Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supporting Information (ESI)

Coexistence of Structurally Similar but Electronically Distinct Isomers of Delocalized Cation Radicals as a Basis for the Development of Functional Materials

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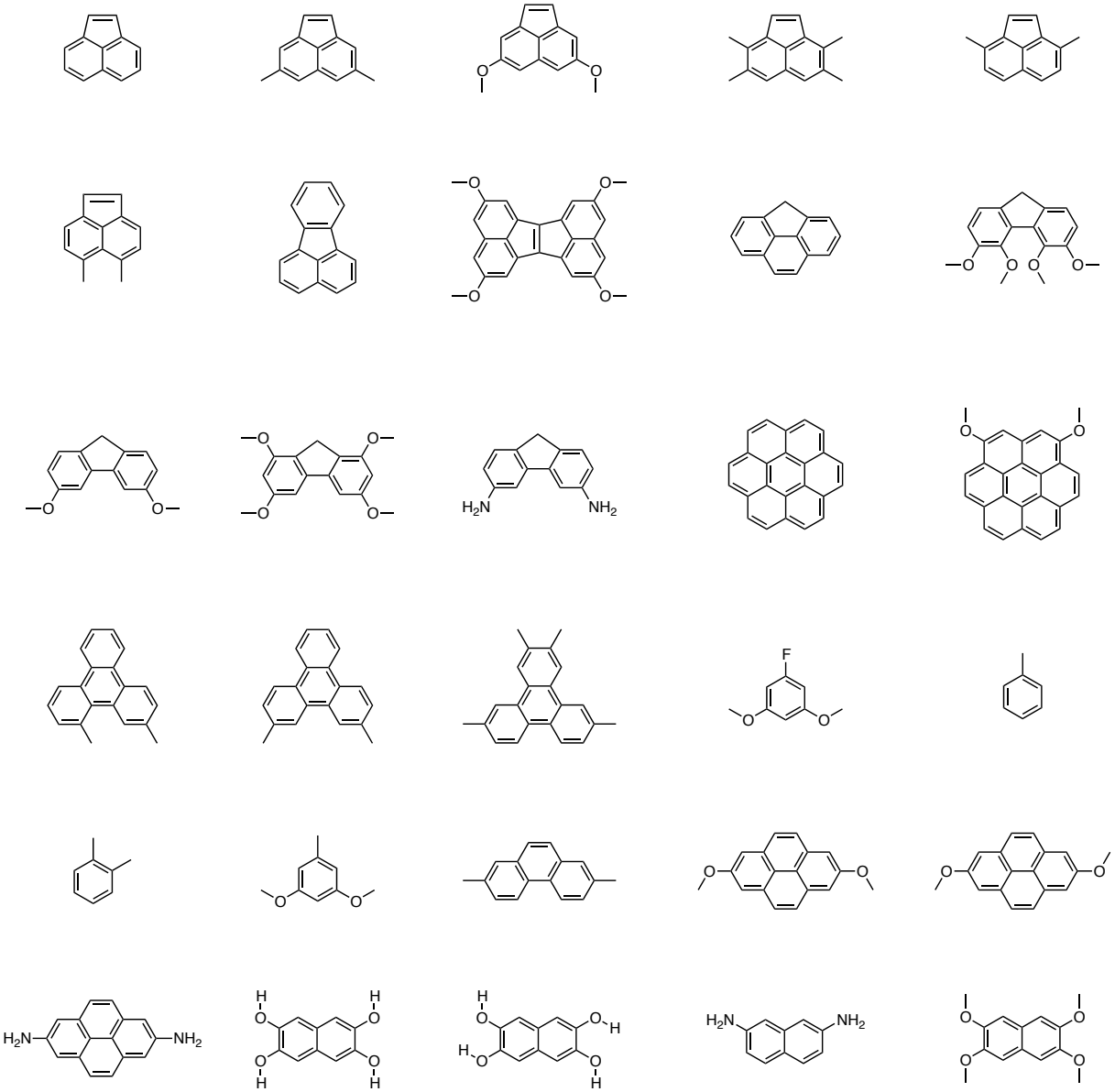
Computational Details

The following protocol was used for the DMRG calculations:

Parameter	Step 1	Step 2	Step 3	Step 4	Step 5	Step 6	Step 7	Step 8	Step 9
Sweeps	0	4	8	12	14	16	18	20	22
MaxMs	200	400	800	1000	1000	1000	1000	1000	1000
Tolerance	1e-5	1e-5	1e-5	1e-5	1e-6	1e-7	1e-8	1e-9	1e-9
Noise	1e-5	1e-5	1e-5	5e-5	5e-5	5e-5	5e-5	5e-5	0

Structural Formula of Molecules Involved in Screening

Chart S1.



