Electronic Supplementary Information for

Theoretical Design of Tetra(arenediyl)bis(allyl) Derivatives as Model Compounds for Cope Rearrangement Transition States

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Gaussian09 full reference

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Theoretical procedure

All structures were optimised at RB3LYP/6-311+G(d) level by using very tight geometry convergence criteria (OPT=VERYTIGHT) at gas phase. Stationary points were characterised by the right number of negative eigenvalues (0 for energy minima; 1 for TS) for the analytical Hessian. UB3LYP/6-311+G(d) single-point calculations (for broken-symmetry singlet and triplet electronic states, GUESS=MIX) were carried out on RB3LYP/6-311+G(d)-optimised geometries. Electronic energies for pure singlet UB3LYP wavefunctions were estimated by means of the Kraka formula:[S1]

$$E_{,pure\ singlet} = \frac{1}{x}E_{,singlet} - \frac{1-x}{x}E_{,triplet}$$

where x is defined as follows:

$$x = \frac{\langle S^2\rangle_{,triplet} - \langle S^2\rangle_{,singlet}}{\langle S^2\rangle_{,triplet} - \langle S^2\rangle_{pure\ singlet}}$$

where $\langle S^2\rangle_{pure\ singlet} = 0$.

Broken-symmetry singlet-state UB3LYP wavefunctions were used for calculations of Nucleus-Independent Chemical Shifts (NICS) and isotropic magnetic susceptibilities. NICS were calculated as the negative of the magnetic shielding computed at different points[S2] by using the Gauge-Independent Atomic Orbital (GIAO) method. Thus, NICS(0) values were computed at the centre of the localised or delocalised ring (by using Cartesian coordinates of all 6 heavy atoms). A "ring plane" was obtained for every structure by least-square fit in order to minimise the distances from that plane to all 6 heavy atoms. A straight passing through the ring centre was calculated as perpendicular to the "ring plane". Every NICS(1) value was calculated at a point placed in the concave ring side at 1 Å far from the ring centre by following the aforementioned straight. NICS(–1) values were analogously obtained for the convex ring side. Isotropic magnetic susceptibility was also calculated for each structure by using the GIAO method.

Gibbs free energies at three different levels (RB3LYP/6-311+G(d), singlet-state UB3LYP/6-311+G(d), and pure singlet UB3LYP/6-311+G(d)) for each estationary point were calculated from the electronic energy at the corresponding level as well as thermal corrections (at 25 ºC) from non-scaled RB3LYP/6-311+G(d) analytical frequencies.

Tables

Table S1. RB3LYP/6-311+G(d) electronic energies.

Ar	R^1	R^2	localised structure		delocalised structure		localised ⇌ delocalised TS	
			E^a	ΔE^b	E^a	ΔE^b	E^a	$\Delta E^{\ddagger b}$
benzene-1,2-diyl	H	H	-1154.100892	0.0	-1154.100103	0.5	-1154.099587	0.8
benzene-1,2-diyl	F	H	-1253.373035	0.0	-1253.370720	1.5	-1253.370480	1.6
benzene-1,2-diyl	Me	H	-1193.421983	0.0	-1193.419008	1.9	-1193.419017	1.9
benzene-1,2-diyl	NO_2	H	-1358.657686	0.0	-1358.655707	1.2	-1358.655406	1.4
benzene-1,2-diyl	Cl	H	-1613.722788	0.0	-1613.719739	1.9	-1613.719687	1.9
benzene-1,2-diyl	F	F	-1352.643144	0.0	-1352.638730	2.8	-1352.638834	2.7
benzene-1,2-diyl	CN	H	-1246.365931	0.0	-1246.362638	2.1	-1246.362613	2.1
benzene-1,2-diyl	C≡CH	H	-1230.261370	0.0	-1230.257344	2.5	-1230.257367	2.5
benzene-1,2-diyl	Me	Me	-1232.742516	0.0	-1232.736564	3.7	-1232.736620	3.7
benzene-1,2-diyl	NH_2	H	-1209.476524	0.0	-1209.470861	3.6	–[c]	–[c]
benzene-1,2-diyl	Cl	Cl	-2073.343216	0.0	-2073.337536	3.6	–[c]	–[c]
benzene-1,2-diyl	CN	CN	-1338.628064	0.0	-1338.621755	4.0	–[c]	–[c]
benzene-1,2-diyl	C≡CH	C≡CH	-1306.421201	0.0	-1306.413482	4.8	–[c]	–[c]
benzene-1,2-diyl	–COCH=CHCO–	–	-1457.013067	0.0	-1457.009247	2.4	-1457.009230	2.4
benzene-1,2-diyl	–NHCONH–	–	-1376.997905	0.0	-1376.993923	2.5	–[c]	–[c]
benzene-1,2-diyl	naphthalene-1,8-diyl	–	-1537.655178	0.0	-1537.650608	2.9	–[c]	–[c]
benzene-1,2-diyl	–COOCO–	–	-1454.858697	0.0	-1454.854174	2.8	–[c]	–[c]
benzene-1,2-diyl	benzene-1,2-diyl	–	-1383.955487	0.0	-1383.950399	3.2	–[c]	–[c]
benzene-1,2-diyl	phenanthrene-4,5-diyl	–	-1691.315812	0.0	-1691.310281	3.5	–[c]	–[c]
naphthalene-1,8-diyl	H	H	-1768.901955	0.0	-1768.890778	7.0	–[c]	–[c]
naphthalene-2,3-diyl	H	H	-1768.803499	0.0	-1768.804786	-0.8	-1768.803050	0.3
thiophene-3,4-diyl	H	H	-2437.134620	0.0	-2437.139563	-3.1	-2437.134616	0.0
pyrrole-3,4-diyl	H	H	–[c]	–[c]	-1065.726548	–	–[c]	–[c]
furan-3,4-diyl	H	H	–[c]	–[c]	-1145.172640	–	–[c]	–[c]
benzene-1,2-diyl	aza	H	-1170.140725	0.0	-1170.138798	1.2	-1170.138795	1.2
benzene-1,2-diyl	aza	aza	-1186.177220	0.0	-1186.174768	1.5	-1186.174739	1.6
furan-3,4-diyl	aza	H	–[c]	–[c]	-1161.207279	–	–[c]	–[c]
furan-3,4-diyl	aza	aza	-1177.235771	0.0	-1177.239646	-2.4	-1177.235432	0.2

[a] Electronic energies (Hartrees). [b] Relative electronic energies (kcal mol^{-1}). [c] Structure could not be obtained.

Table S2. RB3LYP/6-311+G(d) Gibbs free energies.

Ar	R^1	R^2	localised structure		delocalised structure		localised ⇌ delocalised TS	
			G^a	ΔG^b	G^a	ΔG^b	G^a	$\Delta G^{‡b}$
benzene-1,2-diyl	H	H	-1153.772854	0.0	-1153.772324	0.3	-1153.772399	0.3
benzene-1,2-diyl	F	H	-1253.053910	0.0	-1253.053148	0.5	-1253.052563	0.8
benzene-1,2-diyl	Me	H	-1193.067420	0.0	-1193.066402	0.6	-1193.065765	1.0
benzene-1,2-diyl	NO_2	H	-1358.331719	0.0	-1358.330828	0.6	-1358.330239	0.9
benzene-1,2-diyl	Cl	H	-1613.405981	0.0	-1613.404768	0.8	-1613.404060	1.2
benzene-1,2-diyl	F	F	-1352.333029	0.0	-1352.330327	1.7	-1352.330261	1.7
benzene-1,2-diyl	CN	H	-1246.041731	0.0	-1246.040211	1.0	-1246.039458	1.4
benzene-1,2-diyl	C≡CH	H	-1229.927205	0.0	-1229.925477	1.1	-1229.924277	1.8
benzene-1,2-diyl	Me	Me	-1232.361845	0.0	-1232.358179	2.3	-1232.358040	2.4
benzene-1,2-diyl	NH_2	H	-1209.131918	0.0	-1209.127315	2.9	–[c]	–[c]
benzene-1,2-diyl	Cl	Cl	-2073.037812	0.0	-2073.032933	3.1	–[c]	–[c]
benzene-1,2-diyl	CN	CN	-1338.307696	0.0	-1338.302170	3.5	–[c]	–[c]
benzene-1,2-diyl	C≡CH	C≡CH	-1306.080894	0.0	-1306.074109	4.3	–[c]	–[c]
benzene-1,2-diyl	–COCH=CHCO–	–	-1456.659010	0.0	-1456.656807	1.4	-1456.656258	1.7
benzene-1,2-diyl	–NHCONH–	–	-1376.650074	0.0	-1376.647414	1.7	–[c]	–[c]
benzene-1,2-diyl	naphthalene-1,8-diyl	–	-1537.227713	0.0	-1537.224130	2.2	–[c]	–[c]
benzene-1,2-diyl	–COOCO–	–	-1454.531940	0.0	-1454.528214	2.3	–[c]	–[c]
benzene-1,2-diyl	benzene-1,2-diyl	–	-1383.572198	0.0	-1383.567467	3.0	–[c]	–[c]
benzene-1,2-diyl	phenanthrene-4,5-diyl	–	-1690.845597	0.0	-1690.840263	3.3	–[c]	–[c]
naphthalene-1,8-diyl	H	H	-1768.396714	0.0	-1768.386045	6.7	–[c]	–[c]
naphthalene-2,3-diyl	H	H	-1768.303637	0.0	-1768.304341	-0.4	-1768.303543	0.1
thiophene-3,4-diyl	H	H	-2436.940774	0.0	-2436.944656	-2.4	-2436.940197	0.4
pyrrole-3,4-diyl	H	H	–[c]	–[c]	-1065.467186	–	–[c]	–[c]
furan-3,4-diyl	H	H	–[c]	–[c]	-1145.016116	–	–[c]	–[c]
benzene-1,2-diyl	aza	H	-1169.824730	0.0	-1169.824248	0.3	-1169.823826	0.6
benzene-1,2-diyl	aza	aza	-1185.873497	0.0	-1185.872330	0.7	-1185.872147	0.8
furan-3,4-diyl	aza	H	–[c]	–[c]	-1161.008440	–	–[c]	–[c]
furan-3,4-diyl	aza	aza	-1177.048379	0.0	-1177.052693	-2.7	-1177.048552	-0.1

[a] Sum of electronic and thermal free energies (Hartrees). [b] Relative Gibbs free energies (kcal mol^{-1}).
[c] Structure could not be obtained.

Table S3. Singlet-state UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) electronic energies.

Ar	R^1	R^2	localised structure			delocalised structure			localised ⇌ delocalised TS		
			E^a	ΔE^b	$<S^2>$	E^a	ΔE^b	$<S^2>$	E^a	ΔE^b	$<S^2>$
benzene-1,2-diyl	H	H	-1154.100892	0.0	0.0000	-1154.103588	-1.7	0.5391	-1154.099587	0.8	0.0000
benzene-1,2-diyl	F	H	-1253.373035	0.0	0.0000	-1253.373531	-0.3	0.5067	-1253.370914	1.3	0.2627
benzene-1,2-diyl	Me	H	-1193.421983	0.0	0.0000	-1193.421400	0.4	0.4676	-1193.419442	1.6	0.2190
benzene-1,2-diyl	NO_2	H	-1358.657686	0.0	0.0000	-1358.657432	0.2	0.4310	-1358.655410	1.4	0.0233
benzene-1,2-diyl	Cl	H	-1613.722788	0.0	0.0000	-1613.721798	0.6	0.4450	-1613.720102	1.7	0.2164
benzene-1,2-diyl	F	F	-1352.643144	0.0	0.0000	-1352.642270	0.5	0.5382	-1352.640327	1.8	0.3893
benzene-1,2-diyl	CN	H	-1246.365931	0.0	0.0000	-1246.364425	0.9	0.4159	-1246.363087	1.8	0.2314
benzene-1,2-diyl	C≡CH	H	-1230.261370	0.0	0.0000	-1230.259339	1.3	0.4396	-1230.258615	1.7	0.3613
benzene-1,2-diyl	Me	Me	-1232.742516	0.0	0.0000	-1232.739136	2.1	0.4884	-1232.739008	2.2	0.4783
benzene-1,2-diyl	NH_2	H	-1209.476524	0.0	0.0000	-1209.473545	1.9	0.5032	–[c]	–[c]	–[c]
benzene-1,2-diyl	Cl	Cl	-2073.343216	0.0	0.0000	-2073.339454	2.4	0.4176	–[c]	–[c]	–[c]
benzene-1,2-diyl	CN	CN	-1338.628064	0.0	0.0000	-1338.622864	3.3	0.3233	–[c]	–[c]	–[c]
benzene-1,2-diyl	C≡CH	C≡CH	-1306.421201	0.0	0.0000	-1306.414974	3.9	0.4396	–[c]	–[c]	–[c]
benzene-1,2-diyl	–COCH=CHCO–	–	-1457.013067	0.0	0.0000	-1457.010276	1.8	0.3005	-1457.010276	1.8	0.3005
benzene-1,2-diyl	–NHCONH–	–	-1376.997905	0.0	0.0000	-1376.994387	2.2	0.1850	–[c]	–[c]	–[c]
benzene-1,2-diyl	naphthalene-1,8-diyl	–	-1537.655178	0.0	0.0000	-1537.650900	2.7	0.1810	–[c]	–[c]	–[c]
benzene-1,2-diyl	–COOCO–	–	-1454.858697	0.0	0.0000	-1454.854325	2.7	0.0866	–[c]	–[c]	–[c]
benzene-1,2-diyl	benzene-1,2-diyl	–	-1383.955487	0.0	0.0000	-1383.950600	3.1	0.0000	–[c]	–[c]	–[c]
benzene-1,2-diyl	phenanthrene-4,5-diyl	–	-1691.315812	0.0	0.0000	-1691.310790	3.2	0.2052	–[c]	–[c]	–[c]
naphthalene-1,8-diyl	H	H	-1768.901955	0.0	0.0000	-1768.891065	6.8	0.0000	–[c]	–[c]	–[c]
naphthalene-2,3-diyl	H	H	-1768.803499	0.0	0.0000	-1768.809338	-3.7	0.6128	-1768.803050	0.3	0.0000
thiophene-3,4-diyl	H	H	-2437.134620	0.0	0.0000	-2437.157937	-14.6	0.9879	-2437.158508	-15.0	0.9878
pyrrole-3,4-diyl	H	H	–[c]	–[c]	–[c]	-1065.756895	–	1.0634	–[c]	–[c]	–[c]
furan-3,4-diyl	H	H	–[c]	–[c]	–[c]	-1145.208567	–	1.0699	–[c]	–[c]	–[c]
benzene-1,2-diyl	aza	H	-1170.140725	0.0	0.0000	-1170.139737	0.6	0.2790	-1170.138795	1.2	0.0000
benzene-1,2-diyl	aza	aza	-1186.177220	0.0	0.0000	-1186.174965	1.4	0.0777	-1186.174965	1.4	0.0777
furan-3,4-diyl	aza	H	–[c]	–[c]	–[c]	-1161.236655	–	1.0570	–[c]	–[c]	–[c]
furan-3,4-diyl	aza	aza	-1177.235771	0.0	0.0000	-1177.262602	-16.8	1.0101	-1177.235432	0.2	0.0000

[a] Electronic energies (Hartrees). [b] Relative electronic energies (kcal mol^{-1}). [c] Structure could not be obtained.

Table S4. Singlet-state UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) Gibbs free energies.

Ar	R^1	R^2	localised structure		delocalised structure		localised ⇌ delocalised TS	
			G^a	ΔG^b	E^a	ΔG^b	G^a	$\Delta G^{‡b}$
benzene-1,2-diyl	H	H	-1153.772854	0.0	-1153.775808	-1.9	-1153.772399	0.3
benzene-1,2-diyl	F	H	-1253.053910	0.0	-1253.055959	-1.3	-1253.052563	0.8
benzene-1,2-diyl	Me	H	-1193.067420	0.0	-1193.068794	-0.9	-1193.065765	1.0
benzene-1,2-diyl	NO_2	H	-1358.331719	0.0	-1358.332553	-0.5	-1358.330239	0.9
benzene-1,2-diyl	Cl	H	-1613.405981	0.0	-1613.406827	-0.5	-1613.404060	1.2
benzene-1,2-diyl	F	F	-1352.333029	0.0	-1352.333867	-0.5	-1352.330261	1.7
benzene-1,2-diyl	CN	H	-1246.041731	0.0	-1246.041998	-0.2	-1246.039458	1.4
benzene-1,2-diyl	C≡CH	H	-1229.927205	0.0	-1229.927472	-0.2	-1229.924277	1.8
benzene-1,2-diyl	Me	Me	-1232.361845	0.0	-1232.360751	0.7	-1232.358040	2.4
benzene-1,2-diyl	NH_2	H	-1209.131918	0.0	-1209.129999	1.2	–[c]	–[c]
benzene-1,2-diyl	Cl	Cl	-2073.037812	0.0	-2073.034851	1.9	–[c]	–[c]
benzene-1,2-diyl	CN	CN	-1338.307696	0.0	-1338.303279	2.8	–[c]	–[c]
benzene-1,2-diyl	C≡CH	C≡CH	-1306.080894	0.0	-1306.075601	3.3	–[c]	–[c]
benzene-1,2-diyl	–COCH=CHCO–	–	-1456.659010	0.0	-1456.657837	0.7	-1456.656258	1.7
benzene-1,2-diyl	–NHCONH–	–	-1376.650074	0.0	-1376.647879	1.4	–[c]	–[c]
benzene-1,2-diyl	naphthalene-1,8-diyl	–	-1537.227713	0.0	-1537.224422	2.1	–[c]	–[c]
benzene-1,2-diyl	–COOCO–	–	-1454.531940	0.0	-1454.528365	2.2	–[c]	–[c]
benzene-1,2-diyl	benzene-1,2-diyl	–	-1383.572198	0.0	-1383.567668	2.8	–[c]	–[c]
benzene-1,2-diyl	phenanthrene-4,5-diyl	–	-1690.845597	0.0	-1690.840771	3.0	–[c]	–[c]
naphthalene-1,8-diyl	H	H	-1768.396714	0.0	-1768.386332	6.5	–[c]	–[c]
naphthalene-2,3-diyl	H	H	-1768.303637	0.0	-1768.308892	-3.3	-1768.303543	0.1
thiophene-3,4-diyl	H	H	-2436.940774	0.0	-2436.963030	-14.0	-2436.940197	0.4
pyrrole-3,4-diyl	H	H	–[c]	–[c]	-1065.497533	–	–[c]	–[c]
furan-3,4-diyl	H	H	–[c]	–[c]	-1145.052043	–	–[c]	–[c]
benzene-1,2-diyl	aza	H	-1169.824730	0.0	-1169.825187	-0.3	-1169.823826	0.6
benzene-1,2-diyl	aza	aza	-1185.873497	0.0	-1185.872527	0.6	-1185.872147	0.8
furan-3,4-diyl	aza	H	–[c]	–[c]	-1161.037816	–	–[c]	–[c]
furan-3,4-diyl	aza	aza	-1177.048379	0.0	-1177.075649	-17.1	-1177.048552	-0.1

[a] Sum of electronic and thermal free energies (Hartrees). [b] Relative Gibbs free energies (kcal mol^{-1}). [c] Structure could not be obtained.

Table S5. Triplet-state UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) electronic energies.

Ar	R^1	R^2	delocalised structure		localised ⇌ delocalised TS	
			E^a	$<S^2>$	E^a	$<S^2>$
benzene-1,2-diyl	H	H	-1154.085367	2.0626	-1154.056616	2.0519
benzene-1,2-diyl	F	H	-1253.354546	2.0630	-1253.343737	2.0519
benzene-1,2-diyl	Me	H	-1193.400843	2.0649	-1193.390507	2.0611
benzene-1,2-diyl	NO_2	H	-1358.636064	2.0640	-1358.620011	2.0580
benzene-1,2-diyl	Cl	H	-1613.700472	2.0656	-1613.690991	2.0621
benzene-1,2-diyl	F	F	-1352.623950	2.0637	-1352.617231	2.0613
benzene-1,2-diyl	CN	H	-1246.341934	2.0700	-1246.334382	2.0667
benzene-1,2-diyl	C≡CH	H	-1230.237478	2.0732	-1230.234114	2.0718
benzene-1,2-diyl	Me	Me	-1232.719173	2.0672	-1232.718758	2.0671
benzene-1,2-diyl	NH_2	H	-1209.454598	2.0647	–[c]	–[c]
benzene-1,2-diyl	Cl	Cl	-2073.316784	2.0690	–[c]	–[c]
benzene-1,2-diyl	CN	CN	-1338.596647	2.0771	–[c]	–[c]
benzene-1,2-diyl	C≡CH	C≡CH	-1306.389674	2.0833	–[c]	–[c]
benzene-1,2-diyl	–COCH=CHCO–	–	-1456.983906	2.0625	-1456.979787	2.0607
benzene-1,2-diyl	–NHCONH–	–	-1376.962508	2.0680	–[c]	–[c]
benzene-1,2-diyl	naphthalene-1,8-diyl	–	-1537.619680	2.0654	–[c]	–[c]
benzene-1,2-diyl	–COOCO–	–	-1454.819775	2.0647	–[c]	–[c]
benzene-1,2-diyl	benzene-1,2-diyl	–	-1383.911798	2.0736	–[c]	–[c]
benzene-1,2-diyl	phenanthrene-4,5-diyl	–	-1691.280651	2.0635	–[c]	–[c]
naphthalene-1,8-diyl	H	H	-1768.793522	2.0635	–[c]	–[c]
naphthalene-2,3-diyl	H	H	-1768.793970	2.0628	-1768.744474	2.0437
thiophene-3,4-diyl	H	H	-2437.155377	2.0644	-2437.06124	2.0255
pyrrole-3,4-diyl	H	H	-1065.756693	2.0649	–[c]	–[c]
furan-3,4-diyl	H	H	-1145.208434	2.0661	–[c]	–[c]
benzene-1,2-diyl	aza	H	-1170.112278	2.0578	-1170.097276	2.0526
benzene-1,2-diyl	aza	aza	-1186.139607	2.0537	-1186.133714	2.0518
furan-3,4-diyl	aza	H	–[d]	–[d]	–[c]	–[c]
furan-3,4-diyl	aza	aza	-1177.260914	2.0575	-1177.181762	2.0333

[a] Electronic energies (Hartrees). [b] Relative electronic energies (kcal mol^{-1}). [c] Structure could not be obtained. [d] SCF convergence not achieved.

Table S6. Pure singlet UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) electronic energies.

Ar	R^1	R^2	localised structure		delocalised structure		localised ⇌ delocalised TS	
			E^a	ΔE^b	E^a	ΔE^b	E^a	$\Delta E^{‡b}$
benzene-1,2-diyl	H	H	-1154.100892	0.0	-1154.110035	-5.7	-1154.099587	0.8
benzene-1,2-diyl	F	H	-1253.373035	0.0	-1253.379712	-4.2	-1253.374904	-1.2
benzene-1,2-diyl	Me	H	-1193.421983	0.0	-1193.427418	-3.4	-1193.422881	-0.6
benzene-1,2-diyl	NO_2	H	-1358.657686	0.0	-1358.663072	-3.4	-1358.655816	1.2
benzene-1,2-diyl	Cl	H	-1613.722788	0.0	-1613.727654	-3.1	-1613.723515	-0.5
benzene-1,2-diyl	F	F	-1352.643144	0.0	-1352.648733	-3.5	-1352.645704	-1.6
benzene-1,2-diyl	CN	H	-1246.365931	0.0	-1246.370080	-2.6	-1246.366706	-0.5
benzene-1,2-diyl	C≡CH	H	-1230.261370	0.0	-1230.265222	-2.4	-1230.263790	-1.5
benzene-1,2-diyl	Me	Me	-1232.742516	0.0	-1232.745312	-1.8	-1232.745104	-1.6
benzene-1,2-diyl	NH_2	H	-1209.476524	0.0	-1209.479650	-2.0	–[c]	–[c]
benzene-1,2-diyl	Cl	Cl	-2073.343216	0.0	-2073.345187	-1.2	–[c]	–[c]
benzene-1,2-diyl	CN	CN	-1338.628064	0.0	-1338.627697	0.2	–[c]	–[c]
benzene-1,2-diyl	C≡CH	C≡CH	-1306.421201	0.0	-1306.421741	-0.3	–[c]	–[c]
benzene-1,2-diyl	–COCH=CHCO–	–	-1457.013067	0.0	-1457.014774	-1.1	-1457.015482	-1.5
benzene-1,2-diyl	–NHCONH–	–	-1376.997905	0.0	-1376.997520	0.2	–[c]	–[c]
benzene-1,2-diyl	naphthalene-1,8-diyl	–	-1537.655178	0.0	-1537.653899	0.8	–[c]	–[c]
benzene-1,2-diyl	–COOCO–	–	-1454.858697	0.0	-1454.855838	1.8	–[c]	–[c]
benzene-1,2-diyl	benzene-1,2-diyl	–	-1383.955487	0.0	-1383.950600	3.1	–[c]	–[c]
benzene-1,2-diyl	phenanthrene-4,5-diyl	–	-1691.315812	0.0	-1691.314118	1.1	–[c]	–[c]
naphthalene-1,8-diyl	H	H	-1768.901955	0.0	-1768.891065	6.8	–[c]	–[c]
naphthalene-2,3-diyl	H	H	-1768.803499	0.0	-1768.815832	-7.7	-1768.803050	0.3
thiophene-3,4-diyl	H	H	-2437.134620	0.0	-2437.160285	-16.1	-2437.251100	-73.1
pyrrole-3,4-diyl	H	H	–[c]	–[c]	-1065.757109		–[c]	–[c]
furan-3,4-diyl	H	H	–[c]	–[c]	-1145.208709		–[c]	–[c]
benzene-1,2-diyl	aza	H	-1170.140725	0.0	-1170.144044	-2.1	-1170.138795	1.2
benzene-1,2-diyl	aza	aza	-1186.177220	0.0	-1186.176355	0.5	-1186.176589	0.4
furan-3,4-diyl	aza	H	–[c]	–[c]		0.0	–[c]	–[c]
furan-3,4-diyl	aza	aza	-1177.235771	0.0	-1177.264230	-17.9	-1177.235432	0.2

Calculations obtained by using the Kraka formula.[S1] [a] Electronic energies (Hartrees). [b] Relative electronic energies (kcal mol^{-1}). [c] Structure could not be obtained.

Table S7. Pure singlet UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) Gibbs free energies.

Ar	R^1	R^2	localised structure		delocalised structure		localised ⇌ delocalised TS	
			G^a	ΔG^b	G^a	ΔG^b	G^a	$\Delta G^{‡b}$
benzene-1,2-diyl	H	H	-1153.772854	0.0	-1153.782256	-5.9	-1153.771548	0.8
benzene-1,2-diyl	F	H	-1253.053910	0.0	-1253.062141	-5.2	-1253.055779	-1.2
benzene-1,2-diyl	Me	H	-1193.067420	0.0	-1193.074812	-4.6	-1193.068319	-0.6
benzene-1,2-diyl	NO_2	H	-1358.331719	0.0	-1358.338193	-4.1	-1358.329848	1.2
benzene-1,2-diyl	Cl	H	-1613.405981	0.0	-1613.412683	-4.2	-1613.406708	-0.5
benzene-1,2-diyl	F	F	-1352.333029	0.0	-1352.340330	-4.6	-1352.335589	-1.6
benzene-1,2-diyl	CN	H	-1246.041731	0.0	-1246.047653	-3.7	-1246.042507	-0.5
benzene-1,2-diyl	C≡CH	H	-1229.927205	0.0	-1229.933355	-3.9	-1229.929625	-1.5
benzene-1,2-diyl	Me	Me	-1232.361845	0.0	-1232.366927	-3.2	-1232.364433	-1.6
benzene-1,2-diyl	NH_2	H	-1209.131918	0.0	-1209.136104	-2.6	–[c]	–[c]
benzene-1,2-diyl	Cl	Cl	-2073.037812	0.0	-2073.040584	-1.7	–[c]	–[c]
benzene-1,2-diyl	CN	CN	-1338.307696	0.0	-1338.308112	-0.3	–[c]	–[c]
benzene-1,2-diyl	C≡CH	C≡CH	-1306.080894	0.0	-1306.082367	-0.9	–[c]	–[c]
benzene-1,2-diyl	–COCH=CHCO–	–	-1456.659010	0.0	-1456.662334	-2.1	-1456.661425	-1.5
benzene-1,2-diyl	–NHCONH–	–	-1376.650074	0.0	-1376.651011	-0.6	–[c]	–[c]
benzene-1,2-diyl	naphthalene-1,8-diyl	–	-1537.227713	0.0	-1537.227421	0.2	–[c]	–[c]
benzene-1,2-diyl	–COOCO–	–	-1454.531940	0.0	-1454.529878	1.3	–[c]	–[c]
benzene-1,2-diyl	benzene-1,2-diyl	–	-1383.572198	0.0	-1383.567668	2.8	–[c]	–[c]
benzene-1,2-diyl	phenanthrene-4,5-diyl	–	-1690.845597	0.0	-1690.844099	0.9	–[c]	–[c]
naphthalene-1,8-diyl	H	H	-1768.396714	0.0	-1768.386332	6.5	–[c]	–[c]
naphthalene-2,3-diyl	H	H	-1768.303637	0.0	-1768.315387	-7.4	-1768.303188	0.3
thiophene-3,4-diyl	H	H	-2436.940774	0.0	-2436.965378	-15.4	-2437.057254	-73.1
pyrrole-3,4-diyl	H	H	–[c]	–[c]	-1065.497747	–	–[c]	–[c]
furan-3,4-diyl	H	H	–[c]	–[c]	-1145.052186	–	–[c]	–[c]
benzene-1,2-diyl	aza	H	-1169.824730	0.0	-1169.829494	-3.0	-1169.822800	1.2
benzene-1,2-diyl	aza	aza	-1185.873497	0.0	-1185.873917	-0.3	-1185.872866	0.4
furan-3,4-diyl	aza	H	–[c]	–[c]	–[d]	–[d]	–[c]	–[c]
furan-3,4-diyl	aza	aza	-1177.048379	0.0	-1177.077277	-18.1	-1177.048040	0.2

Calculations obtained by using the Kraka formula from singlet and triplet states for UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) calculations.[S1] [a] Sum of electronic and thermal free energies (Hartrees). [b] Relative Gibbs free energies (kcal mol^{-1}). [c] Structure could not be obtained. [d] SCF convergence of the triplet-state UB3LYP wavefunction was not achieved.

Table S8. NICS values for delocalised structures.

Ar	R^1	R^2	NICS (0)	NICS (1)	NICS (-1)
benzene-1,2-diyl	H	H	-7.8122	-3.0651	-7.4170
benzene-1,2-diyl	F	H	-7.1746	-1.2508	-4.5096
benzene-1,2-diyl	Me	H	-7.5722	-0.7971	-5.5466
benzene-1,2-diyl	NO_2	H	-6.8963	-1.1613	-3.2201
benzene-1,2-diyl	Cl	H	-7.0901	-0.9187	-4.7464
benzene-1,2-diyl	F	F	-7.3036	-1.7844	-3.1360
benzene-1,2-diyl	CN	H	-7.1148	-1.1284	-4.6230
benzene-1,2-diyl	C≡CH	H	-6.9312	-0.9293	-4.6902
benzene-1,2-diyl	Me	Me	-5.7726	0.2475	-5.3664
benzene-1,2-diyl	NH_2	H	-6.7001	-0.5436	-4.6734
benzene-1,2-diyl	Cl	Cl	-6.4732	-0.6133	-3.7489
benzene-1,2-diyl	CN	CN	-7.2010	-1.4026	-3.8219
benzene-1,2-diyl	C≡CH	C≡CH	-6.7267	-0.7125	-4.2448
benzene-1,2-diyl	–COCH=CHCO–	–	-6.4489	-1.5960	-2.2645
benzene-1,2-diyl	–NHCONH–	–	-10.7371	-2.0451	-6.1570
benzene-1,2-diyl	naphthalene-1,8-diyl	–	-12.1676	-1.6852	-2.0465
benzene-1,2-diyl	–COOCO–	–	-12.8286	-2.5498	-6.2439
benzene-1,2-diyl	benzene-1,2-diyl	–	-15.6918	-2.5996	-10.0839
benzene-1,2-diyl	phenanthrene-4,5-diyl	–	-8.1157	-0.4546	-2.4491
naphthalene-1,8-diyl	H	H	-15.3263	-6.0956	-10.3720
naphthalene-2,3-diyl	H	H	-4.9050	-0.3774	-4.8506
thiophene-3,4-diyl	H	H	-3.6276	-0.8905	-2.8090
pyrrole-3,4-diyl	H	H	-3.3994	-0.8244	-3.1432
furan-3,4-diyl	H	H	-4.6707	-2.1237	-3.8957
benzene-1,2-diyl	aza	H	-8.7797	-0.7124	-5.7872
benzene-1,2-diyl	aza	aza	-10.8860	-0.7230	-6.9455
furan-3,4-diyl	aza	H	-3.5243	-2.3474	-3.5716
furan-3,4-diyl	aza	aza	-4.7020	-0.6396	-3.2132

Singlet-state UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) calculations.

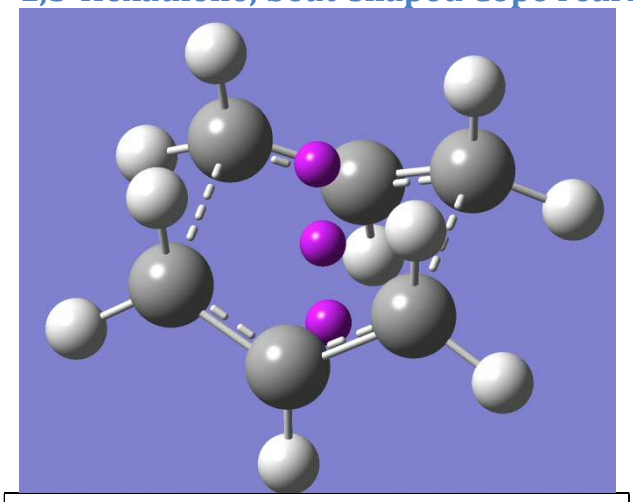
Table S9. Isotropic magnetic susceptibilities.

Ar	R^1	R^2	localised structure	delocalised structure	
			χ	χ	$\Delta\chi$
benzene-1,2-diyl	H	H	-115.9804	-53.6717	62.3087
benzene-1,2-diyl	F	H	-130.9474	-97.1960	33.7514
benzene-1,2-diyl	Me	H	-104.2974	-99.7127	4.5847
benzene-1,2-diyl	NO_2	H	-106.8726	-162.9477	-56.0751
benzene-1,2-diyl	Cl	H	-126.6451	-98.9107	27.7344
benzene-1,2-diyl	F	F	-123.3006	-47.8201	75.4805
benzene-1,2-diyl	CN	H	-133.2188	-163.7740	-30.5552
benzene-1,2-diyl	C≡CH	H	-187.3886	-175.9505	11.4381
benzene-1,2-diyl	Me	Me	-52.2288	-13.6779	38.5509
benzene-1,2-diyl	NH_2	H	-102.4002	-58.5974	43.8028
benzene-1,2-diyl	Cl	Cl	-58.5555	-88.9214	-30.3659
benzene-1,2-diyl	CN	CN	-71.5685	-138.8721	-67.3036
benzene-1,2-diyl	C≡CH	C≡CH	-106.1582	-138.6201	-32.4619
benzene-1,2-diyl	–COCH=CHCO–	–	-153.3849	-14.1726	139.2123
benzene-1,2-diyl	–NHCONH–	–	-99.6966	-118.2847	-18.5881
benzene-1,2-diyl	naphthalene-1,8-diyl	–	-86.6448	-8.0513	78.5935
benzene-1,2-diyl	–COOCO–	–	-57.4671	-117.8085	-60.3414
benzene-1,2-diyl	benzene-1,2-diyl	–	-44.1553	93.7166	137.8719
benzene-1,2-diyl	phenanthrene-4,5-diyl	–	-190.8229	-120.4407	70.3822
naphthalene-1,8-diyl	H	H	-91.6831	-101.6509	-9.9678
naphthalene-2,3-diyl	H	H	-193.0071	-146.2267	46.7804
thiophene-3,4-diyl	H	H	-126.0942	-147.1796	-21.0854
pyrrole-3,4-diyl	H	H	–[a]	-127.6876	-127.6876
furan-3,4-diyl	H	H	–[a]	-109.2152	-109.2152
benzene-1,2-diyl	aza	H	-142.0743	-108.7806	33.2937
benzene-1,2-diyl	aza	aza	-140.6809	-147.1611	-6.4802
furan-3,4-diyl	aza	H	–[a]	-112.8256	-112.8256
furan-3,4-diyl	aza	aza	-83.6701	-103.9644	-20.2943

Isotropic magnetic susceptibilities (cgs-ppm) obtained from singlet-state UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) calculations. [a] Structure could not be obtained.

Selected properties of all structures

1,5-Hexadiene, boat-shaped Cope rearrangement TS



RB3LYP/6-311+G(d) level:
C···C bond length: 2.24919 Å
Electronic energy: -234.598905 Hartrees
Gibbs free energy: -234.488245 Hartrees
Imaginary frequency: 501.4*i* cm^{-1}
Point group: C_{2v}

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -234.598905 Hartrees
<S^2> (singlet): 0.0000
NICS(0): -20.9006 ppm
NICS(1): -10.6357 ppm
NICS(–1): -15.2510 ppm
Isotropic magnetic susceptibility: -74.5927 cgs-ppm
Electronic energy (triplet): -234.463820 Hartrees
<S^2> (triplet): 2.0626

Cartesian coordinates:
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H,0,1.2571377635,-1.30108724,1.1204707409
H,0,-0.3482158218,-2.1442920266,1.3412508974
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H,0,1.2571376693,1.301087418,-1.1204707409
Bq,0,-0.02132513,0.00000004,0,0.00000000
Bq,0,0.97867487,0,0.00000004,0,0.00000000
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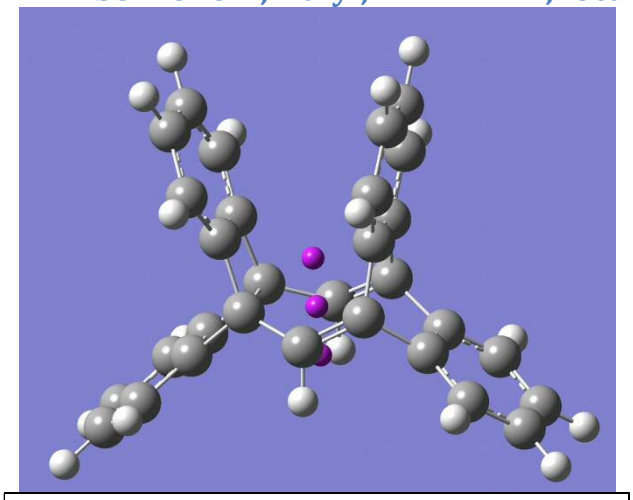
Ar = benzene-1,2-diyl, $R^1 = R^2 = H$, localised structure



RB3LYP/6-311+G(d) level:
Allyl-allyl C–C bond length: 1.78794 Å
Distance between terminal allyl C atoms: 2.44737 Å
Sum of bond angles for terminal allyl C: 350.984°
Electronic energy: -1154.100892 Hartrees
Gibbs free energy: -1153.772854 Hartrees
No imaginary frequencies
Point group: C_s

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1154.100892 Hartrees
<S^2> (singlet): 0.0000
NICS(0): -1.8839 ppm
NICS(1): 0.3222 ppm
NICS(–1): -3.1708 ppm
Isotropic magnetic susceptibility: -115.9804 cgs-ppm

Cartesian coordinates:
C,0,0.1810442538,1.3744728766,1.2236866409
C,0,0.1810442538,1.3744728766,-1.2236866409
C,0,0.4332789285,-1.1070049753,-0.8939680819
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C,0,-0.9752720697,-1.6565269206,0.6957112705
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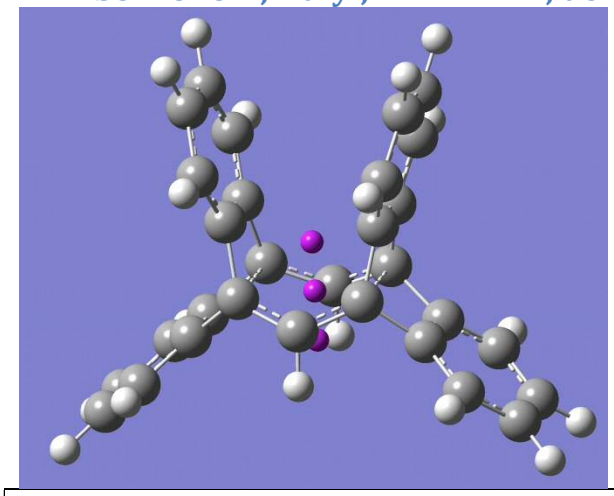
C,0,-3.6126853287,1.6373957534,0.6968399277
H,0,-4.5513448961,1.7181875815,-1.2358076969
H,0,-4.5513448961,1.7181875815,1.2358076969
H,0,-2.0307387012,-2.1931173767,-2.5177762355
H,0,-2.4117462166,1.5344232779,-2.4930773748
C,0,1.5030900441,-2.1817825784,0.6965834536
C,0,1.5030900441,-2.1817825784,-0.6965834536
C,0,2.3179630971,-3.0254604725,1.4321278817
C,0,2.3179630971,-3.0254604725,-1.4321278817
C,0,3.1544943288,-3.8821485278,0.6987635538
H,0,2.3321087926,-3.0287277639,2.5176956512
C,0,3.1544943288,-3.8821485278,-0.6987635538
H,0,2.3321087926,-3.0287277639,-2.5176956512
H,0,3.819931775,-4.5583799142,1.2263965128
H,0,3.819931775,-4.5583799142,-1.2263965128
C,0,0.9702083657,2.5638742,0.7111397114
C,0,1.6552859277,3.5478096182,1.4068804573
C,0,0.9702083657,2.5638742,-0.7111397114
C,0,2.3493552405,4.5365550938,0.6953468578
H,0,1.6617459456,3.5460649684,2.4925465277
C,0,1.6552859277,3.5478096182,-1.4068804573
C,0,2.3493552405,4.5365550938,-0.6953468578
H,0,2.88803772,5.3081441909,1.2362440909
H,0,1.6617459456,3.5460649684,-2.4925465277
H,0,2.88803772,5.3081441909,-1.2362440909
C,0,-2.0215934517,-2.1855162514,1.4324603006
H,0,-2.0307387012,-2.1931173767,2.5177762355
C,0,-2.4123655672,1.5356531783,1.4075783952
H,0,-2.4117462166,1.5344232779,2.4930773748
C,0,0.8378935156,0.2098034799,1.4346613843
H,0,1.9069289367,0.2877217839,1.6250378955
C,0,0.8378935156,0.2098034799,-1.4346613843
H,0,1.9069289367,0.2877217839,-1.6250378955
Bq,0,0.484072233,0.15909046,0.
Bq,0,-0.511070041,0.060643241,0.
Bq,0,1.479214506,0.25753768,0.

Ar = benzene-1,2-diyl, $R^1 = R^2 = H$, delocalised structure

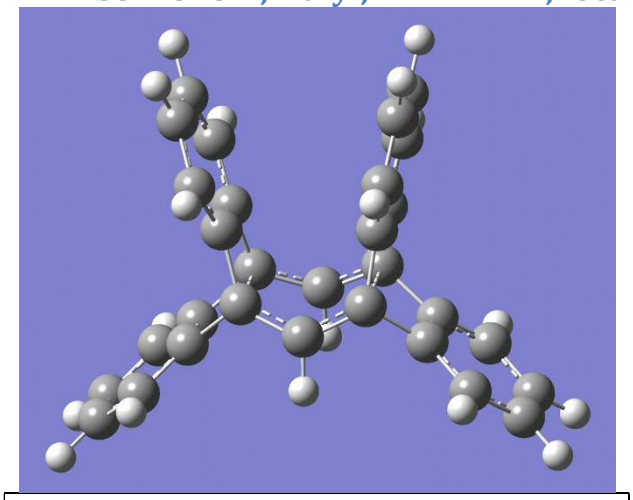


RB3LYP/6-311+G(d) level:
C¨C bond length: 2.29388 Å
Electronic energy: -1154.100103 Hartrees
Gibbs free energy: -1153.772324 Hartrees
No imaginary frequencies
Point group: C_{2v}

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1154.103588 Hartrees
$\langle S^2 \rangle$ (singlet): 0.5391
NICS(0): -7.8122 ppm
NICS(1): -3.0651 ppm
NICS(–1): -7.4170 ppm
Isotropic magnetic susceptibility: -53.6717 cgs-ppm
Electronic energy (triplet): -1154.085367 Hartrees
$\langle S^2 \rangle$ (triplet): 2.0626

Cartesian coordinates:
C,0,-1.251101305,1.1469387341,-0.2989985538
C,0,-1.251101305,-1.1469387341,-0.2989985538
C,0,1.251101305,-1.1469387341,-0.2989985538
C,0,1.251101305,1.1469387341,-0.2989985538
C,0,1.5305618797,0.6969341549,1.1113145221
C,0,1.5305618797,-0.6969341549,1.1113145221
C,0,1.8518711834,-1.4151565377,2.2538871982
C,0,2.1688682462,0.6974448114,3.4141143454
C,0,2.1688682462,-0.6974448114,3.4141143454
H,0,2.4167761879,1.2326745081,4.3253134301
H,0,2.4167761879,-1.2326745081,4.3253134301
C,0,-1.5305618797,-0.6969341549,1.1113145221
C,0,-1.5305618797,0.6969341549,1.1113145221
C,0,-1.8518711834,-1.4151565377,2.2538871982
C,0,-2.1688682462,-0.6974448114,3.4141143454
C,0,-2.1688682462,0.6974448114,3.4141143454
H,0,-2.4167761879,-1.2326745081,4.3253134301
H,0,-2.4167761879,1.2326745081,4.3253134301
H,0,1.849992272,-2.5008352984,2.2559340404
H,0,-1.849992272,-2.5008352984,2.2559340404
C,0,2.3589537312,0.7020296307,-1.2378312173
C,0,2.3589537312,-0.7020296307,-1.2378312173
C,0,3.2571917158,1.4147999858,-2.0159815333
C,0,3.2571917158,-1.4147999858,-2.0159815333
C,0,4.1654335724,0.6962177073,-2.8090469266
H,0,3.2491593463,2.5006394816,-2.0294224155
C,0,4.1654335724,-0.6962177073,-2.8090469266
H,0,3.2491593463,-2.5006394816,-2.0294224155
H,0,4.8727576384,1.232707727,-3.4335457295
H,0,4.8727576384,-1.232707727,-3.4335457295
C,0,-2.3589537312,0.7020296307,-1.2378312173
C,0,-3.2571917158,1.4147999858,-2.0159815333
C,0,-2.3589537312,-0.7020296307,-1.2378312173
C,0,-4.1654335724,0.6962177073,-2.8090469266
H,0,-3.2491593463,2.5006394816,-2.0294224155
C,0,-3.2571917158,-1.4147999858,-2.0159815333
C,0,-4.1654335724,-0.6962177073,-2.8090469266
H,0,-4.8727576384,1.232707727,-3.4335457295
H,0,-3.2491593463,-2.5006394816,-2.0294224155
H,0,-4.8727576384,-1.232707727,-3.4335457295
C,0,1.8518711834,1.4151565377,2.2538871982
H,0,1.849992272,2.5008352984,2.2559340404
C,0,-1.8518711834,1.4151565377,2.2538871982
H,0,-1.849992272,2.5008352984,2.2559340404
C,0,0.,1.460833639,-0.8336765726
H,0,0.,1.6373797819,-1.9078619284
C,0,0.,-1.460833639,-0.8336765726
H,0,0.,-1.6373797819,-1.9078619284
Bq,0,0.,0.,-0.47722456
Bq,0,0.,0.,0.52277544
Bq,0,0.,0.,-1.47722456

Ar = benzene-1,2-diyl, $R^1 = R^2 = H$, localised ⇌ delocalised TS

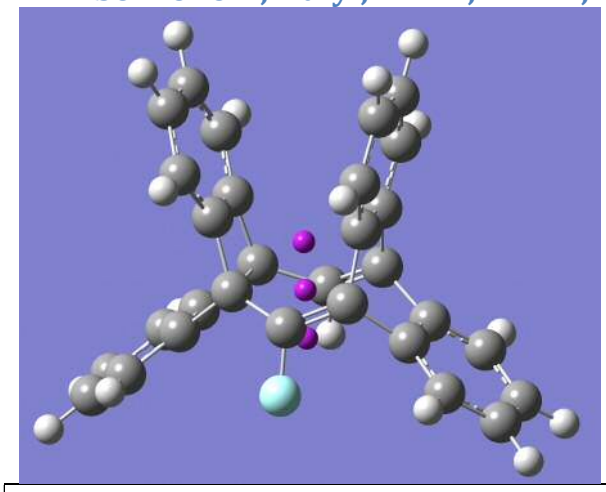


RB3LYP/6-311+G(d) level:
C¨C bond lengths: 2.06480 Å, 2.39382 Å
Electronic energy: -1154.099587 Hartrees
Gibbs free energy: -1153.772399 Hartrees
Imaginary frequency: 217.0*i* cm^{-1}
Point group: C_s

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1154.099587 Hartrees
$<S^2>$ (singlet): 0.0000
Electronic energy (triplet): 2.0519 Hartrees
$<S^2>$ (triplet):

Cartesian coordinates:
C,0,0.1653770798,1.3199629813,1.1969123889
C,0,0.1653770798,1.3199629813,-1.1969123889
C,0,0.4400967003,-1.1623358181,-1.0323975508
C,0,0.4400967003,-1.1623358181,1.0323975508
C,0,-0.9480741507,-1.6597578959,0.6951395986
C,0,-0.9480741507,-1.6597578959,-0.6951395986
C,0,-2.0185504549,-2.1539690256,-1.4240110144
C,0,-3.1121785788,-2.6460360193,0.6983738849
C,0,-3.1121785788,-2.6460360193,-0.6983738849
H,0,-3.9757974819,-3.0338622275,1.2294989536
H,0,-3.9757974819,-3.0338622275,-1.2294989536
C,0,-1.2504289678,1.3983311844,-0.6990089043
C,0,-1.2504289678,1.3983311844,0.6990089043
C,0,-2.4336507115,1.5414392139,-1.4104305903
C,0,-3.6298414736,1.6797494901,-0.6970890809
C,0,-3.6298414736,1.6797494901,0.6970890809
H,0,-4.5665943825,1.7885713397,-1.2345367186
H,0,-4.5665943825,1.7885713397,1.2345367186
H,0,-2.0246695785,-2.1549393665,-2.5095096572
H,0,-2.4336169768,1.5405820316,-2.4960973801
C,0,1.505792022,-2.1948820974,0.6982895279
C,0,1.505792022,-2.1948820974,-0.6982895279
C,0,2.3541750395,-3.0152322494,1.4235490757
C,0,2.3541750395,-3.0152322494,-1.4235490757
C,0,3.221924037,-3.8466181838,0.6973954837
H,0,2.3694044408,-3.0092833637,2.5092325022
C,0,3.221924037,-3.8466181838,-0.6973954837
H,0,2.3694044408,-3.0092833637,-2.5092325022
H,0,3.9097141314,-4.4963896605,1.2293643679
H,0,3.9097141314,-4.4963896605,-1.2293643679
C,0,0.9606811227,2.516726773,0.7062541075
C,0,1.635646527,3.5018407644,1.4100193361
C,0,0.9606811227,2.516726773,-0.7062541075
C,0,2.3223798976,4.4948758903,0.6957477144
H,0,1.6451051641,3.4974340846,2.495863878
C,0,1.635646527,3.5018407644,-1.4100193361
C,0,2.3223798976,4.4948758903,-0.6957477144
H,0,2.8588930467,5.2692702453,1.2348315795
H,0,1.6451051641,3.4974340846,-2.495863878
H,0,2.8588930467,5.2692702453,-1.2348315795
C,0,-2.0185504549,-2.1539690256,1.4240110144
H,0,-2.0246695785,-2.1549393665,2.5095096572
C,0,-2.4336507115,1.5414392139,1.4104305903
H,0,-2.4336169768,1.5405820316,2.4960973801
C,0,0.8327268369,0.1496123701,1.4503364025
H,0,1.9019757211,0.2512326632,1.6278030587
C,0,0.8327268369,0.1496123701,-1.4503364025
H,0,1.9019757211,0.2512326632,-1.6278030587

Ar = benzene-1,2-diyl, R^1 = F, R^2 = H, localised structure

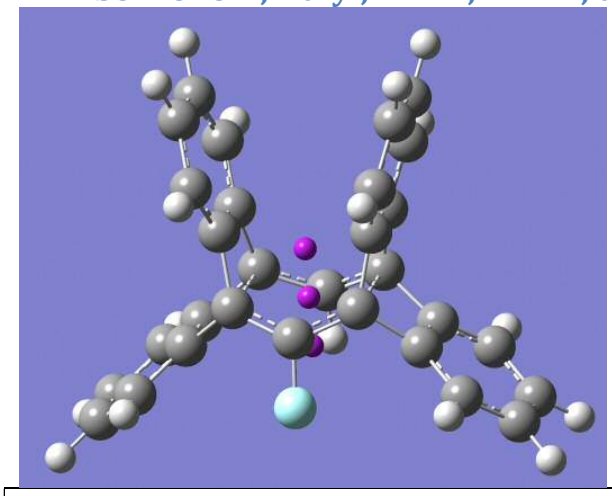


RB3LYP/6-311+G(d) level:
Allyl-allyl C–C bond length: 1.76476 Å
Distance between terminal allyl C atoms: 2.45277 Å
Sum of bond angles for tertiary chloro-conjugated vinyl C: 351.852º
Sum of bond angles for tertiary non-conjugated vinyl C: 350.900º
Electronic energy: -1253.373035 Hartrees
Gibbs free energy: -1253.053910 Hartrees
No imaginary frequencies
Point group: C_1

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1253.373035 Hartrees
<S^2> (singlet): 0.0000
NICS(0): -2.1427 ppm
NICS(1): 0.0602 ppm
NICS(–1): -2.8099 ppm
Isotropic magnetic susceptibility: -130.9474 cgs-ppm

Cartesian coordinates:
C,0,0.0366858903,1.3821113952,1.2104013222
C,0,0.0483220598,1.3663545517,-1.2422859155
C,0,0.2902324347,-1.1129582688,-0.9170206686
C,0,0.2905504269,-1.1135596943,0.8477413163
C,0,-1.122822111,-1.6537029919,0.6621784645
C,0,-1.1239814431,-1.6571146558,-0.7290773819
C,0,-2.1697784988,-2.1904367826,-1.4627152545
C,0,-3.2397034914,-2.7089801725,0.6741221898
C,0,-3.2417391386,-2.713433932,-0.7247739422
H,0,-4.0901051109,-3.1269958213,1.2037085564
H,0,-4.0942316637,-3.1345706859,-1.2486196802
C,0,-1.3568535764,1.4222874656,-0.7248342335
C,0,-1.3616821293,1.4215566401,0.6759495012
C,0,-2.5449286649,1.528497257,-1.4356389561
C,0,-3.7469301802,1.6299761717,-0.7278723502
C,0,-3.7517159708,1.6283851334,0.6660567823
H,0,-4.6838845527,1.7125865614,-1.2694857337
H,0,-4.6919775228,1.7101570552,1.2019105529
H,0,-2.1805218426,-2.2032704619,-2.5478364697
H,0,-2.5413032378,1.528559567,-2.5210883394
C,0,1.360971438,-2.1908991327,0.6638678677
C,0,1.3501143452,-2.2000711521,-0.7279873279
C,0,2.163827037,-3.0428109592,1.4015814215
C,0,2.1395600953,-3.0669554544,-1.4644911037
C,0,2.9753658422,-3.9213799361,0.6679486437
H,0,2.1914772708,-3.0314477432,2.4861614026
C,0,2.963557211,-3.9337179637,-0.7301852188
H,0,2.1434678759,-3.080254222,-2.5499426351
H,0,3.6331508297,-4.6049189612,1.195567681
H,0,3.6108907109,-4.6279196268,-1.256922797
C,0,0.8361146299,2.560564049,0.6885988437
C,0,1.5184323699,3.5473832119,1.3820356359
C,0,0.8324660882,2.5584045355,-0.7319640567
C,0,2.1993564279,4.5418776729,0.6678588409
H,0,1.5353668806,3.5400723098,2.466969988
C,0,1.5060541692,3.547770305,-1.4317792381
C,0,2.1932657,4.5422235245,-0.7232015945
H,0,2.7365662491,5.3159689973,1.2064268358
H,0,1.5081463584,3.5452875835,-2.5173599125
H,0,2.7240306645,5.3178436564,-1.266127432
C,0,-2.1651038417,-2.1814183974,1.4046674356
H,0,-2.1709877017,-2.1878073244,2.4898371769
C,0,-2.5538012891,1.5261502877,1.3802865662
H,0,-2.5549166808,1.526842738,2.4656707557
C,0,0.6621927262,0.2046520441,1.4101886751
C,0,0.7054046606,0.2041245708,-1.4582258505
H,0,1.7748337856,0.2774217217,-1.6464393755
F,0,1.99548276,0.2614019636,1.708423782
Bq,0,0.338898033,0.155120766,-0.024866854
Bq,0,-0.656399791,0.058657022,-0.033641089
Bq,0,1.334195857,0.251584511,-0.016092618

Ar = benzene-1,2-diyl, R^1 = F, R^2 = H, delocalised structure

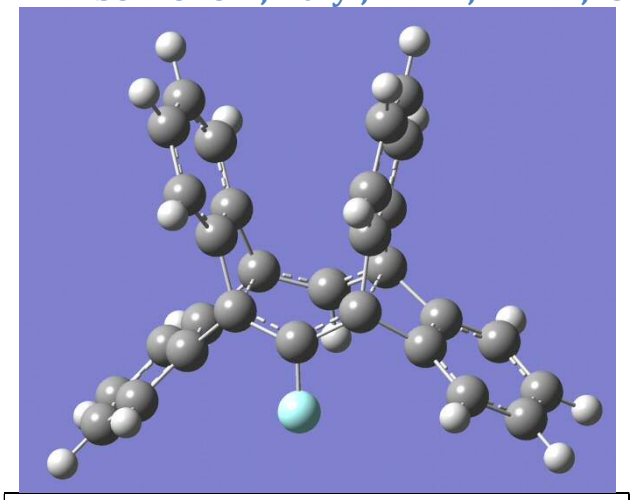


RB3LYP/6-311+G(d) level:
C¨C bond length: 2.28654 Å
Electronic energy: -1253.370720 Hartrees
Gibbs free energy: -1253.053148 Hartrees
No imaginary frequencies
Point group: C_s

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1253.373531 Hartrees
<S^2> (singlet): 0.5067
NICS(0): -7.1746 ppm
NICS(1): -1.2508 ppm
NICS(–1): -4.5096 ppm
Isotropic magnetic susceptibility: -97.1960 cgs-ppm
Electronic energy (triplet): -1253.354546 Hartrees
<S^2> (triplet): 2.0630

Cartesian coordinates:
C,0,0.2760228632,-1.0699067694,1.2573191608
C,0,0.1782250457,1.2145223184,1.2478315394
C,0,0.178225046,1.2145223184,-1.2478315394
C,0,0.2760228634,-1.0699067694,-1.2573191608
C,0,-1.15402211,-0.680015634,-1.5218932206
C,0,-1.2153634407,0.7116626186,-1.5239653892
C,0,-2.3864595276,1.3802259603,-1.8483329325
C,0,-3.4526189451,-0.7826448286,-2.1624304786
C,0,-3.5133196373,0.6111268479,-2.1652309925
H,0,-4.339108008,-1.3572127841,-2.4115088808
H,0,-4.4465264917,1.105298382,-2.4162653688
C,0,-1.215363441,0.7116626186,1.523965389
C,0,-1.1540221103,-0.680015634,1.5218932204
C,0,-2.3864595279,1.3802259603,1.8483329321
C,0,-3.5133196376,0.6111268479,2.1652309919
C,0,-3.4526189454,-0.7826448286,2.162430478
H,0,-4.4465264921,1.105298382,2.416265368
H,0,-4.3391080085,-1.3572127841,2.4115088801
H,0,-2.4358745303,2.464701676,-1.8493293647
H,0,-2.4358745307,2.464701676,1.8493293643
C,0,1.1965811472,-0.5814725359,-2.3622902219
C,0,1.1253742106,0.8188353434,-2.3663501766
C,0,1.9933493627,-1.2575801002,-3.2716977883
C,0,1.8433021716,1.5691812313,-3.2841280045
C,0,2.7262528169,-0.5026837152,-4.1990631829
H,0,2.0692260703,-2.3400666404,-3.2540140816
C,0,2.6522481997,0.8884271186,-4.2061041679
H,0,1.7982799782,2.6540954659,-3.2812271775
H,0,3.3653224105,-1.0089849845,-4.9154422491
H,0,3.2324038869,1.4529344962,-4.9291464775
C,0,1.1965811468,-0.5814725359,2.3622902221
C,0,1.9933493622,-1.2575801002,3.2716977887
C,0,1.1253742102,0.8188353434,2.3663501768
C,0,2.7262528162,-0.5026837152,4.1990631833
H,0,2.0692260698,-2.3400666404,3.254014082
C,0,1.8433021711,1.5691812313,3.2841280048
C,0,2.652248199,0.8884271186,4.2061041684
H,0,3.3653224096,-1.0089849845,4.9154422497
H,0,1.7982799777,2.6540954659,3.2812271778
H,0,3.232403886,1.4529344962,4.9291464781
C,0,-2.2628937506,-1.4490402435,-1.8432922327
H,0,-2.2163353259,-2.5335932045,-1.8419778
C,0,-2.2628937509,-1.4490402435,1.8432922323
H,0,-2.2163353262,-2.5335932045,1.8419777996
C,0,0.7964957471,-1.3645817036,0.0000000001
C,0,0.7048380586,1.5530857812,0.0000000001
F,0,2.1500940399,-1.5854336473,0.0000000002
H,0,1.7706861717,1.7725208886,0.0000000002
Bq,0,0.401638271,0.079622529,0.
Bq,0,1.400935022,0.117119234,0.
Bq,0,-0.597658481,0.042125824,0.

Ar = benzene-1,2-diyl, R^1 = F, R^2 = H, localised ⇌ delocalised TS

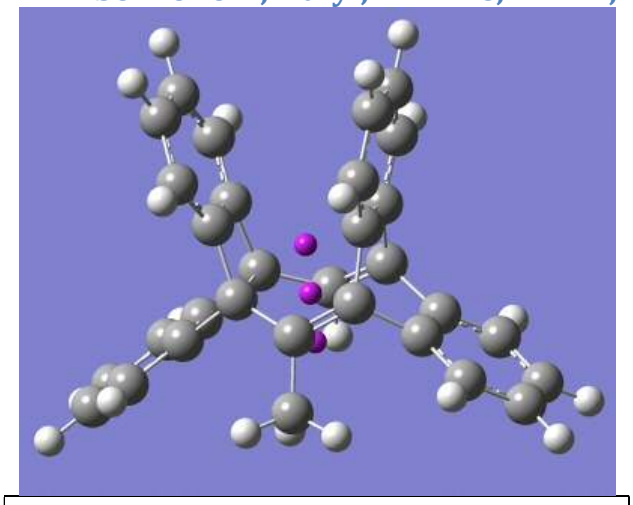


RB3LYP/6-311+G(d) level:
C···C bond lengths: 2.12311 Å, 2.37263 Å
Electronic energy: -1253.370480 Hartrees
Gibbs free energy: -1253.052563 Hartrees
Imaginary frequency: 186.1*i* cm^{-1}
Point group: C_1

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1253.370914 Hartrees
<S^2> (singlet): 0.2627
Electronic energy (triplet): -1253.343737 Hartrees
<S^2> (triplet): 2.0519

Cartesian coordinates:
C,0,0.2509788673,1.3120904418,1.1944689078
C,0,0.2562638753,1.2998849535,-1.17812125
C,0,0.3856539554,-1.1901340564,-1.0613206709
C,0,0.3808582647,-1.1959370748,1.0617773887
C,0,-1.0305472869,-1.5806523791,0.6896841896
C,0,-1.0280488482,-1.5846681848,-0.7005265236
C,0,-2.1293833521,-2.0069187479,-1.4285878161
C,0,-3.2594044039,-2.4145851403,0.6913449251
C,0,-3.2562951875,-2.4199165324,-0.7050331475
H,0,-4.147990414,-2.7405076934,1.2226423898
H,0,-4.1428144364,-2.7496085443,-1.2375245886
C,0,-1.1589967563,1.4675401445,-0.696237264
C,0,-1.1599888907,1.4671375317,0.6997986281
C,0,-2.3268017589,1.6933741343,-1.410906602
C,0,-3.5102941892,1.9141573332,-0.6965908826
C,0,-3.5114996258,1.9139498078,0.6979363439
H,0,-4.4370845513,2.0886079157,-1.2339544567
H,0,-4.4390231331,2.0883661754,1.2339327956
H,0,-2.1319872831,-2.011270597,-2.5140428213
H,0,-2.3265965004,1.6933500368,-2.496532242
C,0,1.3847168187,-2.2774041363,0.6972738681
C,0,1.3773769981,-2.2832280971,-0.699202135
C,0,2.178821529,-3.1518940953,1.4198421654
C,0,2.1587484551,-3.1687842932,-1.4236431022
C,0,2.9786191442,-4.0479506214,0.6948901637
H,0,2.2065207127,-3.1335211457,2.5045145359
C,0,2.9686358851,-4.0571263485,-0.6997993088
H,0,2.1654704058,-3.169178222,-2.5093642073
H,0,3.6229970815,-4.7401210067,1.2275212435
H,0,3.603602071,-4.7576108518,-1.232944329
C,0,1.1235017676,2.455133336,0.7063468336
C,0,1.8448515206,3.4064049734,1.4096582649
C,0,1.115156155,2.4569982587,-0.7018510168
C,0,2.5640460819,4.3716750825,0.6910468457
H,0,1.8692144719,3.3926942089,2.4945899923
C,0,1.8221053243,3.4140576643,-1.4130391963
C,0,2.5527942288,4.3760844815,-0.7011443418
H,0,3.1394675656,5.1198569384,1.2268293054
H,0,1.8233218219,3.4109624599,-2.4988656624
H,0,3.1176300396,5.1288385629,-1.2418789019
C,0,-2.1352906761,-1.9968893966,1.4163357128
H,0,-2.1413318537,-1.9951383339,2.5017401491
C,0,-2.3287924752,1.6931579178,1.4131552459
H,0,-2.3283818435,1.6943665386,2.4987238897
C,0,0.820848901,0.0923380237,1.4590354051
C,0,0.8605491573,0.0931005246,-1.4474940377
H,0,1.9340891527,0.1366303712,-1.6203441707
F,0,2.1624792442,0.1301614519,1.7386603357

Ar = benzene-1,2-diyl, R^1 = Me, R^2 = H, localised structure

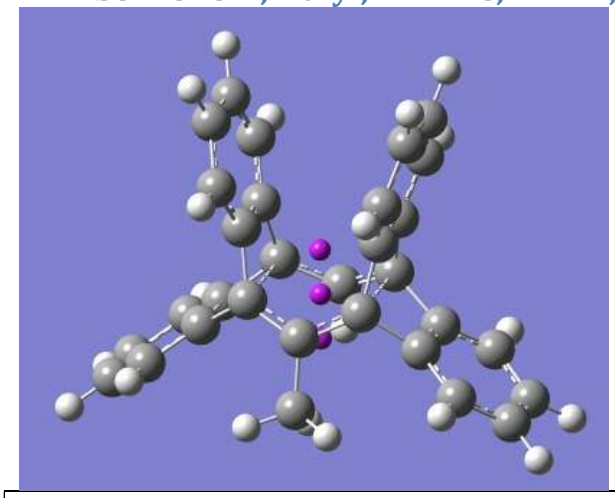


RB3LYP/6-311+G(d) level:
Allyl-allyl C–C bond length: 1.76641 Å
Distance between terminal allyl C atoms: 2.45333 Å
Sum of bond angles for terminal methylallyl C: 351.437°
Sum of bond angles for terminal non-substituted allyl C: 350.921°
Electronic energy: -1193.421983 Hartrees
Gibbs free energy: -1193.067420 Hartrees
No imaginary frequencies
Point group: C_1

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1193.421983 Hartrees
<S^2> (singlet): 0.0000
NICS(0): -2.2012 ppm
NICS(1): 0.9353 ppm
NICS(–1): -3.2145 ppm
Isotropic magnetic susceptibility: -104.2974 cgs-ppm

Cartesian coordinates:
C,0,0.1864012025,1.3697484124,1.1319289718
C,0,0.0582882773,1.366670422,-1.3180526591
C,0,0.3575459465,-1.0986757731,-0.9703443824
C,0,0.4563130665,-1.0890415255,0.793276152
C,0,-0.965110752,-1.6378537668,0.6879991229
C,0,-1.0419502049,-1.6492655499,-0.7012837653
C,0,-2.1178987516,-2.2000780507,-1.3758407206
C,0,-3.0639167949,-2.7259564035,0.815899011
C,0,-3.1418497423,-2.7357275111,-0.5805664656
H,0,-3.8782538878,-3.1542197844,1.3922321798
H,0,-4.0148837642,-3.1711835017,-1.0568538708
C,0,-1.3183470819,1.3862283378,-0.7281542541
C,0,-1.2402424389,1.3706569844,0.6700401277
C,0,-2.5451814514,1.4787079119,-1.3708673664
C,0,-3.7075234624,1.5519737854,-0.5962117524
C,0,-3.6324309469,1.5358468136,0.7955194962
H,0,-4.6749030162,1.6237690629,-1.0832663344
H,0,-4.5420657648,1.5951042791,1.3848302798
H,0,-2.1857827056,-2.2184190105,-2.4589670353
H,0,-2.6022276508,1.4910057163,-2.4548863343
C,0,1.4802632155,-2.2076170487,0.5492965423
C,0,1.413320316,-2.1959442414,-0.8422558085
C,0,2.2728506427,-3.1124917477,1.2358081982
C,0,2.1463281358,-3.0725345044,-1.6241423482
C,0,3.0277200914,-4.0028446393,0.4559724037
H,0,2.3314597715,-3.1403631925,2.319469785
C,0,2.9698313777,-3.9808504983,-0.9404403557
H,0,2.1034162787,-3.0675483502,-2.7089694087
H,0,3.6739332277,-4.7244695113,0.9461175572
H,0,3.5733388498,-4.6845811403,-1.5052752732
C,0,0.870381267,2.6091255643,0.5742036552
C,0,1.485711258,3.6680849026,1.2258561186
C,0,0.8157134165,2.591714939,-0.8482975624
C,0,2.066087826,4.7004034982,0.476385028
H,0,1.5236788538,3.694394949,2.3106362742
C,0,1.390106595,3.6178771632,-1.5828021939
C,0,2.0240873566,4.6732183843,-0.91336788
H,0,2.5489879913,5.5275902228,0.9870486666
H,0,1.3492796839,3.6016827328,-2.6675967775
H,0,2.4760560131,5.4777142814,-1.4848570366
C,0,-1.9588455046,-2.1797473707,1.4851893046
H,0,-1.9071885553,-2.1826496661,2.5694062847
C,0,-2.3940999278,1.4474834395,1.4395276222
H,0,-2.3352004626,1.437511365,2.5234871681
C,0,0.9100579163,0.2353961278,1.3325852685
C,0,0.7286406285,0.21521406,-1.5484192981
H,0,1.78610499,0.3044399112,-1.7921949422
C,0,2.383658226,0.3231857972,1.6597655384
H,0,2.646926801,-0.390519403,2.4456606638
H,0,3.0084849435,0.0728622662,0.7947764948
H,0,2.6647713408,1.3173542006,2.0013017405
Bq,0,0.449541173,0.166551954,-0.096504325
Bq,0,-0.542452376,0.055165332,-0.036991134
Bq,0,1.441534722,0.277938576,-0.15601751

Ar = benzene-1,2-diyl, R^1 = Me, R^2 = H, delocalised structure

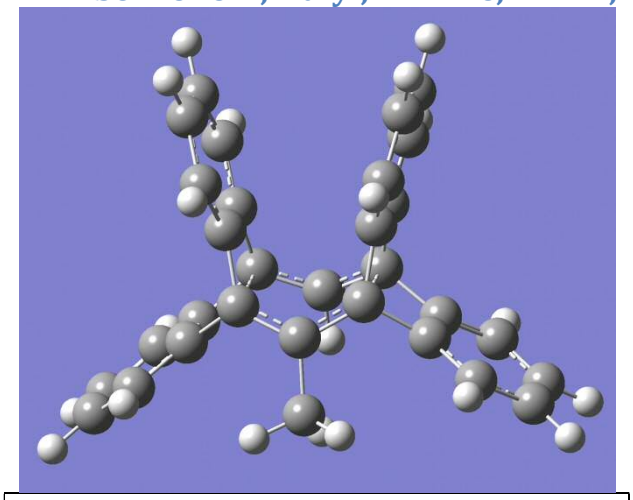


RB3LYP/6-311+G(d) level:
C¨C bond length: 2.28525 Å
Electronic energy: -1193.419008 Hartrees
Gibbs free energy: -1193.066402 Hartrees
No imaginary frequencies
Point group: C_s

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1193.421400 Hartrees
<S^2> (singlet): 0.4676
NICS(0): -7.5722 ppm
NICS(1): -0.7971 ppm
NICS(–1): -5.5466 ppm
Isotropic magnetic susceptibility: -99.7127 cgs-ppm
Electronic energy (triplet): -1193.400843 Hartrees
<S^2> (triplet): 2.0649

Cartesian coordinates:
C,0,0.3189318159,-1.0533957193,1.2366937679
C,0,0.167662932,1.2268212477,1.2459498327
C,0,0.1676629339,1.2268212477,-1.2459498324
C,0,0.3189318178,-1.0533957193,-1.2366937675
C,0,-1.1252202157,-0.6995124592,-1.4890218785
C,0,-1.2176692445,0.6901624463,-1.5060443387
C,0,-2.4031854959,1.3293237897,-1.8365084105
C,0,-3.4215911181,-0.8586440167,-2.1302225926
C,0,-3.5135201898,0.5332668247,-2.1459883408
H,0,-4.2950497926,-1.4553142576,-2.373929557
H,0,-4.4573353013,1.0044690879,-2.4018282479
C,0,-1.2176692468,0.6901624463,1.5060443368
C,0,-1.125220218,-0.6995124592,1.4890218768
C,0,-2.4031854987,1.3293237897,1.8365084068
C,0,-3.5135201931,0.5332668247,2.1459883354
C,0,-3.4215911214,-0.8586440167,2.1302225874
H,0,-4.457335305,1.0044690879,2.4018282411
H,0,-4.2950497962,-1.4553142576,2.3739295505
H,0,-2.4757946402,2.4125669846,-1.849010693
H,0,-2.475794643,2.4125669846,1.8490106893
C,0,1.1679814153,-0.5555405416,-2.4006312284
C,0,1.0924474468,0.8463245353,-2.3867100409
C,0,1.8940859299,-1.215451754,-3.3808136739
C,0,1.7556879314,1.6084554083,-3.3359850187
C,0,2.5703518572,-0.4481406861,-4.3410124727
H,0,1.9552122583,-2.2995344603,-3.401660304
C,0,2.5077083922,0.9431095278,-4.3156830913
H,0,1.7036149507,2.6930343342,-3.3195616824
H,0,3.1525249688,-0.9451635187,-5.1106074969
H,0,3.0432068434,1.5185473584,-5.0641979832
C,0,1.1679814116,-0.5555405416,2.4006312302
C,0,1.8940859247,-1.215451754,3.3808136768
C,0,1.0924474432,0.8463245353,2.3867100426
C,0,2.5703518506,-0.4481406861,4.3410124766
H,0,1.9552122531,-2.2995344603,3.401660307
C,0,1.7556879263,1.6084554083,3.3359850214
C,0,2.5077083856,0.9431095278,4.3156830951
H,0,3.152524961,-0.9451635187,5.1106075017
H,0,1.7036149456,2.6930343342,3.319561685
H,0,3.0432068357,1.5185473584,5.0641979878
C,0,-2.2172496973,-1.4951428809,-1.8043843041
H,0,-2.1477343411,-2.5786279473,-1.7929403754
C,0,-2.2172497001,-1.4951428809,1.8043843007
H,0,-2.1477343438,-2.5786279473,1.7929403721
C,0,0.9173465661,-1.3540525594,0.0000000007
C,0,0.6927333331,1.5721700441,0.0000000005
C,0,2.4175195679,-1.6048329097,0.0000000018
H,0,2.728059214,-2.1652567859,-0.8805563805
H,0,2.9794671254,-0.6635201882,0.0000000023
H,0,2.7280592126,-2.1652567859,0.8805563846
H,0,1.7530759598,1.8195598424,0.0000000013
Bq,0,0.4305449,0.094161424,0.
Bq,0,-0.566837627,0.021855855,0.
Bq,0,1.427927427,0.166466992,0.

Ar = benzene-1,2-diyl, R^1 = Me, R^2 = H, localised ⇌ delocalised TS

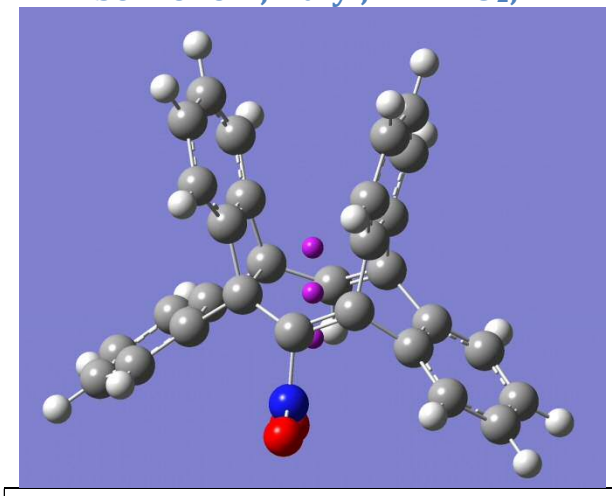


RB3LYP/6-311+G(d) level:
C···C bond lengths: 2.16173 Å, 2.36012 Å
Electronic energy: -1193.419017 Hartrees
Gibbs free energy: -1193.065765 Hartrees
Imaginary frequency: 139.1*i* cm^{-1}
Point group: C_1

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1193.419442 Hartrees
<S^2> (singlet): 0.2190
Electronic energy (triplet): -1193.390507 Hartrees
<S^2> (triplet): 2.0611

Cartesian coordinates:
C,0,0.3070482778,-0.9902003991,1.2049982044
C,0,0.1895577007,1.1683297498,1.2057664769
C,0,0.1970658987,1.2640055202,-1.2838847526
C,0,0.3286851939,-1.0923826597,-1.2672077665
C,0,-1.1028783823,-0.6854987726,-1.4981966419
C,0,-1.1816961877,0.7073072242,-1.5206861777
C,0,-2.3700305915,1.3527734017,-1.8300190843
C,0,-3.4179812434,-0.8222760684,-2.0928186359
C,0,-3.4957243981,0.5699238767,-2.1137758861
H,0,-4.3011548773,-1.4123272247,-2.3167756509
H,0,-4.4384776533,1.051390473,-2.353979517
C,0,-1.2203782422,0.7070506402,1.4947693951
C,0,-1.145364623,-0.6814773072,1.4846573772
C,0,-2.3867554724,1.3686756291,1.8461317183
C,0,-3.4978070555,0.5836186042,2.1829195184
C,0,-3.4228594387,-0.8103183417,2.1738819423
H,0,-4.4316442797,1.0653484488,2.4553298707
H,0,-4.2996048044,-1.3927329551,2.4394082126
H,0,-2.4301165593,2.4367434961,-1.8471435092
H,0,-2.4484396557,2.4525492612,1.8539112884
C,0,1.1782515467,-0.5723615593,-2.420770711
C,0,1.1175967702,0.8354193058,-2.4107817073
C,0,1.9051598427,-1.2359178507,-3.3984107343
C,0,1.7975397336,1.582521794,-3.3605490203
C,0,2.596487846,-0.4811075063,-4.3570743008
H,0,1.9520988292,-2.3207849087,-3.416969553
C,0,2.5490922447,0.9100423793,-4.3349671847
H,0,1.7546794249,2.6675367388,-3.3473745247
H,0,3.1754847484,-0.9879353663,-5.1226648962
H,0,3.0931660662,1.4797096725,-5.0817085464
C,0,1.1646091832,-0.557054922,2.3894425929
C,0,1.8698696767,-1.230191097,3.3749978319
C,0,1.1057440089,0.8408106985,2.3705240949
C,0,2.5440882689,-0.4636602847,4.3379949038
H,0,1.9206112443,-2.3145806158,3.4002249431
C,0,1.7649558537,1.605017901,3.32029914
C,0,2.4978163333,0.9293310574,4.3081268344
H,0,3.1148395372,-0.9625673891,5.1149200183
H,0,1.7285175078,2.6901270124,3.3010160222
H,0,3.0344877121,1.4982557456,5.0607972547
C,0,-2.2131933146,-1.4666027345,-1.7875520796
H,0,-2.1531274492,-2.5506375269,-1.7727280551
C,0,-2.2347864018,-1.4678526451,1.8276972948
H,0,-2.1809833948,-2.5521825447,1.8218039647
C,0,0.9128539685,-1.3563665668,-0.0353930772
C,0,0.7210136054,1.5661529311,-0.0439113076
C,0,2.406889595,-1.6310337174,0.0049154956
H,0,2.7603330542,-2.0690867084,-0.9261661796
H,0,2.9786091939,-0.7113143519,0.1742438245
H,0,2.6600991267,-2.3153945691,0.8156237746
H,0,1.7835177813,1.8037196218,-0.0287850948

Ar = benzene-1,2-diyl, $R^1 = NO_2$, $R^2 = H$, localised structure

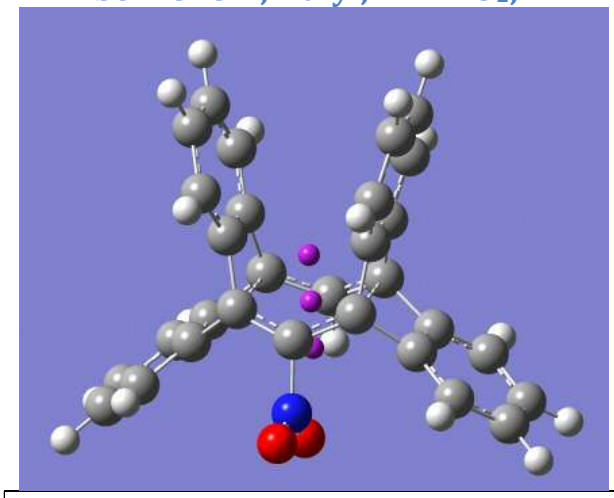


RB3LYP/6-311+G(d) level:
Allyl-allyl C–C bond length: 1.76478 Å
Distance between terminal allyl C atoms: 2.43775 Å
Sum of bond angles for terminal nitroallyl C: 351.963º
Sum of bond angles for terminal non-substituted allyl C: 351.172º
Electronic energy: -1358.657686 Hartrees
Gibbs free energy: -1358.331719 Hartrees
No imaginary frequencies
Point group: C_1

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1358.657686 Hartrees
<S^2> (singlet): 0.0000
NICS(0): -2.0146 ppm
NICS(1): 0.6141 ppm
NICS(–1): -2.4320 ppm
Isotropic magnetic susceptibility: -106.8726 cgs-ppm

Cartesian coordinates:
C,0,0.1708303489,1.3837607066,1.2444895347
C,0,0.129960818,1.3730304869,-1.1928963554
C,0,0.3789722511,-1.1046204736,-0.8620735718
C,0,0.4405534163,-1.1073364494,0.9016303394
C,0,-0.9866202382,-1.6317063764,0.7657409393
C,0,-1.0352214181,-1.6317477638,-0.6243241119
C,0,-2.1072480979,-2.1622560802,-1.3209639176
C,0,-3.1037493382,-2.6808243227,0.8514550325
C,0,-3.1543295719,-2.6832735398,-0.5464854591
H,0,-3.935442917,-3.0986260943,1.4099900386
H,0,-4.0247958093,-3.1029396676,-1.0410074551
C,0,-1.2668314916,1.424730769,-0.6513815989
C,0,-1.2412325087,1.4160431162,0.7473121385
C,0,-2.4713121473,1.5367525948,-1.3321739097
C,0,-3.6548531578,1.6374960361,-0.593456066
C,0,-3.6260320639,1.6270642133,0.80026262
H,0,-4.6048135156,1.7253702211,-1.1107855658
H,0,-4.5527062379,1.707174942,1.359235792
H,0,-2.1549203962,-2.176829954,-2.4050273555
H,0,-2.494524771,1.5428347009,-2.4172394946
C,0,1.472596695,-2.2159434499,0.683165851
C,0,1.4197174682,-2.2155868345,-0.7082582754
C,0,2.2583212981,-3.1041169004,1.3948768099
C,0,2.1569018525,-3.1041518046,-1.4699522088
C,0,3.0198545437,-4.0042892988,0.6332255174
H,0,2.3126982879,-3.1063724143,2.4787087583
C,0,2.9714221528,-4.0035619414,-0.7633845658
H,0,2.1300366999,-3.1113468648,-2.5550611222
H,0,3.6656171862,-4.7150532897,1.1388907216
H,0,3.5804930172,-4.714701545,-1.3124986028
C,0,0.9313851667,2.5900700463,0.7243835853
C,0,1.5944925897,3.5939733508,1.4106567502
C,0,0.9088232375,2.5765629074,-0.6969503661
C,0,2.2478390908,4.5974387252,0.6826325923
H,0,1.6223367298,3.5929656148,2.49502367
C,0,1.5574275484,3.5748702736,-1.405796826
C,0,2.230913038,4.5864867994,-0.7076230895
H,0,2.773694792,5.385503374,1.2114323969
H,0,1.5516643784,3.5662145441,-2.4911765835
H,0,2.7433494752,5.3677313556,-1.2597241582
C,0,-2.0027980289,-2.157059485,1.5445938111
H,0,-1.9686908532,-2.166652871,2.629147752
C,0,-2.4122454741,1.5163865457,1.4858304843
H,0,-2.3868633445,1.508734222,2.5707027004
C,0,0.808093202,0.2141508837,1.4755318468
C,0,0.7876320504,0.2103569714,-1.4110359684
H,0,1.8538007823,0.2825341732,-1.6098843486
N,0,2.2587870839,0.3445946014,1.8225601158
O,0,3.0812041387,0.190421784,0.9340243665
O,0,2.5173151319,0.5930231816,2.9914533715
Bq,0,0.452673681,0.161557021,0.025940971
Bq,0,-0.542036792,0.060246497,0.042889487
Bq,0,1.447384154,0.262867545,0.008992454

Ar = benzene-1,2-diyl, $R^1 = NO_2$, $R^2 = H$, delocalised structure

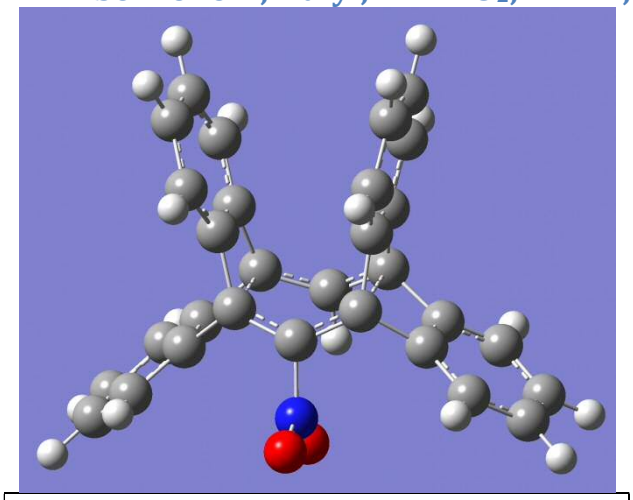


RB3LYP/6-311+G(d) level:
C¨C bond length: 2.27597 Å
Electronic energy: -1358.655707 Hartrees
Gibbs free energy: -1358.330828 Hartrees
No imaginary frequencies
Point group: C_s

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1358.657432 Hartrees
<S^2> (singlet): 0.4310
NICS(0): -6.8963 ppm
NICS(1): -1.1613 ppm
NICS(–1): -3.2201 ppm
Isotropic magnetic susceptibility: -162.9477 cgs-ppm
Electronic energy (triplet): -1358.636064 Hartrees
<S^2> (triplet): 2.0640

Cartesian coordinates:
C,0,0.2621906333,-0.7810264338,1.2528984118
C,0,-0.1751271894,1.4429685328,1.0463532815
C,0,-0.2400143657,1.2172109069,-1.4321843478
C,0,0.1965026369,-1.0095680038,-1.2562112838
C,0,-1.2862644685,-0.863708487,-1.4874862059
C,0,-1.5536405277,0.4976568343,-1.6028718106
C,0,-2.820262741,0.9561254461,-1.9323064623
C,0,-3.5589053938,-1.3596968792,-2.019682549
C,0,-3.8271933891,0.0043143874,-2.1372862453
H,0,-4.3559941254,-2.0778602237,-2.1831038115
H,0,-4.8303440095,0.331709131,-2.3911169445
C,0,-1.4747097686,0.7722732115,1.4120837914
C,0,-1.2072498612,-0.5888007817,1.5306673508
C,0,-2.7246827349,1.288667372,1.7186082066
C,0,-3.7151089775,0.3942766274,2.1440390031
C,0,-3.4468407855,-0.9698045202,2.2608748181
H,0,-4.7052719818,0.7668572083,2.3862980577
H,0,-4.2309712563,-1.6428849748,2.5924131318
H,0,-3.0319135112,2.0170110103,-2.0220660743
H,0,-2.9364027709,2.3493128687,1.6262135061
C,0,0.9800382892,-0.5061253126,-2.4577869195
C,0,0.709242009,0.8663641122,-2.5639558119
C,0,1.8047788801,-1.1469362229,-3.3671864711
C,0,1.2642655545,1.6255471265,-3.5802892175
C,0,2.3731721675,-0.3794645906,-4.3949918967
H,0,2.0277048721,-2.2052795228,-3.27734759
C,0,2.1085342934,0.983598794,-4.4991228709
H,0,1.0683635531,2.6906106241,-3.6582201927
H,0,3.0334845213,-0.8540742754,-5.1134689186
H,0,2.5647933066,1.5586097778,-5.298482101
C,0,1.1046362,-0.0726253182,2.3015259945
C,0,1.9784773584,-0.5426071665,3.2676325639
C,0,0.8332296093,1.2977420161,2.1720591148
C,0,2.5958072723,0.3951237008,4.1090790623
H,0,2.2014409293,-1.6008198825,3.3589050423
C,0,1.4366520108,2.2253125419,3.0044279392
C,0,2.3304897232,1.7558229072,3.978992607
H,0,3.2947503456,0.0549165594,4.8661878177
H,0,1.2400259586,3.2878572648,2.8988438245
H,0,2.824892554,2.4635430194,4.6366271405
C,0,-2.2746133396,-1.8140959932,-1.6944480847
H,0,-2.0657610046,-2.8752779609,-1.6027097802
C,0,-2.179023346,-1.4815213358,1.9568239069
H,0,-1.9701991614,-2.542802351,2.0474740378
C,0,0.780450103,-1.1231697072,0.0046715098
C,0,0.2659161454,1.7472553188,-0.2433086565
N,0,2.2858270742,-1.2136627207,-0.026496032
O,0,2.7552259056,-2.3380006723,0.0636231257
O,0,2.9293762911,-0.1844165963,-0.1370899411
H,0,1.2872233518,2.1136832132,-0.3034221758
Bq,0,0.181652994,0.248945102,-0.104630181
Bq,0,-0.800802339,0.067299459,-0.062364611
Bq,0,1.164108327,0.430590746,-0.146895751

Ar = benzene-1,2-diyl, $R^1 = NO_2$, $R^2 = H$, localised ⇌ delocalised TS

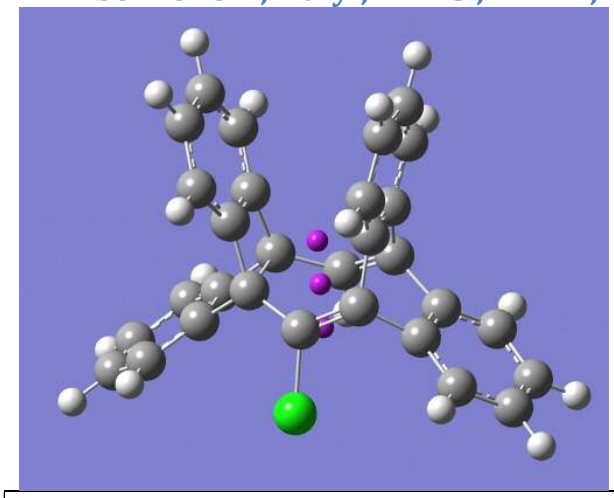


RB3LYP/6-311+G(d) level:
C···C bond lengths: 2.11780 Å, 2.35767 Å
Electronic energy: -1358.655406 Hartrees
Gibbs free energy: -1358.330239 Hartrees
Imaginary frequency: 179.4*i* cm^{-1}
Point group: C_1

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1358.655410 Hartrees
<S^2> (singlet): 0.0233
Electronic energy (triplet): -1358.620011 Hartrees
<S^2> (triplet): 2.0580

Cartesian coordinates:
C,0,0.2311355236,1.32114625,1.2811835982
C,0,0.1692115716,1.4394693163,-1.0726980174
C,0,0.3397449779,-1.047253564,-1.0995088981
C,0,0.4030318132,-1.1763487433,1.0134022165
C,0,-1.0187530516,-1.5543555542,0.6664872952
C,0,-1.0595306054,-1.4770190204,-0.7205936225
C,0,-2.178138083,-1.8726710695,-1.4368523822
C,0,-3.2334767075,-2.4200491709,0.6908201897
C,0,-3.2750503354,-2.3440838534,-0.7028984907
H,0,-4.0997005492,-2.7904730739,1.2296514085
H,0,-4.1733730825,-2.656855666,-1.2256339899
C,0,-1.2372453876,1.5521594156,-0.5502573166
C,0,-1.1999599415,1.4725160809,0.841691899
C,0,-2.4281338673,1.7970795352,-1.2184233187
C,0,-3.5935299704,1.9553077752,-0.4589326361
C,0,-3.5548917842,1.8738774246,0.9327184896
H,0,-4.5381604747,2.1441776419,-0.958860202
H,0,-4.4693821749,1.9998363941,1.5033248629
H,0,-2.2158838649,-1.8152896246,-2.5200643981
H,0,-2.4594588354,1.8592921564,-2.3017086128
C,0,1.3870718859,-2.2437677324,0.5604168704
C,0,1.3436175234,-2.1570175265,-0.8335211322
C,0,2.1786263098,-3.177728579,1.2063836132
C,0,2.0969653089,-3.0005183246,-1.6317132476
C,0,2.9511726204,-4.0315940373,0.4040806075
H,0,2.2265459613,-3.237457214,2.2889334961
C,0,2.911936646,-3.9441261754,-0.9866767316
H,0,2.0787367498,-2.9303798121,-2.7149253793
H,0,3.595877357,-4.7669071612,0.8744479578
H,0,3.5265424924,-4.6133863276,-1.5801556265
C,0,1.0475455022,2.5278236274,0.8477173156
C,0,1.7376865724,3.4735006211,1.5879044327
C,0,1.0089461385,2.5956821656,-0.5591372103
C,0,2.4073293626,4.4981000378,0.9033929863
H,0,1.7788234666,3.4128008556,2.6706440177
C,0,1.6671261547,3.6108848155,-1.2332453681
C,0,2.373910316,4.564748316,-0.4861549952
H,0,2.9616148936,5.2429536921,1.464975485
H,0,1.6500277367,3.6603585341,-2.3176763779
H,0,2.902392673,5.3619378333,-0.9989844162
C,0,-2.0923810726,-2.0280707123,1.4036078432
H,0,-2.0619222632,-2.0895160564,2.4867332818
C,0,-2.3492496086,1.6328559416,1.601902878
H,0,-2.317796866,1.569117611,2.6849886811
C,0,0.8211444446,0.0965859001,1.4834884458
C,0,0.787598967,0.2613609943,-1.4288511813
H,0,1.8545367266,0.3325238961,-1.6231031822
N,0,2.2877934468,0.1596845974,1.8225975285
O,0,3.0949341584,0.2089486696,0.9103763782
O,0,2.5621737846,0.1496329099,3.0131909046

Ar = benzene-1,2-diyl, R^1 = Cl, R^2 = H, localised structure

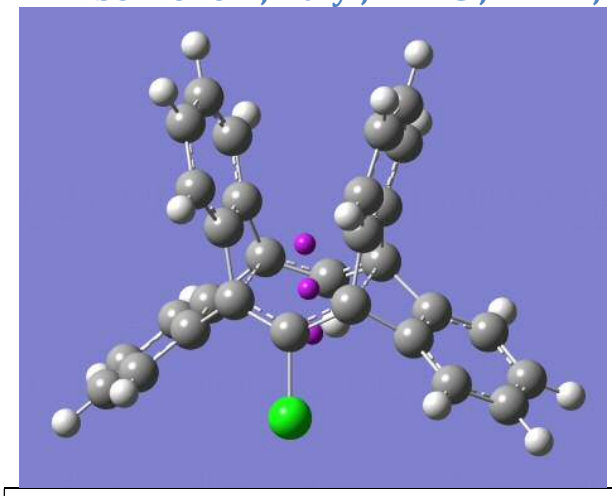


RB3LYP/6-311+G(d) level:
Allyl-allyl C–C bond length: 1.76080 Å
Distance between terminal allyl C atoms: 2.44569 Å
Sum of bond angles for terminal chloroallyl C: 351.852º
Sum of bond angles for terminal non-substituted allyl C: 350.900º
Electronic energy: -1613.722788 Hartrees
Gibbs free energy: -1613.405981 Hartrees
No imaginary frequencies
Point group: C_1

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1613.722788 Hartrees
<S^2> (singlet): 0.0000
NICS(0): -1.8603 ppm
NICS(1): 0.9468 ppm
NICS(–1): -2.8443 ppm
Isotropic magnetic susceptibility: -126.6451 cgs-ppm

Cartesian coordinates:
C,0,1.3480175124,0.1139029963,0.978918299
C,0,1.2829589297,0.4453404644,-1.4433348526
C,0,-1.1655444093,0.0232023373,-1.08755132
C,0,-1.1282700568,-0.2315482831,0.6543275291
C,0,-1.7303135614,1.1727218639,0.686005221
C,0,-1.7636346774,1.3722978252,-0.6905833262
C,0,-2.3681136079,2.4806213946,-1.2579739879
C,0,-2.8969954586,3.2036263693,1.0173367797
C,0,-2.9312599804,3.4057139122,-0.3663105169
H,0,-3.3492040667,3.9441921382,1.6696554304
H,0,-3.409161386,4.2989930007,-0.7564321535
C,0,1.2639778335,1.7687436474,-0.7417524961
C,0,1.2801041237,1.5747474903,0.64433103
C,0,1.2982186376,3.0488388961,-1.2770820665
C,0,1.3434502226,4.1419995921,-0.4055308413
C,0,1.3566645204,3.9484817957,0.9748473045
H,0,1.3697067216,5.1495615662,-0.8081554924
H,0,1.3933600919,4.8060846975,1.638967716
H,0,-2.4076996171,2.6443696768,-2.3300988891
H,0,1.2866051651,3.1991666742,-2.3520012085
C,0,-2.1950390961,-1.2837342854,0.3383413122
C,0,-2.2202293124,-1.0829339355,-1.0386907606
C,0,-3.0462733177,-2.1750335266,0.9683729033
C,0,-3.092339572,-1.7681367711,-1.8676380351
C,0,-3.9295303344,-2.88274377,0.139693481
H,0,-3.0289124008,-2.3465537847,2.0393895754
C,0,-3.9508760534,-2.6867552082,-1.2448302578
H,0,-3.1178079149,-1.6217068263,-2.9429812568
H,0,-4.6102114957,-3.604260139,0.5806633161
H,0,-4.6480590406,-3.2596035393,-1.8483075588
C,0,2.5889467967,-0.4877666024,0.3475113338
C,0,3.6637230124,-1.1386379775,0.9315710319
C,0,2.5437165628,-0.3036822678,-1.0612133254
C,0,4.6986640093,-1.6185433323,0.1187372168
H,0,3.6937956519,-1.2902238125,2.0053629281
C,0,3.5720102846,-0.782937088,-1.8581104514
C,0,4.6518133259,-1.4463418308,-1.2607765895
H,0,5.5412895948,-2.1313106276,0.5713563883
H,0,3.5366110169,-0.6486171895,-2.9347362982
H,0,5.458550406,-1.8242999945,-1.8806977699
C,0,-2.2976954361,2.0661169599,1.5778641658
H,0,-2.2833067098,1.9146000409,2.6523765252
C,0,1.3267789234,2.6576811335,1.5121347519
H,0,1.3402759625,2.5051499188,2.5866141672
C,0,0.222905781,-0.6173799029,1.1573463684
C,0,0.1536550672,-0.2497838802,-1.7073607353
H,0,0.2776778165,-1.2811743496,-2.0316853003
Cl,0,0.4217523954,-2.3633875668,1.4216599345
Bq,0,0.118953804,-0.086044378,-0.241275785
Bq,0,-0.030007442,0.893236002,-0.104088011
Bq,0,0.26791505,-1.065324758,-0.37846356

Ar = benzene-1,2-diyl, R^1 = Cl, R^2 = H, delocalised structure

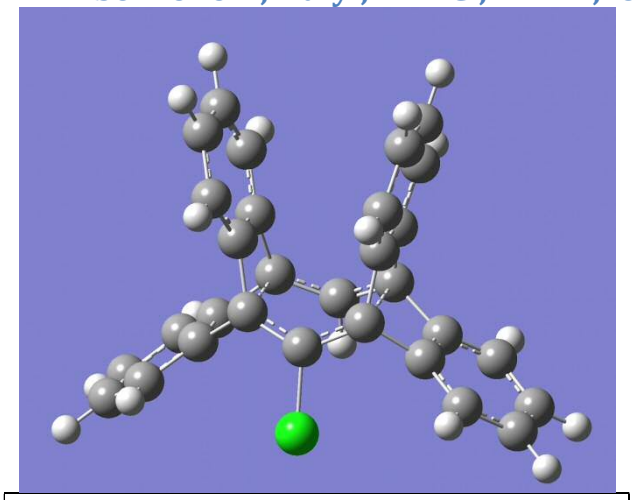


RB3LYP/6-311+G(d) level:
C¨C bond length: 2.27676 Å
Electronic energy: -1613.719739 Hartrees
Gibbs free energy: -1613.404768 Hartrees
No imaginary frequencies
Point group: C_{2v}

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1613.721798 Hartrees
<S^2> (singlet): 0.4450
NICS(0): -7.0901 ppm
NICS(1): -0.9187 ppm
NICS(–1): -4.7464 ppm
Isotropic magnetic susceptibility: -98.9107 cgs-ppm
Electronic energy (triplet): -1613.700472 Hartrees
<S^2> (triplet): 2.0656

Cartesian coordinates:
C,0,-1.2520176465,1.1413725106,0.0213602694
C,0,-1.2454521515,-1.1353817889,0.0226090504
C,0,1.2454521515,-1.1353817889,0.0226090504
C,0,1.2520176465,1.1413725106,0.0213602694
C,0,1.4978029916,0.6927206146,1.4415192864
C,0,1.507922801,-0.6996550532,1.4418728914
C,0,1.8344984434,-1.4166619194,2.5828018363
C,0,2.1328804381,0.6997726236,3.7429696299
C,0,2.1450056023,-0.6952342282,3.7427208228
H,0,2.377154131,1.2368033179,4.6539925546
H,0,2.398727174,-1.2279523701,4.6537200771
C,0,-1.507922801,-0.6996550532,1.4418728914
C,0,-1.4978029916,0.6927206146,1.4415192864
C,0,-1.8344984434,-1.4166619194,2.5828018363
C,0,-2.1450056023,-0.6952342282,3.7427208228
C,0,-2.1328804381,0.6997726236,3.7429696299
H,0,-2.398727174,-1.2279523701,4.6537200771
H,0,-2.377154131,1.2368033179,4.6539925546
H,0,1.8432243978,-2.5022264092,2.5847795789
H,0,-1.8432243978,-2.5022264092,2.5847795789
C,0,2.4002954143,0.6996575904,-0.8718794559
C,0,2.3895331485,-0.70261285,-0.8756746272
C,0,3.3657783429,1.4068271457,-1.5702609567
C,0,3.3378390998,-1.4237124423,-1.5838427464
C,0,4.3250338288,0.6815482091,-2.2911482144
H,0,3.3665353387,2.4918012422,-1.5843232711
C,0,4.3100962665,-0.7116414137,-2.3012759246
H,0,3.3240251491,-2.5093927283,-1.5958120637
H,0,5.0845436645,1.2133391845,-2.8553500543
H,0,5.0583667195,-1.2522545916,-2.8721022998
C,0,-2.4002954143,0.6996575904,-0.8718794559
C,0,-3.3657783429,1.4068271457,-1.5702609567
C,0,-2.3895331485,-0.70261285,-0.8756746272
C,0,-4.3250338288,0.6815482091,-2.2911482144
H,0,-3.3665353387,2.4918012422,-1.5843232711
C,0,-3.3378390998,-1.4237124423,-1.5838427464
C,0,-4.3100962665,-0.7116414137,-2.3012759246
H,0,-5.0845436645,1.2133391845,-2.8553500543
H,0,-3.3240251491,-2.5093927283,-1.5958120637
H,0,-5.0583667195,-1.2522545916,-2.8721022998
C,0,1.8111190488,1.4157086851,2.5829642918
H,0,1.8032973841,2.5012325099,2.583594168
C,0,-1.8111190488,1.4157086851,2.5829642918
H,0,-1.8032973841,2.5012325099,2.583594168
C,0,0.,1.4878510051,-0.4976759135
C,0,0.,-1.4429919592,-0.5270134183
Cl,0,0.,1.959462892,-2.2195753124
H,0,0.,-1.6076410804,-1.6025153228
Bq,0,0.,0.009473415,-0.156125115
Bq,0,0.,0.006582354,0.843870706
Bq,0,0.,0.012364476,-1.156120936

Ar = benzene-1,2-diyl, R^1 = Cl, R^2 = H, localised ⇌ delocalised TS

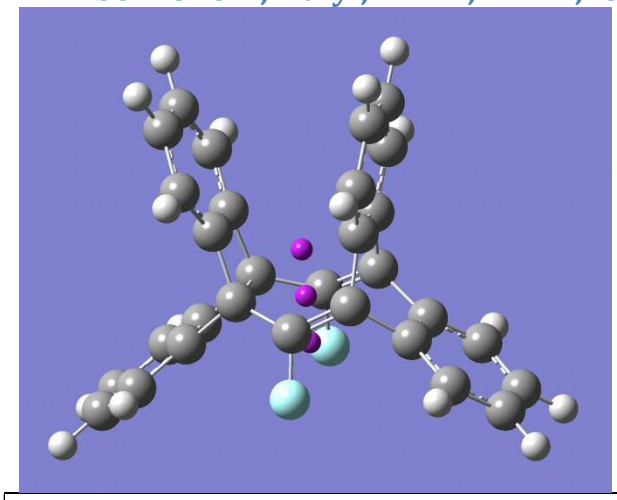


RB3LYP/6-311+G(d) level:
C···C bond lengths: 2.16127 Å, 2.34645 Å
Electronic energy: -1613.719687 Hartrees
Gibbs free energy: -1613.404060 Hartrees
Imaginary frequency: 145.6*i* cm^{-1}
Point group: C_1

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1613.720102 Hartrees
<S^2> (singlet): 0.2164
Electronic energy (triplet): -1613.690991 Hartrees
<S^2> (triplet): 2.0621

Cartesian coordinates:
C,0,0.2800374802,-1.002935718,1.2848119106
C,0,0.0200400792,1.3290613689,1.2786976494
C,0,0.0186098999,1.2330893808,-1.2108482724
C,0,0.2603008963,-0.9146144246,-1.2171121247
C,0,-1.2093268085,-0.6865927423,-1.4907934172
C,0,-1.3636666605,0.695254349,-1.4987278308
C,0,-2.5667389072,1.2881340432,-1.848171399
C,0,-3.4757804321,-0.9479399825,-2.173127682
C,0,-3.6305329774,0.4393923249,-2.1828043231
H,0,-4.3177084532,-1.5799485627,-2.4373530417
H,0,-4.5908445673,0.8662298906,-2.4544074969
C,0,-1.3293074259,0.7074810126,1.5210408943
C,0,-1.1748885681,-0.6783732223,1.5088052735
C,0,-2.5512041597,1.288460347,1.8261909501
C,0,-3.6312325864,0.4450483087,2.1141747853
C,0,-3.4772002632,-0.9409372169,2.100309758
H,0,-4.5992740172,0.8746064005,2.3518021639
H,0,-4.3266436754,-1.5773505515,2.3270589573
H,0,-2.6912950963,2.36644357,-1.856310414
H,0,-2.6718524092,2.3673121825,1.8365904314
C,0,1.1037282413,-0.4317969946,-2.3871886227
C,0,0.9518861974,0.9577331518,-2.3764427785
C,0,1.8598250382,-1.0656554753,-3.3596080092
C,0,1.5580367577,1.7579345251,-3.3315700011
C,0,2.4806474745,-0.262401256,-4.3271287135
H,0,1.9954377821,-2.1421474482,-3.3620481109
C,0,2.3358276283,1.1245132389,-4.3122778321
H,0,1.4507363932,2.8383223299,-3.3193771656
H,0,3.0911429887,-0.7268979383,-5.094969898
H,0,2.8343408163,1.7219664459,-5.0689712309
C,0,1.1133535691,-0.4341775186,2.4216257334
C,0,1.8952558112,-1.0543873847,3.3830249898
C,0,0.9626227364,0.964713857,2.4108183738
C,0,2.5414818266,-0.2565242405,4.3372862537
H,0,2.0261789715,-2.1315355053,3.3837327256
C,0,1.599188759,1.7543985051,3.3555269561
C,0,2.3991165022,1.1286344076,4.3221983259
H,0,3.1650906804,-0.724520222,5.0923023476
H,0,1.4905070396,2.8346829091,3.3420147082
H,0,2.9117643018,1.7304993206,5.0658199365
C,0,-2.2512005261,-1.5360236151,-1.8294689358
H,0,-2.1331702226,-2.6150376307,-1.8243306461
C,0,-2.2387725062,-1.5203615226,1.7993877377
H,0,-2.1180552026,-2.5991562057,1.7903671141
C,0,0.8249304704,-1.2543424605,0.0391956616
C,0,0.5301985022,1.6553838792,0.0380163265
Cl,0,2.587496501,-1.5315060856,0.0088431829
H,0,1.5806661202,1.9385971755,0.0233947991

Ar = benzene-1,2-diyl, R^1 = F, R^2 = F, localised structure

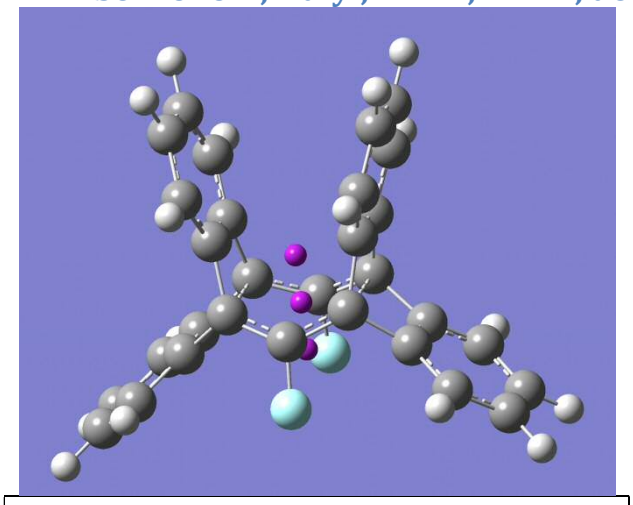


RB3LYP/6-311+G(d) level:
Allyl-allyl C–C bond length: 1.74443 Å
Distance between terminal allyl C atoms: 2.46674 Å
Sum of bond angles for terminal chloroallyl C: 350.275°
Electronic energy: -1352.643144 Hartrees
Gibbs free energy: -1352.333029 Hartrees
No imaginary frequencies
Point group: C_s

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1352.643144 Hartrees
<S^2> (singlet): 0.0000
NICS(0): -1.9100 ppm
NICS(1): -0.3383 ppm
NICS(–1): -1.5837 ppm
Isotropic magnetic susceptibility: -123.3006 cgs-ppm

Cartesian coordinates:
C,0.1955407976,1.3997912798,1.233371931
C,0.1955407976,1.3997912798,-1.233371931
C,0.4408561456,-1.0944218024,-0.8722151773
C,0.4408561456,-1.0944218024,0.8722151773
C,-0.9753534636,-1.6352090127,0.6956779308
C,-0.9753534636,-1.6352090127,-0.6956779308
C,-2.0162701606,-2.1692664593,-1.434799846
C,-3.0873645643,-2.697618974,0.6995137984
C,-3.0873645643,-2.697618974,-0.6995137984
H,-3.9373020295,-3.1204817927,1.2258775986
H,-3.9373020295,-3.1204817927,-1.2258775986
C,-1.2022628328,1.4355390773,-0.7001762212
C,-1.2022628328,1.4355390773,0.7001762212
C,-2.3928464684,1.536259571,-1.4079645355
C,-3.5930447031,1.6323048283,-0.6970421629
C,-3.5930447031,1.6323048283,0.6970421629
H,-4.5319217503,1.7111172109,-1.2357248732
H,-4.5319217503,1.7111172109,1.2357248732
H,-2.024360001,-2.1799182758,-2.5197888382
H,-2.3908047705,1.5379875463,-2.4932776512
C,1.5067671386,-2.1784915955,0.6954403917
C,1.5067671386,-2.1784915955,-0.6954403917
C,2.2894032392,-3.0484967068,1.4341127875
C,2.2894032392,-3.0484967068,-1.4341127875
C,3.0935722277,-3.9317941403,0.6994243071
H,2.3069886245,-3.0470730385,2.5188450405
C,3.0935722277,-3.9317941403,-0.6994243071
H,2.3069886245,-3.0470730385,-2.5188450405
H,3.7374122602,-4.6290615353,1.2261954534
H,3.7374122602,-4.6290615353,-1.2261954534
C,0.994117118,2.5763683734,0.7101394739
C,1.6730394228,3.5639826727,1.4065766389
C,0.994117118,2.5763683734,-0.7101394739
C,2.3548231061,4.5590266703,0.6956490069
H,1.6856752144,3.5560304588,2.4914687943
C,1.6730394228,3.5639826727,-1.4065766389
C,2.3548231061,4.5590266703,-0.6956490069
H,2.8896179938,5.3331638308,1.2365241346
H,1.6856752144,3.5560304588,-2.4914687943
H,2.8896179938,5.3331638308,-1.2365241346
C,-2.0162701606,-2.1692664593,1.434799846
H,-2.024360001,-2.1799182758,2.5197888382
C,-2.3928464684,1.536259571,1.4079645355
H,-2.3908047705,1.5379875463,2.4932776512
C,0.8185777608,0.2238122207,1.4430548466
C,0.8185777608,0.2238122207,-1.4430548466
F,2.1446028959,0.2711588914,1.7619717989
F,2.1446028959,0.2711588914,-1.7619717989
Bq,0,0.484991568,0.176393899,0.
Bq,0,-0.510445327,0.080971744,0.
Bq,0,1.480428463,0.271816055,0.

Ar = benzene-1,2-diyl, R^1 = F, R^2 = F, delocalised structure

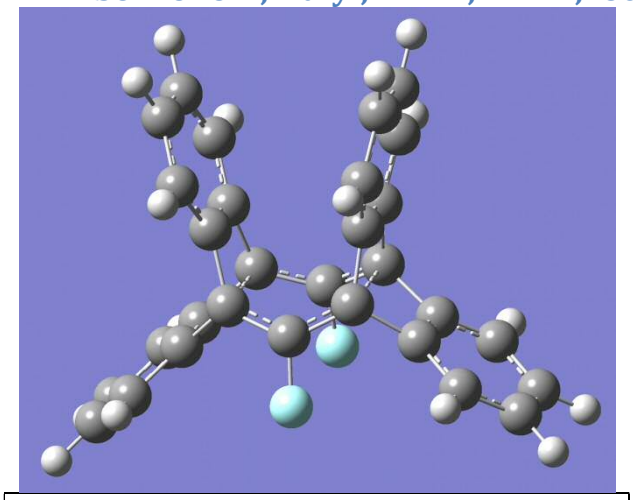


RB3LYP/6-311+G(d) level:
C¨C bond length: 2.28786 Å
Electronic energy: -1352.638730 Hartrees
Gibbs free energy: -1352.330327 Hartrees
No imaginary frequencies
Point group: C_{2v}

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1352.642270 Hartrees
<S^2> (singlet): 0.5382
NICS(0): -7.3036 ppm
NICS(1): -1.7844 ppm
NICS(–1): -3.1360 ppm
Isotropic magnetic susceptibility: -47.8201 cgs-ppm
Electronic energy (triplet): -1352.623950 Hartrees
<S^2> (triplet): 2.0637

Cartesian coordinates:
C,0,-1.2541244394,1.1439324795,0.0065437077
C,0,-1.2541244394,-1.1439324795,0.0065437077
C,0,1.2541244394,-1.1439324795,0.0065437077
C,0,1.2541244394,1.1439324795,0.0065437077
C,0,1.5170806051,0.6962208957,1.4195342946
C,0,1.5170806051,-0.6962208957,1.4195342946
C,0,1.8417311196,-1.416543361,2.559384683
C,0,2.160924079,0.6975851613,3.7181672327
C,0,2.160924079,-0.6975851613,3.7181672327
H,0,2.4127713094,1.2322184263,4.6284712913
H,0,2.4127713094,-1.2322184263,4.6284712913
C,0,-1.5170806051,-0.6962208957,1.4195342946
C,0,-1.5170806051,0.6962208957,1.4195342946
C,0,-1.8417311196,-1.416543361,2.559384683
C,0,-2.160924079,-0.6975851613,3.7181672327
C,0,-2.160924079,0.6975851613,3.7181672327
H,0,-2.4127713094,-1.2322184263,4.6284712913
H,0,-2.4127713094,1.2322184263,4.6284712913
H,0,1.8429191828,-2.5020011657,2.560205023
H,0,-1.8429191828,-2.5020011657,2.560205023
C,0,2.3634384693,0.7005082871,0.930464761
C,0,2.3634384693,-0.7005082871,-0.930464761
C,0,3.2844306129,1.4156612816,-1.6785575916
C,0,3.2844306129,-1.4156612816,-1.6785575916
C,0,4.2173330043,0.6967291863,-2.4387784175
H,0,3.2712005435,2.5006271424,-1.6967351685
C,0,4.2173330043,-0.6967291863,-2.4387784175
H,0,3.2712005435,-2.5006271424,-1.6967351685
H,0,4.9426448017,1.2327771042,-3.0424597238
H,0,4.9426448017,-1.2327771042,-3.0424597238
C,0,-2.3634384693,0.7005082871,-0.930464761
C,0,-3.2844306129,1.4156612816,-1.6785575916
C,0,-2.3634384693,-0.7005082871,-0.930464761
C,0,-4.2173330043,0.6967291863,-2.4387784175
H,0,-3.2712005435,2.5006271424,-1.6967351685
C,0,-3.2844306129,-1.4156612816,-1.6785575916
C,0,-4.2173330043,-0.6967291863,-2.4387784175
H,0,-4.9426448017,1.2327771042,-3.0424597238
H,0,-3.2712005435,-2.5006271424,-1.6967351685
H,0,-4.9426448017,-1.2327771042,-3.0424597238
C,0,1.8417311196,1.416543361,2.559384683
H,0,1.8429191828,2.5020011657,2.560205023
C,0,-1.8417311196,1.416543361,2.559384683
H,0,-1.8429191828,2.5020011657,2.560205023
C,0,0.,1.470839741,-0.5028307419
C,0,0.,-1.470839741,-0.5028307419
F,0,0.,1.7735727901,-1.8374102582
F,0,0.,-1.7735727901,-1.8374102582
Bq,0,0.,0.,-0.163247776
Bq,0,0.,0.,0.836752225
Bq,0,0,0.,-1.163247776

Ar = benzene-1,2-diyl, R^1 = F, R^2 = F, localised ⇌ delocalised TS

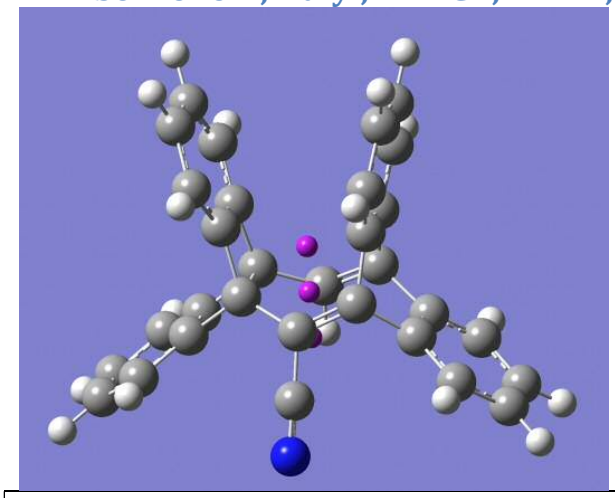


RB3LYP/6-311+G(d) level:
C···C bond lengths: 2.19000 Å, 2.35279 Å
Electronic energy: -1352.638834 Hartrees
Gibbs free energy: -1352.015941 Hartrees
Imaginary frequency: 126.3*i* cm^{-1}
Point group: C_s

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1352.640327 Hartrees
<S^2> (singlet): 0.3893
Electronic energy (triplet): -1352.617231 Hartrees
<S^2> (triplet): 2.0613

Cartesian coordinates:
C,0,0.2445674507,1.2944760094,1.1763928779
C,0,0.2445674507,1.2944760094,-1.1763928779
C,0,0.3962382026,-1.2081183478,-1.0950005789
C,0,0.3962382026,-1.2081183478,1.0950005789
C,0,-1.0075797026,-1.5860452379,0.6952875939
C,0,-1.0075797026,-1.5860452379,-0.6952875939
C,0,-2.1128048985,-2.0037074025,-1.4205040765
C,0,-3.2396482318,-2.4175497548,0.6979461343
C,0,-3.2396482318,-2.4175497548,-0.6979461343
H,0,-4.1268813768,-2.7443126563,1.2308265493
H,0,-4.1268813768,-2.7443126563,-1.2308265493
C,0,-1.1726017385,1.4461951579,-0.6971762971
C,0,-1.1726017385,1.4461951579,0.6971762971
C,0,-2.3384272644,1.6752215913,-1.413658592
C,0,-3.5205230362,1.8979241698,-0.6973827377
C,0,-3.5205230362,1.8979241698,0.6973827377
H,0,-4.4476523301,2.0744320273,-1.233301204
H,0,-4.4476523301,2.0744320273,1.233301204
H,0,-2.115450993,-2.0054194334,-2.5058819754
H,0,-2.3380610675,1.6767169547,-2.4991454042
C,0,1.4034529392,-2.273737807,0.698630411
C,0,1.4034529392,-2.273737807,-0.698630411
C,0,2.1966496876,-3.1508781105,1.4196347407
C,0,2.1966496876,-3.1508781105,-1.4196347407
C,0,3.0049408393,-4.0401088487,0.6972197056
H,0,2.215724396,-3.1374018763,2.5045182824
C,0,3.0049408393,-4.0401088487,-0.6972197056
H,0,2.215724396,-3.1374018763,-2.5045182824
H,0,3.6484160994,-4.7319363029,1.231253336
H,0,3.6484160994,-4.7319363029,-1.231253336
C,0,1.1071463539,2.450168333,0.7024726142
C,0,1.8030520354,3.4152178758,1.4127015979
C,0,1.1071463539,2.450168333,-0.7024726142
C,0,2.5085552999,4.3915585076,0.6964074943
H,0,1.8198710327,3.4035904688,2.4977257395
C,0,1.8030520354,3.4152178758,-1.4127015979
C,0,2.5085552999,4.3915585076,-0.6964074943
H,0,3.0672186129,5.1509949885,1.2340090802
H,0,1.8198710327,3.4035904688,-2.4977257395
H,0,3.0672186129,5.1509949885,-1.2340090802
C,0,-2.1128048985,-2.0037074025,1.4205040765
H,0,-2.115450993,-2.0054194334,2.5058819754
C,0,-2.3384272644,1.6752215913,1.413658592
H,0,-2.3380610675,1.6767169547,2.4991454042
C,0,0.8280806317,0.0797087571,1.4680806688
C,0,0.8280806317,0.0797087571,-1.4680806688
F,0,2.1612607917,0.139402092,1.7705163402
F,0,2.1612607917,0.139402092,-1.7705163402

Ar = benzene-1,2-diyl, R^1 = CN, R^2 = H, localised structure

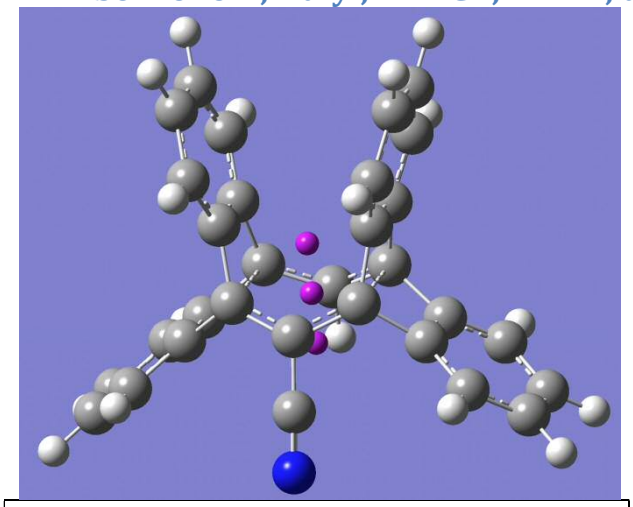


RB3LYP/6-311+G(d) level:
Allyl-allyl C–C bond length: 1.75757 Å
Distance between terminal allyl C atoms: 2.43594 Å
Sum of bond angles for terminal cyanoallyl C: 352.810º
Sum of bond angles for terminal non-substituted allyl C: 350.490º
Electronic energy: -1246.365931 Hartrees
Gibbs free energy: -1246.041731 Hartrees
Point group: C_1
No imaginary frequencies

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1246.365931 Hartrees
<S^2> (singlet): 0.0000
NICS(0): -1.9547 ppm
NICS(1): 0.4268 ppm
NICS(–1): -2.9005 ppm
Isotropic magnetic susceptibility: -133.2188 cgs-ppm

Cartesian coordinates:
C,0,0.2263415121,1.3859231804,1.1861783992
C,0,0.2205270967,1.3851642861,-1.249755792
C,0,0.4505980112,-1.0953243327,-0.8857016832
C,0,0.4643852423,-1.1035233769,0.8717959357
C,0,-0.9573253167,-1.6309499792,0.6998997209
C,0,-0.9684923818,-1.6274135766,-0.6918991299
C,0,-2.0198060492,-2.1572259155,-1.4200702929
C,0,-3.0747712676,-2.6857056197,0.721814348
C,0,-3.0872299584,-2.682615287,-0.6769717693
H,0,-3.9207654453,-3.1073897689,1.2555141904
H,0,-3.9431881791,-3.1015456925,-1.1968507009
C,0,-1.1834228175,1.4383542003,-0.7320086151
C,0,-1.1757828034,1.4182453232,0.6677913332
C,0,-2.3785716957,1.5519346892,-1.428189863
C,0,-3.5726728608,1.6448264501,-0.7057509846
C,0,-3.5631129858,1.6231271112,0.6878959363
H,0,-4.515308942,1.735023719,-1.2358730465
H,0,-4.4975093961,1.6966320357,1.234746583
H,0,-2.0372518434,-2.1677249182,-2.5051290593
H,0,-2.3864824566,1.5653403886,-2.5133786494
C,0,1.5097294566,-2.2057690928,0.6781648484
C,0,1.4946341182,-2.2003619943,-0.7138262311
C,0,2.2895003459,-3.0882627697,1.4052476844
C,0,2.2588118272,-3.0796415228,-1.4617829929
C,0,3.0764560409,-3.9786938434,0.659698747
H,0,2.3232464357,-3.0892086148,2.4894536221
C,0,3.0618303171,-3.9748435647,-0.7384601627
H,0,2.2588472179,-3.0825050304,-2.5473015633
H,0,3.718509255,-4.6833290226,1.178519723
H,0,3.6908949347,-4.6788345821,-1.2741611516
C,0,0.9895336681,2.5952204803,0.6839622479
C,0,1.6404402208,3.5996150631,1.3812663311
C,0,0.9915354797,2.586855104,-0.7386085678
C,0,2.3029212012,4.6065312847,0.6672415117
H,0,1.6541546884,3.59617466,2.4659512593
C,0,1.6503563064,3.5879426875,-1.434321258
C,0,2.3092093197,4.5999509325,-0.7232032998
H,0,2.8188934604,5.3936413292,1.2070771693
H,0,1.6618070717,3.581557849,-2.5196957104
H,0,2.8283975716,5.3840741004,-1.2647563454
C,0,-1.9940448264,-2.1631491044,1.4470342083
H,0,-1.9903946763,-2.1784896679,2.5321756509
C,0,-2.3588114108,1.5087345389,1.3891223956
H,0,-2.3497030429,1.4923744946,2.474173354
C,0,0.8773022446,0.2168447431,1.4585517958
C,0,0.8765280595,0.2167510177,-1.4334213421
H,0,1.9481668248,0.2836335578,-1.6121095585
C,0,2.2400072313,0.2978316164,1.9014138485
N,0,3.3177175959,0.3455421639,2.3187891756
Bq,0,0.519280361,0.167639253,-0.008725448
Bq,0,-0.476568021,0.076758382,-0.00356137
Bq,0,1.515128743,0.258520124,-0.013889525

Ar = benzene-1,2-diyl, R^1 = CN, R^2 = H, delocalised structure

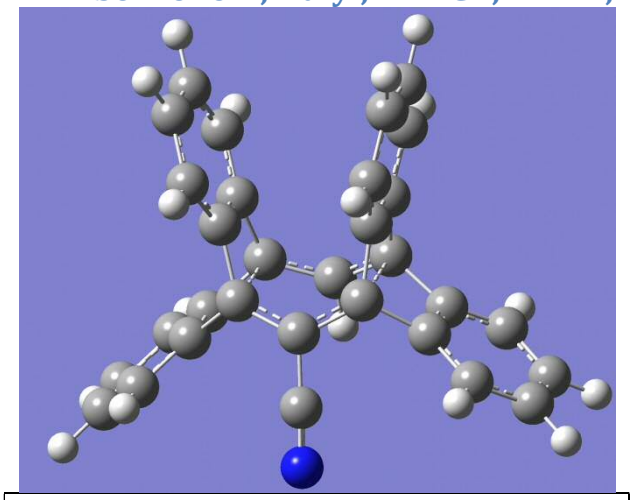


RB3LYP/6-311+G(d) level:
C¨C bond length: 2.26877 Å
Electronic energy: -1246.362638 Hartrees
Gibbs free energy: -1246.040211 Hartrees
No imaginary frequencies
Point group: C_s

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1246.364425 Hartrees
<S^2> (singlet): 0.4159
NICS(0): -7.1148 ppm
NICS(1): -1.1284 ppm
NICS(–1): -4.6230 ppm
Isotropic magnetic susceptibility: -163.7740 cgs-ppm
Electronic energy (triplet): -1246.341934 Hartrees
<S^2> (triplet): 2.0700

Cartesian coordinates:
C,0,-0.0460981333,1.2624133663,1.247259433
C,0,-0.2716112503,-0.9951102777,1.2553527315
C,0,-0.2716112503,-0.9951102777,-1.2553527315
C,0,-0.0460981333,1.2624133663,-1.247259433
C,0,1.3219742625,0.6894549071,-1.5152837898
C,0,1.1828289096,-0.6962537094,-1.5082746307
C,0,2.2465081483,-1.5291077657,-1.822980664
C,0,3.6109736537,0.456865072,-2.1511674312
C,0,3.4719153279,-0.931242416,-2.1428994161
H,0,4.5706729091,0.8965092914,-2.4033580511
H,0,4.3248187712,-1.5557887185,-2.3885625075
C,0,1.1828289096,-0.6962537094,1.5082746307
C,0,1.3219742625,0.6894549071,1.5152837898
C,0,2.2465081483,-1.5291077657,1.822980664
C,0,3.4719153279,-0.931242416,2.1428994161
C,0,3.6109736537,0.456865072,2.1511674312
H,0,4.3248187712,-1.5557887185,2.3885625075
H,0,4.5706729091,0.8965092914,2.4033580511
H,0,2.1394996824,-2.6092959784,-1.8177960942
H,0,2.1394996824,-2.6092959784,1.8177960942
C,0,-0.9946936531,0.9247276103,-2.3839102801
C,0,-1.1321517209,-0.4714885844,-2.3940179581
C,0,-1.6468609671,1.7136976332,-3.3174247605
C,0,-1.9233319897,-1.1053344433,-3.3379931081
C,0,-2.4544127226,1.0765947966,-4.271351618
H,0,-1.5517427902,2.7952150604,-3.3045748727
C,0,-2.5894478306,-0.3096688658,-4.2813143622
H,0,-2.0516131784,-2.182761782,-3.3337926784
H,0,-2.9854533902,1.6722337944,-5.0068816713
H,0,-3.2265896738,-0.7808356356,-5.0226078703
C,0,-0.9946936531,0.9247276103,2.3839102801
C,0,-1.6468609671,1.7136976332,3.3174247605
C,0,-1.1321517209,-0.4714885844,2.3940179581
C,0,-2.4544127226,1.0765947966,4.271351618
H,0,-1.5517427902,2.7952150604,3.3045748727
C,0,-1.9233319897,-1.1053344433,3.3379931081
C,0,-2.5894478306,-0.3096688658,4.2813143622
H,0,-2.9854533902,1.6722337944,5.0068816713
H,0,-2.0516131784,-2.182761782,3.3337926784
H,0,-3.2265896738,-0.7808356356,5.0226078703
C,0,2.5291134027,1.2899424495,-1.8389801747
H,0,2.6396368893,2.3698057891,-1.8444866223
C,0,2.5291134027,1.2899424495,1.8389801747
H,0,2.6396368893,2.3698057891,1.8444866223
C,0,-0.558020713,1.6256792452,0.
C,0,-0.8433049167,-1.284994293,0.
C,0,-2.2655641349,-1.5307044568,0.
N,0,-3.3931729763,-1.7827742035,0.
H,0,-1.61153457,1.8983605186,0.
Bq,0,-0.339457399,0.145881855,0.
Bq,0,0.65553961,0.045977145,0.
Bq,0,-1.334454409,0.245786565,0.

Ar = benzene-1,2-diyl, R^1 = CN, R^2 = H, localised ⇌ delocalised TS



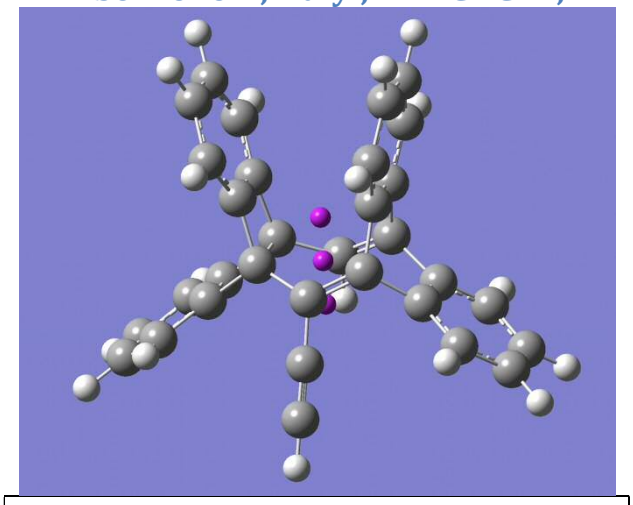
RB3LYP/6-311+G(d) level:
C···C bond lengths: 2.16835 Å, 2.33192 Å
Electronic energy: -1246.362613 Hartrees
Gibbs free energy: -1246.039458 Hartrees
Imaginary frequency: 132.4*i* cm^{-1}
Point group: C_1

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1246.363087 Hartrees
<S^2> (singlet): 0.2314
Electronic energy (triplet): -1246.334382 Hartrees
<S^2> (triplet): 2.0667

Cartesian coordinates:

C,0,0.2747706652,1.2950554956,1.1532251767
C,0,0.2662571948,1.2884896665,-1.1786755915
C,0,0.417488556,-1.2009050024,-1.0915844043
C,0,0.4237573768,-1.2088948602,1.076741837
C,0,-0.9870886812,-1.5774054785,0.6885092521
C,0,-0.9904071172,-1.5835300545,-0.7023296066
C,0,-2.0987494948,-2.0007664944,-1.4226232366
C,0,-3.2222729463,-2.4001102616,0.7006715262
C,0,-3.2251913364,-2.4074803536,-0.6952263215
H,0,-4.109334613,-2.7212370456,1.2372673659
H,0,-4.1147149963,-2.7342242161,-1.2243516475
C,0,-1.15467768,1.446829287,-0.7081897884
C,0,-1.1477544663,1.4376576001,0.6863583249
C,0,-2.3251450824,1.6762054368,-1.4159213248
C,0,-3.503688761,1.8923229192,-0.6914026512
C,0,-3.4963754303,1.8825049234,0.7031455444
H,0,-4.4340166854,2.070447256,-1.2211750044
H,0,-4.4208483624,2.0527462908,1.2454971971
H,0,-2.1049374649,-2.0069743878,-2.5080452859
H,0,-2.3320402311,1.6829244877,-2.5014083984
C,0,1.4038924841,-2.3044495946,0.6866221318
C,0,1.4015483826,-2.294321101,-0.7122309491
C,0,2.1764677499,-3.2057307945,1.3999901578
C,0,2.1726358513,-3.1852429225,-1.440571835
C,0,2.9648426066,-4.1065845112,0.6690299286
H,0,2.2010470338,-3.2011480108,2.4846949152
C,0,2.9637362518,-4.0967178625,-0.7249123229
H,0,2.1831313314,-3.172999479,-2.5261736819
H,0,3.5939881372,-4.8153969667,1.1975169068
H,0,3.5899850452,-4.8000201619,-1.264390157
C,0,1.1040408952,2.4802411281,0.6868586203
C,0,1.7766748751,3.4661555151,1.3902173345
C,0,1.1013601332,2.4709548537,-0.7203981312
C,0,2.4605094588,4.452580516,0.6656657327
H,0,1.7991682114,3.462576963,2.475019242
C,0,1.7733064152,3.4481634825,-1.4367227664
C,0,2.4599233771,4.4437110638,-0.7264491048
H,0,3.0033536653,5.2267164108,1.1980682418
H,0,1.7817048913,3.4370175743,-2.5223863131
H,0,3.0002497439,5.2127560061,-1.269033585
C,0,-2.0924816506,-1.9865324724,1.4187168338
H,0,-2.0928178534,-1.9834070329,2.504144983
C,0,-2.3102181618,1.6567361897,1.4115882666
H,0,-2.304654722,1.6498312368,2.4970375257
C,0,0.8886219867,0.0823853217,1.4672845371
C,0,0.8846367302,0.0826686364,-1.4525685842
H,0,1.9580739483,0.139414918,-1.6224666144
C,0,2.2771279073,0.1530700848,1.8521215029
N,0,3.3729888812,0.2047518706,2.2150509916

Ar = benzene-1,2-diyl, R^1 = C≡C–H, R^2 = H, localised structure

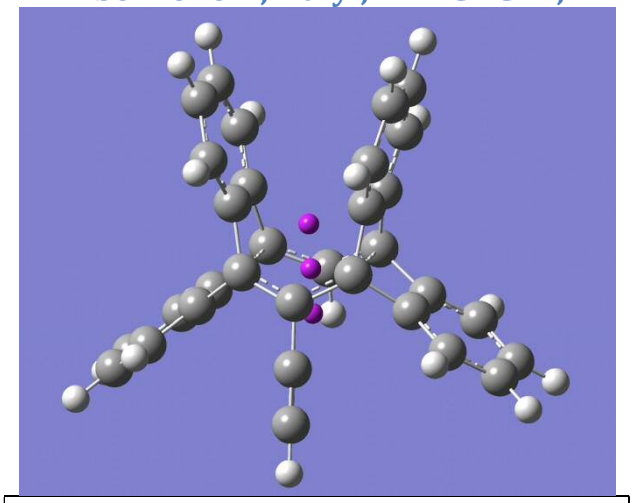


RB3LYP/6-311+G(d) level:
Allyl-allyl C–C bond length: 1.75312 Å
Distance between terminal allyl C atoms: 2.44627 Å
Sum of bond angles for terminal ethynylallyl C: 350.443°
Sum of bond angles for terminal non-substituted allyl C: 352.300°
Electronic energy: -1230.261370 Hartrees
Gibbs free energy: -1229.927205 Hartrees
No imaginary frequencies
Point group: C_1

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1230.261370 Hartrees
<S^2> (singlet): 0.0000
NICS(0): -2.1387 ppm
NICS(1): 0.3933 ppm
NICS(–1): -2.7982 ppm
Isotropic magnetic susceptibility: -187.3886 cgs-ppm

Cartesian coordinates:
C,0,0.2510796425,-0.7371098619,1.1228803951
C,0,0.0515891569,1.0046127567,1.1166227866
C,0,0.061632409,1.3784865226,-1.3700389335
C,0,0.322101765,-1.0538740534,-1.3695902294
C,0,-1.1134883534,-0.6745888896,-1.5520318682
C,0,-1.2656408836,0.7174470442,-1.5761222076
C,0,-2.5053871449,1.2895151415,-1.8251328159
C,0,-3.4516446785,-0.9347073335,-2.0220061557
C,0,-3.602175022,0.4507303204,-2.0484822747
H,0,-4.31115983,-1.5737814028,-2.1973983477
H,0,-4.5783624446,0.8828417987,-2.2442788742
C,0,-1.3912754634,0.6573986608,1.4825793994
C,0,-1.232414261,-0.7255235584,1.4846110913
C,0,-2.5667291748,1.2635543251,1.8910729515
C,0,-3.6016717017,0.4054692685,2.2918708793
C,0,-3.4409569624,-0.984038367,2.2944607494
H,0,-4.5497743607,0.8267479244,2.6116610272
H,0,-4.2677047277,-1.6096226671,2.6165650745
H,0,-2.6223015541,2.3685189456,-1.8425629827
H,0,-2.700504816,2.3405873143,1.9005101028
C,0,1.1471544284,-0.4531110298,-2.490551847
C,0,1.0047249335,0.9626993194,-2.4812319446
C,0,1.9632772718,-1.0642220535,-3.429004802
C,0,1.6871188524,1.7356191462,-3.4076910763
C,0,2.6479743399,-0.2745452922,-4.3620421638
H,0,2.0826598638,-2.142528896,-3.4300124372
C,0,2.5141954116,1.1097342208,-4.3499681608
H,0,1.5848365855,2.8163404908,-3.3978794761
H,0,3.2888757595,-0.7494673331,-5.0980432023
H,0,3.0504387012,1.7115486111,-5.0768365646
C,0,1.1234976425,0.4512683429,2.3493716061
C,0,1.8484106276,-1.1034042289,3.3317727866
C,0,0.967367629,0.9319053718,2.3396796863
C,0,2.4343225974,-0.2917407364,4.3148210238
H,0,1.9839989371,-2.1796955576,3.3445809715
C,0,1.5335270963,1.7447985078,3.3071665981
C,0,2.2830933334,1.0985381203,4.3021095483
H,0,3.0232283341,-0.7506598464,5.1029886348
H,0,1.4214757252,2.8246526844,3.3069156464
H,0,2.7573173846,1.6881414706,5.0806171108
C,0,-2.2012794816,-1.5094154402,-1.7736661601
H,0,-2.0826583815,-2.5881308775,-1.7550218488
C,0,-2.2374350162,-1.5840448186,1.8958446141
H,0,-2.1208718282,-2.6630434625,1.9089469468
C,0,0.8853495533,-1.2615525558,-0.1401823581
C,0,0.562397279,1.615292026,-0.1367231811
C,0,2.281239533,-1.5522114089,-0.0604340164
C,0,3.4486034326,-1.8427674137,0.0255333812
H,0,4.4825684884,-2.0833690366,0.0964784761
H,0,1.6104343688,1.9040074728,-0.0827275448
Bq,0,0.355691634,0.157642472,-0.129505253
Bq,0,-0.637689436,0.044602561,-0.149902008
Bq,0,1.349072705,0.270682384,-0.109108499

Ar = benzene-1,2-diyl, R^1 = C≡C–H, R^2 = H, delocalised structure

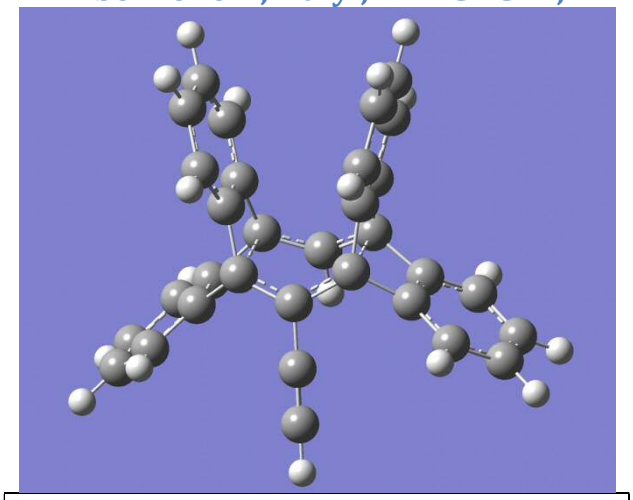


RB3LYP/6-311+G(d) level:
C¨¨C bond length: 2.27341 Å
Electronic energy: -1230.257344 Hartrees
Gibbs free energy: -1229.925477 Hartrees
No imaginary frequencies
Point group: C_s

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1230.259339 Hartrees
<S^2> (singlet): 0.4396
NICS(0): -6.9312 ppm
NICS(1): -0.9293 ppm
NICS(–1): -4.6902 ppm
Isotropic magnetic susceptibility: -175.9505 cgs-ppm
Electronic energy (triplet): -1230.237478 Hartrees
<S^2> (triplet): 2.0732

Cartesian coordinates:
C,0,0.282095611,-0.9918979493,1.2483903691
C,0,0.0388476991,1.2684612408,1.2470422184
C,0,0.0388476758,1.2684612408,-1.2470422191
C,0,0.2820955877,-0.9918979492,-1.2483903743
C,0,-1.1753538869,-0.7021959366,-1.4974162902
C,0,-1.3249869694,0.6825400124,-1.5110651216
C,0,-2.5363747892,1.2726024831,-1.8382017472
C,0,-3.4638626686,-0.9559822933,-2.1317025113
C,0,-3.6128560025,0.4310181649,-2.1466294947
H,0,-4.3125025676,-1.5878623013,-2.3739486217
H,0,-4.5757911918,0.8628455062,-2.4004820545
C,0,-1.3249869412,0.6825400124,1.5110651463
C,0,-1.175353859,-0.7021959366,1.4974163121
C,0,-2.536374755,1.2726024831,1.8382017945
C,0,-3.6128559625,0.4310181649,2.146629562
C,0,-3.4638626288,-0.9559822934,2.1317025759
H,0,-4.575791147,0.8628455062,2.4004821398
H,0,-4.3125025233,-1.5878623013,2.3739487021
H,0,-2.6542880394,2.3517850943,-1.848349653
H,0,-2.654288005,2.3517850943,1.8483497025
C,0,1.1250568383,-0.4624450694,-2.3976350282
C,0,0.9825684367,0.9331127386,-2.3876883869
C,0,1.9026771,-1.0926693464,-3.3557012224
C,0,1.6207660984,1.7239810249,-3.3299433292
C,0,2.5531740895,-0.2959992164,-4.3090824629
H,0,2.029134843,-2.1704487155,-3.3557533262
C,0,2.4174823063,1.0905542526,-4.2952520473
H,0,1.5201915689,2.8051301436,-3.3166099699
H,0,3.1762927591,-0.765770522,-5.0635656636
H,0,2.9353183581,1.6879039902,-5.0390217705
C,0,1.125056883,-0.4624450694,2.3976350073
C,0,1.9026771626,-1.0926693464,3.355701187
C,0,0.9825684812,0.9331127386,2.3876883686
C,0,2.5531741698,-0.2959992164,4.3090824153
H,0,2.0291349056,-2.1704487155,3.3557532883
C,0,1.6207661604,1.7239810249,3.3299432991
C,0,2.4174823864,1.0905542526,4.2952520023
H,0,3.1762928535,-0.765770522,5.0635656044
H,0,1.5201916307,2.8051301436,3.3166099416
H,0,2.935318452,1.6879039902,5.0390217158
C,0,-2.233913807,-1.5431080167,-1.8090738398
H,0,-2.1192883661,-2.6226164157,-1.7985172659
C,0,-2.2339137733,-1.5431080167,1.8090738814
H,0,-2.1192883326,-2.6226164157,1.7985173054
C,0,0.8756566385,-1.281475702,-0.0000000082
C,0,0.5504063251,1.6314705204,-0.0000000051
C,0,2.2937466121,-1.5150556224,-0.0000000214
C,0,3.475021734,-1.7502798286,-0.0000000324
H,0,4.5210327317,-1.9449625812,-0.0000000421
H,0,1.6025975896,1.9090895851,-0.0000000149
Bq,0,0.344658256,0.150520234,0.
Bq,0,-0.649194321,0.039808652,0.
Bq,0,1.338510834,0.261231815,0.

Ar = benzene-1,2-diyl, R^1 = C≡C–H, R^2 = H, localised ⇌ delocalised TS

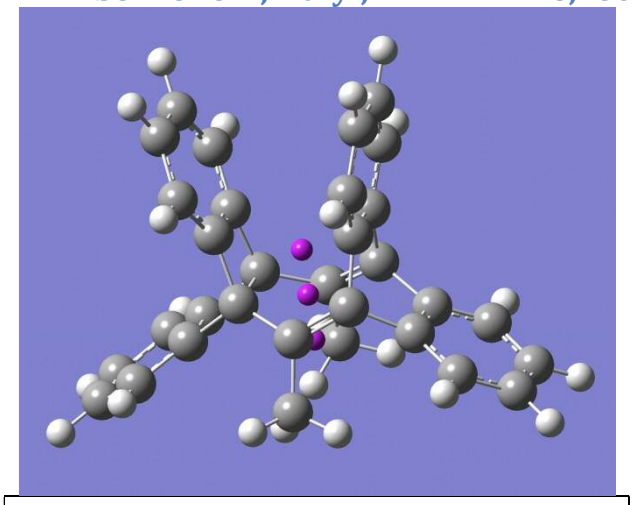


RB3LYP/6-311+G(d) level:
C···C bond lengths: 2.20984 Å, 2.32013 Å
Electronic energy: -1230.257367 Hartrees
Gibbs free energy: -1229.924277 Hartrees
Imaginary frequency: 84.1*i* cm^{-1}
Point group: C_1

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1230.258615 Hartrees
<S^2> (singlet): 0.3613
Electronic energy (triplet): -1230.234114 Hartrees
<S^2> (triplet): 2.0718

Cartesian coordinates:
C,0,0.2749757527,-0.9613611148,1.228038136
C,0,0.0398463861,1.2359380061,1.2258085307
C,0,0.0404607555,1.2958521834,-1.2676712909
C,0,0.2876263121,-1.011076595,-1.2679489625
C,0,-1.1655215151,-0.6969177529,-1.5032930118
C,0,-1.3149914088,0.6891500295,-1.5189148913
C,0,-2.5316578228,1.2758451337,-1.8332849904
C,0,-3.4640559145,-0.9509957331,-2.1108390875
C,0,-3.6127483144,0.4356686719,-2.1275722783
H,0,-4.3149028329,-1.5840471531,-2.3419577592
H,0,-4.5778425026,0.8682249831,-2.3717881565
C,0,-1.3355776145,0.6802231339,1.5046213948
C,0,-1.187395914,-0.7033815884,1.4928444512
C,0,-2.5404412644,1.2755022912,1.8449678305
C,0,-3.6125676416,0.4332291034,2.1679725676
C,0,-3.4646496349,-0.9544180846,2.1551008819
H,0,-4.5727355223,0.8651369312,2.4320380631
H,0,-4.3115956292,-1.5839060964,2.4092953633
H,0,-2.6484045405,2.3551617957,-1.8448741384
H,0,-2.658620645,2.3546256125,1.8541045643
C,0,1.1275556077,-0.4611356477,-2.4093632976
C,0,0.9854327868,0.9374065206,-2.4001130106
C,0,1.9113510669,-1.0882483764,-3.3646195827
C,0,1.6309753932,1.7245037662,-3.3406561605
C,0,2.5678311199,-0.293691599,-4.3153303733
H,0,2.0361708932,-2.166224795,-3.364039265
C,0,2.4327667144,1.0924085506,-4.3022952669
H,0,1.5298320664,2.805605172,-3.3279281875
H,0,3.1935535653,-0.7649805814,-5.0666928146
H,0,2.9535336799,1.690387165,-5.0435061671
C,0,1.1212202636,-0.4621070308,2.3888235476
C,0,1.8894167498,-1.0973363399,3.3508996463
C,0,0.9799002256,0.9307454254,2.3782655278
C,0,2.5324972099,-0.2992650984,4.3084232748
H,0,2.0158583197,-2.1750854678,3.352159851
C,0,1.6093156959,1.7246577579,3.3236913802
C,0,2.3978276644,1.0880760938,4.293945178
H,0,3.1505296884,-0.7682854707,5.0675661406
H,0,1.5105417751,2.8059505212,3.310581541
H,0,2.9116855252,1.6836437822,5.0419071583
C,0,-2.2302573295,-1.5358061293,-1.800595913
H,0,-2.1150570955,-2.6152523216,-1.7886617771
C,0,-2.2396327264,-1.5457117705,1.81979218
H,0,-2.1269475381,-2.6254016477,1.8111050015
C,0,0.8748805465,-1.2795548193,-0.0232972938
C,0,0.5514067332,1.6315813611,-0.0231259342
C,0,2.2921366893,-1.5156051938,-0.0094848038
C,0,3.4728446414,-1.7535716707,0.0046115028
H,0,4.518374123,-1.9504516719,0.0156839902
H,0,1.6036594156,1.9088824184,-0.0143932891

Ar = benzene-1,2-diyl, $R^1 = R^2$ = Me, localised structure

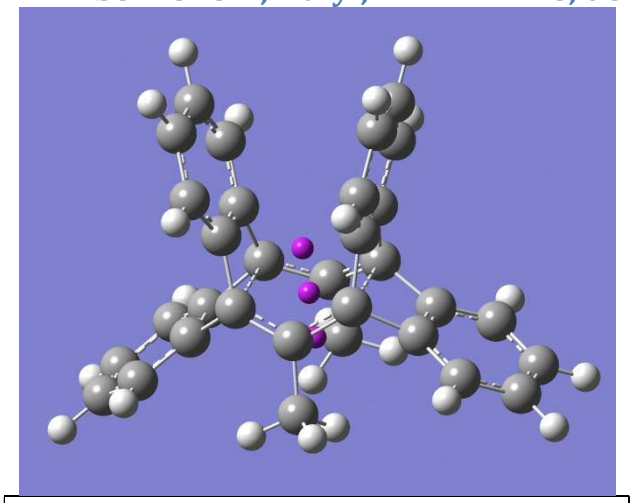


RB3LYP/6-311+G(d) level:
Allyl-allyl C–C bond length: 1.75014 Å
Distance between terminal allyl C atoms: 2.46986 Å
Sum of bond angles for terminal methylallyl C: 351.272°
Electronic energy: -1232.736564 Hartrees
Gibbs free energy: -1232.358179 Hartrees
No imaginary frequencies
Point group: C_s

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1232.736564 Hartrees
<S^2> (singlet): 0.0000
NICS(0): -2.0522 ppm
NICS(1): 0.3287 ppm
NICS(–1): -3.0108 ppm
Isotropic magnetic susceptibility: -52.2288 cgs-ppm

Cartesian coordinates:
C,0,0.0108720595,1.8368067822,-0.2340148641
C,0,-1.8272370445,0.187094129,-0.2347102904
C,0,0.0866987562,-1.4066725799,-0.1919632066
C,0,1.389184933,-0.2376842356,-0.1914706053
C,0,1.4897255885,-0.6187087276,1.2870556527
C,0,0.4540567846,-1.5482268968,1.2866639547
C,0,0.1811022446,-2.3479114997,2.3827821387
C,0,2.0363415111,-1.2235201454,3.509629872
C,0,0.9955385212,-2.157646443,3.5092362176
H,0,2.6438979414,-1.1114594623,4.4024107931
H,0,0.8183119668,-2.7499327714,4.4017203048
C,0,-1.5418373329,0.6701408872,1.1533216785
C,0,-0.5006881575,1.6045776877,1.1537155307
C,0,-2.2236297537,0.3705622495,2.3256342201
C,0,-1.8488669344,1.0149913408,3.5088755403
C,0,-0.8114468994,1.9460810511,3.5092680079
H,0,-2.3722216479,0.790500639,4.4330079538
H,0,-0.5322755163,2.441861588,4.4337040203
H,0,-0.6192352923,-3.0811728073,2.3920332741
H,0,-3.0333501535,-0.352628796,2.3235114827
C,0,2.1010488557,-1.2976496789,-1.0428165054
C,0,1.0641740518,-2.2282504607,-1.0432085998
C,0,3.3267652676,-1.5637163205,-1.6306031221
C,0,1.1969091009,-3.4752740062,-1.6314084032
C,0,3.4678639163,-2.8165004321,-2.2473275632
H,0,4.1455826329,-0.8509563857,-1.6317872143
C,0,2.4274636829,-3.7502654498,-2.2477208565
H,0,0.4000967121,-4.2125506355,-1.6332034158
H,0,4.4052607835,-3.0698790499,-2.7327838554
H,0,2.5785983715,-4.709318762,-2.7334743703
C,0,-1.1463379435,2.3457997873,-1.0772889781
C,0,-1.2943090297,3.5440317791,-1.7608383224
C,0,-2.2082642213,1.3927153927,-1.07769064
C,0,-2.480941856,3.8058677841,-2.4586285424
H,0,-0.4929722563,4.2766184045,-1.7549348305
C,0,-3.3832990294,1.6691524836,-1.7616283692
C,0,-3.5154989424,2.8773475012,-2.4590197614
H,0,-2.5934012061,4.7432929533,-2.9941416695
H,0,-4.1979429878,0.9513879931,-1.7563361031
H,0,-4.4351316238,3.0903304446,-2.9948381656
C,0,2.3136997293,-0.4338938386,2.3835887029
H,0,3.1289003715,0.2827989333,2.3934508067
C,0,-0.1299033292,2.249692423,2.3264262896
H,0,0.6763012216,2.9768023421,2.3249149287
C,0,0.995498561,1.0838663098,-0.7911392654
C,0,-1.1845044009,-0.8726980515,-0.7919641059
C,0,1.4178838032,1.3075634134,-2.2250044583
H,0,0.9613835057,2.2022666714,-2.6452354267
H,0,2.5050191024,1.4291492713,-2.2820403132
H,0,1.1720042629,0.4609903419,-2.8718533305
C,0,-1.4517967237,-1.2679901755,-2.226090375
H,0,-1.6897547161,-2.3356815229,-2.2836276932
H,0,-2.2919446779,-0.7176125856,-2.6464668634
H,0,-0.5833925633,-1.1144888636,-2.8725172836
Bq,0,-0.088247856,0.098452059,-0.405877056
Bq,0,-0.102229516,0.113608989,0.593910311
Bq,0,-0.074266196,0.083295129,-1.405664424

Ar = benzene-1,2-diyl, $R^1 = R^2$ = Me, delocalised structure

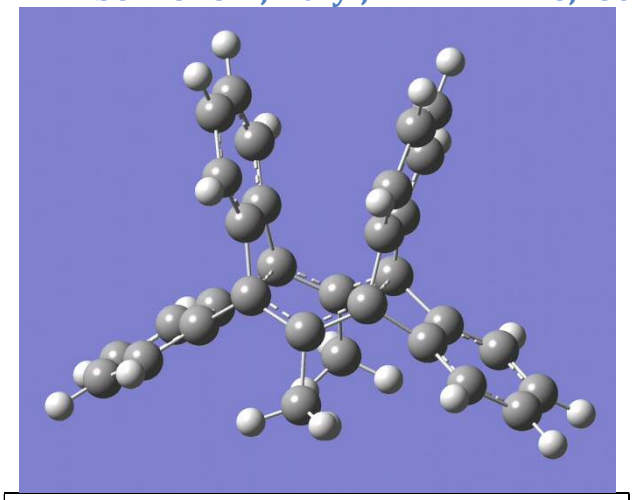


RB3LYP/6-311+G(d) level:
C¨¨C bond length: 2.29258 Å
Electronic energy: -1232.736564 Hartrees
Gibbs free energy: -1232.358179 Hartrees
No imaginary frequencies
Point group: C_2

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1232.739136 Hartrees
<S^2> (singlet): 0.4884
NICS(0): -5.7726 ppm
NICS(1): 0.2475 ppm
NICS(–1): -5.3664 ppm
Isotropic magnetic susceptibility: -13.6779 cgs-ppm
Electronic energy (triplet): -1232.719173 Hartrees
<S^2> (triplet): 2.0672

Cartesian coordinates:
C,0,-1.1416247887,-1.2318948307,-0.1909413995
C,0,1.1508934431,-1.2321626924,-0.207283968
C,0,1.1416247887,1.2318948307,-0.1909413995
C,0,-1.1508934431,1.2321626924,-0.207283968
C,0,-0.7095048734,1.4698647844,1.2160278401
C,0,0.6825982745,1.4645195586,1.2268363721
C,0,1.3931041527,1.7888707306,2.3731389757
C,0,-0.7276262655,2.120509587,3.514915526
C,0,0.6672449033,2.1128278235,3.5267283232
H,0,-1.2692417116,2.3776605868,4.4198428055
H,0,1.1962114249,2.3636346643,4.4408906652
C,0,0.7095048734,-1.4698647844,1.2160278401
C,0,-0.6825982745,-1.4645195586,1.2268363721
C,0,1.4367355651,-1.8025382136,2.3493222462
C,0,0.7276262655,-2.120509587,3.514915526
C,0,-0.6672449033,-2.1128278235,3.5267283232
H,0,1.2692417116,-2.3776605868,4.4198428055
H,0,-1.1962114249,-2.3636346643,4.4408906652
H,0,2.4788916611,1.7866969503,2.3834206605
H,0,2.522515343,-1.8106534058,2.3405649251
C,0,-0.70129701,2.4182028525,-1.0503009153
C,0,0.7038301129,2.416960582,-1.0396816639
C,0,-1.4045146206,3.4261926587,-1.6938109295
C,0,1.420665684,3.4184349312,-1.6771904395
C,0,-0.6813540616,4.4326607348,-2.350997306
H,0,-2.4905128602,3.4348356442,-1.7017216079
C,0,0.7112555686,4.4282934497,-2.343790011
H,0,2.5065433469,3.418997285,-1.6741771581
H,0,-1.2135172308,5.2238694422,-2.8696577104
H,0,1.2537128519,5.2155536374,-2.8578039103
C,0,-0.7038301129,-2.416960582,-1.0396816639
C,0,-1.420665684,-3.4184349312,-1.6771904395
C,0,0.70129701,-2.4182028525,-1.0503009153
C,0,-0.7112555686,-4.4282934497,-2.343790011
H,0,-2.5065433469,-3.418997285,-1.6741771581
C,0,1.4045146206,-3.4261926587,-1.6938109295
C,0,0.6813540616,-4.4326607348,-2.350997306
H,0,-1.2537128519,-5.2155536374,-2.8578039103
H,0,2.4905128602,-3.4348356442,-1.7017216079
H,0,1.2135172308,-5.2238694422,-2.8696577104
C,0,-1.4367355651,1.8025382136,2.3493222462
H,0,-2.522515343,1.8106534058,2.3405649251
C,0,-1.3931041527,-1.7888707306,2.3731389757
H,0,-2.4788916611,-1.7866969503,2.3834206605
C,0,-1.4898720108,-0.0046267219,-0.7828520018
C,0,1.4898720108,0.0046267219,-0.7828520018
C,0,-1.9095981647,-0.0361849011,-2.2442949461
H,0,-2.8511124982,-0.5806806448,-2.3555963789
H,0,-2.0579480543,0.9637214882,-2.646778883
H,0,-1.1760673297,-0.5479197933,-2.8718552292
C,0,1.9095981647,0.0361849011,-2.2442949461
H,0,2.8511124982,0.5806806448,-2.3555963789
H,0,2.0579480543,-0.9637214882,-2.646778883
H,0,1.1760673297,0.5479197933,-2.8718552292
Bq,0,0.,0.,-0.393692456
Bq,0,0.007127545,-0.006605257,0.606260327
Bq,0,-0.007127545,0.006605257,-1.39364524

Ar = benzene-1,2-diyl, $R^1 = R^2$ = Me, localised ⇌ delocalised TS

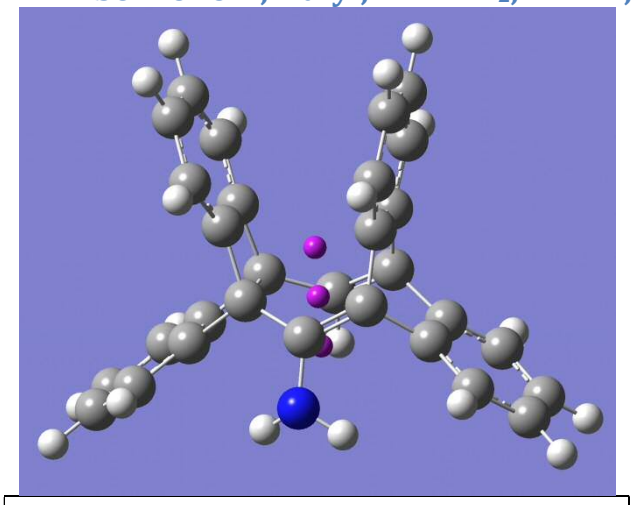


RB3LYP/6-311+G(d) level:
C···C bond lengths: 2.27784 Å, 2.30408 Å
Electronic energy: -1232.736620 Hartrees
Gibbs free energy: -1232.358040 Hartrees
Imaginary frequency: 86.5*i* cm^{-1}
Point group: C_1

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1232.739008 Hartrees
<S^2> (singlet): 0.4783
Electronic energy (triplet): -1232.718758 Hartrees
<S^2> (triplet): 2.0671

Cartesian coordinates:
C,0,0.0262970905,1.6931486387,-0.1948943438
C,0,-1.6807865358,0.1457995604,-0.2133182444
C,0,-0.0131476453,-1.6672286344,-0.2006511751
C,0,1.675533668,-0.1385490223,-0.2063447427
C,0,1.5124919726,-0.6122541937,1.2171758064
C,0,0.478110175,-1.5435829659,1.2208812441
C,0,0.1674492075,-2.2685699959,2.3618658879
C,0,1.9589545738,-1.0947799224,3.5133016788
C,0,0.9213181607,-2.0272306951,3.5178171386
H,0,2.5306129589,-0.92604741,4.4205627575
H,0,0.6970801876,-2.573670727,4.4285946129
C,0,-1.5056538051,0.6185627098,1.2088481509
C,0,-0.4732541881,1.5528875389,1.2207651219
C,0,-2.2631975227,0.3702187957,2.3440146966
C,0,-1.9519635196,1.0797220831,3.5110295818
C,0,-0.9172970199,2.0151451128,3.5232431071
H,0,-2.5230223108,0.9009700035,4.4167509081
H,0,-0.6939746997,2.5546336258,4.4383763182
H,0,-0.6375656564,-2.997224672,2.3665543564
H,0,-3.0704663874,-0.3559521667,2.3349520692
C,0,2.1480171621,-1.3143341317,-1.0510354149
C,0,1.1059102242,-2.255633888,-1.0481420787
C,0,3.3503755877,-1.5879876484,-1.6863932792
C,0,1.2495876582,-3.4786730541,-1.6859474844
C,0,3.4937428638,-2.8189879133,-2.3435203246
H,0,4.1616193823,-0.8658962472,-1.6879914665
C,0,2.4579865824,-3.7502564071,-2.3444571791
H,0,0.4448980762,-4.207783054,-1.6890166242
H,0,4.4226737823,-3.0481789899,-2.8561641006
H,0,2.587736207,-4.6973109777,-2.8587608144
C,0,-1.0954226108,2.2719854671,-1.0451281043
C,0,-1.2385239922,3.4958256688,-1.6815652412
C,0,-2.1383865917,1.3294340582,-1.0553805051
C,0,-2.442695656,3.769029157,-2.3468590762
H,0,-0.4354491717,4.2267313041,-1.676402524
C,0,-3.3363768831,1.6054755707,-1.6982810526
C,0,-3.4775021772,2.8372338365,-2.3542369471
H,0,-2.5697595035,4.7177092007,-2.8588221875
H,0,-4.1468153854,0.8825275925,-1.7056000761
H,0,-4.4038894067,3.0664426664,-2.8714542983
C,0,2.2725704135,-0.3753427567,2.3527408223
H,0,3.0819151851,0.3485084632,2.3501559741
C,0,-0.1653412845,2.2680821181,2.3687156903
H,0,0.6375935571,2.9989619058,2.3787981213
C,0,1.1001405153,1.008681356,-0.7842052805
C,0,-1.1035387609,-0.996285808,-0.7897610934
C,0,1.3744369881,1.2896518754,-2.2541907927
H,0,1.5521961099,2.3550628637,-2.4149616995
H,0,2.2481572939,0.7495885071,-2.6134417801
H,0,0.526592839,1.0127076428,-2.8868623518
C,0,-1.4120459543,-1.3161605196,-2.2440555975
H,0,-1.8547270519,-2.3137745781,-2.3218432552
H,0,-2.1186094602,-0.6102646402,-2.676143383
H,0,-0.5145852416,-1.3227663032,-2.8661375259

Ar = benzene-1,2-diyl, $R^1 = NH_2$, $R^2 = H$, localised structure

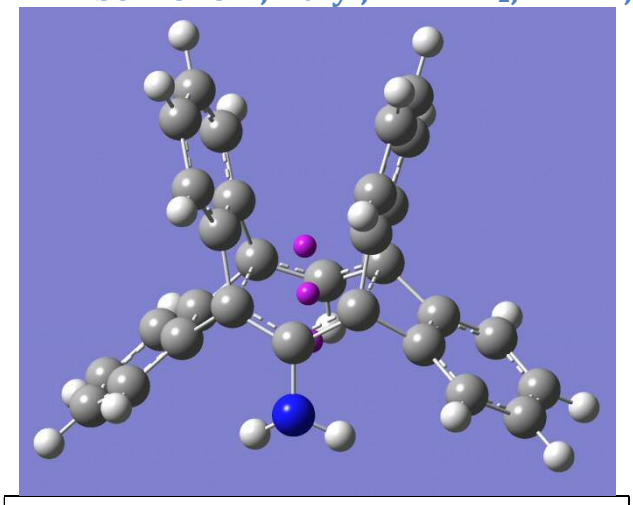


RB3LYP/6-311+G(d) level:
Allyl-allyl C–C bond length: 1.73717 Å
Distance between terminal allyl C atoms: 2.48119 Å
Sum of bond angles for terminal aminoallyl C: 348.747º
Sum of bond angles for terminal non-substituted allyl C: 351.131º
Electronic energy: -1209.476524 Hartrees
Gibbs free energy: -1209.131918 Hartrees
No imaginary frequencies
Point group: C_1

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1209.476524 Hartrees
$\langle S^2 \rangle$ (singlet): 0.0000
NICS(0): -1.1916 ppm
NICS(1): 0.9474 ppm
NICS(–1): -2.5898 ppm
Isotropic magnetic susceptibility: -102.4002 cgs-ppm

Cartesian coordinates:
C,0,-1.3973853206,-0.1428265204,-1.1856440367
C,0,-1.382833551,-0.0394864595,1.2933514125
C,0,1.0847135767,-0.3174701731,0.9475378815
C,0,1.0811682749,-0.4167510301,-0.7867928959
C,0,1.6292836229,1.0051224411,-0.6987701865
C,0,1.6383833853,1.0854282138,0.6907522638
C,0,2.18724187,2.1632806973,1.363381311
C,0,2.7140334674,3.102958442,-0.8320549296
C,0,2.7221066164,3.184809094,0.5644511797
H,0,3.1410554268,3.9168875239,-1.4097841219
H,0,3.1550672114,4.060514988,1.038082981
C,0,-1.4126954162,1.3369969754,0.7083703271
C,0,-1.3952844926,1.2698395299,-0.6920352027
C,0,-1.5076004135,2.5558913922,1.3667881081
C,0,-1.5747748731,3.7282675895,0.6074740889
C,0,-1.5514028868,3.6692300064,-0.7850717535
H,0,-1.6467382456,4.6896990237,1.1062900047
H,0,-1.6057854,4.586003541,-1.3639806345
H,0,2.2034649511,2.2358184617,2.4461484072
H,0,-1.5229796287,2.5990622881,2.4515421264
C,0,2.1949018486,-1.4479226878,-0.554228468
C,0,2.1858016678,-1.3745578417,0.8377588852
C,0,3.087631894,-2.253321215,-1.243616101
C,0,3.0616894594,-2.107967997,1.619296536
C,0,3.9755040037,-3.0104129915,-0.4616414251
H,0,3.1070542008,-2.3160048661,-2.3270812088
C,0,3.9612103299,-2.941027717,0.9342768917
H,0,3.0628467943,-2.0604218094,2.7038283628
H,0,4.6903992298,-3.6650930188,-0.9501884895
H,0,4.6644994904,-3.5449749723,1.4991658638
C,0,-2.5954877964,-0.8707798305,-0.6032628499
C,0,-3.6108565744,-1.5594540972,-1.2548117923
C,0,-2.5884524092,-0.8208754514,0.8212812884
C,0,-4.61158867,-2.2005010993,-0.5091179735
H,0,-3.6330217584,-1.5942713753,-2.3403268845
C,0,-3.583444694,-1.4501849478,1.5523823672
C,0,-4.5975318132,-2.1471186237,0.8796765579
H,0,-5.4047720639,-2.7349305997,-1.02258782
H,0,-3.5728962295,-1.4106560535,2.6373802048
H,0,-5.3778285427,-2.6421851563,1.4491187676
C,0,2.1702394464,1.9958340918,-1.4996913224
H,0,2.1728041285,1.9411388343,-2.5835599648
C,0,-1.4666545502,2.4381363604,-1.4427296949
H,0,-1.4565786662,2.3913554206,-2.527304517
C,0,-0.2408283364,-0.8596490362,-1.3511088516
C,0,-0.2289109694,-0.6984716224,1.5348319803
H,0,-0.3075652841,-1.7559838961,1.7811679128
N,0,-0.2775823146,-2.1955278766,-1.7296705875
H,0,-1.1920837037,-2.6258818129,-1.7547968031
H,0,0.4416573679,-2.7997026261,-1.3600976151
Bq,0,-0.180679388,-0.412442474,0.075362582
Bq,0,-0.289507413,-1.405166527,0.126893305
Bq,0,-0.071851362,0.580281579,0.023831859

Ar = benzene-1,2-diyl, $R^1 = NH_2$, $R^2 = H$, delocalised structure

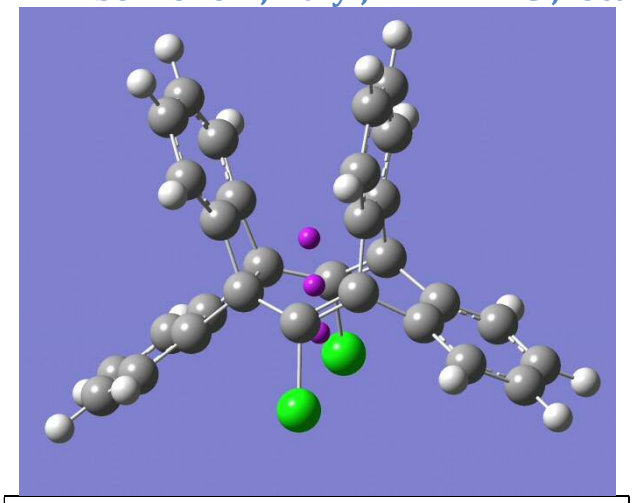


RB3LYP/6-311+G(d) level:
C¨C bond length: 2.29192 Å
Electronic energy: -1209.470861 Hartrees
Gibbs free energy: -1209.127315 Hartrees
Imaginary frequency: 14.6*i* cm^{-1}
Point group: C_s

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1209.473545 Hartrees
<S^2> (singlet): 0.5032
NICS(0): -6.7001 ppm
NICS(1): -0.5436 ppm
NICS(–1): -4.6734 ppm
Isotropic magnetic susceptibility: -58.5974 cgs-ppm
Electronic energy (triplet): -1209.454598 Hartrees
<S^2> (triplet): 2.0647

Cartesian coordinates:
C,0,0.3010565639,1.0582742154,-1.2417612088
C,0,0.1741183282,-1.2301276533,-1.2452495146
C,0,0.174118329,-1.2301276533,1.2452495145
C,0,0.3010565647,1.0582742154,1.2417612086
C,0,-1.1360423973,0.6866970167,1.4884527371
C,0,-1.2146377942,-0.7043903655,1.5093985964
C,0,-2.3920790576,-1.356251343,1.8440380635
C,0,-3.4357523519,0.8210033141,2.1278965538
C,0,-3.5116730631,-0.571814748,2.1499915687
H,0,-4.3163268282,1.4085121969,2.3683037794
H,0,-4.4502268112,-1.0527744583,2.4071309814
C,0,-1.2146377952,-0.7043903655,-1.5093985956
C,0,-1.1360423983,0.6866970167,-1.4884527363
C,0,-2.3920790588,-1.356251343,-1.8440380619
C,0,-3.5116730645,-0.5718147479,-2.1499915664
C,0,-3.4357523532,0.8210033141,-2.1278965515
H,0,-4.4502268127,-1.0527744583,-2.4071309785
H,0,-4.3163268297,1.4085121969,-2.3683037765
H,0,-2.4524911165,-2.4402282375,1.8596759032
H,0,-2.4524911177,-2.4402282375,-1.8596759016
C,0,1.1691049109,0.5589465597,2.3875620703
C,0,1.1050371307,-0.8442300731,2.3784288238
C,0,1.9267697043,1.2283001403,3.3384360641
C,0,1.8004024273,-1.5978582684,3.3103969018
C,0,2.6377243697,0.4679267833,4.2810943283
H,0,1.9823678725,2.3129758814,3.3485386073
C,0,2.5779573873,-0.9229316667,4.2649300248
H,0,1.7587445253,-2.6829175103,3.2980581875
H,0,3.2427085701,0.9708565982,5.0288689316
H,0,3.1387237783,-1.4925530364,4.999269573
C,0,1.1691049093,0.5589465597,-2.387562071
C,0,1.9267697021,1.2283001403,-3.3384360654
C,0,1.1050371291,-0.8442300731,-2.3784288245
C,0,2.637724367,0.4679267834,-4.28109433
H,0,1.9823678703,2.3129758814,-3.3485386086
C,0,1.8004024251,-1.5978582684,-3.310396903
C,0,2.5779573845,-0.9229316667,-4.2649300265
H,0,3.2427085668,0.9708565983,-5.0288689337
H,0,1.7587445231,-2.6829175103,-3.2980581886
H,0,3.138723775,-1.4925530364,-4.999269575
C,0,-2.2383987849,1.4699097792,1.801044515
H,0,-2.1804505396,2.5539574944,1.7862034406
C,0,-2.2383987861,1.4699097792,-1.8010445136
H,0,-2.1804505407,2.5539574944,-1.7862034392
C,0,0.8962951496,1.3674414649,-0.0000000003
C,0,0.7008914169,-1.5757709071,-0.0000000002
N,0,2.2601287812,1.6937858682,-0.0000000007
H,0,2.7644720428,1.4415623973,-0.8383276639
H,0,2.7644720433,1.4415623973,0.8383276621
H,0,1.7625727485,-1.8168034999,-0.0000000006
Bq,0,0.424589392,-0.092006053,-1.33333E-10
Bq,0,-0.573512975,-0.03042955,1.47528E-10
Bq,0,1.422691759,-0.153582556,-4.14194E-10

Ar = benzene-1,2-diyl, $R^1 = R^2$ = Cl, localised structure

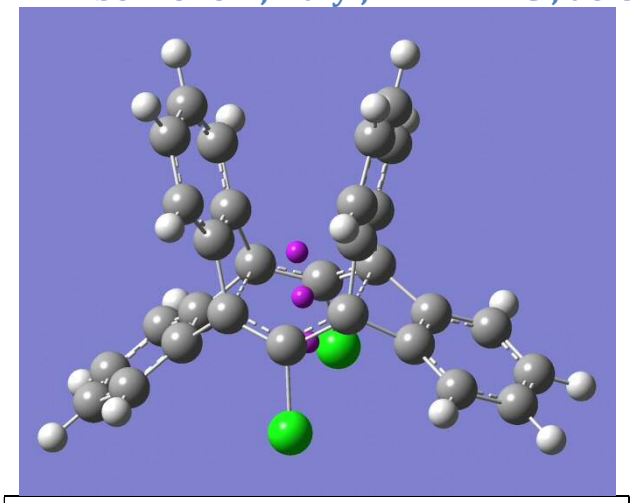


RB3LYP/6-311+G(d) level:
Allyl-allyl C–C bond length: 1.73920 Å
Distance between terminal allyl C atoms: 2.45394 Å
Sum of bond angles for terminal chloroallyl C: 351.852º
Electronic energy: -2073.343216 Hartrees
Gibbs free energy: -2073.037812 Hartrees
No imaginary frequencies
Point group: C_s

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -2073.343216 Hartrees
<S^2> (singlet): 0.0000
NICS(0): -0.2226 ppm
NICS(1): 1.2443 ppm
NICS(–1): -1.3167 ppm
Isotropic magnetic susceptibility: -58.5555 cgs-ppm

Cartesian coordinates:
C,0,0.2732969298,1.4001160052,1.2269700486
C,0,0.2732969298,1.4001160052,-1.2269700486
C,0,0.5170740337,-1.0802908006,-0.8695983374
C,0,0.5170740337,-1.0802908006,0.8695983374
C,0,-0.9148110232,-1.593360863,0.695794479
C,0,-0.9148110232,-1.593360863,-0.695794479
C,0,-1.9555483173,-2.1277300547,-1.4341845601
C,0,-3.0284384073,-2.6541549285,0.6993330402
C,0,-3.0284384073,-2.6541549285,-0.6993330402
H,0,-3.8782418201,-3.0768291623,1.2261564834
H,0,-3.8782418201,-3.0768291623,-1.2261564834
C,0,-1.1287591082,1.4073119726,-0.6987907068
C,0,-1.1287591082,1.4073119726,0.6987907068
C,0,-2.3179208554,1.5017447111,-1.4087504249
C,0,-3.518113079,1.5944576466,-0.6970675871
C,0,-3.518113079,1.5944576466,0.6970675871
H,0,-4.4573372159,1.6699155474,-1.2355228865
H,0,-4.4573372159,1.6699155474,1.2355228865
H,0,-1.9617625182,-2.1421622953,-2.5192235788
H,0,-2.3159061924,1.5033225096,-2.4940117007
C,0,1.5211186538,-2.2227228703,0.6953394613
C,0,1.5211186538,-2.2227228703,-0.6953394613
C,0,2.2243253094,-3.1594301437,1.4333713191
C,0,2.2243253094,-3.1594301437,-1.4333713191
C,0,2.9551223741,-4.1043353425,0.6995941064
H,0,2.2367375399,-3.1637038288,2.518021688
C,0,2.9551223741,-4.1043353425,-0.6995941064
H,0,2.2367375399,-3.1637038288,-2.518021688
H,0,3.5377920667,-4.8532379567,1.2267788655
H,0,3.5377920667,-4.8532379567,-1.2267788655
C,0,1.00038073,2.6255807251,0.7111183919
C,0,1.5973886432,3.6650129577,1.4065275281
C,0,1.00038073,2.6255807251,-0.7111183919
C,0,2.1981612953,4.7108849088,0.6954943606
H,0,1.6091946044,3.6599514754,2.491233894
C,0,1.5973886432,3.6650129577,-1.4065275281
C,0,2.1981612953,4.7108849088,-0.6954943606
H,0,2.6681967833,5.5257713699,1.2365452132
H,0,1.6091946044,3.6599514754,-2.491233894
H,0,2.6681967833,5.5257713699,-1.2365452132
C,0,-1.9555483173,-2.1277300547,1.4341845601
H,0,-1.9617625182,-2.1421622953,2.5192235788
C,0,-2.3179208554,1.5017447111,1.4087504249
H,0,-2.3159061924,1.5033225096,2.4940117007
C,0,0.9152653464,0.2335358533,1.464434265
C,0,0.9152653464,0.2335358533,-1.464434265
Cl,0,2.6047350785,0.3126108586,1.9938720301
Cl,0,2.6047350785,0.3126108586,-1.9938720301
Bq,0,0.568545437,0.184453686,0.
Bq,0,-0.426918386,0.089312859,0.
Bq,0,1.56400926,0.279594513,0.

Ar = benzene-1,2-diyl, $R^1 = R^2 = Cl$, delocalised structure

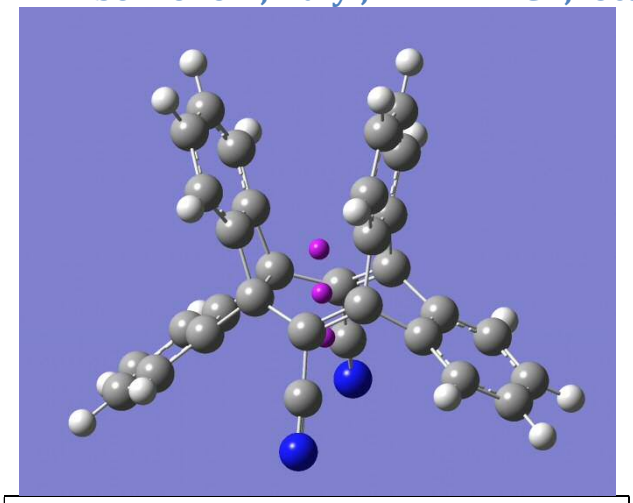


RB3LYP/6-311+G(d) level:
C¨C bond length: 2.26908 Å
Electronic energy: -2073.337536 Hartrees
Gibbs free energy: -2073.032933 Hartrees
Imaginary frequency: 71.9*i* cm^{-1}
Point group: C_{2v}

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -2073.339454 Hartrees
<S²> (singlet): 0.4176
NICS(0): -6.4732 ppm
NICS(1): -0.6133 ppm
NICS(–1): -3.7489 ppm
Isotropic magnetic susceptibility: -88.9214 cgs-ppm
Electronic energy (triplet): -2073.316784 Hartrees
<S²> (triplet): 2.0690

Cartesian coordinates:
C,0,-1.2471761949,1.1345376806,-0.0436474555
C,0,-1.2471761949,-1.1345376806,-0.0436474555
C,0,1.2471761949,-1.1345376806,-0.0436474555
C,0,1.2471761949,1.1345376806,-0.0436474555
C,0,1.4843686056,0.6955410196,1.3807972643
C,0,1.4843686056,-0.6955410196,1.3807972643
C,0,1.8085030064,-1.4172381592,2.5193577615
C,0,2.127934052,0.6976021457,3.6780132438
C,0,2.127934052,-0.6976021457,3.6780132438
H,0,2.3810834278,1.2320906769,4.5880464077
H,0,2.3810834278,-1.2320906769,4.5880464077
C,0,-1.4843686056,-0.6955410196,1.3807972643
C,0,-1.4843686056,0.6955410196,1.3807972643
C,0,-1.8085030064,-1.4172381592,2.5193577615
C,0,-2.127934052,-0.6976021457,3.6780132438
C,0,-2.127934052,0.6976021457,3.6780132438
H,0,-2.3810834278,-1.2320906769,4.5880464077
H,0,-2.3810834278,1.2320906769,4.5880464077
H,0,1.8124081454,-2.5026802266,2.5198136884
H,0,-1.8124081454,-2.5026802266,2.5198136884
C,0,2.415258048,0.7007565807,-0.9127185287
C,0,2.415258048,-0.7007565807,-0.9127185287
C,0,3.4040274492,1.4156330847,-1.5693475928
C,0,3.4040274492,-1.4156330847,-1.5693475928
C,0,4.4018136176,0.6968334078,-2.2416175212
H,0,3.3966197246,2.5005085432,-1.5841102417
C,0,4.4018136176,-0.6968334078,-2.2416175212
H,0,3.3966197246,-2.5005085432,-1.5841102417
H,0,5.1810907663,1.2330720856,-2.7736417509
H,0,5.1810907663,-1.2330720856,-2.7736417509
C,0,-2.415258048,0.7007565807,-0.9127185287
C,0,-3.4040274492,1.4156330847,-1.5693475928
C,0,-2.415258048,-0.7007565807,-0.9127185287
C,0,-4.4018136176,0.6968334078,-2.2416175212
H,0,-3.3966197246,2.5005085432,-1.5841102417
C,0,-3.4040274492,-1.4156330847,-1.5693475928
C,0,-4.4018136176,-0.6968334078,-2.2416175212
H,0,-5.1810907663,1.2330720856,-2.7736417509
H,0,-3.3966197246,-2.5005085432,-1.5841102417
H,0,-5.1810907663,-1.2330720856,-2.7736417509
C,0,1.8085030064,1.4172381592,2.5193577615H,0,1.8124081454,2.5026802266,2.5198136884
C,0,-1.8085030064,1.4172381592,2.5193577615
H,0,-1.8124081454,2.5026802266,2.5198136884
C,0,0.,1.4838752324,-0.5708964731
C,0,0.,-1.4838752324,-0.5708964731
Cl,0,0.,-1.9854011279,-2.2792929966
Cl,0,0.,1.9854011279,-2.2792929966
Bq,0,0.,0.,-0.219397128
Bq,0,0.,0.,0.780602872
Bq,0,0.,0.,-1.219397128

Ar = benzene-1,2-diyl, $R^1 = R^2 = CN$, localised structure

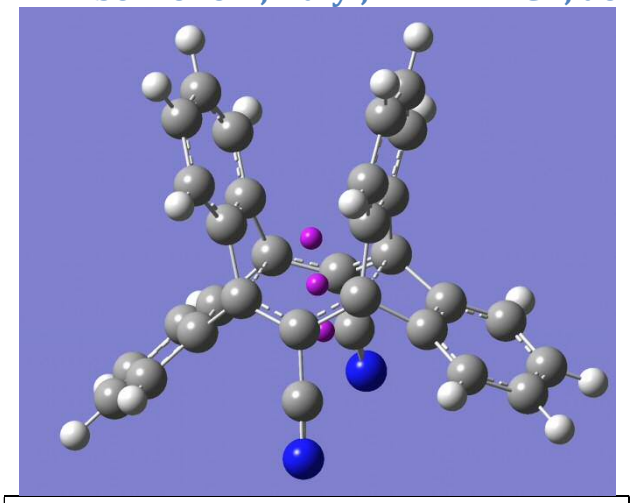


RB3LYP/6-311+G(d) level:
Allyl-allyl C–C bond length: 1.73512 Å
Distance between terminal allyl C atoms: 2.43076 Å
Sum of bond angles for terminal cyanoallyl C: 352.320º
Electronic energy: -1338.628064 Hartrees
Gibbs free energy: -1338.307696 Hartrees
No imaginary frequencies
Point group: C_s

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1338.628064 Hartrees
<S^2> (singlet): 0.0000
NICS(0): -1.7178 ppm
NICS(1): 0.4083 ppm
NICS(–1): -2.3044 ppm
Isotropic magnetic susceptibility: cgs-ppm

Cartesian coordinates:
C,0,0.0395880324,1.3748617161,1.2153819057
C,0,0.0395880324,1.3748617161,-1.2153819057
C,0,0.3543456185,-1.103919528,-0.8675601529
C,0,0.3543456185,-1.103919528,0.8675601529
C,0,-1.0530288871,-1.6754605599,0.6962039882
C,0,-1.0530288871,-1.6754605599,-0.6962039882
C,0,-2.0745067315,-2.2468953657,-1.4344880498
C,0,-3.1282490693,-2.8098958844,0.6994400255
C,0,-3.1282490693,-2.8098958844,-0.6994400255
H,0,-3.9622877793,-3.2629063112,1.2260819994
H,0,-3.9622877793,-3.2629063112,-1.2260819994
C,0,-1.361492918,1.3494931573,-0.698735282
C,0,-1.361492918,1.3494931573,0.698735282
C,0,-2.5525784046,1.3948913268,-1.4099542763
C,0,-3.7542141659,1.4457540607,-0.6970410953
C,0,-3.7542141659,1.4457540607,0.6970410953
H,0,-4.6954780878,1.4857378658,-1.235222858
H,0,-4.6954780878,1.4857378658,1.235222858
H,0,-2.0798268712,-2.2631754303,-2.5194962461
H,0,-2.5513630533,1.3919480996,-2.4949767718
C,0,1.4255896726,-2.1849950946,0.6956547694
C,0,1.4255896726,-2.1849950946,-0.6956547694
C,0,2.203345259,-3.059160954,1.4350611196
C,0,2.203345259,-3.059160954,-1.4350611196
C,0,3.0057956796,-3.9427187649,0.6993345633
H,0,2.2236849971,-3.0582771704,2.5194791091
C,0,3.0057956796,-3.9427187649,-0.6993345633
H,0,2.2236849971,-3.0582771704,-2.5194791091
H,0,3.6503661619,-4.6390862351,1.2259882439
H,0,3.6503661619,-4.6390862351,-1.2259882439
C,0,0.7460895854,2.6172275101,0.7119850877
C,0,1.3482114987,3.6516149336,1.40845542
C,0,0.7460895854,2.6172275101,-0.7119850877
C,0,1.9520787927,4.6947421602,0.6950402984
H,0,1.3673434825,3.6442704538,2.4928938544
C,0,1.3482114987,3.6516149336,-1.40845542
C,0,1.9520787927,4.6947421602,-0.6950402984
H,0,2.4297695935,5.5048032285,1.2358484355
H,0,1.3673434825,3.6442704538,-2.4928938544
H,0,2.4297695935,5.5048032285,-1.2358484355
C,0,-2.0745067315,-2.2468953657,1.4344880498
H,0,-2.0798268712,-2.2631754303,2.5194962461
C,0,-2.5525784046,1.3948913268,1.4099542763
H,0,-2.5513630533,1.3919480996,2.4949767718
C,0,0.7319584851,0.2260952044,1.4659858434
C,0,0.7319584851,0.2260952044,-1.4659858434
C,0,2.0847997408,0.3416749175,1.9294582852
N,0,3.1467405618,0.4181149631,2.3807624962
C,0,2.0847997408,0.3416749175,-1.9294582852
N,0,3.1467405618,0.4181149631,-2.3807624962
Bq,0,0.375297379,0.165679131,0.
Bq,0,-0.61708317,0.042468548,0.
Bq,0,1.367677927,0.288889713,0.

Ar = benzene-1,2-diyl, $R^1 = R^2$ = CN, delocalised structure

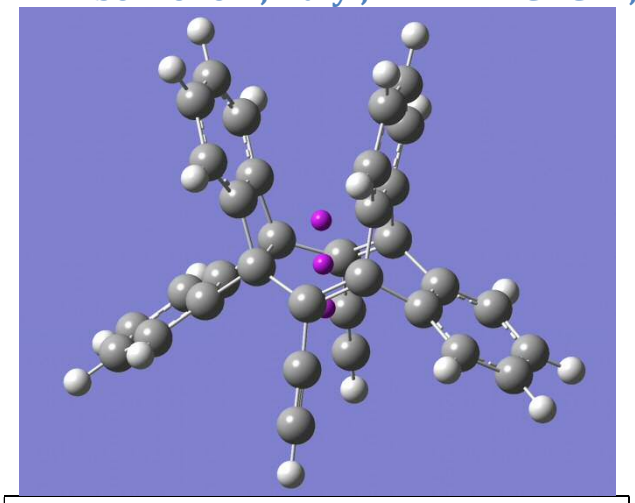


RB3LYP/6-311+G(d) level:
C¨¨C bond length: 2.24694 Å
Electronic energy: -1338.621755 Hartrees
Gibbs free energy: -1338.302170 Hartrees
Imaginary frequency: 121.4*i* cm^{-1}
Point group: C_{2v}

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1338.622864 Hartrees
<S^2> (singlet): 0.3233
NICS(0): -7.2010 ppm
NICS(1): -1.4026 ppm
NICS(–1): -3.8219 ppm
Isotropic magnetic susceptibility: -138.8721 cgs-ppm
Electronic energy (triplet): -1338.596647 Hartrees
<S^2> (triplet): 2.0771

Cartesian coordinates:
C,0,-1.2518849405,1.1234676254,-0.0413656619
C,0,-1.2518849405,-1.1234676254,-0.0413656619
C,0,1.2518849405,-1.1234676254,-0.0413656619
C,0,1.2518849405,1.1234676254,-0.0413656619
C,0,1.5005826775,0.6955942794,1.3810290052
C,0,1.5005826775,-0.6955942794,1.3810290052
C,0,1.8222346328,-1.4182878325,2.5198077492
C,0,2.1406197603,0.697685242,3.6778671162
C,0,2.1406197603,-0.697685242,3.6778671162
H,0,2.3930314327,1.2317715839,4.5881600033
H,0,2.3930314327,-1.2317715839,4.5881600033
C,0,-1.5005826775,-0.6955942794,1.3810290052
C,0,-1.5005826775,0.6955942794,1.3810290052
C,0,-1.8222346328,-1.4182878325,2.5198077492
C,0,-2.1406197603,-0.697685242,3.6778671162
C,0,-2.1406197603,0.697685242,3.6778671162
H,0,-2.3930314327,-1.2317715839,4.5881600033
H,0,-2.3930314327,1.2317715839,4.5881600033
H,0,1.8252913742,-2.5035937596,2.5211624304
H,0,-1.8252913742,-2.5035937596,2.5211624304
C,0,2.406828282,0.7013275648,-0.9346001991
C,0,2.406828282,-0.7013275648,-0.9346001991
C,0,3.3641394251,1.4177738411,-1.6329673615
C,0,3.3641394251,-1.4177738411,-1.6329673615
C,0,4.3315866409,0.6964892311,-2.346820206
H,0,3.3534641933,2.5024030833,-1.654511897
C,0,4.3315866409,-0.6964892311,-2.346820206
H,0,3.3534641933,-2.5024030833,-1.654511897
H,0,5.0837571774,1.2321762076,-2.9164427647
H,0,5.0837571774,-1.2321762076,-2.9164427647
C,0,-2.406828282,0.7013275648,-0.9346001991
C,0,-3.3641394251,1.4177738411,-1.6329673615
C,0,-2.406828282,-0.7013275648,-0.9346001991
C,0,-4.3315866409,0.6964892311,-2.346820206
H,0,-3.3534641933,2.5024030833,-1.654511897
C,0,-3.3641394251,-1.4177738411,-1.6329673615
C,0,-4.3315866409,-0.6964892311,-2.346820206
H,0,-5.0837571774,1.2321762076,-2.9164427647
H,0,-3.3534641933,-2.5024030833,-1.654511897
H,0,-5.0837571774,-1.2321762076,-2.9164427647
C,0,1.8222346328,1.4182878325,2.5198077492
H,0,1.8252913742,2.5035937596,2.5211624304
C,0,-1.8222346328,1.4182878325,2.5198077492
H,0,-1.8252913742,2.5035937596,2.5211624304
C,0,0.,1.4751390995,-0.5851789232
C,0,0.,-1.4751390995,-0.5851789232
C,0,0.,1.8971246258,-1.9647626768
N,0,0.,2.3144128482,-3.041880834
C,0,0.,-1.8971246258,-1.9647626768
N,0,0.,-2.3144128482,-3.041880834
Bq,0,0.,0.,-0.222636749
Bq,0,0.,0.,0.777363251
Bq,0,0.,0.,-1.222636749

Ar = benzene-1,2-diyl, $R^1 = R^2 = C{\equiv}C{-}H$, localised structure

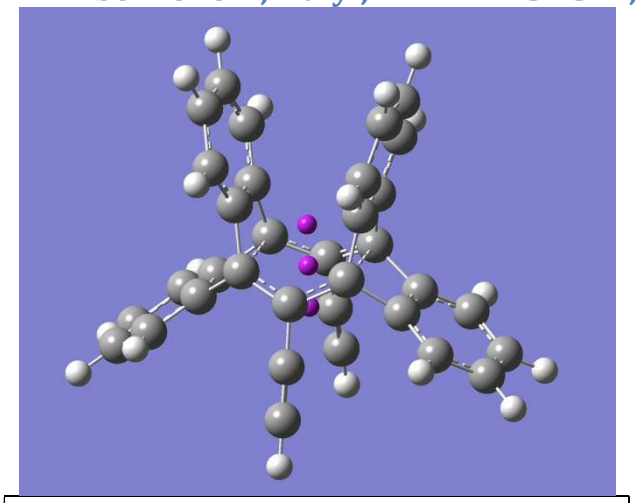


RB3LYP/6-311+G(d) level:
Allyl-allyl C–C bond length: 1.75312 Å
Distance between terminal allyl C atoms: 2.44627 Å
Sum of bond angles for terminal ethynylallyl C: 351.834°
Electronic energy: -1306.421201 Hartrees
Gibbs free energy: -1306.080894 Hartrees
No imaginary frequencies
Point group: C_s

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1306.421201 Hartrees
<S^2> (singlet): 0.0000
NICS(0): -1.1161 ppm
NICS(1): 1.0153 ppm
NICS(–1): -1.8121 ppm
Isotropic magnetic susceptibility: -106.1582 cgs-ppm

Cartesian coordinates:
C,0,0.0590457854,1.3759013944,1.2242492371
C,0,0.0590457854,1.3759013944,-1.2242492371
C,0,0.3830663923,-1.090388634,-0.8648618307
C,0,0.3830663923,-1.090388634,0.8648618307
C,0,-1.0273300076,-1.6586179852,0.6963637656
C,0,-1.0273300076,-1.6586179852,-0.6963637656
C,0,-2.0493851022,-2.2301303204,-1.4337442422
C,0,-3.1035382164,-2.793802388,0.6993537213
C,0,-3.1035382164,-2.793802388,-0.6993537213
H,0,-3.9383403259,-3.2455756391,1.2262601936
H,0,-3.9383403259,-3.2455756391,-1.2262601936
C,0,-1.3392970672,1.3390697606,-0.6992984963
C,0,-1.3392970672,1.3390697606,0.6992984963
C,0,-2.5322561637,1.3857379083,-1.4082715789
C,0,-3.735131347,1.4333486711,-0.6970206625
C,0,-3.735131347,1.4333486711,0.6970206625
H,0,-4.6765032113,1.4716023898,-1.2357216012
H,0,-4.6765032113,1.4716023898,1.2357216012
H,0,-2.0556788753,-2.2447912243,-2.5189636919
H,0,-2.5305860416,1.3848125928,-2.4936075566
C,0,1.4329636241,-2.1929742317,0.6955229831
C,0,1.4329636241,-2.1929742317,-0.6955229831
C,0,2.1844290407,-3.0916696787,1.4334407003
C,0,2.1844290407,-3.0916696787,-1.4334407003
C,0,2.9618647475,-3.999101743,0.699598258
H,0,2.1969476313,-3.0958735575,2.5182291092
C,0,2.9618647475,-3.999101743,-0.699598258
H,0,2.1969476313,-3.0958735575,-2.5182291092
H,0,3.5806114804,-4.718955907,1.2265466134
H,0,3.5806114804,-4.718955907,-1.2265466134
C,0,0.7456769402,2.6255089471,0.712153722
C,0,1.3242478516,3.675814253,1.4065242837
C,0,0.7456769402,2.6255089471,-0.712153722
C,0,1.9048691451,4.7335750115,0.695343492
H,0,1.3367738951,3.6708473376,2.4913157966
C,0,1.3242478516,3.675814253,-1.4065242837
C,0,1.9048691451,4.7335750115,-0.695343492
H,0,2.3584926591,5.5578020637,1.2364999721
H,0,1.3367738951,3.6708473376,-2.4913157966
H,0,2.3584926591,5.5578020637,-1.2364999721
C,0,-2.0493851022,-2.2301303204,1.4337442422
H,0,-2.0556788753,-2.2447912243,2.5189636919
C,0,-2.5322561637,1.3857379083,1.4082715789
H,0,-2.5305860416,1.3848125928,2.4936075566
C,0,0.7765710529,0.238191065,1.4680254706
C,0,0.7765710529,0.238191065,-1.4680254706
C,0,2.1268877656,0.348104884,1.9166617921
C,0,2.1268877656,0.348104884,-1.9166617921
C,0,3.2480685778,0.4190038202,2.3548953315
H,0,4.2466742586,0.486601873,2.7155835869
C,0,3.2480685778,0.4190038202,-2.3548953315
H,0,4.2466742586,0.486601873,-2.7155835869
Bq,0,0.406227744,0.174567942,0.
Bq,0,-0.585625586,0.047182808,0.
Bq,0,1.398081073,0.301953076,0.

Ar = benzene-1,2-diyl, $R^1 = R^2 = C{\equiv}C{-}H$, delocalised structure

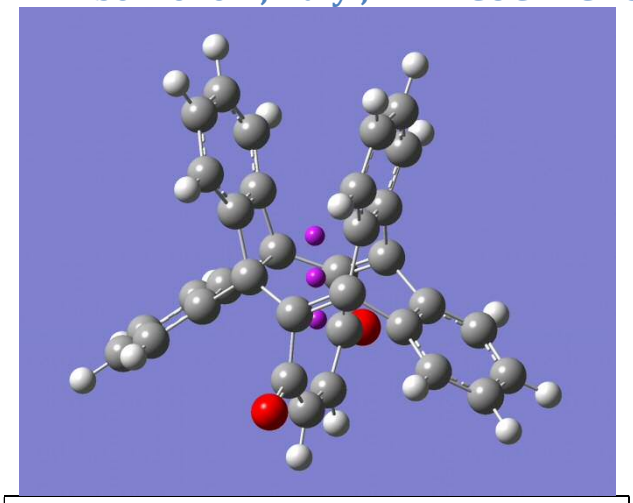


RB3LYP/6-311+G(d) level:
C¨¨C bond length: 2.25625 Å
Electronic energy: -1306.413482 Hartrees
Gibbs free energy: -1306.074109 Hartrees
Imaginary frequency: 156.9*i* cm^{-1}
Point group: C_{2v}

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1306.414974 Hartrees
<S^2> (singlet): 0.4396
NICS(0): -6.7267 ppm
NICS(1): -0.7125 ppm
NICS(–1): -4.2448 ppm
Isotropic magnetic susceptibility: -138.6201 cgs-ppm
Electronic energy (triplet): -1306.389674 Hartrees
<S^2> (triplet): 2.0833

Cartesian coordinates:
C,0,-1.2448176116,1.1281272467,-0.0495048128
C,0,-1.2448176116,-1.1281272467,-0.0495048128
C,0,1.2448176116,-1.1281272467,-0.0495048128
C,0,1.2448176116,1.1281272467,-0.0495048128
C,0,1.4867327172,0.6958038521,1.3735527864
C,0,1.4867327172,-0.6958038521,1.3735527864
C,0,1.8092534778,-1.417101613,2.5132705019
C,0,2.1269261637,0.6976432929,3.6724318547
C,0,2.1269261637,-0.6976432929,3.6724318547
H,0,2.3778818108,1.2321024349,4.5831927624
H,0,2.3778818108,-1.2321024349,4.5831927624
C,0,-1.4867327172,-0.6958038521,1.3735527864
C,0,-1.4867327172,0.6958038521,1.3735527864
C,0,-1.8092534778,-1.417101613,2.5132705019
C,0,-2.1269261637,-0.6976432929,3.6724318547
C,0,-2.1269261637,0.6976432929,3.6724318547
H,0,-2.3778818108,-1.2321024349,4.5831927624
H,0,-2.3778818108,1.2321024349,4.5831927624
H,0,1.8119517179,-2.5026626696,2.5144118495
H,0,-1.8119517179,-2.5026626696,2.5144118495
C,0,2.4131426286,0.7011687883,-0.9223065625
C,0,2.4131426286,-0.7011687883,-0.9223065625
C,0,3.3922791262,1.4159896206,-1.5930826528
C,0,3.3922791262,-1.4159896206,-1.5930826528
C,0,4.3807792167,0.696834862,-2.2795690182
H,0,3.3850319686,2.5010010507,-1.6075998024
C,0,4.3807792167,-0.696834862,-2.2795690182
H,0,3.3850319686,-2.5010010507,-1.6075998024
H,0,5.1534771549,1.2328142137,-2.8216959651
H,0,5.1534771549,-1.2328142137,-2.8216959651
C,0,-2.4131426286,0.7011687883,-0.9223065625
C,0,-3.3922791262,1.4159896206,-1.5930826528
C,0,-2.4131426286,-0.7011687883,-0.9223065625
C,0,-4.3807792167,0.696834862,-2.2795690182
H,0,-3.3850319686,2.5010010507,-1.6075998024
C,0,-3.3922791262,-1.4159896206,-1.5930826528
C,0,-4.3807792167,-0.696834862,-2.2795690182
H,0,-5.1534771549,1.2328142137,-2.8216959651
H,0,-3.3850319686,-2.5010010507,-1.6075998024
H,0,-5.1534771549,-1.2328142137,-2.8216959651
C,0,1.8092534778,1.417101613,2.5132705019
H,0,1.8119517179,2.5026626696,2.5144118495
C,0,-1.8092534778,1.417101613,2.5132705019
H,0,-1.8119517179,2.5026626696,2.5144118495
C,0,0.,1.4831451209,-0.6130272904
C,0,0.,-1.4831451209,-0.6130272904
C,0,0.,1.8993437679,-1.9876736583
C,0,0.,-1.8993437679,-1.9876736583
C,0,0.,-2.3124586706,-3.118830285
H,0,0.,-2.6501094695,-4.1277307257
C,0,0.,2.3124586706,-3.118830285
H,0,0.,2.6501094695,-4.1277307257
Bq,0,0.,0.,-0.237345639
Bq,0,0.,0.,0.762654361
Bq,0,0.,0.,-1.237345639

Ar = benzene-1,2-diyl, R^1 = –COCH=CHCO–, R^2 = –, localised structure

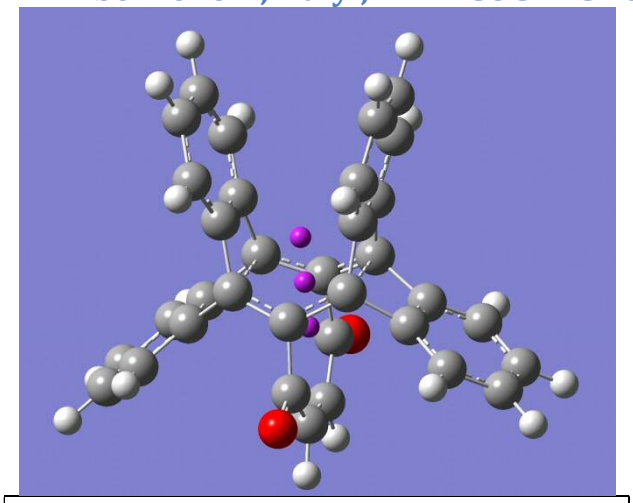


RB3LYP/6-311+G(d) level:
Allyl-allyl C–C bond length: 1.74459 Å
Distance between terminal allyl C atoms: 2.43337 Å
Sum of bond angles for terminal allyl C: 350.728º
Electronic energy: -1457.013067 Hartrees
Gibbs free energy: -1456.659010 Hartrees
No imaginary frequencies
Point group: C_s

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1457.013067 Hartrees
<S^2> (singlet):
NICS(0): -1.3477 ppm
NICS(1): 0.6038 ppm
NICS(–1): 0.4235 ppm
Isotropic magnetic susceptibility: -153.3849 cgs-ppm

Cartesian coordinates:
C,0,-0.6873963687,1.1490451852,1.2166848148
C,0,-0.6873963687,1.1490451852,-1.2166848148
C,0,0.3657742841,-1.1116429522,-0.8722929095
C,0,0.3657742841,-1.1116429522,0.8722929095
C,0,-0.8184019801,-2.0600757949,0.6956390592
C,0,-0.8184019801,-2.0600757949,-0.6956390592
C,0,-1.6383624873,-2.8948685195,-1.4346220487
C,0,-2.4884617832,-3.7338613549,0.6996373548
C,0,-2.4884617832,-3.7338613549,-0.6996373548
H,0,-3.1610453013,-4.4036886311,1.2262164124
H,0,-3.1610453013,-4.4036886311,-1.2262164124
C,0,-2.0273231348,0.7186634362,-0.7014226647
C,0,-2.0273231348,0.7186634362,0.7014226647
C,0,-3.1864707616,0.4327134247,-1.4088178643
C,0,-4.354652709,0.1410268262,-0.6968363628
C,0,-4.354652709,0.1410268262,0.6968363628
H,0,-5.2691618394,-0.0852126444,-1.2355989939
H,0,-5.2691618394,-0.0852126444,1.2355989939
H,0,-1.6405976125,-2.9082335543,-2.5196209451
H,0,-3.1859875842,0.4340055741,-2.4940594536
C,0,1.6986282307,-1.8483162397,0.6965597985
C,0,1.6986282307,-1.8483162397,-0.6965597985
C,0,2.705300994,-2.4451853821,1.4350908294
C,0,2.705300994,-2.4451853821,-1.4350908294
C,0,3.7372999754,-3.0491167691,0.6989500329
H,0,2.7225764453,-2.4382680027,2.5198851916
C,0,3.7372999754,-3.0491167691,-0.6989500329
H,0,2.7225764453,-2.4382680027,-2.5198851916
H,0,4.5586602369,-3.5242290338,1.2259791053
H,0,4.5586602369,-3.5242290338,-1.2259791053
C,0,-0.3971147651,2.5509689525,0.7111162118
C,0,-0.1426239735,3.7207548446,1.4088183979
C,0,-0.3971147651,2.5509689525,-0.7111162118
C,0,0.1157313507,4.8997872672,0.6951979798
H,0,-0.1296344954,3.7198902553,2.4937967534
C,0,-0.1426239735,3.7207548446,-1.4088183979
C,0,0.1157313507,4.8997872672,-0.6951979798
H,0,0.3171422755,5.8189388163,1.2357666698
H,0,-0.1296344954,3.7198902553,-2.4937967534
H,0,0.3171422755,5.8189388163,-1.2357666698
C,0,-1.6383624873,-2.8948685195,1.4346220487
H,0,-1.6405976125,-2.9082335543,2.5196209451
C,0,-3.1864707616,0.4327134247,1.4088178643
H,0,-3.1859875842,0.4340055741,2.4940594536
C,0,0.3387218631,0.2844407401,1.3970423319
C,0,0.3387218631,0.2844407401,-1.3970423319
C,0,1.7005313559,0.8625039704,1.7162401081
O,0,2.0319873086,0.9836116948,2.8823324783
C,0,1.7005313559,0.8625039704,-1.7162401081
O,0,2.0319873086,0.9836116948,-2.8823324783
C,0,2.678770856,1.2986482037,0.6728671607
H,0,3.5699914776,1.6949791018,1.1544189745
C,0,2.678770856,1.2986482037,-0.6728671607
H,0,3.5699914776,1.6949791018,-1.1544189745
Bq,0,0.005699926,0.107280991,0.
Bq,0,-0.902398691,-0.311475385,0.
Bq,0,0.913798543,0.526037367,0.

Ar = benzene-1,2-diyl, R^1 = –COCH=CHCO–, R^2 = –, delocalised structure

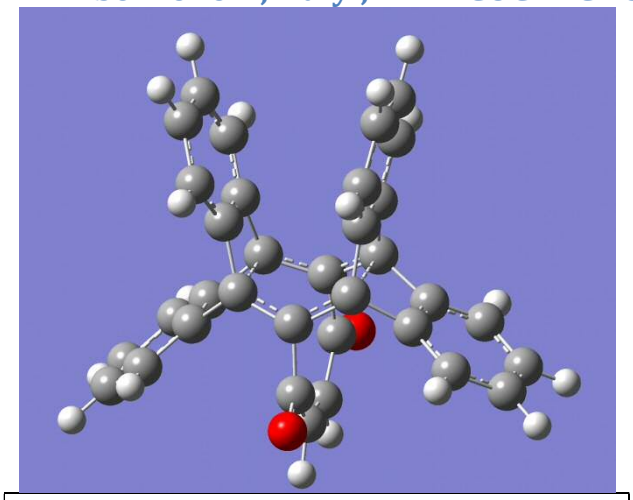


RB3LYP/6-311+G(d) level:
C¨¨C bond length: 2.25205 Å
Electronic energy: -1457.009247 Hartrees
Gibbs free energy: -1456.656807 Hartrees
No imaginary frequencies
Point group: C_{2v}

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1457.010276 Hartrees
<S^2> (singlet): 0.3005
NICS(0): -6.4489 ppm
NICS(1): -1.5960 ppm
NICS(–1): -2.2645 ppm
Isotropic magnetic susceptibility: -14.1726 cgs-ppm
Electronic energy (triplet): -1456.983906 Hartrees
<S^2> (triplet): 2.0625

Cartesian coordinates:
C,0,-1.1260251429,-1.2474864628,0.1644606552
C,0,1.1260251429,-1.2474864628,0.1644606552
C,0,1.1260251429,1.2474864628,0.1644606552
C,0,-1.1260251429,1.2474864628,0.1644606552
C,0,-0.6966549449,1.499821913,1.5884010854
C,0,0.6966549449,1.499821913,1.5884010854
C,0,1.4175684502,1.8225988042,2.7280813067
C,0,-0.6977189435,2.14037392,3.886679228
C,0,0.6977189435,2.14037392,3.886679228
H,0,-1.2320631197,2.3921326478,4.7971976435
H,0,1.2320631197,2.3921326478,4.7971976435
C,0,0.6966549449,-1.499821913,1.5884010854
C,0,-0.6966549449,-1.499821913,1.5884010854
C,0,1.4175684502,-1.8225988042,2.7280813067
C,0,0.6977189435,-2.14037392,3.886679228
C,0,-0.6977189435,-2.14037392,3.886679228
H,0,1.2320631197,-2.3921326478,4.7971976435
H,0,-1.2320631197,-2.3921326478,4.7971976435
H,0,2.5029877524,1.8252370892,2.729088947
H,0,2.5029877524,-1.8252370892,2.729088947
C,0,-0.7013396051,2.4121746584,-0.7168655795
C,0,0.7013396051,2.4121746584,-0.7168655795
C,0,-1.4178781792,3.3648201671,-1.422380522
C,0,1.4178781792,3.3648201671,-1.422380522
C,0,-0.6964073195,4.3304417509,-2.141836346
H,0,-2.502931903,3.3545175037,-1.4409360062
C,0,0.6964073195,4.3304417509,-2.141836346
H,0,2.502931903,3.3545175037,-1.4409360062
H,0,-1.2322130171,5.0833309337,-2.7108824483
H,0,1.2322130171,5.0833309337,-2.7108824483
C,0,-0.7013396051,-2.4121746584,-0.7168655795
C,0,-1.4178781792,-3.3648201671,-1.422380522
C,0,0.7013396051,-2.4121746584,-0.7168655795
C,0,-0.6964073195,-4.3304417509,-2.141836346
H,0,-2.502931903,-3.3545175037,-1.4409360062
C,0,1.4178781792,-3.3648201671,-1.422380522
C,0,0.6964073195,-4.3304417509,-2.141836346
H,0,-1.2322130171,-5.0833309337,-2.7108824483
H,0,2.502931903,-3.3545175037,-1.4409360062
H,0,1.2322130171,-5.0833309337,-2.7108824483
C,0,-1.4175684502,1.8225988042,2.7280813067
H,0,-2.5029877524,1.8252370892,2.729088947
C,0,-1.4175684502,-1.8225988042,2.7280813067
H,0,-2.5029877524,-1.8252370892,2.729088947
C,0,-1.4182974134,0.,-0.3969133525
C,0,1.4182974134,0.,-0.3969133525
C,0,-1.7246192069,0.,-1.8853445624
O,0,-2.8872801063,0.,-2.2467801194
C,0,1.7246192069,0.,-1.8853445624
O,0,2.8872801063,0.,-2.2467801194
C,0,-0.6730255243,0.,-2.9481439762
H,0,-1.1505632884,0.,-3.9254890815
C,0,0.6730255243,0.,-2.9481439762
H,0,1.1505632884,0.,-3.9254890815
Bq,0,0.,0.,-0.022664014
Bq,0,0.,0.,0.977335986
Bq,0,0.,0.,-1.022664014

Ar = benzene-1,2-diyl, R^1 = –COCH=CHCO–, R^2 = –, localised ⇌ delocalised TS

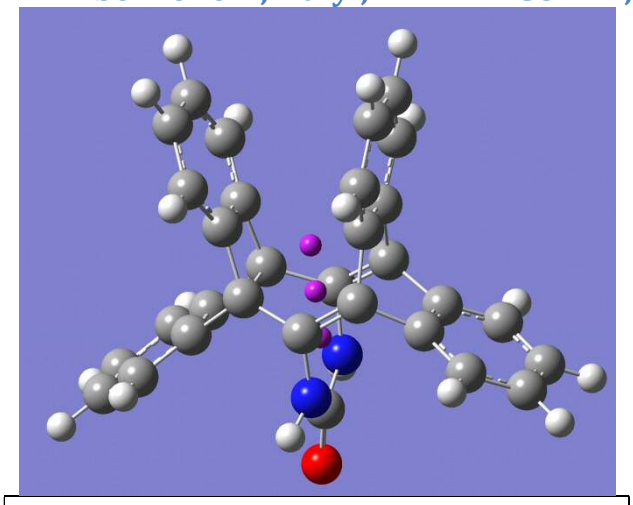


RB3LYP/6-311+G(d) level:
C¨C bond lengths: 2.14465 Å, 2.32733 Å
Electronic energy: -1457.009230 Hartrees
Gibbs free energy: -1456.656258 Hartrees
Imaginary frequency: 94.7*i* cm^{-1}
Point group: C_s

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1457.010276 Hartrees
<S^2> (singlet): 0.3005
Electronic energy (triplet): -1456.979787 Hartrees
<S^2> (triplet): 2.0607

Cartesian coordinates:
C,0,-0.6718619685,1.0604155667,1.1533257625
C,0,-0.6718619685,1.0604155667,-1.1533257625
C,0,0.403849078,-1.1896359636,-1.08976545
C,0,0.403849078,-1.1896359636,1.08976545
C,0,-0.7716334997,-2.0521902426,0.6957638063
C,0,-0.7716334997,-2.0521902426,-0.6957638063
C,0,-1.6457345898,-2.8475744918,-1.4205016412
C,0,-2.5405549407,-3.6475277304,0.6980296413
C,0,-2.5405549407,-3.6475277304,-0.6980296413
H,0,-3.2439600735,-4.2792534374,1.231049271
H,0,-3.2439600735,-4.2792534374,-1.231049271
C,0,-2.0513830989,0.659767518,-0.6975588148
C,0,-2.0513830989,0.659767518,0.6975588148
C,0,-3.2179051387,0.4407631551,-1.4151212523
C,0,-4.3977832365,0.2098683588,-0.6974891359
C,0,-4.3977832365,0.2098683588,0.6974891359
H,0,-5.3247360099,0.031078875,-1.2329625769
H,0,-5.3247360099,0.031078875,1.2329625769
H,0,-1.6463012679,-2.8513469398,-2.5058805174
H,0,-3.2192089555,0.4434096036,-2.5005606383
C,0,1.7092506445,-1.8673383761,0.6998633489
C,0,1.7092506445,-1.8673383761,-0.6998633489
C,0,2.7529558584,-2.4233125057,1.4209487204
C,0,2.7529558584,-2.4233125057,-1.4209487204
C,0,3.8162295101,-2.9853525107,0.6968128737
H,0,2.7669871758,-2.4049306741,2.5058869145
C,0,3.8162295101,-2.9853525107,-0.6968128737
H,0,2.7669871758,-2.4049306741,-2.5058869145
H,0,4.6550994387,-3.4197915875,1.2309777184
H,0,4.6550994387,-3.4197915875,-1.2309777184
C,0,-0.3817359101,2.4837480186,0.7029483403
C,0,-0.1527240659,3.6495193083,1.4153917515
C,0,-0.3817359101,2.4837480186,-0.7029483403
C,0,0.0825537139,4.8315453661,0.6960577891
H,0,-0.1332114984,3.6480637927,2.5005217668
C,0,-0.1527240659,3.6495193083,-1.4153917515
C,0,0.0825537139,4.8315453661,-0.6960577891
H,0,0.2715563999,5.7554191305,1.233149741
H,0,-0.1332114984,3.6480637927,-2.5005217668
H,0,0.2715563999,5.7554191305,-1.233149741
C,0,-1.6457345898,-2.8475744918,1.4205016412
H,0,-1.6463012679,-2.8513469398,2.5058805174
C,0,-3.2179051387,0.4407631551,1.4151212523
H,0,-3.2192089555,0.4434096036,2.5005606383
C,0,0.3701829329,0.1832731341,1.4170134232
C,0,0.3701829329,0.1832731341,-1.4170134232
C,0,1.717826146,0.8142698938,1.7239716895
O,0,2.0562589438,0.942765419,2.8864659136
C,0,1.717826146,0.8142698938,-1.7239716895
O,0,2.0562589438,0.942765419,-2.8864659136
C,0,2.6668380402,1.2944713314,0.673023324
H,0,3.5430278915,1.7271554549,1.1508539174
C,0,2.6668380402,1.2944713314,-0.673023324
H,0,3.5430278915,1.7271554549,-1.1508539174

Ar = benzene-1,2-diyl, R^1 = –NHCONH–, R^2 = –, localised structure

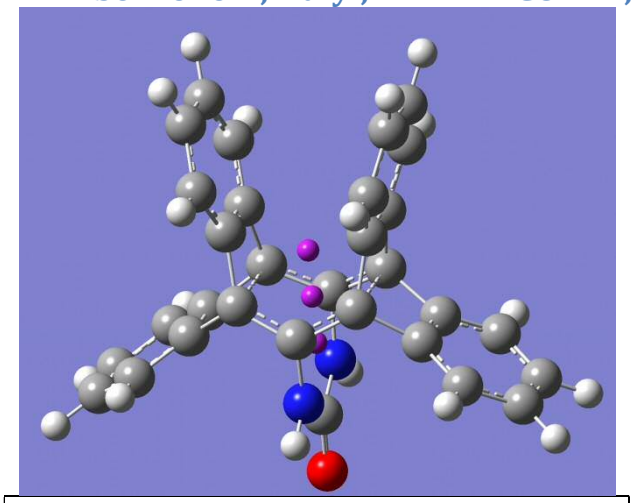


RB3LYP/6-311+G(d) level:
Allyl-allyl C–C bond length: 1.74720 Å
Distance between terminal allyl C atoms: 2.41841 Å
Sum of bond angles for terminal allyl C: 348.979º
Electronic energy: -1376.997905 Hartrees
Gibbs free energy: -1376.650074 Hartrees
No imaginary frequencies
Point group: C_s

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1376.997905 Hartrees
<S^2> (singlet): 0.0000
NICS(0): -4.0101 ppm
NICS(1): -0.1161 ppm
NICS(–1): -3.7916 ppm
Isotropic magnetic susceptibility: -99.6966 cgs-ppm

Cartesian coordinates:
C,0,1.3480893182,1.2092062848,0.0467577306
C,0,1.3480893182,-1.2092062848,0.0467577306
C,0,-1.1529725358,-0.8736002674,0.0075382412
C,0,-1.1529725358,0.8736002674,0.0075382412
C,0,-1.4561892275,0.6965395319,-1.4764232276
C,0,-1.4561892275,-0.6965395319,-1.4764232276
C,0,-1.8431500822,-1.4334367528,-2.5826391347
C,0,-2.2185964063,0.6994732878,-3.716942909
C,0,-2.2185964063,-0.6994732878,-3.716942909
H,0,-2.523575526,1.2262595482,-4.6157297223
H,0,-2.523575526,-1.2262595482,-4.6157297223
C,0,1.527175585,-0.7067409018,-1.3594233288
C,0,1.527175585,0.7067409018,-1.3594233288
C,0,1.7870795381,-1.407401584,-2.5269851254
C,0,2.037837017,-0.6961105514,-3.7058514463
C,0,2.037837017,0.6961105514,-3.7058514463
H,0,2.2405923889,-1.2357201304,-4.6253518586
H,0,2.2405923889,1.2357201304,-4.6253518586
H,0,-1.8596642951,-2.5185900072,-2.5904200425
H,0,1.7961041492,-2.4926700736,-2.5267714465
C,0,-2.4160819187,0.6960496688,0.8561371676
C,0,-2.4160819187,-0.6960496688,0.8561371676
C,0,-3.4194876891,1.4334978794,1.4603485869
C,0,-3.4194876891,-1.4334978794,1.4603485869
C,0,-4.4375351949,0.6991870487,2.0869099618
H,0,-3.4306669312,2.5189840203,1.4689231063
C,0,-4.4375351949,-0.6991870487,2.0869099618
H,0,-3.4306669312,-2.5189840203,1.4689231063
H,0,-5.2441956996,1.2260262963,2.5866531565
H,0,-5.2441956996,-1.2260262963,2.5866531565
C,0,2.5163977403,0.7074106725,0.8704408747
C,0,3.5135112747,1.4079457163,1.5307649539
C,0,2.5163977403,-0.7074106725,0.8704408747
C,0,4.5169731048,0.6961696336,2.198104589
H,0,3.5106528104,2.4932098113,1.5386424972
C,0,3.5135112747,-1.4079457163,1.5307649539
C,0,4.5169731048,-0.6961696336,2.198104589
H,0,5.3004339171,1.2359470229,2.7201728029
H,0,3.5106528104,-2.4932098113,1.5386424972
H,0,5.3004339171,-1.2359470229,2.7201728029
C,0,-1.8431500822,1.4334367528,-2.5826391347
H,0,-1.8596642951,2.5185900072,-2.5904200425
C,0,1.7870795381,1.407401584,-2.5269851254
H,0,1.7961041492,2.4926700736,-2.5267714465
C,0,0.1319938263,1.3066268746,0.6394155518
C,0,0.1319938263,-1.3066268746,0.6394155518
C,0,-0.0324975185,0.,2.7818222495
O,0,-0.2479057277,0.,3.9824547088
N,0,0.1058083461,1.1945201286,2.0775685838
H,0,-0.1903317682,1.9859307177,2.6300760358
N,0,0.1058083461,-1.1945201286,2.0775685838
H,0,-0.1903317682,-1.9859307177,2.6300760358
Bq,0,0.10903687,0.,0.231237175
Bq,0,0.130948177,0.,-0.768522744
Bq,0,0.087125563,0.,1.230997093

Ar = benzene-1,2-diyl, R^1 = –NHCONH–, R^2 = –, delocalised structure



RB3LYP/6-311+G(d) level:
C¨¨C bond length: 2.23683 Å
Electronic energy: -1376.993923 Hartrees
Gibbs free energy: -1376.647414 Hartrees
Imaginary frequency: 49.7*i* cm^{-1}
Point group: C_{2v}

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1376.994387 Hartrees
<S^2> (singlet): 0.1850
NICS(0): -10.7371 ppm
NICS(1): -2.0451 ppm
NICS(–1): -6.1570 ppm
Isotropic magnetic susceptibility: -118.2847 cgs-ppm
Electronic energy (triplet): -1376.962508 Hartrees
<S^2> (triplet): 2.0680

Cartesian coordinates:
C,0,1.2499613848,1.1184174737,0.0158826407
C,0,1.2499613848,-1.1184174737,0.0158826407
C,0,-1.2499613848,-1.1184174737,0.0158826407
C,0,-1.2499613848,1.1184174737,0.0158826407
C,0,-1.4821346796,0.6995619746,-1.417399934
C,0,-1.4821346796,-0.6995619746,-1.417399934
C,0,-1.8078894134,-1.4165275689,-2.5578884933
C,0,-2.1248883793,0.6973770461,-3.7173142177
C,0,-2.1248883793,-0.6973770461,-3.7173142177
H,0,-2.3789424134,1.2321906418,-4.6269114537
H,0,-2.3789424134,-1.2321906418,-4.6269114537
C,0,1.4821346796,-0.6995619746,-1.417399934
C,0,1.4821346796,0.6995619746,-1.417399934
C,0,1.8078894134,-1.4165275689,-2.5578884933
C,0,2.1248883793,-0.6973770461,-3.7173142177
C,0,2.1248883793,0.6973770461,-3.7173142177
H,0,2.3789424134,-1.2321906418,-4.6269114537
H,0,2.3789424134,1.2321906418,-4.6269114537
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H,0,1.817096063,-2.5020136067,-2.5588159928
C,0,-2.4422818527,0.6988096747,0.8585632488
C,0,-2.4422818527,-0.6988096747,0.8585632488
C,0,-3.4393280996,1.4171554953,1.4992432066
C,0,-3.4393280996,-1.4171554953,1.4992432066
C,0,-4.4474305097,0.6974056275,2.1539267256
H,0,-3.4379198478,2.5028461945,1.5081562825
C,0,-4.4474305097,-0.6974056275,2.1539267256
H,0,-3.4379198478,-2.5028461945,1.5081562825
H,0,-5.237483994,1.2322016631,2.6712056872
H,0,-5.237483994,-1.2322016631,2.6712056872
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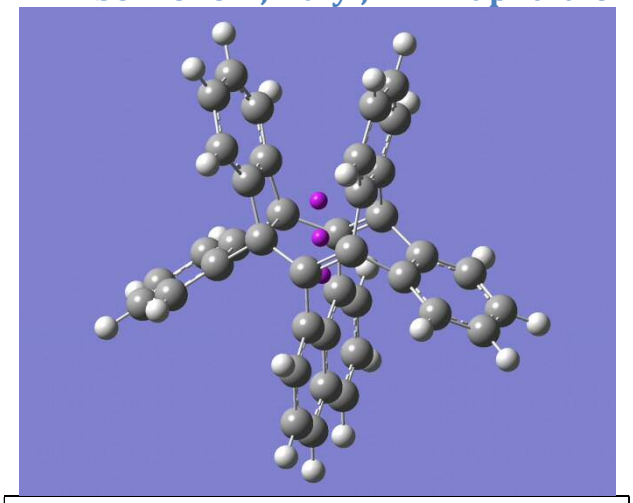
C,0,3.4393280996,1.4171554953,1.4992432066
C,0,2.4422818527,-0.6988096747,0.8585632488
C,0,4.4474305097,0.6974056275,2.1539267256
H,0,3.4379198478,2.5028461945,1.5081562825
C,0,3.4393280996,-1.4171554953,1.4992432066
C,0,4.4474305097,-0.6974056275,2.1539267256
H,0,5.237483994,1.2322016631,2.6712056872
H,0,3.4379198478,-2.5028461945,1.5081562825
H,0,5.237483994,-1.2322016631,2.6712056872
C,0,-1.8078894134,1.4165275689,-2.5578884933
H,0,-1.817096063,2.5020136067,-2.5588159928
C,0,1.8078894134,1.4165275689,-2.5578884933
H,0,1.817096063,2.5020136067,-2.5588159928
C,0,0.,1.3223893687,0.6211370705
C,0,0.,-1.3223893687,0.6211370705
C,0,0.,0.,2.7721374089
O,0,0.,0.,3.9939513719
N,0,0.,1.1913938641,2.0588015279
H,0,0.,2.0052759965,2.6537755784
N,0,0.,-1.1913938641,2.0588015279
H,0,0.,-2.0052759965,2.6537755784
Bq,0,0.,0.,0.217634117
Bq,0,0.,0.,-0.782365883
Bq,0,0.,0.,1.217634117

Ar = benzene-1,2-diyl, R^1 = naphthalene-1,8-diyl, R^2 = –, localised structure



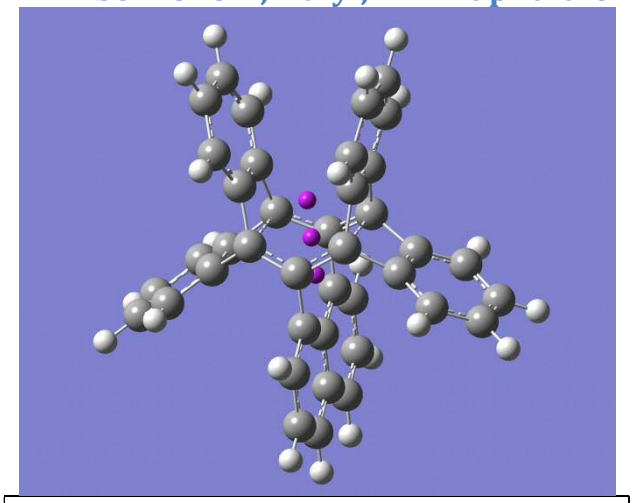
RB3LYP/6-311+G(d) level:
Allyl-allyl C–C bond length: 1.73410 Å
Distance between terminal allyl C atoms: 2.43140 Å
Sum of bond angles for terminal allyl C: 348.982º
Electronic energy: -1537.655178 Hartrees
Gibbs free energy: -1537.227713 Hartrees
No imaginary frequencies
Point group: C_s

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1537.655178 Hartrees
<S^2> (singlet): 0.0000
NICS(0): -3.5382 ppm
NICS(1): 0.5747 ppm
NICS(–1): 0.3569 ppm
Isotropic magnetic susceptibility: -86.6448 cgs-ppm

Cartesian coordinates:

C,0,0.5598587175,-1.3317958695,1.2156991318
C,0,0.5598587175,-1.3317958695,-1.2156991318
C,0,-0.0398600295,-0.1187727285,-1.3211233195
C,0,0.5934384893,1.1589685683,-0.8670517716
C,0,0.5934384893,1.1589685683,0.8670517716
C,0,-0.0398600295,-0.1187727285,1.3211233195
C,0,-1.5442020734,-0.0685280394,-1.272916156
C,0,-2.2193244355,-0.0324513631,0.
C,0,-2.2747746974,-0.0563693066,-2.440060946
C,0,-1.5442020734,-0.0685280394,1.272916156
C,0,-3.652135456,0.0133701276,0.
C,0,-3.6858205885,-0.0064881329,-2.4272226906
H,0,-1.7491879081,-0.0881663264,-3.3893269346
C,0,-2.2747746974,-0.0563693066,2.440060946
C,0,-4.357006419,0.0298472191,1.2324772334
C,0,-4.357006419,0.0298472191,-1.2324772334
H,0,-4.2316400048,0.0013323083,-3.365325269
C,0,-3.6858205885,-0.0064881329,2.4272226906
H,0,-1.7491879081,-0.0881663264,3.3893269346
H,0,-5.4422231506,0.0672807197,1.210608658
H,0,-5.4422231506,0.0672807197,-1.210608658
H,0,-4.2316400048,0.0013323083,3.365325269
C,0,2.0807839138,1.4622680306,0.6961358066
C,0,2.0807839138,1.4622680306,-0.6961358066
C,0,3.1852176885,1.8524307427,-1.4335398164
C,0,4.3189597433,2.230137797,0.6995242856
C,0,4.3189597433,2.230137797,-0.6995242856
H,0,5.2174798226,2.536578213,1.2262161672
H,0,5.2174798226,2.536578213,-1.2262161672
C,0,1.9643702477,-1.5127451196,-0.7056490056
C,0,1.9643702477,-1.5127451196,0.7056490056
C,0,3.1315398955,-1.7761041423,-1.4067911028
C,0,4.3103371624,-2.0297044553,-0.6962505536
C,0,4.3103371624,-2.0297044553,0.6962505536
H,0,5.2296298214,-2.2338865828,-1.2360238761
H,0,5.2296298214,-2.2338865828,1.2360238761
H,0,3.192266202,1.8693488301,-2.5187437512
H,0,3.1310647136,-1.7845495764,-2.4922729972
C,0,-0.2381041748,2.4360119345,0.6960843795
C,0,-0.2381041748,2.4360119345,-0.6960843795
C,0,-0.8244826187,3.449908118,1.4336053223
C,0,-0.8244826187,3.449908118,-1.4336053223
C,0,-1.4310282825,4.4802261882,0.6993376746
H,0,-0.8374250425,3.4575193459,2.5187853317
C,0,-1.4310282825,4.4802261882,-0.6993376746
H,0,-0.8374250425,3.4575193459,-2.5187853317
H,0,-1.9145643023,5.2969465112,1.2263478361
H,0,-1.9145643023,5.2969465112,-1.2263478361
C,0,-0.2572680924,-2.5057339209,0.7089825557
C,0,-0.9184797203,-3.5041664492,1.407115698
C,0,-0.2572680924,-2.5057339209,-0.7089825557
C,0,-1.587821526,-4.5079226889,0.6958837845
H,0,-0.9256782855,-3.5023207426,2.492377741
C,0,-0.9184797203,-3.5041664492,-1.407115698
C,0,-1.587821526,-4.5079226889,-0.6958837845
H,0,-2.1087791837,-5.2920099205,1.2362448573
H,0,-0.9256782855,-3.5023207426,-2.492377741
H,0,-2.1087791837,-5.2920099205,-1.2362448573
C,0,3.1852176885,1.8524307427,1.4335398164
H,0,3.192266202,1.8693488301,2.5187437512
C,0,3.1315398955,-1.7761041423,1.4067911028
H,0,3.1310647136,-1.7845495764,2.4922729972
Bq,0,0.371145726,-0.09720001,0.
Bq,0,1.370958727,-0.116538143,0.
Bq,0,-0.628667275,-0.077861877,0.

Ar = benzene-1,2-diyl, R^1 = naphthalene-1,8-diyl, R^2 = –, delocalised structure



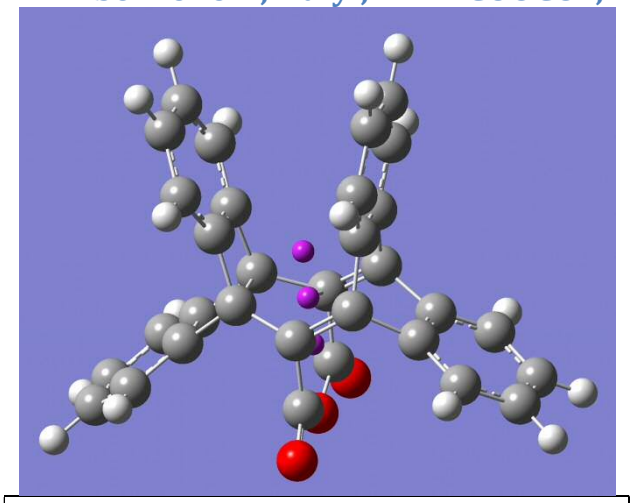
RB3LYP/6-311+G(d) level:
C¨¨C bond length: 2.23698 Å
Electronic energy: -1537.650608 Hartrees
Gibbs free energy: -1537.224130 Hartrees
Imaginary frequency: 18.6*i* cm^{-1}
Point group: C_{2v}

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1537.650900 Hartrees
<S^2> (singlet): 0.1810
NICS(0): -12.1676 ppm
NICS(1): -1.6852 ppm
NICS(–1): -2.0465 ppm
Isotropic magnetic susceptibility: -8.0513 cgs-ppm
Electronic energy (triplet): -1537.619680 Hartrees
<S^2> (triplet): 2.0654

Cartesian coordinates:

C,0,1.2507633752,0.5616748629,1.1184908443
C,0,1.2507633752,0.5616748629,-1.1184908443
C,0,-0.0024300356,-0.0291139559,-1.339829806
C,0,-1.2366622695,0.6003281585,-1.1184892266
C,0,-1.2366622695,0.6003281585,1.1184892266
C,0,-0.0024300356,-0.0291139559,1.339829806
C,0,-0.0258952749,-1.5391396776,-1.2769364788
C,0,-0.0363130036,-2.2095351724,0.
C,0,-0.0373025849,-2.2732179941,-2.4413866918
C,0,-0.0258952749,-1.5391396776,1.2769364788
C,0,-0.0586022947,-3.6438813006,0.
C,0,-0.0592320766,-3.6844117131,-2.427433258
H,0,-0.0291532453,-1.7487987899,-3.391987945
C,0,-0.0373025849,-2.2732179941,2.4413866918
C,0,-0.0696091728,-4.3521908955,1.2306195094
C,0,-0.0696091728,-4.3521908955,-1.2306195094
H,0,-0.0677453031,-4.2322522856,-3.3643305701
C,0,-0.0592320766,-3.6844117131,2.427433258
H,0,-0.0291532453,-1.7487987899,3.391987945
H,0,-0.0864799379,-5.4378498175,1.2048478108
H,0,-0.0864799379,-5.4378498175,-1.2048478108
H,0,-0.0677453031,-4.2322522856,3.3643305701
C,0,-1.4460162211,2.0386540244,0.6986229155
C,0,-1.4460162211,2.0386540244,-0.6986229155
C,0,-1.7540933301,3.1838705026,-1.4162813887
C,0,-2.0533605538,4.3483226816,0.6974919238
C,0,-2.0533605538,4.3483226816,-0.6974919238
H,0,-2.2928622174,5.2620295628,1.2323296982
H,0,-2.2928622174,5.2620295628,-1.2323296982
C,0,1.5047062931,1.9928009422,-0.6986229916
C,0,1.5047062931,1.9928009422,0.6986229916
C,0,1.8482174205,3.1278924398,-1.4162812585
C,0,2.1835206206,4.2824839921,-0.6974919133
C,0,2.1835206206,4.2824839921,0.6974919133
H,0,2.4512962541,5.1883081842,-1.2323297437
H,0,2.4512962541,5.1883081842,1.2323297437
H,0,-1.762358541,3.1848936925,-2.5019441589
H,0,1.8565104077,3.1286582971,-2.5019440283
C,0,-2.4542700537,-0.208399809,0.6994113812
C,0,-2.4542700537,-0.208399809,-0.6994113812
C,0,-3.4717701557,-0.8173465561,1.4167762705
C,0,-3.4717701557,-0.8173465561,-1.4167762705
C,0,-4.5007109211,-1.4404714617,0.6972761408
H,0,-3.4692665496,-0.8284214068,2.5022900669
C,0,-4.5007109211,-1.4404714617,-0.6972761408
H,0,-3.4692665496,-0.8284214068,-2.5022900669
H,0,-5.3073596832,-1.9314987141,1.2325165975
H,0,-5.3073596832,-1.9314987141,-1.2325165975
C,0,2.4426545073,-0.284495203,0.6994114669
C,0,3.4407424714,-0.9247633911,1.4167761428
C,0,2.4426545073,-0.284495203,-0.6994114669
C,0,4.4498249592,-1.5795583289,0.6972761238
H,0,3.4378959177,-0.9357550848,2.5022899397
C,0,3.4407424714,-0.9247633911,-1.4167761428
C,0,4.4498249592,-1.5795583289,-0.6972761238
H,0,5.2408271984,-2.0954123553,1.2325166463
H,0,3.4378959177,-0.9357550848,-2.5022899397
H,0,5.2408271984,-2.0954123553,-1.2325166463
C,0,-1.7540933301,3.1838705026,1.4162813887
H,0,-1.762358541,3.1848936925,2.5019441589
C,0,1.8482174205,3.1278924398,1.4162812585
H,0,1.8565104077,3.1286582971,2.5019440283
Bq,0,0.003890357,0.377629689,0.
Bq,0,-0.011647245,-0.622249596,0.
Bq,0,0.019427959,1.377508973,0.

Ar = benzene-1,2-diyl, R^1 = –COOCO–, R^2 = –, localised structure

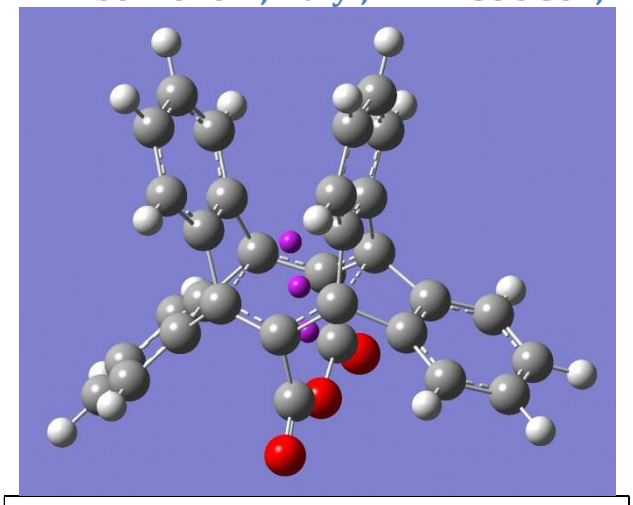


RB3LYP/6-311+G(d) level:
Allyl-allyl C–C bond length: 1.73282 Å
Distance between terminal allyl C atoms: 2.41028 Å
Sum of bond angles for terminal allyl C: 349.728º
Electronic energy: -1454.858697 Hartrees
Gibbs free energy: -1454.531940 Hartrees
No imaginary frequencies
Point group: C_s

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1454.858697 Hartrees
<S^2> (singlet): 0.0000
NICS(0): -4.0922 ppm
NICS(1): 0.5517 ppm
NICS(–1): -3.0021 ppm
Isotropic magnetic susceptibility: -57.4671 cgs-ppm

Cartesian coordinates:
C,0,1.1713902731,0.8664115158,-0.0654158312
C,0,1.1713902731,-0.8664115158,-0.0654158312
C,0,-1.3350675711,-1.205139207,-0.0302078323
C,0,-1.3350675711,1.205139207,-0.0302078323
C,0,-1.5327934492,0.7045196935,-1.4349586648
C,0,-1.5327934492,-0.7045196935,-1.4349586648
C,0,-1.7944226604,-1.4089717807,-2.6001483082
C,0,-2.0492653014,0.6964000044,-3.7770639457
C,0,-2.0492653014,-0.6964000044,-3.7770639457
H,0,-2.2547380444,1.2353655578,-4.6962093403
H,0,-2.2547380444,-1.2353655578,-4.6962093403
C,0,1.4799715219,-0.6959134653,-1.5500871264
C,0,1.4799715219,0.6959134653,-1.5500871264
C,0,1.8623549439,-1.434983119,-2.6560948251
C,0,2.2333716983,-0.6996898211,-3.7907601405
C,0,2.2333716983,0.6996898211,-3.7907601405
H,0,2.5351852354,-1.2258775346,-4.6908554763
H,0,2.5351852354,1.2258775346,-4.6908554763
H,0,-1.8007736903,-2.4941255165,-2.5994019323
H,0,1.877837098,-2.5199075131,-2.6633180351
C,0,-2.4872180663,0.7083664986,0.8229023689
C,0,-2.4872180663,-0.7083664986,0.8229023689
C,0,-3.4463969087,1.4109668056,1.5348157921
C,0,-3.4463969087,-1.4109668056,1.5348157921
C,0,-4.4144526063,0.6958317768,2.2511510346
H,0,-3.4359978402,2.4955583952,1.551709058
C,0,-4.4144526063,-0.6958317768,2.2511510346
H,0,-3.4359978402,-2.4955583952,1.551709058
H,0,-5.1672376661,1.2349200183,2.8167373028
H,0,-5.1672376661,-1.2349200183,2.8167373028
C,0,2.4253605347,0.6963642142,0.799682186
C,0,3.4051242956,1.4365542996,1.4374216782
C,0,2.4253605347,-0.6963642142,0.799682186
C,0,4.4037092018,0.6991966958,2.0917499939
H,0,3.4053675493,2.5211401758,1.4593131245
C,0,3.4051242956,-1.4365542996,1.4374216782
C,0,4.4037092018,-0.6991966958,2.0917499939
H,0,5.1928720913,1.2251920467,2.619319049
H,0,3.4053675493,-2.5211401758,1.4593131245
H,0,5.1928720913,-1.2251920467,2.619319049
C,0,-1.7944226604,1.4089717807,-2.6001483082
H,0,-1.8007736903,2.4941255165,-2.5994019323
C,0,1.8623549439,1.434983119,-2.6560948251
H,0,1.877837098,2.5199075131,-2.6633180351
C,0,-0.1115920446,1.3244471207,0.5396973903
C,0,-0.1115920446,-1.3244471207,0.5396973903
C,0,-0.0738696526,1.2711586085,2.0474690799
O,0,-0.0943191153,2.2133027178,2.7776460465
C,0,-0.0738696526,-1.2711586085,2.0474690799
O,0,-0.0943191153,-2.2133027178,2.7776460465
O,0,0.0112001664,0.,2.6396327696
Bq,0,-0.091756448,0.,0.148024576
Bq,0,-0.11090661,0.,-0.851792043
Bq,0,-0.072606285,0.,1.147841194

Ar = benzene-1,2-diyl, R^1 = –COOCO–, R^2 = –, delocalised structure



RB3LYP/6-311+G(d) level:
C¨¨C bond length: 2.21731 Å
Electronic energy: -1454.854174 Hartrees
Gibbs free energy: -1454.528214 Hartrees
Imaginary frequency: 100.7*i* cm^{-1}
Point group: C_{2v}

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1454.854325 Hartrees
<S^2> (singlet): 0.0866
NICS(0): -12.8286 ppm
NICS(1): -2.5498 ppm
NICS(–1): -6.2439 ppm
Isotropic magnetic susceptibility: -117.8085 cgs-ppm
Electronic energy (triplet): -1454.819775 Hartrees
<S^2> (triplet): 2.0647

Cartesian coordinates:
C,0,1.2528154122,1.1086534118,-0.051973859
C,0,1.2528154122,-1.1086534118,-0.051973859
C,0,-1.2528154122,-1.1086534118,-0.051973859
C,0,-1.2528154122,1.1086534118,-0.051973859
C,0,-1.4993141869,0.6980040993,-1.4857699528
C,0,-1.4993141869,-0.6980040993,-1.4857699528
C,0,-1.8221903313,-1.4184411006,-2.6249330778
C,0,-2.1387806293,0.6977046074,-3.7832713426
C,0,-2.1387806293,-0.6977046074,-3.7832713426
H,0,-2.3922802421,1.2316943543,-4.6934024956
H,0,-2.3922802421,-1.2316943543,-4.6934024956
C,0,1.4993141869,-0.6980040993,-1.4857699528
C,0,1.4993141869,0.6980040993,-1.4857699528
C,0,1.8221903313,-1.4184411006,-2.6249330778
C,0,2.1387806293,-0.6977046074,-3.7832713426
C,0,2.1387806293,0.6977046074,-3.7832713426
H,0,2.3922802421,-1.2316943543,-4.6934024956
H,0,2.3922802421,1.2316943543,-4.6934024956
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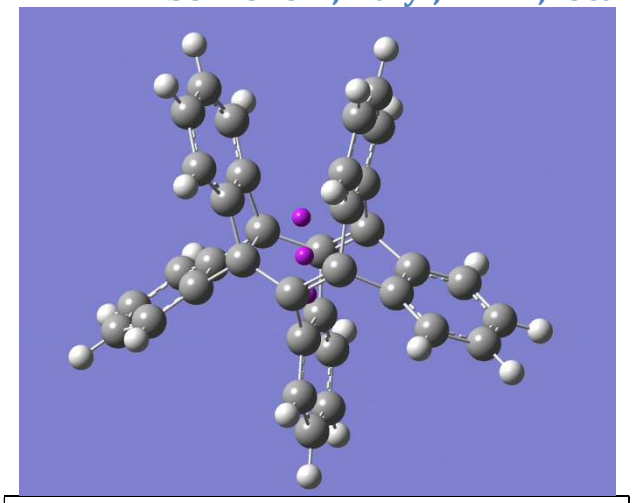
H,0,1.8292348203,-2.5037595995,-2.6259364946
C,0,-2.4329961299,0.699465196,0.8142103932
C,0,-2.4329961299,-0.699465196,0.8142103932
C,0,-3.3970594618,1.4204945362,1.4994323148
C,0,-3.3970594618,-1.4204945362,1.4994323148
C,0,-4.3762620489,0.6971157778,2.1951792099
H,0,-3.3854130965,2.5052585545,1.5212094874
C,0,-4.3762620489,-0.6971157778,2.1951792099
H,0,-3.3854130965,-2.5052585545,1.5212094874
H,0,-5.1399109585,1.2311834723,2.7510481717
H,0,-5.1399109585,-1.2311834723,2.7510481717
C,0,2.4329961299,0.699465196,0.8142103932
C,0,3.3970594618,1.4204945362,1.4994323148
C,0,2.4329961299,-0.699465196,0.8142103932
C,0,4.3762620489,0.6971157778,2.1951792099
H,0,3.3854130965,2.5052585545,1.5212094874
C,0,3.3970594618,-1.4204945362,1.4994323148
C,0,4.3762620489,-0.6971157778,2.1951792099
H,0,5.1399109585,1.2311834723,2.7510481717
H,0,3.3854130965,-2.5052585545,1.5212094874
H,0,5.1399109585,-1.2311834723,2.7510481717
C,0,-1.8221903313,1.4184411006,-2.6249330778
H,0,-1.8292348203,2.5037595995,-2.6259364946
C,0,1.8221903313,1.4184411006,-2.6249330778
H,0,1.8292348203,2.5037595995,-2.6259364946
C,0,0.,1.3400577435,0.5275342128
C,0,0.,-1.3400577435,0.5275342128
C,0,0.,1.275673997,2.0411170364
O,0,0.,2.2135676363,2.776326062
C,0,0.,-1.275673997,2.0411170364
O,0,0.,-2.2135676363,2.776326062
O,0,0.,0.,2.6304486696
Bq,0,0.,0.,0.141195498
Bq,0,0.,0.,-0.858804502
Bq,0,0.,0.,1.141195498

Ar = R^1 = benzene-1,2-diyl, R^2 = –, localised structure

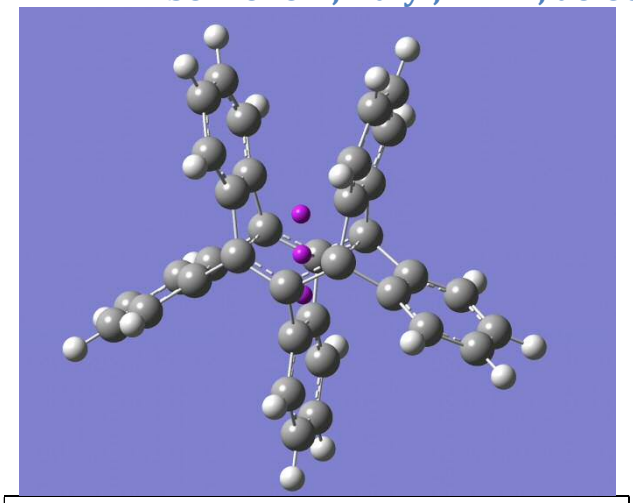


RB3LYP/6-311+G(d) level:
Allyl-allyl C–C bond length: 1.73159 Å
Distance between terminal allyl C atoms: 2.41017 Å
Sum of bond angles for terminal allyl C: 348.078º
Electronic energy: -1383.955487 Hartrees
Gibbs free energy: -1383.572198 Hartrees
No imaginary frequencies
Point group: C_s

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1383.955487 Hartrees
<S^2> (singlet): 0.0000
NICS(0): -6.5249 ppm
NICS(1): 0.4163 ppm
NICS(–1): -5.9224 ppm
Isotropic magnetic susceptibility: -44.1553 cgs-ppm

Cartesian coordinates:
C,0,-0.5588722134,-1.063919325,0.8657971139
C,0,-0.5588722134,-1.063919325,-0.8657971139
C,0,-0.3034041446,0.3610640742,-1.2556163855
C,0,0.9287912935,0.9405456454,-1.2050844185
C,0,0.9287912935,0.9405456454,1.2050844185
C,0,-0.3034041446,0.3610640742,1.2556163855
C,0,-1.436521451,1.203002755,-0.7147761378
C,0,-1.436521451,1.203002755,0.7147761378
C,0,-2.4029379349,1.9190039631,-1.403095306
C,0,-3.3679148685,2.6447748348,-0.6951962817
H,0,-2.4056010432,1.9217945955,-2.4884099098
C,0,-3.3679148685,2.6447748348,0.6951962817
H,0,-4.1202524283,3.2088992664,-1.2372403959
H,0,-4.1202524283,3.2088992664,1.2372403959
C,0,2.1628939745,0.2202806668,0.7094371767
C,0,2.1628939745,0.2202806668,-0.7094371767
C,0,3.2544450728,-0.2712448567,-1.4071070282
C,0,4.346580697,-0.783029533,0.6957927201
C,0,4.346580697,-0.783029533,-0.6957927201
H,0,5.2027182471,-1.1749394546,1.2357195976
H,0,5.2027182471,-1.1749394546,-1.2357195976
C,0,0.4498991478,-2.1981033349,-0.6967936186
C,0,0.4498991478,-2.1981033349,0.6967936186
C,0,1.0936784214,-3.1775031302,-1.4332968601
C,0,1.7696087691,-4.1628564534,-0.6994291915
C,0,1.7696087691,-4.1628564534,0.6994291915
H,0,2.2993283936,-4.9506453347,-1.2261029372
H,0,2.2993283936,-4.9506453347,1.2261029372
H,0,3.2615314979,-0.2619240013,-2.492519708
H,0,1.086224135,-3.1974249414,-2.518461963
C,0,1.0302855165,2.3684050389,0.7065752439
C,0,1.0302855165,2.3684050389,-0.7065752439
C,0,1.1496626115,3.556426702,1.4089197379
C,0,1.1496626115,3.556426702,-1.4089197379
C,0,1.270744173,4.7568674772,0.6959339317
H,0,1.1451056887,3.558880237,2.4944895248
C,0,1.270744173,4.7568674772,-0.6959339317
H,0,1.1451056887,3.558880237,-2.4944895248
H,0,1.367427004,5.6938040311,1.2353779927
H,0,1.367427004,5.6938040311,-1.2353779927
C,0,-1.9904738406,-1.5865713963,0.6960142824
C,0,-3.0698591295,-2.0379229257,1.4342786043
C,0,-1.9904738406,-1.5865713963,-0.6960142824
C,0,-4.1752926405,-2.4944643992,0.6992506814
H,0,-3.0840273181,-2.037342338,2.5196949897
C,0,-3.0698591295,-2.0379229257,-1.4342786043
C,0,-4.1752926405,-2.4944643992,-0.6992506814
H,0,-5.0530663628,-2.8559452286,1.2260148477
H,0,-3.0840273181,-2.037342338,-2.5196949897
H,0,-5.0530663628,-2.8559452286,-1.2260148477
C,0,3.2544450728,-0.2712448567,1.4071070282
H,0,3.2615314979,-0.2619240013,2.492519708
C,0,1.0936784214,-3.1775031302,1.4332968601
H,0,1.086224135,-3.1974249414,2.518461963
C,0,-2.4029379349,1.9190039631,1.403095306
H,0,-2.4056010432,1.9217945955,2.4884099098
Bq,0,0.022171645,0.079230132,0.
Bq,0,0.829518281,-0.510847329,0.
Bq,0,-0.78517499,0.669307593,0.

Ar = R^1 = benzene-1,2-diyl, R^2 = –, delocalised structure

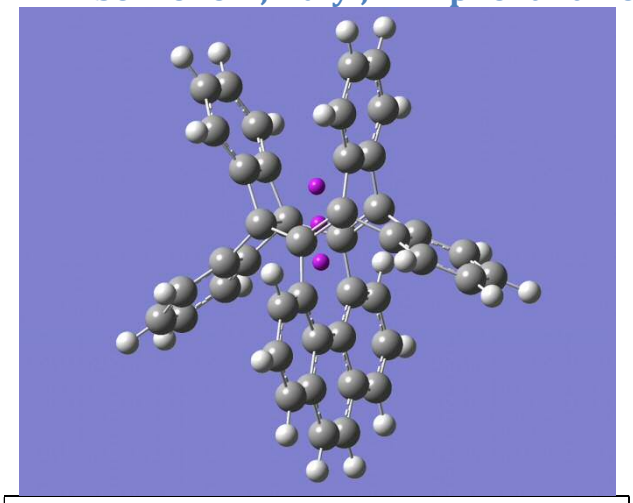


RB3LYP/6-311+G(d) level:
C¨C bond length: 2.20657 Å
Electronic energy: -1383.950399 Hartrees
Gibbs free energy: -1383.567467 Hartrees
Imaginary frequency: 175.7*i* cm^{-1}
Point group: C_{2v}

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1383.950600 Hartrees
<S^2> (singlet): 0.0000
NICS(0): -15.6918 ppm
NICS(1): -2.5996 ppm
NICS(–1): -10.0839 ppm
Isotropic magnetic susceptibility: 93.7166 cgs-ppm
Electronic energy (triplet): -1383.911798 Hartrees
<S^2> (triplet): 2.0736

Cartesian coordinates:
C,0,-1.2462190327,-1.103286123,-0.2000696093
C,0,-1.2462190327,1.103286123,-0.2000696093
C,0,0.,1.2698345866,0.4347864865
C,0,1.2462190327,1.103286123,-0.2000696093
C,0,1.2462190327,-1.103286123,-0.2000696093
C,0,0.,-1.2698345866,0.4347864865
C,0,0.,0.7163201987,1.8462425792
C,0,0.,-0.7163201987,1.8462425792
C,0,0.,1.4022287775,3.0491087624
C,0,0.,0.6945625528,4.2581304731
H,0,0.,2.4875450661,3.053629027
C,0,0.,-0.6945625528,4.2581304731
H,0,0.,1.2373109488,5.1981280566
H,0,0.,-1.2373109488,5.1981280566
C,0,1.4745701782,-0.700771051,-1.6448714821
C,0,1.4745701782,0.700771051,-1.6448714821
C,0,1.8019249923,1.4168469585,-2.7849321319
C,0,2.1180250028,-0.6973511569,-3.9447824949
C,0,2.1180250028,0.6973511569,-3.9447824949
H,0,2.3722499328,-1.2320799454,-4.854539703
H,0,2.3722499328,1.2320799454,-4.854539703
C,0,-1.4745701782,0.700771051,-1.6448714821
C,0,-1.4745701782,-0.700771051,-1.6448714821
C,0,-1.8019249923,1.4168469585,-2.7849321319
C,0,-2.1180250028,0.6973511569,-3.9447824949
C,0,-2.1180250028,-0.6973511569,-3.9447824949
H,0,-2.3722499328,1.2320799454,-4.854539703
H,0,-2.3722499328,-1.2320799454,-4.854539703
H,0,1.81331088,2.5024265215,-2.785854937
H,0,-1.81331088,2.5024265215,-2.785854937
C,0,2.4677337758,-0.6979965482,0.6081897432
C,0,2.4677337758,0.6979965482,0.6081897432
C,0,3.4791473548,-1.4187008051,1.2212263521
C,0,3.4791473548,1.4187008051,1.2212263521
C,0,4.5074292238,-0.6973703488,1.8450122696
H,0,3.4767997027,-2.5044477611,1.23152613
C,0,4.5074292238,0.6973703488,1.8450122696
H,0,3.4767997027,2.5044477611,1.23152613
H,0,5.3145209467,-1.2315838504,2.3364495312
H,0,5.3145209467,1.2315838504,2.3364495312
C,0,-2.4677337758,-0.6979965482,0.6081897432
C,0,-3.4791473548,-1.4187008051,1.2212263521
C,0,-2.4677337758,0.6979965482,0.6081897432
C,0,-4.5074292238,-0.6973703488,1.8450122696
H,0,-3.4767997027,-2.5044477611,1.23152613
C,0,-3.4791473548,1.4187008051,1.2212263521
C,0,-4.5074292238,0.6973703488,1.8450122696
H,0,-5.3145209467,-1.2315838504,2.3364495312
H,0,-3.4767997027,2.5044477611,1.23152613
H,0,-5.3145209467,1.2315838504,2.3364495312
C,0,1.8019249923,-1.4168469585,-2.7849321319
H,0,1.81331088,-2.5024265215,-2.785854937
C,0,-1.8019249923,-1.4168469585,-2.7849321319
H,0,-1.81331088,-2.5024265215,-2.785854937
C,0,0.,-1.4022287775,3.0491087624
H,0,0.,-2.4875450661,3.053629027
Bq,0,0.,0.,0.011549089
Bq,0,0.,0.,-0.988450911
Bq,0,0.,0.,1.011549089

Ar = benzene-1,2-diyl, R^1 = phenanthrene-4,5-diyl, R^2 = –, localised structure



RB3LYP/6-311+G(d) level:
Allyl-allyl C–C bond length: 1.71663 Å
Distance between terminal allyl C atoms: 2.43227 Å
Sum of bond angles for terminal allyl C: 349.138º
Electronic energy: -1691.315812 Hartrees
Gibbs free energy: -1690.845597 Hartrees
No imaginary frequencies
Point group: C_s

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1691.315812 Hartrees
<S^2> (singlet): 0.0000
NICS(0): -24.0643 ppm
NICS(1): -0.6730 ppm
NICS(–1): 1.0442 ppm
Isotropic magnetic susceptibility: -190.8229 cgs-ppm

Cartesian coordinates:

C,0,1.1218125758,0.926267929,0.8583147853
C,0,1.1218125758,0.926267929,-0.8583147853
C,0,-0.1504847912,0.3016104886,-1.3333697304
C,0,-1.3707120405,0.8765164973,-1.2161327728
C,0,-1.3707120405,0.8765164973,1.2161327728
C,0,-0.1504847912,0.3016104886,1.3333697304
C,0,0.0676646735,-2.2821268435,-0.7481407355
C,0,0.0676646735,-2.2821268435,0.7481407355
C,0,0.1882561116,-3.560645804,-1.4054366495
C,0,0.3264662327,-4.7795481623,-0.6726487718
C,0,0.3264662327,-4.7795481623,0.6726487718
H,0,0.4242483916,-5.7054933469,-1.2305361915
H,0,0.4242483916,-5.7054933469,1.2305361915
C,0,-1.5651435585,2.2725144751,0.7031503323
C,0,-1.5651435585,2.2725144751,-0.7031503323
C,0,-1.8284678941,3.439196226,-1.4070127727
C,0,-2.0853292321,4.6167013253,0.6966347668
C,0,-2.0853292321,4.6167013253,-0.6966347668
H,0,-2.2907545673,5.5360640041,1.2359218219
H,0,-2.2907545673,5.5360640041,-1.2359218219
C,0,1.4294744638,2.41467087,-0.6959197503
C,0,1.4294744638,2.41467087,0.6959197503
C,0,1.8113531415,3.5215657015,-1.4340986222
C,0,2.1836444688,4.6568356282,-0.6995928962
C,0,2.1836444688,4.6568356282,0.6995928962
H,0,2.4847107222,5.5572670002,-1.226127517
H,0,2.4847107222,5.5572670002,1.226127517
H,0,-1.8352640003,3.4389562608,-2.4925627697
H,0,1.8258836753,3.5305466565,-2.5193517909
C,0,-2.5233358311,0.027919875,0.7103737183
C,0,-2.5233358311,0.027919875,-0.7103737183
C,0,-3.5049035282,-0.6608713816,1.4066338474
C,0,-3.5049035282,-0.6608713816,-1.4066338474
C,0,-4.4893762358,-1.3584430799,0.6957926593
H,0,-3.5032697625,-0.6688822315,2.4917658366
C,0,-4.4893762358,-1.3584430799,-0.6957926593
H,0,-3.5032697625,-0.6688822315,-2.4917658366
H,0,-5.2581961089,-1.9012673732,1.2366491227
H,0,-5.2581961089,-1.9012673732,-1.2366491227
C,0,2.3925288262,0.0839527847,0.6959477511
C,0,3.4047252487,-0.5062283426,1.4341323923
C,0,2.3925288262,0.0839527847,-0.6959477511
C,0,4.4310385422,-1.1177796361,0.69962541
H,0,3.4119101621,-0.5199665893,2.5191116601
C,0,3.4047252487,-0.5062283426,-1.4341323923
C,0,4.4310385422,-1.1177796361,-0.69962541
H,0,5.2452264773,-1.6059052662,1.2263933845
H,0,3.4119101621,-0.5199665893,-2.5191116601
H,0,5.2452264773,-1.6059052662,-1.2263933845
C,0,-1.8284678941,3.439196226,1.4070127727
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C,0,0.1715546227,-3.6997075786,-2.8105175964
C,0,0.0275742392,-2.6127663822,-3.6313581965
H,0,0.2689582684,-4.6980431752,-3.2254802406
H,0,0.0042483076,-2.7156017489,-4.7112568115
C,0,0.1715546227,-3.6997075786,2.8105175964
C,0,0.0275742392,-2.6127663822,3.6313581965
H,0,0.2689582684,-4.6980431752,3.2254802406
H,0,0.0042483076,-2.7156017489,4.7112568115
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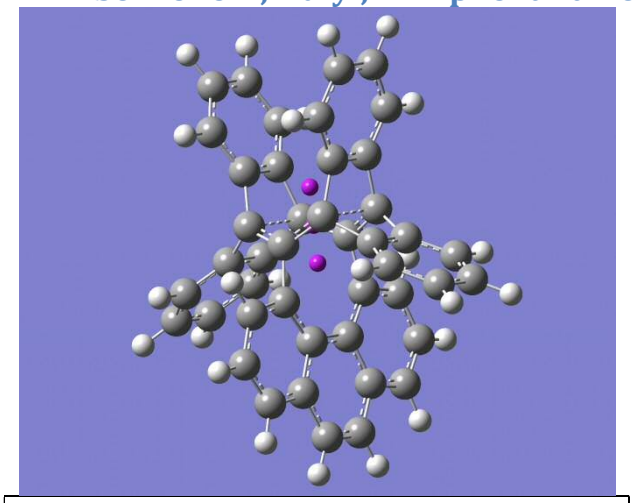
C,0,-0.0633465188,-1.1649386055,-1.6525575158
H,0,-0.1951335413,-0.4809419604,-3.6605242905
C,0,-0.0876765846,-1.3581963195,3.0322643172
C,0,-0.0633465188,-1.1649386055,1.6525575158
H,0,-0.1951335413,-0.4809419604,3.6605242905
Bq,0,-0.133128085,0.701464972,0.
Bq,0,-0.271416271,1.688129999,-0.085839973
Bq,0,0.005160101,-0.285200056,0.085839973

Ar = benzene-1,2-diyl, R^1 = phenanthrene-4,5-diyl, R^2 = –, delocalised structure



RB3LYP/6-311+G(d) level:
C¨¨C bond length: 2.23458 Å
Electronic energy: -1691.310281 Hartrees
Gibbs free energy: -1690.840263 Hartrees
Imaginary frequency: 68.6*i* cm^{-1}
Point group: C_{2v}

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1691.310790 Hartrees
<S^2> (singlet): 0.2052
NICS(0): -8.1157 ppm
NICS(1): -0.4546 ppm
NICS(–1): -2.4491 ppm
Isotropic magnetic susceptibility: -120.4407 cgs-ppm
Electronic energy (triplet): -1691.280651 Hartrees
<S^2> (triplet): 2.0635

Cartesian coordinates:

C,0,-1.244691001,1.1172875868,0.9143907224
C,0,-1.244691001,-1.1172875868,0.9143907224
C,0,0.,-1.3563931555,0.3220076971
C,0,1.244691001,-1.1172875868,0.9143907224
C,0,1.244691001,1.1172875868,0.9143907224
C,0,0.,1.3563931555,0.3220076971
C,0,0.,-0.7496524845,-2.2751171495
C,0,0.,0.7496524845,-2.2751171495
C,0,0.,-1.4052300497,-3.5620742941
C,0,0.,-0.6722021909,-4.7890505534
C,0,0.,0.6722021909,-4.7890505534
H,0,0.,-1.2303331591,-5.7199756074
H,0,0.,1.2303331591,-5.7199756074
C,0,1.4852061514,0.6970536773,2.3442676393
C,0,1.4852061514,-0.6970536773,2.3442676393
C,0,1.8100081494,-1.416731233,3.4842150759
C,0,2.1282527698,0.6977382959,4.6432101116
C,0,2.1282527698,-0.6977382959,4.6432101116
H,0,2.3818863565,1.2321621529,5.5533697588
H,0,2.3818863565,-1.2321621529,5.5533697588
C,0,-1.4852061514,-0.6970536773,2.3442676393
C,0,-1.4852061514,0.6970536773,2.3442676393
C,0,-1.8100081494,-1.416731233,3.4842150759
C,0,-2.1282527698,-0.6977382959,4.6432101116
C,0,-2.1282527698,0.6977382959,4.6432101116
H,0,-2.3818863565,-1.2321621529,5.5533697588
H,0,-2.3818863565,1.2321621529,5.5533697588
H,0,1.8166243374,-2.5024443931,3.4854730716
H,0,-1.8166243374,-2.5024443931,3.4854730716
C,0,2.4331997491,0.6998366641,0.0622087005
C,0,2.4331997491,-0.6998366641,0.0622087005
C,0,3.4284780563,1.4167037491,-0.5843007001
C,0,3.4284780563,-1.4167037491,-0.5843007001
C,0,4.4322584964,0.6973284428,-1.2466360193
H,0,3.4245105583,2.5019907165,-0.597309392
C,0,4.4322584964,-0.6973284428,-1.2466360193
H,0,3.4245105583,-2.5019907165,-0.597309392
H,0,5.2184599425,1.232662647,-1.7697062553
H,0,5.2184599425,-1.232662647,-1.7697062553
C,0,-2.4331997491,0.6998366641,0.0622087005
C,0,-3.4284780563,1.4167037491,-0.5843007001
C,0,-2.4331997491,-0.6998366641,0.0622087005
C,0,-4.4322584964,0.6973284428,-1.2466360193
H,0,-3.4245105583,2.5019907165,-0.597309392
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C,0,-4.4322584964,-0.6973284428,-1.2466360193
H,0,-5.2184599425,1.232662647,-1.7697062553
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H,0,-5.2184599425,-1.232662647,-1.7697062553
C,0,1.8100081494,1.416731233,3.4842150759
H,0,1.8166243374,2.5024443931,3.4854730716
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C,0,0.,-2.8095063282,-3.7045833496
C,0,0.,-3.636638146,-2.612436978
H,0,0.,-3.2195465897,-4.709641369
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H,0,0.,3.2195465897,-4.709641369
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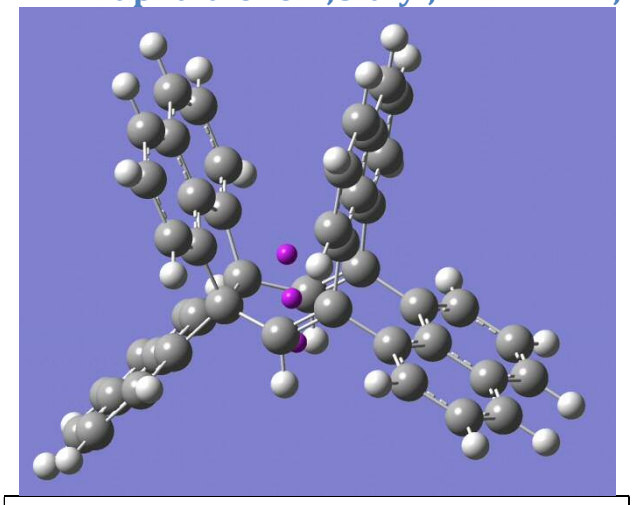
C,0,0.,-1.6612477936,-1.1568286955
H,0,0.,-3.6719397786,-0.4703577004
C,0,0.,3.0406833794,-1.3524723921
C,0,0.,1.6612477936,-1.1568286955
H,0,0.,3.6719397786,-0.4703577004
Bq,0,0.,0.,0.716929714
Bq,0,0.100547222,-0.063327458,1.709844559
Bq,0,-0.100547222,0.063327458,-0.275985131

Ar = naphthalene-1,8-diyl, $R^1 = R^2 = H$, localised structure



RB3LYP/6-311+G(d) level:
Allyl-allyl C–C bond length: 1.74009 Å
Distance between terminal allyl C atoms: 2.64978 Å
Sum of bond angles for terminal allyl C: 359.909º
Electronic energy: -1768.901955 Hartrees
Gibbs free energy: -1768.396714 Hartrees
No imaginary frequencies
Point group: C_s

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1768.901955 Hartrees
<S^2> (singlet): 0.0000
NICS(0): -2.8998 ppm
NICS(1): 0.7162 ppm
NICS(–1): -3.7283 ppm
Isotropic magnetic susceptibility: -91.6831 cgs-ppm

Cartesian coordinates:

C,0,0.8700463567,1.2766810262,-0.4083397065
C,0,-0.8700463567,1.2766810262,-0.4083397065
C,0,-1.3248880849,-1.2452639868,-0.4438762958
C,0,1.3248880849,-1.2452639868,-0.4438762958
C,0,1.2740399563,-2.4386661994,-1.3568658118
C,0,0.,-2.9848000147,-1.7546710708
C,0,2.4403165102,-3.0145689171,-1.8154139241
C,0,-1.2740399563,-2.4386661994,-1.3568658118
C,0,0.,-4.1251456408,-2.6278120137
C,0,2.426371085,-4.1348424164,-2.6735069642
H,0,3.3916042203,-2.5921047474,-1.5083442185
C,0,-2.4403165102,-3.0145689171,-1.8154139241
C,0,-1.2311792895,-4.6792663138,-3.0662120638
C,0,1.2311792895,-4.6792663138,-3.0662120638
H,0,3.3641670659,-4.5593761603,-3.0174704361
C,0,-2.426371085,-4.1348424164,-2.6735069642
H,0,-3.3916042203,-2.5921047474,-1.5083442185
H,0,-1.2077501541,-5.5417017053,-3.7258600826
H,0,1.2077501541,-5.5417017053,-3.7258600826
H,0,-3.3641670659,-4.5593761603,-3.0174704361
C,0,-1.2498495428,-1.5752367058,1.0161845316
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C,0,-2.425977071,-1.7773194762,1.7098070379
C,0,1.2498495428,-1.5752367058,1.0161845316
C,0,0.,-2.1763215491,3.0536266359
C,0,-2.4237740761,-2.1708197826,3.064404118
H,0,-3.3731519856,-1.6268699631,1.2020772993
C,0,2.425977071,-1.7773194762,1.7098070379
C,0,1.2357968415,-2.3694669372,3.72197467
C,0,-1.2357968415,-2.3694669372,3.72197467
H,0,-3.367631467,-2.315218338,3.5804758036
C,0,2.4237740761,-2.1708197826,3.064404118
H,0,3.3731519856,-1.6268699631,1.2020772993
H,0,1.2252744573,-2.6742608021,4.7643277124
H,0,-1.2252744573,-2.6742608021,4.7643277124
H,0,3.367631467,-2.315218338,3.5804758036
C,0,-1.1815955507,2.4563326084,-1.3241847422
C,0,0.,3.0713668659,-1.7830159587
C,0,-2.3952994176,2.9503786711,-1.7417846238
C,0,1.1815955507,2.4563326084,-1.3241847422
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C,0,-2.4236211361,4.0736557803,-2.610285295
H,0,-3.3298377015,2.4994433414,-1.4233457488
C,0,2.3952994176,2.9503786711,-1.7417846238
C,0,1.2685861861,4.681791577,-3.0573067279
C,0,-1.2685861861,4.681791577,-3.0573067279
H,0,-3.3860749071,4.4591466837,-2.9326307864
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H,0,3.3298377015,2.4994433414,-1.4233457488
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H,0,-1.3257270781,5.5364274301,-3.72501385
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C,0,0.,1.8219773757,1.7804232697
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C,0,1.1825881638,1.6093485773,1.0443742467
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C,0,-2.4235522577,2.1897355614,3.0267943237
H,0,-3.3303675573,1.6408893541,1.1350188829
C,0,2.3955996373,1.7940503045,1.6643690419
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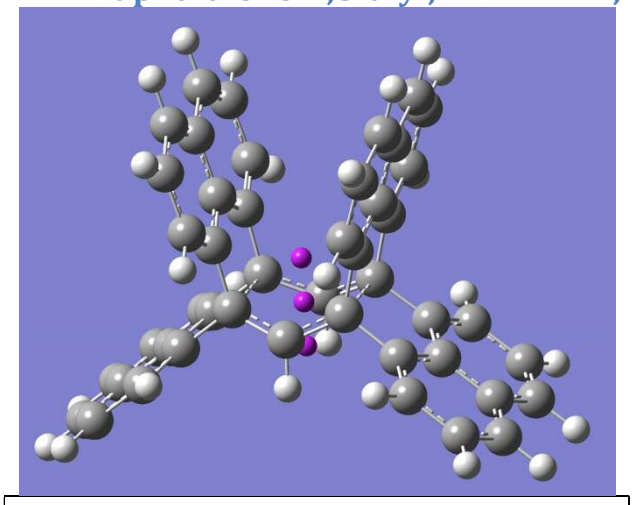
C,0,-1.2680579358,2.4011145779,3.7506570219
H,0,-3.3861684253,2.3302941862,3.5089988449
C,0,2.4235522577,2.1897355614,3.0267943237
H,0,3.3303675573,1.6408893541,1.1350188829
H,0,1.3242382918,2.7051515145,4.7918035444
H,0,-1.3242382918,2.7051515145,4.7918035444
H,0,3.3861684253,2.3302941862,3.5089988449
C,0,1.363113696,-0.0172877857,-0.9864882036
H,0,1.4449956558,0.0100269267,-2.0719175723
C,0,-1.363113696,-0.0172877857,-0.9864882036
H,0,-1.4449956558,0.0100269267,-2.0719175723
Bq,0,0.,0.004709751,-0.612901402
Bq,0,0.,-0.014512367,0.386913836
Bq,0,0.,0.023931869,-1.61271664

Ar = naphthalene-1,8-diyl, $R^1 = R^2 = H$, delocalised structure



RB3LYP/6-311+G(d) level:
C¨¨C bond length: 2.33282 Å
Electronic energy (RB3LYP, singlet state): -1768.890778 Hartrees
Electronic energy (UB3LYP, singlet state): -1768.890778 Hartrees
$\langle S^2 \rangle$ (UB3LYP, singlet state): 0.0000
Electronic energy (UB3LYP, triplet state): -1768.793522 Hartrees
$\langle S^2 \rangle$ (UB3LYP, triplet state): 2.0661
Gibbs free energy: -1768.386045 Hartrees
Imaginary frequency: 276.9*i* cm^{-1}
Point group: C_{2v}

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1768.891065 Hartrees
$\langle S^2 \rangle$ (singlet): 0.0000
NICS(0): -15.3263 ppm
NICS(1): -6.0956 ppm
NICS(–1): -10.3720 ppm
Isotropic magnetic susceptibility: -101.6509 cgs-ppm
Electronic energy (triplet): -1768.793522 Hartrees
$\langle S^2 \rangle$ (triplet): 2.0635

Cartesian coordinates:

C,0,1.1664118272,1.2585385944,-0.4298423076
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C,0,1.2321994011,-2.4463649132,-1.3469362388
C,0,0.,-3.0299491803,-1.7647767553
C,0,2.4190819745,-2.9872170375,-1.7952085183
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C,0,0.,-4.1629400751,-2.6330234806
C,0,2.4246942656,-4.1144762721,-2.6498936677
H,0,3.3629251228,-2.5474680358,-1.488886836
C,0,-2.4190819745,-2.9872170375,-1.7952085183
C,0,-1.246332435,-4.6928128165,-3.0571228497
C,0,1.246332435,-4.6928128165,-3.0571228497
H,0,3.3736509208,-4.5203610462,-2.98626002
C,0,-2.4246942656,-4.1144762721,-2.6498936677
H,0,-3.3629251228,-2.5474680358,-1.488886836
H,0,-1.2559047414,-5.5554522198,-3.7169388603
H,0,1.2559047414,-5.5554522198,-3.7169388603
H,0,-3.3736509208,-4.5203610462,-2.98626002
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C,0,-2.413092159,-1.7811959521,1.6997123468
C,0,1.222011405,-1.5931536901,1.030309902
C,0,0.,-2.2142924331,3.0877530777
C,0,-2.4236822704,-2.1859369065,3.054232998
H,0,-3.3547696217,-1.6199998363,1.185229258
C,0,2.413092159,-1.7811959521,1.6997123468
C,0,1.248412293,-2.4015210712,3.7348307333
C,0,-1.248412293,-2.4015210712,3.7348307333
H,0,-3.375373183,-2.3259883577,3.5573551412
C,0,2.4236822704,-2.1859369065,3.054232998
H,0,3.3547696217,-1.6199998363,1.185229258
H,0,1.263765167,-2.7106863913,4.7758828354
H,0,-1.263765167,-2.7106863913,4.7758828354
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C,0,0.,3.0299491803,-1.7647767553
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C,0,-2.4246942656,4.1144762721,-2.6498936677
H,0,-3.3629251228,2.5474680358,-1.488886836
C,0,2.4190819745,2.9872170375,-1.7952085183
C,0,1.246332435,4.6928128165,-3.0571228497
C,0,-1.246332435,4.6928128165,-3.0571228497
H,0,-3.3736509208,4.5203610462,-2.98626002
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H,0,3.3629251228,2.5474680358,-1.488886836
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C,0,0.,1.810574626,1.7202594451
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H,0,3.3547696217,1.6199998363,1.185229258
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H,0,-1.263765167,2.7106863913,4.7758828354
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H,0,1.5283211225,0.,-2.0611571319
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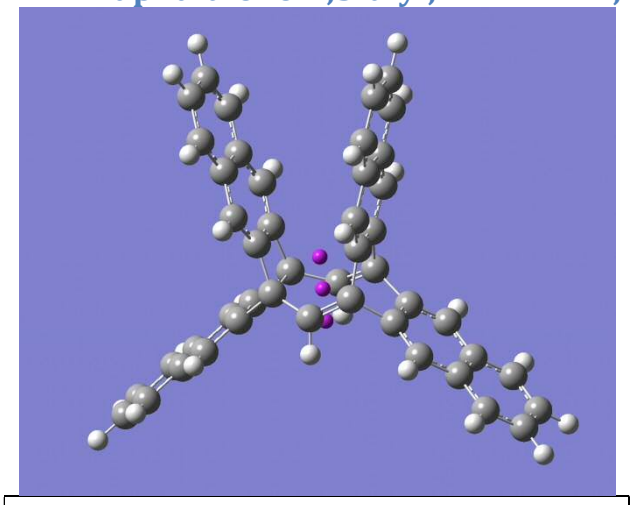
Bq,0,0.,0.,-0.612015202
Bq,0,0.,0.,0.387984798
Bq,0,0.,0.,-1.612015202

Ar = naphthalene-2,3-diyl, $R^1 = R^2 = H$, localised structure



RB3LYP/6-311+G(d) level:
Allyl-allyl C–C bond length: 1.81935 Å
Distance between terminal allyl C atoms: 2.45432 Å
Sum of bond angles for terminal allyl C: 351.589º
Electronic energy: -1768.803499 Hartrees
Gibbs free energy: -1768.303637 Hartrees
No imaginary frequencies
Point group: C_s

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1768.803499 Hartrees
<S^2> (singlet): 0.0000
NICS(0): -2.2315 ppm
NICS(1): 0.2657 ppm
NICS(–1): -3.0380 ppm
Isotropic magnetic susceptibility: -193.0071 cgs-ppm

Cartesian coordinates:

C,0,-1.1017453605,0.9096752808,-0.5226547162
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C,0,1.3871034913,-1.2271600742,-0.5633229426
C,0,1.3871034913,1.2271600742,-0.5633229426
C,0,1.6149915676,0.7118946482,0.8229748193
C,0,1.6149915676,-0.7118946482,0.8229748193
C,0,1.8651413467,-1.4138316499,1.9709143414
C,0,2.1260555108,0.7165401206,3.1844039705
C,0,-1.477561499,-0.705782356,0.9378411876
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C,0,-1.8471837922,-1.438059051,2.0282014207
C,0,-2.2273542045,0.7198679538,3.203147848
H,0,1.8634302027,-2.5000709745,1.97012093
H,0,-1.8487694638,-2.5240890194,2.0376470587
C,0,2.4797104284,0.7235611567,-1.4814087444
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C,0,3.3538378686,1.4140403637,-2.2726341255
C,0,4.2765722891,0.7154568705,-3.10758103
H,0,3.3471534942,2.5004143543,-2.2840996103
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C,0,-2.2982640402,0.7071714616,-1.4467271059
C,0,-3.2039376032,1.4377582759,-2.158671551
C,0,-2.2982640402,-0.7071714616,-1.4467271059
C,0,-4.1786998283,0.719395496,-2.9206110671
H,0,-3.200684035,2.5239870682,-2.1792210901
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C,0,-1.8471837922,1.438059051,2.0282014207
H,0,-1.8487694638,2.5240890194,2.0376470587
C,0,0.1537074628,1.4464772776,-1.0791370738
H,0,0.1071617358,1.637259122,-2.1498483542
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H,0,0.1071617358,-1.637259122,-2.1498483542
C,0,-4.1786998283,-0.719395496,-2.9206110671
C,0,-5.1562497283,-1.3973498615,-3.6924397443
C,0,-6.092781063,-0.7059697326,-4.4263206475
H,0,-5.1562903722,-2.4836444929,-3.6942576757
C,0,-5.1562497283,1.3973498615,-3.6924397443
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C,0,-2.6137512591,-1.3975340608,4.3878905238
C,0,-2.9841368527,-0.7062421807,5.5180077843
H,0,-2.6135376168,-2.4838358494,4.3891083163
C,0,-2.6137512591,1.3975340608,4.3878905238
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C,0,2.3929131515,-1.3991160273,4.3985446375
C,0,2.6490471852,-0.7066097724,5.5592941409
H,0,2.3935941453,-2.4854098193,4.3984619027
C,0,2.3929131515,1.3991160273,4.3985446375
C,0,2.6490471852,0.7066097724,5.5592941409
H,0,2.8522495278,-1.2443289147,6.4799190371
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H,0,2.8522495278,1.2443289147,6.4799190371
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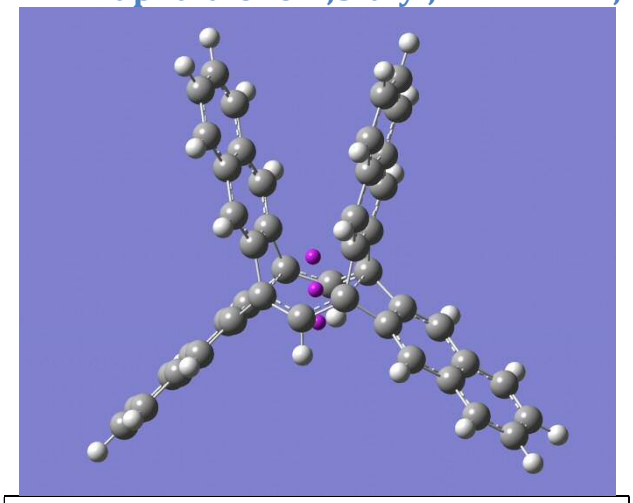
C,0,3.3538378686,-1.4140403637,-2.2726341255
H,0,3.3471534942,-2.5004143543,-2.2840996103
Bq,0,0.146355198,0.,-0.721704911
Bq,0,0.165124674,0.,0.278118927
Bq,0,0.127585722,0.,-1.721528749

Ar = naphthalene-2,3-diyl, $R^1 = R^2 = H$, delocalised structure



RB3LYP/6-311+G(d) level:
C¨¨C bond length: 2.32570 Å
Electronic energy (RB3LYP, singlet state): -1768.804786 Hartrees
Electronic energy (UB3LYP, singlet state): -1768.804786 Hartrees
$\langle S^2 \rangle$ (UB3LYP, singlet state): 0.0000
Electronic energy (UB3LYP, triplet state): -1768.793970 Hartrees
$\langle S^2 \rangle$ (UB3LYP, triplet state): 2.0628
Gibbs free energy: -1768.304341 Hartrees
No imaginary frequencies
Point group: C_{2v}

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1768.809338 Hartrees
$\langle S^2 \rangle$ (singlet): 0.6128
NICS(0): -4.9050 ppm
NICS(1): -3.3774 ppm
NICS(–1): -4.8506 ppm
Isotropic magnetic susceptibility: -146.2267 cgs-ppm
Electronic energy (triplet): -1768.793970 Hartrees
$\langle S^2 \rangle$ (triplet): 2.0628

Cartesian coordinates:

C,0,-1.1628488539,1.2489212905,0.4769380358
C,0,1.1628488539,1.2489212905,0.4769380358
C,0,1.1628488539,-1.2489212905,0.4769380358
C,0,-1.1628488539,-1.2489212905,0.4769380358
C,0,-0.7078976784,-1.5280329708,-0.9275915773
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C,0,1.4203229494,-1.8301534529,-2.0550571514
C,0,-0.7174615934,-2.147323168,-3.2543933702
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C,0,-0.7174615934,2.147323168,-3.2543933702
H,0,2.5067109848,-1.8217218676,-2.0577848668
H,0,2.5067109848,1.8217218676,-2.0577848668
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C,0,0.7141822334,-2.3489450386,1.4148452467
C,0,-1.4203686034,-3.2015419491,2.214958948
C,0,-0.7164919843,-4.1172349975,3.0570073961
H,0,-2.5065969103,-3.1806487516,2.2402022133
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C,0,-1.4203686034,3.2015419491,2.214958948
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H,0,-2.5065969103,3.1806487516,2.2402022133
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H,0,1.2443769571,6.5851728594,5.3588014108
H,0,-2.4841661229,5.0221865652,3.9080299504
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C,0,1.3985389354,2.4663309894,-4.4560725482
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H,0,2.4848131074,-2.4657570181,-4.4566316113
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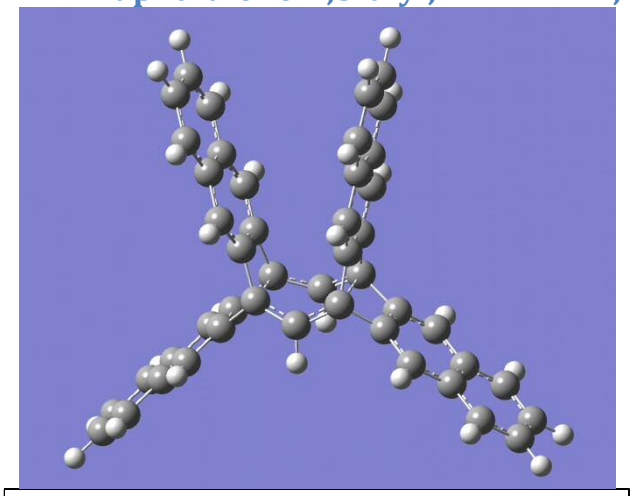
Bq,0,0.,0.,0.654489146
Bq,0,0.,0.,1.654489146
Bq,0,0.,0.,-0.345510854

Ar = naphthalene-2,3-diyl, $R^1 = R^2 = H$, localised ⇌ delocalised TS



RB3LYP/6-311+G(d) level:
C···C bond lengths: 1.99903 Å, 2.42696 Å
Electronic energy: -1768.803050 Hartrees
Gibbs free energy: -1768.303543 Hartrees
Imaginary frequency: 220.7*i* cm^{-1}
Point group: C_s

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1768.803050 Hartrees
<S^2> (singlet): 0.0000
Electronic energy (triplet): -1768.744474 Hartrees
<S^2> (triplet): 2.0437

Cartesian coordinates:

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C,0,2.7108029282,-0.1775957914,-1.415344896
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H,0,-3.8278006821,-0.6010423465,2.5184427621
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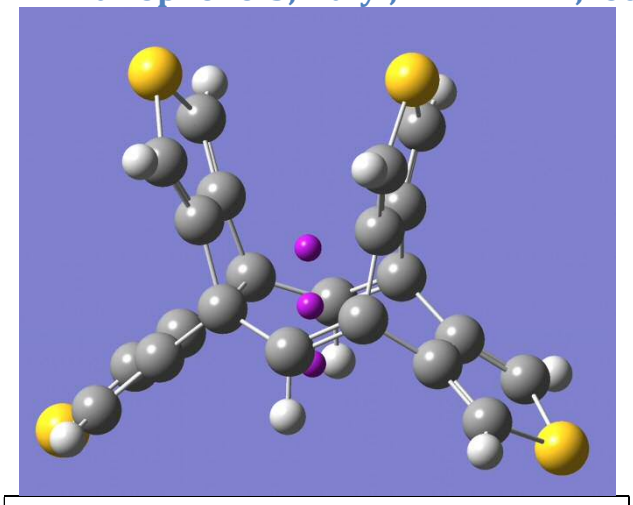
H,0,6.5440129739,-2.7492957133,-1.2444032047
H,0,4.77338507,-1.5629273369,2.4851782354
H,0,6.5440129739,-2.7492957133,1.2444032047
C,0,1.047208733,6.3917787131,1.3981722759
C,0,1.047208733,6.3917787131,-1.3981722759
C,0,1.144359785,7.5781890334,0.7058802439
H,0,1.0466121858,6.391847076,2.4845022812
C,0,1.144359785,7.5781890334,-0.7058802439
H,0,1.0466121858,6.391847076,-2.4845022812
H,0,1.2206428174,8.5173290676,1.2445301507
H,0,1.2206428174,8.5173290676,-1.2445301507
C,0,0.8493388591,3.9134752143,-1.4155790264
H,0,0.8323472944,3.9166610556,-2.5020294698

Ar = thiophene-3,4-diyl, $R^1 = R^2 = H$, localised structure

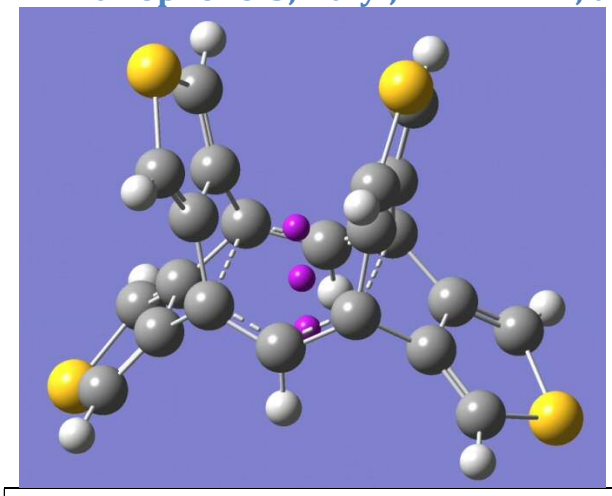


RB3LYP/6-311+G(d) level:
Allyl-allyl C–C bond length: 1.87569 Å
Distance between terminal allyl C atoms: 2.52583 Å
Sum of bonds for terminal allyl C: 349.554°
Electronic energy: -2437.134620 Hartrees
Gibbs free energy: -2436.940774 Hartrees
No imaginary frequencies
Point group: C_s

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -2437.134620 Hartrees
$\langle S^2 \rangle$ (singlet): 0.0000
NICS(0): -0.2888 ppm
NICS(1): 1.4980 ppm
NICS(–1): -1.5031 ppm
Isotropic magnetic susceptibility: -126.0942 cgs-ppm

Cartesian coordinates:
C,0,0.2183127211,1.3672651064,1.2629151702
C,0,0.2183127211,1.3672651064,-1.2629151702
C,0,0.4324144764,-1.1155601399,-0.9378458623
C,0,0.4324144764,-1.1155601399,0.9378458623
C,0,-0.9784726834,-1.6332301834,0.7076259615
C,0,-0.9784726834,-1.6332301834,-0.7076259615
C,0,-2.0925717099,-2.1685227361,-1.272393512
C,0,-1.1702674641,1.4444660528,-0.7169116701
C,0,-1.1702674641,1.4444660528,0.7169116701
H,0,-2.3816299823,-2.2974621221,-2.3050748037
C,0,1.4735926177,-2.2060075316,0.7088461957
C,0,1.4735926177,-2.2060075316,-0.7088461957
C,0,2.3285073474,-3.0990546833,1.272282384
H,0,2.5590317088,-3.3161455306,2.3052597156
C,0,1.0116527887,2.5371002831,0.7282128848
C,0,1.0116527887,2.5371002831,-0.7282128848
C,0,1.7369840773,3.5566586721,-1.2551641223
H,0,1.9189549754,3.7962381524,-2.2928824855
C,0,-2.4118001658,1.5828723488,1.2539051161
H,0,-2.7097748804,1.6097735743,2.291857229
C,0,2.3285073474,-3.0990546833,-1.272282384
H,0,2.5590317088,-3.3161455306,-2.3052597156
C,0,-2.0925717099,-2.1685227361,1.272393512
H,0,-2.3816299823,-2.2974621221,2.3050748037
C,0,1.7369840773,3.5566586721,1.2551641223
H,0,1.9189549754,3.7962381524,2.2928824855
C,0,-2.4118001658,1.5828723488,-1.2539051161
H,0,-2.7097748804,1.6097735743,-2.291857229
S,0,-3.6141172057,1.7088362789,0.
S,0,3.1634262758,-3.9678391855,0.
S,0,2.4456800862,4.5411884967,0.
S,0,-3.1847617361,-2.6706936163,0.
C,0,0.8610750709,0.1905354384,1.4614155418
H,0,1.9314590625,0.2516650144,1.6462122369
C,0,0.8610750709,0.1905354384,-1.4614155418
H,0,1.9314590625,0.2516650144,-1.6462122369
Bq,0,0.503934089,0.147413468,0.
Bq,0,-0.492561271,0.06376542,0.
Bq,0,1.50042945,0.231061516,0.

Ar = thiophene-3,4-diyl, $R^1 = R^2 = H$, delocalised structure

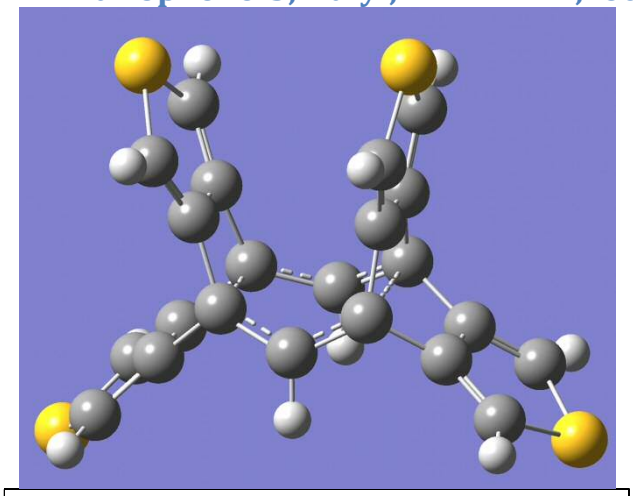


RB3LYP/6-311+G(d) level:
C¨C bond length: 2.44110 Å
Electronic energy: -2437.139563 Hartrees
Gibbs free energy: -2436.944656 Hartrees
No imaginary frequencies
Point group: C_{2v}

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -2437.157937 Hartrees
<S^2> (singlet): 0.9879
NICS(0): -3.6276 ppm
NICS(1): -0.8905 ppm
NICS(–1): -2.8090 ppm
Isotropic magnetic susceptibility: -147.1796 cgs-ppm
Electronic energy (triplet): -2437.155377 Hartrees
<S^2> (triplet): 2.0644

Cartesian coordinates:
C,0,-1.2205475236,-1.2528851527,-0.2861026306
C,0,1.2205475236,-1.2528851527,-0.2861026306
C,0,1.2205475236,1.2528851527,-0.2861026306
C,0,-1.2205475236,1.2528851527,-0.2861026306
C,0,-0.7118017776,1.5182587646,1.0993288119
C,0,0.7118017776,1.5182587646,1.0993288119
C,0,1.2578932301,1.8408845177,2.302592226
C,0,0.7118017776,-1.5182587646,1.0993288119
C,0,-0.7118017776,-1.5182587646,1.0993288119
H,0,2.2952879519,1.9016891208,2.5983941213
C,0,-0.7177871025,2.3239714255,-1.2270048398
C,0,0.7177871025,2.3239714255,-1.2270048398
C,0,-1.2587348163,3.2261995898,-2.0870212711
H,0,-2.2960626002,3.4237353204,-2.3173541476
C,0,-0.7177871025,-2.3239714255,-1.2270048398
C,0,0.7177871025,-2.3239714255,-1.2270048398
C,0,1.2587348163,-3.2261995898,-2.0870212711
H,0,2.2960626002,-3.4237353204,-2.3173541476
C,0,-1.2578932301,-1.8408845177,2.302592226
H,0,-2.2952879519,-1.9016891208,2.5983941213
C,0,-1.5344441639,0.,-0.8189596399
H,0,-1.723926123,0.,-1.8900156412
C,0,1.5344441639,0.,-0.8189596399
H,0,1.723926123,0.,-1.8900156412
C,0,1.2587348163,3.2261995898,-2.0870212711
H,0,2.2960626002,3.4237353204,-2.3173541476
C,0,-1.2578932301,1.8408845177,2.302592226
H,0,-2.2952879519,1.9016891208,2.5983941213
C,0,-1.2587348163,-3.2261995898,-2.0870212711
H,0,-2.2960626002,-3.4237353204,-2.3173541476
C,0,1.2578932301,-1.8408845177,2.302592226
H,0,2.2952879519,-1.9016891208,2.5983941213
S,0,0.,-2.1507747898,3.4716589347
S,0,0.,4.1100980749,-2.9195476584
S,0,0.,-4.1100980749,-2.9195476584
S,0,0.,2.1507747898,3.4716589347
Bq,0,0.,0.,-0.463721634
Bq,0,0.,0.,0.536278366
Bq,0,0.,0.,-1.463721634

Ar = thiophene-3,4-diyl, $R^1 = R^2 = H$, localised ⇌ delocalised TS

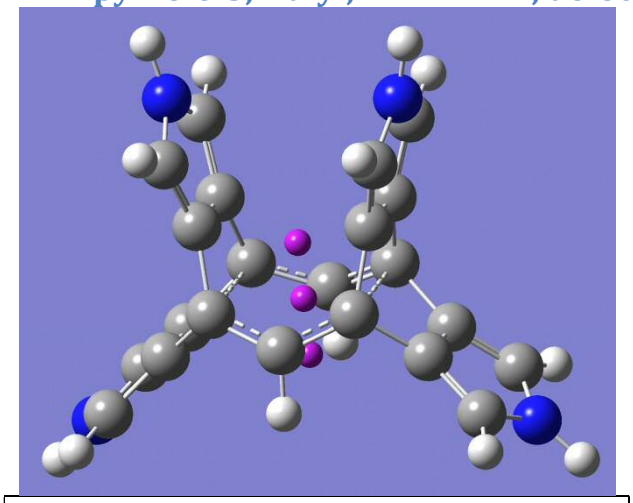


RB3LYP/6-311+G(d) level:
C···C bond lengths: 1.90915 Å, 2.52292 Å
Electronic energy: -2437.134616 Hartrees
Gibbs free energy: -2436.940197 Hartrees
Imaginary frequency: 104.8*i* cm^{-1}
Point group: C_s

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -2437.158508 Hartrees
<S^2> (singlet): 0.9878
Electronic energy (triplet): -2437.06124 Hartrees
<S^2> (triplet): 2.0255

Cartesian coordinates:
C,0,0.3477286985,1.3289928519,1.2614596776
C,0,0.3477286985,1.3289928519,-1.2614596776
C,0,0.307932277,-1.1630376567,-0.9545750057
C,0,0.307932277,-1.1630376567,0.9545750057
C,0,-1.1451971576,-1.5282028866,0.7075323171
C,0,-1.1451971576,-1.5282028866,-0.7075323171
C,0,-2.3103635739,-1.9418414558,-1.2717461992
C,0,-1.0263113559,1.5499387593,-0.7166157444
C,0,-1.0263113559,1.5499387593,0.7166157444
H,0,-2.6111286551,-2.0381316924,-2.3046585597
C,0,1.2318461199,-2.3493030351,0.7090307978
C,0,1.2318461199,-2.3493030351,-0.7090307978
C,0,1.9958217203,-3.3218052983,1.2716652844
H,0,2.2047958176,-3.5588266335,2.3048651339
C,0,1.2584653563,2.4106791331,0.727511444
C,0,1.2584653563,2.4106791331,-0.727511444
C,0,2.0858576822,3.3489273691,-1.2553470704
H,0,2.2925271707,3.567609192,-2.2930790966
C,0,-2.246293122,1.8177822284,1.2540913558
H,0,-2.539971975,1.8754711611,2.2920331761
C,0,0.86677798,0.0918673613,1.4654579319
H,0,1.9380559825,0.0451020579,1.6492461691
C,0,0.86677798,0.0918673613,-1.4654579319
H,0,1.9380559825,0.0451020579,-1.6492461691
C,0,1.9958217203,-3.3218052983,-1.2716652844
H,0,2.2047958176,-3.5588266335,-2.3048651339
C,0,-2.3103635739,-1.9418414558,1.2717461992
H,0,-2.6111286551,-2.0381316924,2.3046585597
C,0,2.0858576822,3.3489273691,1.2553470704
H,0,2.2925271707,3.567609192,2.2930790966
C,0,-2.246293122,1.8177822284,-1.2540913558
H,0,-2.539971975,1.8754711611,-2.2920331761
S,0,-3.4287859756,2.0692440645,0.
S,0,2.7417173057,-4.2686847472,0.
S,0,2.8928856147,4.2546648231,0.
S,0,-3.4498482556,-2.3256663727,0.

Ar = pyrrole-3,4-diyl, $R^1 = R^2 = H$, delocalised structure

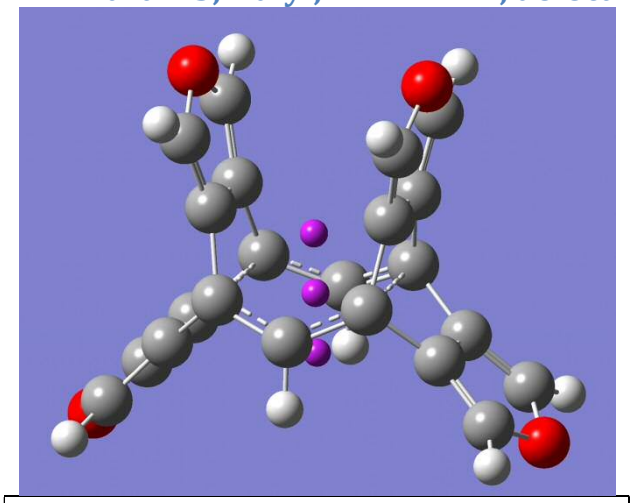


RB3LYP/6-311+G(d) level:
C¨C bond length: 2.49995 Å
Electronic energy: -1065.726548 Hartrees
Gibbs free energy: -1065.467186 Hartrees
No imaginary frequencies
Point group: C_{2v}

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1065.756895 Hartrees
<S^2> (singlet): 1.0634
NICS(0): -3.3994 ppm
NICS(1): -0.8244 ppm
NICS(–1): -3.1432 ppm
Isotropic magnetic susceptibility: -127.6876 cgs-ppm
Electronic energy (triplet): -1065.756693 Hartrees
<S^2> (triplet): 2.0649

Cartesian coordinates:
C,0,1.2499761855,1.2601411718,-0.2388555267
C,0,-1.2499761855,1.2601411718,-0.2388555267
C,0,-1.2499761855,-1.2601411718,-0.2388555267
C,0,1.2499761855,-1.2601411718,-0.2388555267
C,0,0.708068076,-1.5086821055,1.1341707218
C,0,-0.708068076,-1.5086821055,1.1341707218
C,0,-1.1376367829,-1.8334711394,2.3957226846
C,0,-0.708068076,1.5086821055,1.1341707218
C,0,0.708068076,1.5086821055,1.1341707218
H,0,-2.1213287693,-1.9243309172,2.8311904959
C,0,0.7131584116,-2.3057684332,-1.1883843636
C,0,-0.7131584116,-2.3057684332,-1.1883843636
C,0,1.1380755955,-3.2749823732,-2.0609939593
H,0,2.122078419,-3.5901513693,-2.3747923829
C,0,0.7131584116,2.3057684332,-1.1883843636
C,0,-0.7131584116,2.3057684332,-1.1883843636
C,0,-1.1380755955,3.2749823732,-2.0609939593
H,0,-2.122078419,3.5901513693,-2.3747923829
C,0,1.1376367829,1.8334711394,2.3957226846
H,0,2.1213287693,1.9243309172,2.8311904959
C,0,1.5501744893,0.,-0.7690844112
H,0,1.7369372517,0.,-1.8406026134
C,0,-1.5501744893,0.,-0.7690844112
H,0,-1.7369372517,0.,-1.8406026134
C,0,-1.1380755955,-3.2749823732,-2.0609939593
H,0,-2.122078419,-3.5901513693,-2.3747923829
C,0,1.1376367829,-1.8334711394,2.3957226846
H,0,2.1213287693,-1.9243309172,2.8311904959
C,0,1.1380755955,3.2749823732,-2.0609939593
H,0,2.122078419,3.5901513693,-2.3747923829
C,0,-1.1376367829,1.8334711394,2.3957226846
H,0,-2.1213287693,1.9243309172,2.8311904959
N,0,0.,-3.8647709497,-2.588291936
H,0,0.,-4.580912534,-3.2944902666
N,0,0.,-2.027010455,3.1611335086
H,0,0.,-2.2589400613,4.1398221461
N,0,0.,2.027010455,3.1611335086
H,0,0.,2.2589400613,4.1398221461
N,0,0.,3.8647709497,-2.588291936
H,0,0.,4.580912534,-3.2944902666
Bq,0,0.,0.,-0.415598488
Bq,0,0.,0.,0.584401512
Bq,0,0.,0.,-1.415598488

Ar = furan-3,4-diyl, $R^1 = R^2 = H$, delocalised structure

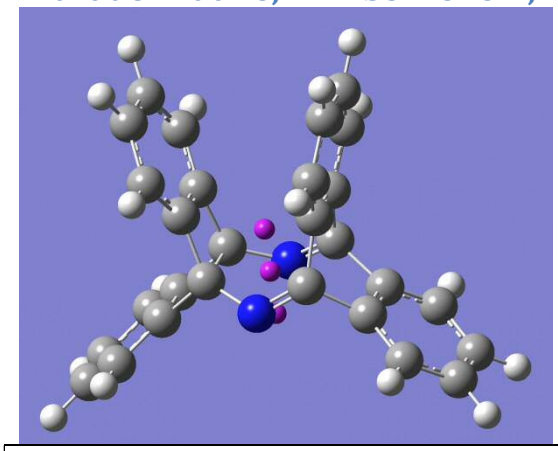


RB3LYP/6-311+G(d) level:
C¨¨C bond length: 2.54486 Å
Electronic energy: -1145.172640 Hartrees
Gibbs free energy: -1145.016116 Hartrees
No imaginary frequencies
Point group: C_{2v}

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1145.208567 Hartrees
$\langle S^2 \rangle$ (singlet): 1.0699
NICS(0): -4.6707 ppm
NICS(1): -2.1237 ppm
NICS(–1): -3.8957 ppm
Isotropic magnetic susceptibility: -109.2152 cgs-ppm
Electronic energy (triplet): -1145.208434 Hartrees
$\langle S^2 \rangle$ (triplet): 2.0661

Cartesian coordinates:
C,0,1.2724307421,1.2570191051,-0.2137488906
C,0,-1.2724307421,1.2570191051,-0.2137488906
C,0,-1.2724307421,-1.2570191051,-0.2137488906
C,0,1.2724307421,-1.2570191051,-0.2137488906
C,0,0.7141095752,-1.4990891486,1.1494302758
C,0,-0.7141095752,-1.4990891486,1.1494302758
C,0,-1.1075783864,-1.7871899502,2.4128769303
C,0,-0.7141095752,1.4990891486,1.1494302758
C,0,0.7141095752,1.4990891486,1.1494302758
H,0,-2.0559097329,-1.8766696533,2.9175495482
C,0,0.7200158669,-2.2877963552,-1.1628510453
C,0,-0.7200158669,-2.2877963552,-1.1628510453
C,0,1.1086252196,-3.2068973578,-2.0775237742
H,0,2.0573518509,-3.5473473233,-2.4603880065
C,0,0.7200158669,2.2877963552,-1.1628510453
C,0,-0.7200158669,2.2877963552,-1.1628510453
C,0,-1.1086252196,3.2068973578,-2.0775237742
H,0,-2.0573518509,3.5473473233,-2.4603880065
C,0,1.1075783864,1.7871899502,2.4128769303
H,0,2.0559097329,1.8766696533,2.9175495482
C,0,1.5886345425,0.,-0.7421971104
H,0,1.7909265181,0.,-1.8102451529
C,0,-1.5886345425,0.,-0.7421971104
H,0,-1.7909265181,0.,-1.8102451529
C,0,-1.1086252196,-3.2068973578,-2.0775237742
H,0,-2.0573518509,-3.5473473233,-2.4603880065
C,0,1.1075783864,-1.7871899502,2.4128769303
H,0,2.0559097329,-1.8766696533,2.9175495482
C,0,1.1086252196,3.2068973578,-2.0775237742
H,0,2.0573518509,3.5473473233,-2.4603880065
C,0,-1.1075783864,1.7871899502,2.4128769303
H,0,-2.0559097329,1.8766696533,2.9175495482
O,0,0.,-1.9643433292,3.2030839858
O,0,0.,-3.7850703037,-2.6477544413
O,0,0.,1.9643433292,3.2030839858
O,0,0.,3.7850703037,-2.6477544413
Bq,0,0.,0.,-0.389898297
Bq,0,0.,0.,0.610101703
Bq,0,0.,0.,-1.389898297

Diazaderivative, Ar = benzene-1,2-diyl, $R^1 = R^2 = –$, localised structure

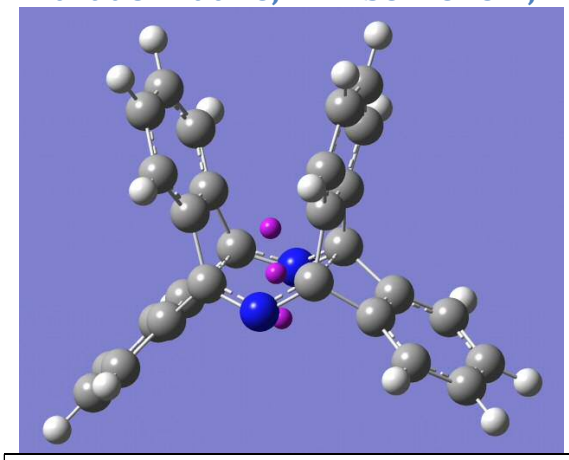


RB3LYP/6-311+G(d) level:
Allyl-allyl C–C bond length: 1.75449 Å
Distance between terminal allyl C atoms: 2.36523 Å
Sum of bond angles for terminal allyl C: 352.908 Å
Electronic energy: -1186.177220 Hartrees
Gibbs free energy: -1185.873497 Hartrees
No imaginary frequencies
Point group: C_s

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1186.177220 Hartrees
<S^2> (singlet): 0.0000
NICS(0): -6.2368 ppm
NICS(1): 0.6406 ppm
NICS(–1): -5.1293 ppm
Isotropic magnetic susceptibility: -140.6809 cgs-ppm

Cartesian coordinates:
C,0,0.1676688693,1.2794674433,1.1826143389
C,0,0.1676688693,1.2794674433,-1.1826143389
C,0,0.4494182114,-1.0473187162,-0.8772468416
C,0,0.4494182114,-1.0473187162,0.8772468416
C,0,-0.9558633916,-1.6367126059,0.69691672
C,0,-0.9558633916,-1.6367126059,-0.69691672
C,0,-1.9784300741,-2.2112246843,-1.4324703309
C,0,-3.0327847595,-2.7753798134,0.6993041622
C,0,-3.0327847595,-2.7753798134,-0.6993041622
H,0,-3.8663965313,-3.2290011184,1.226476956
H,0,-3.8663965313,-3.2290011184,-1.226476956
C,0,-1.2612333263,1.3510245847,-0.6999468506
C,0,-1.2612333263,1.3510245847,0.6999468506
C,0,-2.4444489044,1.4811253809,-1.4110307482
C,0,-3.6411313952,1.608144449,-0.6969085917
C,0,-3.6411313952,1.608144449,0.6969085917
H,0,-4.5783424856,1.7099013204,-1.2344153258
H,0,-4.5783424856,1.7099013204,1.2344153258
H,0,-1.9837988625,-2.227961986,-2.5177534667
H,0,-2.4462144151,1.4828842265,-2.4964164429
C,0,1.5484548091,-2.0950574862,0.6964236962
C,0,1.5484548091,-2.0950574862,-0.6964236962
C,0,2.3852049671,-2.9133914223,1.4334334307
C,0,2.3852049671,-2.9133914223,-1.4334334307
C,0,3.2437091843,-3.7463638793,0.6990804379
H,0,2.4060378821,-2.9075776402,2.5184545207
C,0,3.2437091843,-3.7463638793,-0.6990804379
H,0,2.4060378821,-2.9075776402,-2.5184545207
H,0,3.9306513727,-4.4013191179,1.2261136397
H,0,3.9306513727,-4.4013191179,-1.2261136397
C,0,0.9297479841,2.5133953133,0.7098008412
C,0,1.5909106275,3.5064624305,1.4101797513
C,0,0.9297479841,2.5133953133,-0.7098008412
C,0,2.2528025211,4.5144636915,0.6956459393
H,0,1.6105334928,3.4961399626,2.4951836164
C,0,1.5909106275,3.5064624305,-1.4101797513
C,0,2.2528025211,4.5144636915,-0.6956459393
H,0,2.7737391755,5.2990111057,1.234984544
H,0,1.6105334928,3.4961399626,-2.4951836164
H,0,2.7737391755,5.2990111057,-1.234984544
C,0,-1.9784300741,-2.2112246843,1.4324703309
H,0,-1.9837988625,-2.227961986,2.5177534667
C,0,-2.4444489044,1.4811253809,1.4110307482
H,0,-2.4462144151,1.4828842265,2.4964164429
N,0,0.8580950131,0.2132527032,1.3769386088
N,0,0.8580950131,0.2132527032,-1.3769386088
Bq,0,0.491727365,0.148467143,0.
Bq,0,-0.501545758,0.03267205,0.
Bq,0,1.485000487,0.264262237,0.

Diazaderivative, Ar = benzene-1,2-diyl, $R^1 = R^2 = –$, delocalised structure

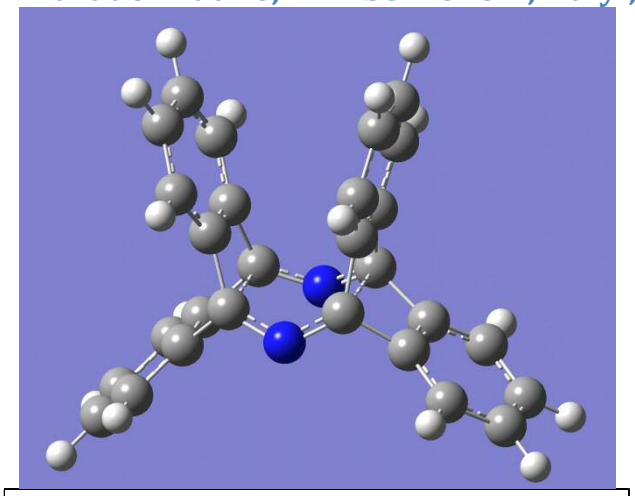


RB3LYP/6-311+G(d) level:
C¨¨C bond length: 2.20491 Å
Electronic energy: -1186.174768 Hartrees
Gibbs free energy: -1185.872330 Hartrees
No imaginary frequencies
Point group: C_{2v}

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1186.174965 Hartrees
<S^2> (singlet): 0.0777
NICS(0): -10.8860 ppm
NICS(1): -0.7230 ppm
NICS(–1): -6.9455 ppm
Isotropic magnetic susceptibility: -147.1611 cgs-ppm
Electronic energy (triplet): -1186.139607 Hartrees
<S^2> (triplet): 2.0537

Cartesian coordinates:
C,0,-1.1771873711,1.1024551098,-0.3107305384
C,0,-1.1771873711,-1.1024551098,-0.3107305384
C,0,1.1771873711,-1.1024551098,-0.3107305384
C,0,1.1771873711,1.1024551098,-0.3107305384
C,0,1.491524373,0.6964805695,1.1176484074
C,0,1.491524373,-0.6964805695,1.1176484074
C,0,1.8452858748,-1.4185241782,2.2470829912
C,0,2.193307255,0.6978143198,3.3967170775
C,0,2.193307255,-0.6978143198,3.3967170775
H,0,2.4701307184,1.231429066,4.3004074515
H,0,2.4701307184,-1.231429066,4.3004074515
C,0,-1.491524373,-0.6964805695,1.1176484074
C,0,-1.491524373,0.6964805695,1.1176484074
C,0,-1.8452858748,-1.4185241782,2.2470829912
C,0,-2.193307255,-0.6978143198,3.3967170775
C,0,-2.193307255,0.6978143198,3.3967170775
H,0,-2.4701307184,-1.231429066,4.3004074515
H,0,-2.4701307184,1.231429066,4.3004074515
H,0,1.8499027347,-2.5041299291,2.2499719233
H,0,-1.8499027347,-2.5041299291,2.2499719233
C,0,2.3014432389,0.7006480105,-1.2566168085
C,0,2.3014432389,-0.7006480105,-1.2566168085
C,0,3.195422111,1.4185153075,-2.0317594234
C,0,3.195422111,-1.4185153075,-2.0317594234
C,0,4.1058393637,0.696920568,-2.8181168976
H,0,3.1804987048,2.5036690983,-2.0535612138
C,0,4.1058393637,-0.696920568,-2.8181168976
H,0,3.1804987048,-2.5036690983,-2.0535612138
H,0,4.814547854,1.2314815606,-3.4426851776
H,0,4.814547854,-1.2314815606,-3.4426851776
C,0,-2.3014432389,0.7006480105,-1.2566168085
C,0,-3.195422111,1.4185153075,-2.0317594234
C,0,-2.3014432389,-0.7006480105,-1.2566168085
C,0,-4.1058393637,0.696920568,-2.8181168976
H,0,-3.1804987048,2.5036690983,-2.0535612138
C,0,-3.195422111,-1.4185153075,-2.0317594234
C,0,-4.1058393637,-0.696920568,-2.8181168976
H,0,-4.814547854,1.2314815606,-3.4426851776
H,0,-3.1804987048,-2.5036690983,-2.0535612138
H,0,-4.814547854,-1.2314815606,-3.4426851776
C,0,1.8452858748,1.4185241782,2.2470829912
H,0,1.8499027347,2.5041299291,2.2499719233
C,0,-1.8452858748,1.4185241782,2.2470829912
H,0,-1.8499027347,2.5041299291,2.2499719233
N,0,0.,1.3861291178,-0.8564330631
N,0,0.,-1.3861291178,-0.8564330631
Bq,0,0.,0.,-0.49263138
Bq,0,0.,0.,0.50736862
Bq,0,0.,0.,-1.49263138

Diazaderivative, Ar = benzene-1,2-diyl, $R^1 = R^2 = –$, localised ⇌ delocalised TS

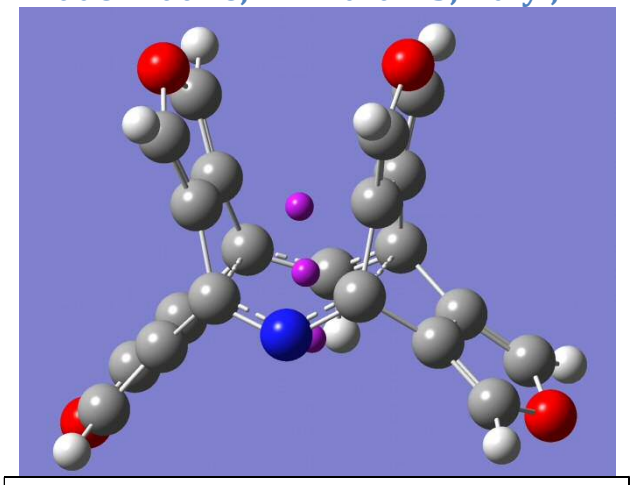


RB3LYP/6-311+G(d) level:
C···C bond lengths: 2.12399 Å, 2.26079 Å
Electronic energy: -1186.174739 Hartrees
Gibbs free energy: -1185.872147 Hartrees
Imaginary frequency: 113.3*i* cm^{-1}
Point group: C_s

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1186.174965 Hartrees
<S^2> (singlet): 0.0777
Electronic energy (triplet): -1186.133714 Hartrees
<S^2> (triplet): 2.0518

Cartesian coordinates:
C,0,0.2274987768,1.2042358084,1.1303941268
C,0,0.2274987768,1.2042358084,-1.1303941268
C,0,0.3725523111,-1.1444923094,-1.061996944
C,0,0.3725523111,-1.1444923094,1.061996944
C,0,-1.040715594,-1.567263438,0.6959138382
C,0,-1.040715594,-1.567263438,-0.6959138382
C,0,-2.1367370718,-2.0071842705,-1.4216017033
C,0,-3.2552051793,-2.4420345927,0.6981311681
C,0,-3.2552051793,-2.4420345927,-0.6981311681
H,0,-4.1357105061,-2.7878855322,1.2303157993
H,0,-4.1357105061,-2.7878855322,-1.2303157993
C,0,-1.210626628,1.4125045562,-0.6971763943
C,0,-1.210626628,1.4125045562,0.6971763943
C,0,-2.3658328394,1.678980142,-1.4161709872
C,0,-3.5393153492,1.9390755397,-0.6975731168
C,0,-3.5393153492,1.9390755397,0.6975731168
H,0,-4.4607135276,2.1465612381,-1.2322994863
H,0,-4.4607135276,2.1465612381,1.2322994863
H,0,-2.1405323362,-2.012929529,-2.507157592
H,0,-2.3681023657,1.6832246917,-2.5017790349
C,0,1.3910838376,-2.2166143664,0.6990999715
C,0,1.3910838376,-2.2166143664,-0.6990999715
C,0,2.2122771271,-3.064359679,1.4216871678
C,0,2.2122771271,-3.064359679,-1.4216871678
C,0,3.0477163732,-3.9280883989,0.697336181
H,0,2.2339086112,-3.0493702198,2.5068018705
C,0,3.0477163732,-3.9280883989,-0.697336181
H,0,2.2339086112,-3.0493702198,-2.5068018705
H,0,3.7123019117,-4.6007821224,1.2302551757
H,0,3.7123019117,-4.6007821224,-1.2302551757
C,0,1.0955553742,2.3815267455,0.7023705433
C,0,1.8172582225,3.3223404245,1.4160489063
C,0,1.0955553742,2.3815267455,-0.7023705433
C,0,2.5474023875,4.2796424797,0.6966034679
H,0,1.8389572927,3.3085931443,2.5012221836
C,0,1.8172582225,3.3223404245,-1.4160489063
C,0,2.5474023875,4.2796424797,-0.6966034679
H,0,3.1264485537,5.025015316,1.232484193
H,0,1.8389572927,3.3085931443,-2.5012221836
H,0,3.1264485537,5.025015316,-1.232484193
C,0,-2.1367370718,-2.0071842705,1.4216017033
H,0,-2.1405323362,-2.012929529,2.507157592
C,0,-2.3658328394,1.678980142,1.4161709872
H,0,-2.3681023657,1.6832246917,2.5017790349
N,0,0.8447046399,0.0703595656,1.3845844113
N,0,0.8447046399,0.0703595656,-1.3845844113

Azaderivative, Ar = furan-3,4-diyl, R^1 = –, R^2 = H, delocalised structure

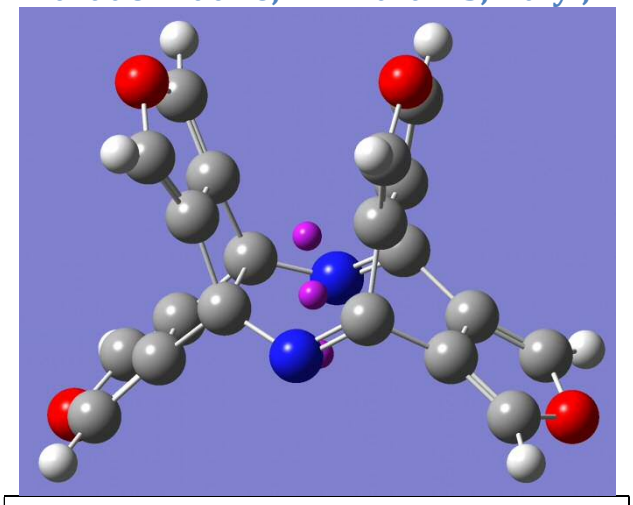


RB3LYP/6-311+G(d) level:
C¨C bond length: 2.48888 Å
Electronic energy: -1161.207209 Hartrees
Gibbs free energy: -1161.008440 Hartrees
No imaginary frequencies
Point group: C_s

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1161.236655 Hartrees
<S^2> (singlet): 1.0570
NICS(0): -3.5243 ppm
NICS(1): -2.3474 ppm
NICS(–1): -3.5716 ppm
Isotropic magnetic susceptibility: -112.8256 cgs-ppm
SCF convergence not achieved for triplet UB3LYP wavefunction.

Cartesian coordinates:
C,0,1.2269819908,1.1868357428,-0.2358796809
C,0,-1.2610353352,1.2497757256,-0.2180266873
C,0,-1.2610353352,-1.2497757256,-0.2180266873
C,0,1.2269819908,-1.1868357428,-0.2358796809
C,0,0.7128890616,-1.4721181453,1.1505641807
C,0,-0.7146871994,-1.4912402514,1.1509772924
C,0,-1.1064487783,-1.8134010247,2.4070356611
C,0,-0.7146871994,1.4912402514,1.1509772924
C,0,0.7128890616,1.4721181453,1.1505641807
H,0,-2.0531612974,-1.9326307752,2.9084928871
C,0,0.7234286543,-2.2562535783,-1.1758074204
C,0,-0.7141344239,-2.283152394,-1.168605839
C,0,1.1244811273,-3.1803705981,-2.0771208731
H,0,2.0759238867,-3.5045754761,-2.466194003
C,0,0.7234286543,2.2562535783,-1.1758074204
C,0,-0.7141344239,2.283152394,-1.168605839
C,0,-1.0942323178,3.2186047384,-2.0707898719
H,0,-2.0380746313,3.582464832,-2.443793444
C,0,1.1104445994,1.7899113783,2.4045072816
H,0,2.0585471733,1.8842949226,2.9085099357
C,0,-1.6037022443,0.,-0.7465172771
H,0,-1.8076217784,0.,-1.8134271884
C,0,-1.0942323178,-3.2186047384,-2.0707898719
H,0,-2.0380746313,-3.582464832,-2.443793444
C,0,1.1104445994,-1.7899113783,2.4045072816
H,0,2.0585471733,-1.8842949226,2.9085099357
C,0,1.1244811273,3.1803705981,-2.0771208731
H,0,2.0759238867,3.5045754761,-2.466194003
C,0,-1.1064487783,1.8134010247,2.4070356611
H,0,-2.0531612974,1.9326307752,2.9084928871
O,0,0.0036780574,-1.9955785765,3.1903067722
O,0,0.0220475103,-3.7843059363,-2.6341661439
O,0,0.0036780574,1.9955785765,3.1903067722
O,0,0.0220475103,3.7843059363,-2.6341661439
N,0,1.4671008673,0.,-0.7802716323
Bq,0,-0.0328341,0.,-0.22683976
Bq,0,-0.02665034,0.,0.86692582
Bq,0,-0.03901786,0.,-1.32060533

Diazaderivative, Ar = furan-3,4-diyl, $R^1 = R^2 = –$, localised structure

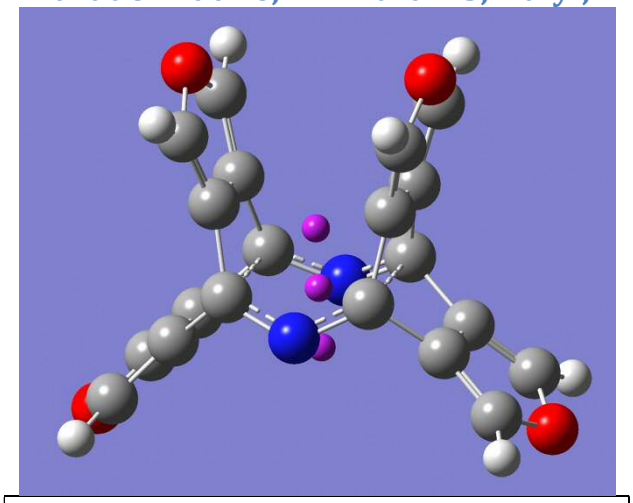


RB3LYP/6-311+G(d) level:
Allyl-allyl C–C bond length: 1.81371 Å
Distance between terminal allyl C atoms: 2.48414 Å
Sum of bond angles for terminal azaallyl C: 350.258º
Electronic energy: -1177.235771 Hartrees
Gibbs free energy: -1177.048379 Hartrees
No imaginary frequencies
Point group: C_s

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1177.235771 Hartrees
<S^2> (singlet): 0.0000
NICS(0): -3.8005 ppm
NICS(1): 1.2497 ppm
NICS(–1): -2.8549 ppm
Isotropic magnetic susceptibility: -83.6701 cgs-ppm

Cartesian coordinates:
C,0,0.1925180585,1.2648347407,1.242071977
C,0,0.1925180585,1.2648347407,-1.242071977
C,0,0.3454308895,-1.0718294756,-0.9068531734
C,0,0.3454308895,-1.0718294756,0.9068531734
C,0,-1.0859750849,-1.5723728205,0.7115453028
C,0,-1.0859750849,-1.5723728205,-0.7115453028
C,0,-2.2469670007,-2.1354195082,-1.1187655791
C,0,-1.2071493966,1.3983845775,-0.7191688205
C,0,-1.2071493966,1.3983845775,0.7191688205
H,0,-2.7262619751,-2.3548434043,-2.0583665689
C,0,1.3682651026,-2.1805327024,0.7106574778
C,0,1.3682651026,-2.1805327024,-0.7106574778
C,0,2.2344467049,-3.1346086783,1.1194549126
H,0,2.6078181148,-3.505648515,2.0593273886
C,0,0.9967358683,2.439455413,0.7305838447
C,0,0.9967358683,2.439455413,-0.7305838447
C,0,1.7574578213,3.4886203569,-1.1076534235
H,0,2.0720066336,3.8901090281,-2.0566133547
C,0,-2.4883257932,1.5899324039,1.1061062013
H,0,-2.9931485852,1.6566595529,2.0554829118
C,0,2.2344467049,-3.1346086783,-1.1194549126
H,0,2.6078181148,-3.505648515,-2.0593273886
C,0,-2.2469670007,-2.1354195082,1.1187655791
H,0,-2.7262619751,-2.3548434043,2.0583665689
C,0,1.7574578213,3.4886203569,1.1076534235
H,0,2.0720066336,3.8901090281,2.0566133547
C,0,-2.4883257932,1.5899324039,-1.1061062013
H,0,-2.9931485852,1.6566595529,-2.0554829118
O,0,2.7767790774,-3.7252933655,0.
O,0,-2.9783286533,-2.4643132223,0.
O,0,-3.2870305489,1.7011674665,0.
O,0,2.2309463359,4.1415860564,0.
N,0,0.8263630262,0.1602470382,1.4068568126
N,0,0.8263630262,0.1602470382,-1.4068568126
Bq,0,0.454770658,0.117750768,0.
Bq,0,-0.543348986,0.056454955,0.
Bq,0,1.452890302,0.17904658,0.

Diazaderivative, Ar = furan-3,4-diyl, $R^1 = R^2 = –$, delocalised structure

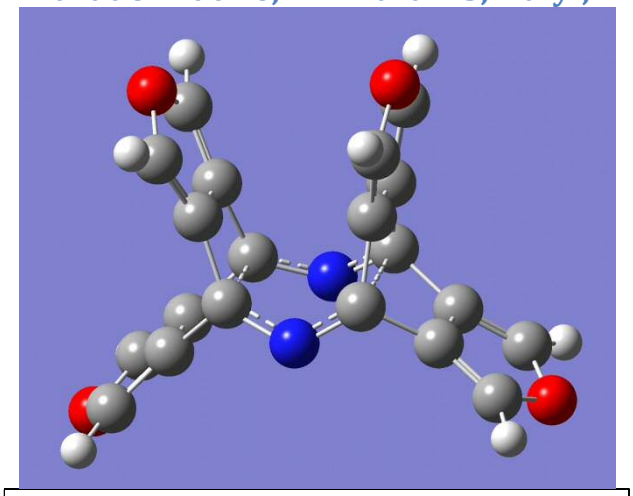


RB3LYP/6-311+G(d) level:
C¨¨C bond length: 2.42377 Å
Electronic energy: -1177.239646 Hartrees
Gibbs free energy: -1177.052693 Hartrees
No imaginary frequencies
Point group: C_{2v}

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1177.262602 Hartrees
<S^2> (singlet): 1.0101
NICS(0): -4.7020 ppm
NICS(1): -0.6396 ppm
NICS(–1): -3.2132 ppm
Isotropic magnetic susceptibility: -103.9644 cgs-ppm
Electronic energy (triplet): -1177.260914 Hartrees
<S^2> (triplet): 2.0575

Cartesian coordinates:
C,0,1.2118853639,1.1810331481,-0.2358606793
C,0,-1.2118853639,1.1810331481,-0.2358606793
C,0,-1.2118853639,-1.1810331481,-0.2358606793
C,0,1.2118853639,-1.1810331481,-0.2358606793
C,0,0.7133525847,-1.4652271855,1.157192437
C,0,-0.7133525847,-1.4652271855,1.157192437
C,0,-1.1094635439,-1.8159960819,2.4031394499
C,0,-0.7133525847,1.4652271855,1.157192437
C,0,0.7133525847,1.4652271855,1.157192437
H,0,-2.0561684285,-1.9394249323,2.9033072566
C,0,0.7181165607,-2.2545999644,-1.1770828032
C,0,-0.7181165607,-2.2545999644,-1.1770828032
C,0,1.1104976678,-3.195229845,-2.0655109143
H,0,2.057573723,-3.5426354625,-2.4447574157
C,0,0.7181165607,2.2545999644,-1.1770828032
C,0,-0.7181165607,2.2545999644,-1.1770828032
C,0,-1.1104976678,3.195229845,-2.0655109143
H,0,-2.057573723,3.5426354625,-2.4447574157
C,0,1.1094635439,1.8159960819,2.4031394499
H,0,2.0561684285,1.9394249323,2.9033072566
C,0,-1.1104976678,-3.195229845,-2.0655109143
H,0,-2.057573723,-3.5426354625,-2.4447574157
C,0,1.1094635439,-1.8159960819,2.4031394499
H,0,2.0561684285,-1.9394249323,2.9033072566
C,0,1.1104976678,3.195229845,-2.0655109143
H,0,2.057573723,3.5426354625,-2.4447574157
C,0,-1.1094635439,1.8159960819,2.4031394499
H,0,-2.0561684285,1.9394249323,2.9033072566
O,0,0.,-2.0256218819,3.1819255483
O,0,0.,-3.786528562,-2.6157492822
O,0,0.,2.0256218819,3.1819255483
O,0,0.,3.786528562,-2.6157492822
N,0,1.482726113,0.,-0.7797548977
N,0,-1.482726113,0.,-0.7797548977
Bq,0,0.,0.,-0.417158752
Bq,0,0.,0.,0.582841248
Bq,0,0.,0.,-1.417158752

Diazaderivative, Ar = furan-3,4-diyl, $R^1 = R^2 = –$, localised ⇌ delocalised TS

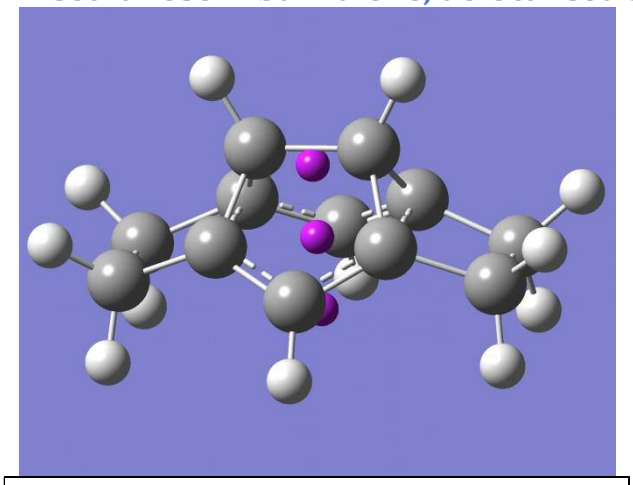


RB3LYP/6-311+G(d) level:
C···C bond lengths: 1.96865 Å, 2.47414 Å
Electronic energy: -1177.235432 Hartrees
Gibbs free energy: -1177.048552 Hartrees
Imaginary frequency: 247.3*i* cm^{-1}
Point group: C_s

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -1177.235432 Hartrees
$<S^2>$ (singlet): 0.0000
Electronic energy (triplet): -1177.181762 Hartrees
$<S^2>$ (triplet): 2.0333

Cartesian coordinates:
C,0,0.2034098247,1.2462224683,1.2370684134
C,0,0.2034098247,1.2462224683,-1.2370684134
C,0,0.3458253214,-1.0955224434,-0.9843248002
C,0,0.3458253214,-1.0955224434,0.9843248002
C,0,-1.0755133271,-1.5615969999,0.7106593048
C,0,-1.0755133271,-1.5615969999,-0.7106593048
C,0,-2.2551455165,-2.0859333886,-1.1171995492
C,0,-1.1982732988,1.3996242185,-0.7175377459
C,0,-1.1982732988,1.3996242185,0.7175377459
H,0,-2.7407859533,-2.2851371634,-2.0581676883
C,0,1.3591617939,-2.1889939484,0.7111208787
C,0,1.3591617939,-2.1889939484,-0.7111208787
C,0,2.2404537197,-3.1303569991,1.1178127468
H,0,2.6211409803,-3.490602718,2.0591038754
C,0,1.0291070647,2.4074405737,0.7268321824
C,0,1.0291070647,2.4074405737,-0.7268321824
C,0,1.8067145716,3.4433109517,-1.1084056582
H,0,2.1313587865,3.8380849066,-2.0568989083
C,0,-2.4749299392,1.6173782614,1.1068876473
H,0,-2.9798668394,1.6939203861,2.055611439
C,0,2.2404537197,-3.1303569991,-1.1178127468
H,0,2.6211409803,-3.490602718,-2.0591038754
C,0,-2.2551455165,-2.0859333886,1.1171995492
H,0,-2.7407859533,-2.2851371634,2.0581676883
C,0,1.8067145716,3.4433109517,1.1084056582
H,0,2.1313587865,3.8380849066,2.0568989083
C,0,-2.4749299392,1.6173782614,-1.1068876473
H,0,-2.9798668394,1.6939203861,-2.055611439
O,0,2.7904116143,-3.7153862072,0.
O,0,-2.9960713856,-2.3939725649,0.
O,0,-3.2714091013,1.7442278935,0.
O,0,2.2906101022,4.0888626279,0.
N,0,0.8256271896,0.1289600273,1.4213204597
N,0,0.8256271896,0.1289600273,-1.4213204597

Bisethanosemibullvalene, delocalised structure

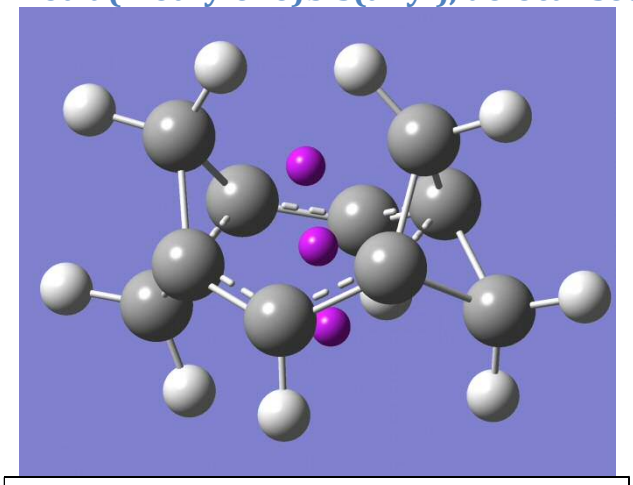


RB3LYP/6-311+G(d) level:
C¨¨C bond length: 2.05339 Å
Electronic energy: -464.475021 Hartrees
Gibbs free energy: -464.303564 Hartrees
No imaginary frequencies
Point group: C_{2v}

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -464.475021 Hartrees
<S^2> (singlet): 0.0000
NICS(0): -18.6176 ppm
NICS(1): -44.0539 ppm
NICS(–1): -10.7924 ppm
Isotropic magnetic susceptibility: -102.3801 cgs-ppm
Electronic energy (triplet): -464.411842 Hartrees
<S^2> (triplet): 2.0520

Cartesian coordinates:
C,0,0.,0.7661955499,1.189435542
C,0,0.,-0.7661955499,1.189435542
H,0,0.,1.2858266188,2.1500031003
H,0,0.,-1.2858266188,2.1500031003
C,0,-1.5814943505,0.,-0.414043256
C,0,1.5814943505,0.,-0.414043256
H,0,2.1786466339,0.,-1.320911332
H,0,-2.1786466339,0.,-1.320911332
C,0,-1.0266929298,1.1468556815,0.1517614946
C,0,-1.0266929298,-1.1468556815,0.1517614946
C,0,1.0266929298,-1.1468556815,0.1517614946
C,0,1.0266929298,1.1468556815,0.1517614946
C,0,0.7812236666,-2.5392425585,-0.4041323276
H,0,1.2179667621,-3.3335843944,0.215388364
H,0,1.1792857897,-2.6595291471,-1.4139178109
C,0,0.7812236666,2.5392425585,-0.4041323276
H,0,1.2179667621,3.3335843944,0.215388364
H,0,1.1792857897,2.6595291471,-1.4139178109
C,0,-0.7812236666,2.5392425585,-0.4041323276
H,0,-1.1792857897,2.6595291471,-1.4139178109
H,0,-1.2179667621,3.3335843944,0.215388364
C,0,-0.7812236666,-2.5392425585,-0.4041323276
H,0,-1.1792857897,-2.6595291471,-1.4139178109
H,0,-1.2179667621,-3.3335843944,0.215388364
Bq,0,0.,0.,-0.036840089
Bq,0,0.,0.,0.963159911
Bq,0,0.,0.,-1.036840089

Tetra(methylene)bis(allyl), delocalised structure

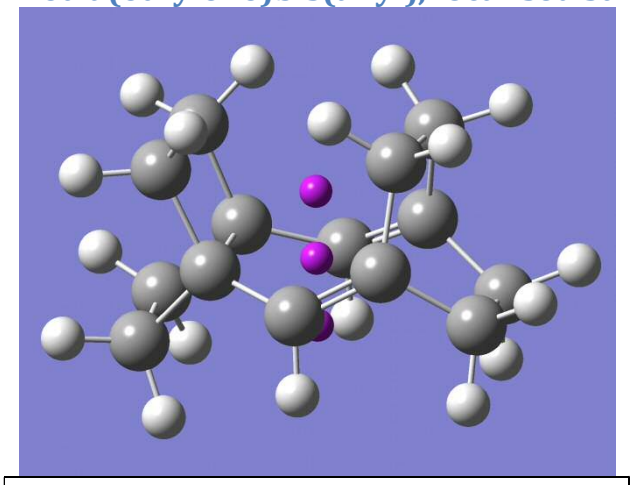


RB3LYP/6-311+G(d) level:
C¨¨C bond length: 1.77332 Å
Electronic energy: -386.923824 Hartrees
Gibbs free energy: -386.786481 Hartrees
No imaginary frequencies
Point group: C_{2v}

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -386.923824 Hartrees
<S^2> (singlet): 0.0000
NICS(0): -16.0021 ppm
NICS(1): -6.4935 ppm
NICS(–1): -10.5419 ppm
Isotropic magnetic susceptibility: -91.1144 cgs-ppm
Electronic energy (triplet): -386.824367 Hartrees
<S^2> (triplet): 2.0155

Cartesian coordinates:
C,0,-1.3699055846,0.,-0.4044824811
C,0,1.3699055846,0.,-0.4044824811
C,0,0.8866621897,-1.2409062072,0.0476836578
C,0,-0.8866621897,-1.2409062072,0.0476836578
H,0,1.6748365568,0.,-1.4502301782
C,0,0.8866621897,1.2409062072,0.0476836578
C,0,0.,-2.1004315121,-0.8705389469
C,0,0.,-1.5004429356,1.2475119053
C,0,-0.8866621897,1.2409062072,0.0476836578
H,0,-1.6748365568,0.,-1.4502301782
C,0,0.,2.1004315121,-0.8705389469
C,0,0.,1.5004429356,1.2475119053
H,0,0.,1.8616658695,-1.9330318066
H,0,0.,3.176038863,-0.6829762517
H,0,0.,0.8560071248,2.1109722299
H,0,0.,2.549474229,1.5547035066
H,0,0.,-1.8616658695,-1.9330318066
H,0,0.,-3.176038863,-0.6829762517
H,0,0.,-0.8560071248,2.1109722299
H,0,0.,-2.549474229,1.5547035066
Bq,0,0.,0.,-0.103038389
Bq,0,0.,0.,0.896961611
Bq,0,0.,0.,-1.103038389

Tetra(ethylene)bis(allyl), localised structure

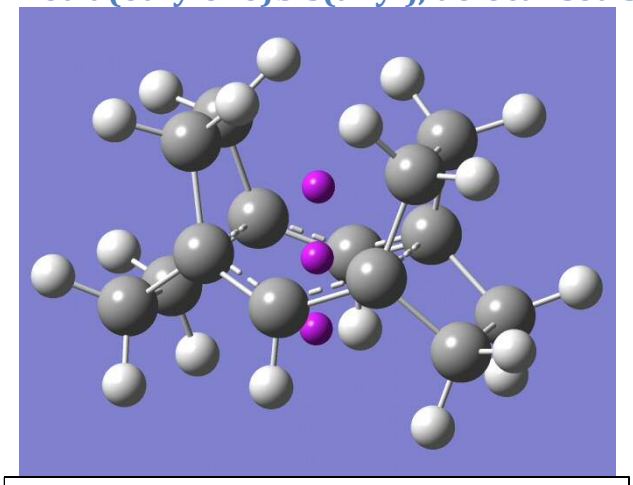


RB3LYP/6-311+G(d) level:
Electronic energy: -544.292422 Hartrees
Gibbs free energy: -544.043458 Hartrees
No imaginary frequencies
Point group: C_1

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -544.292422 Hartrees
<S^2> (singlet): 0.0000
NICS(0): -2.8446 ppm
NICS(1): -2.8022 ppm
NICS(–1): -0.0977 ppm
Isotropic magnetic susceptibility: -105.8671 cgs-ppm

Cartesian coordinates:
C,0,-0.0603599301,-0.5671932649,-1.4235554957
C,0,-0.0596612105,-0.590271343,1.3929351841
C,0,-1.3093983305,-0.1117106104,1.2196815739
C,0,-1.2767807288,-0.0265971215,-1.204864267
H,0,-0.0006281458,-1.6695119894,1.5472279549
C,0,1.2141445126,-0.0411609646,0.8328970084
C,0,-1.6421029458,1.3143865099,0.8393580663
C,0,-2.4494120401,-0.9264237955,-0.8382907837
C,0,-2.4171816781,-1.0503768088,0.7626962419
C,0,-1.5104537762,1.3891286291,-0.72262397
C,0,1.2372819841,-0.1098671823,-0.8329041639
H,0,-0.0613650678,-1.6311613377,-1.6661194759
H,0,-3.4084615671,-0.5102940952,-1.1644213988
H,0,-2.3510045185,-1.9182312109,-1.2850416007
H,0,-3.3953075214,-0.7879039745,1.1799497298
H,0,-2.2013887857,-2.0836749682,1.0434565581
H,0,-0.7099700557,2.0630718661,-1.0164716835
H,0,-2.4286054641,1.7855000737,-1.1700404047
H,0,-1.0049149632,2.0442038656,1.3337755142
H,0,-2.6670138658,1.5416851612,1.1501196237
C,0,2.3708991346,-1.1606979846,-0.7270659244
C,0,2.4365291413,-1.0045984889,0.8195496918
C,0,1.7971588657,1.3436480143,-0.8171146933
C,0,1.6521594896,1.4444615962,0.7308290504
H,0,2.2701968429,-1.9358116156,1.3660471097
H,0,3.3575880321,-0.5557891356,1.2015864235
H,0,2.044430394,-2.1589440774,-1.0300785946
H,0,3.2843173393,-0.92355995,-1.2808533061
H,0,0.8968617173,2.1628559555,1.0399852475
H,0,2.5676967243,1.6761464387,1.2829262625
H,0,1.2217894158,2.0749875016,-1.3821801496
H,0,2.8272044815,1.3947539972,-1.1813952988
Bq,0,-0.042462284,-0.241133414,-0.002635027
Bq,0,0.061761044,-1.233294557,0.066312521
Bq,0,-0.146685612,0.751027728,-0.071582575

Tetra(ethylene)bis(allyl), delocalised structure



RB3LYP/6-311+G(d) level:
C···C bond length: 2.15694 Å
Electronic energy: -544.279219 Hartrees
Gibbs free energy: -544.030120 Hartrees
Imaginary frequency: 376.1*i* cm^{-1}
Point group: C_2

UB3LYP/6-311+G(d)//RB3LYP/6-311+G(d) level:
Electronic energy (singlet): -544.2792223 Hartrees
<S^2> (singlet): 0.0000
NICS(0): -12.2735 ppm
NICS(1): -2.8646 ppm
NICS(–1): -6.9919 ppm
Isotropic magnetic susceptibility: -108.3894 cgs-ppm
Electronic energy (triplet): -544.231671 Hartrees
<S^2> (triplet): 2.0587

Cartesian coordinates:
C,0,1.435357388,0.0026447168,-0.5697383523
C,0,-1.435357388,-0.0026447168,-0.5697383523
C,0,-1.0805962125,1.2410222229,-0.0412835497
C,0,1.0752271726,1.2712525739,-0.1038080276
H,0,-1.6109263525,0.0248359577,-1.6468600748
C,0,-1.0752271726,-1.2712525739,-0.1038080276
C,0,-0.7399490939,1.5724797027,1.4104550729
C,0,0.7378444321,2.3872015651,-1.0982346439
C,0,-0.8185657746,2.4264746269,-0.9815569225
C,0,0.8003812243,1.7062944284,1.3374858948
C,0,1.0805962125,-1.2410222229,-0.0412835497
H,0,1.6109263525,-0.0248359577,-1.6468600748
H,0,1.2210262593,3.3421627895,-0.8531364813
H,0,1.0460936481,2.1169563248,-2.1114139325
H,0,-1.1960239387,3.3709736831,-0.5704883168
H,0,-1.2983370471,2.2846068593,-1.9532261082
H,0,1.323284497,1.1089473474,2.0820035871
H,0,1.1423715538,2.7380480885,1.4816388103
H,0,-1.0491172901,0.7946725956,2.1031718859
H,0,-1.2455067427,2.4918936172,1.7320103287
C,0,0.8185657746,-2.4264746269,-0.9815569225
C,0,-0.7378444321,-2.3872015651,-1.0982346439
C,0,0.7399490939,-1.5724797027,1.4104550729
C,0,-0.8003812243,-1.7062944284,1.3374858948
H,0,-1.0460936481,-2.1169563248,-2.1114139325
H,0,-1.2210262593,-3.3421627895,-0.8531364813
H,0,1.2983370471,-2.2846068593,-1.9532261082
H,0,1.1960239387,-3.3709736831,-0.5704883168
H,0,-1.323284497,-1.1089473474,2.0820035871
H,0,-1.1423715538,-2.7380480885,1.4816388103
H,0,1.0491172901,-0.7946725956,2.1031718859
H,0,1.2455067427,-2.4918936172,1.7320103287

References

(S1) J. Gräfenstein, A. M. Hjerpe, E. Kraka, D. Cremer, *J. Phys. Chem. A* 2000, **104**, 1748.
(S2) Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. v. R. Schleyer, *Chem. Rev.* 2005, **105**, 3842.