Relative Energies of the Cation Radicals of Molecules from Scheme 1

Table S1. Relative energies of the isomeric forms of **1**$^{+\bullet}$, computed using DFT and ab initio methods.

Electronic State	$Q(A_2)$	Q(N)	$Q(B_2)$
B1LYP40/6-31G(d)			
$\Psi(A_2)$	3.0	30.3	47.7
$\Psi(B_2)$	45.6	28.3	0.0
UCCSD(T)/*aug*-cc-pVDZ			
$\Psi(A_2)$	0.0	22.7	42.1
$\Psi(B_2)$	44.1	24.6	2.0
CASPT2(all-p_z)/6-31G(d)			
$\Psi(A_2)$	0.0	23.3	41.8
$\Psi(B_2)$	43.9	29.4	3.7
B1LYP40/6-31G(d)+PCM(DCM)			
$\Psi(A_2)$	0.0	-	-
$\Psi(B_2)$	-	-	1.4

Table S2. Relative energies of the isomeric forms of **2**$^{+\bullet}$, computed using DFT and ab initio methods.

Electronic State	$Q(A_2)$	Q(N)	$Q(B_2)$
B1LYP40/6-31G(d)			
$\Psi(A_2)$	6.0	20.6	46.3
$\Psi(B_2)$	39.5	13.7	0.0
CASPT2(all-p_z)/6-31G(d)			
$\Psi(A_2)$	4.0	15.2	32.6
$\Psi(B_2)$	43.3	16.6	0.0
B1LYP40/6-31G(d)+PCM(DCM)			
$\Psi(A_2)$	8.8	-	-
$\Psi(B_2)$	-	-	0.0

Table S3. Relative energies of the isomeric forms of **3**$^{+\bullet}$, computed using DFT and ab initio methods.

Electronic State	$Q(A_2)$	Q(N)	$Q(B_2)$
B1LYP40/6-31G(d)			
$\Psi(A_2)$	4.8	25.2	38.0
$\Psi(B_2)$	33.5	12.1	0.0
CASPT2(all-p_z)/6-31G(d)			
$\Psi(A_2)$	23.9	39.9	48.6
$\Psi(B_2)$	30.4	11.4	0.0
B1LYP40/6-31G(d)+PCM(DCM)			
$\Psi(A_2)$	9.0 ‡	-	-
$\Psi(B_2)$	-	-	0.0

Table S4. Relative energies of the isomeric forms of **4**$^{+\bullet}$, computed w DFT and ab initio methods.

Electronic State	$Q(A_2)$	Q(N)	$Q(B_2)$
B1LYP40/6-31G(d)			
$\Psi(A_2)$	33.0	45.4	71.6
$\Psi(B_2)$	37.8	24.5	0.0
CASPT2(all-p_z)/6-31G(d)			
$\Psi(A_2)$	30.7	42.4	63.1
$\Psi(B_2)$	36.9	25.3	0.0
B1LYP40/6-31G(d)+PCM(DCM)			
$\Psi(A_2)$	30.1	-	-
$\Psi(B_2)$	-	-	0.0

Table S5. Relative energies of the isomeric forms of **5**$^{+\bullet}$, computed using DFT and ab initio methods.

Electronic State	$Q(A_2)$	Q(N)	$Q(B_2)$
B1LYP40/6-31G(d)			
$\Psi(A_2)$	6.0	20.6	46.3
$\Psi(B_2)$	39.5	13.7	0.0
CASPT2(all-p_z)/6-31G(d)			
$\Psi(A_2)$	4.0	15.2	32.6
$\Psi(B_2)$	43.3	16.6	0.0
B1LYP40/6-31G(d)+PCM(DCM)			
$\Psi(A_2)$	14.8 ‡	-	-
$\Psi(B_2)$	-	-	0.0

Table S6. Relative energies of the isomeric forms of **6**$^{+\bullet}$, computed using DFT and ab initio methods.

Electronic State	$Q(B_{2u})$	Q(N)	$Q(A_u)$
B1LYP40/6-31G(d)			
$\Psi(B_{2u})$	0.0	23.6	20.4
$\Psi(A_u)$	47.8	42.0	27.0
CASPT2(all-p_z)/6-31G(d)			
$\Psi(B_{2u})$	0.0	18.2	14.0
$\Psi(A_u)$	39.3	32.4	21.0

Table S7. Relative energies of the isomeric forms of **7**$^{+\bullet}$, computed using DFT and ab initio methods.

Electronic State	$Q(A_2)$	$Q(B_2)$
B1LYP40/6-31G(d)		
$\Psi(A_2)$	0.0	21.2
$\Psi(B_2)$	39.1	18.3
CASPT2(all-p_z)/6-31G(d)		
$\Psi(A_2)$	0.0	21.3
$\Psi(B_2)$	44.4	27.4

Cation Radical Geometries

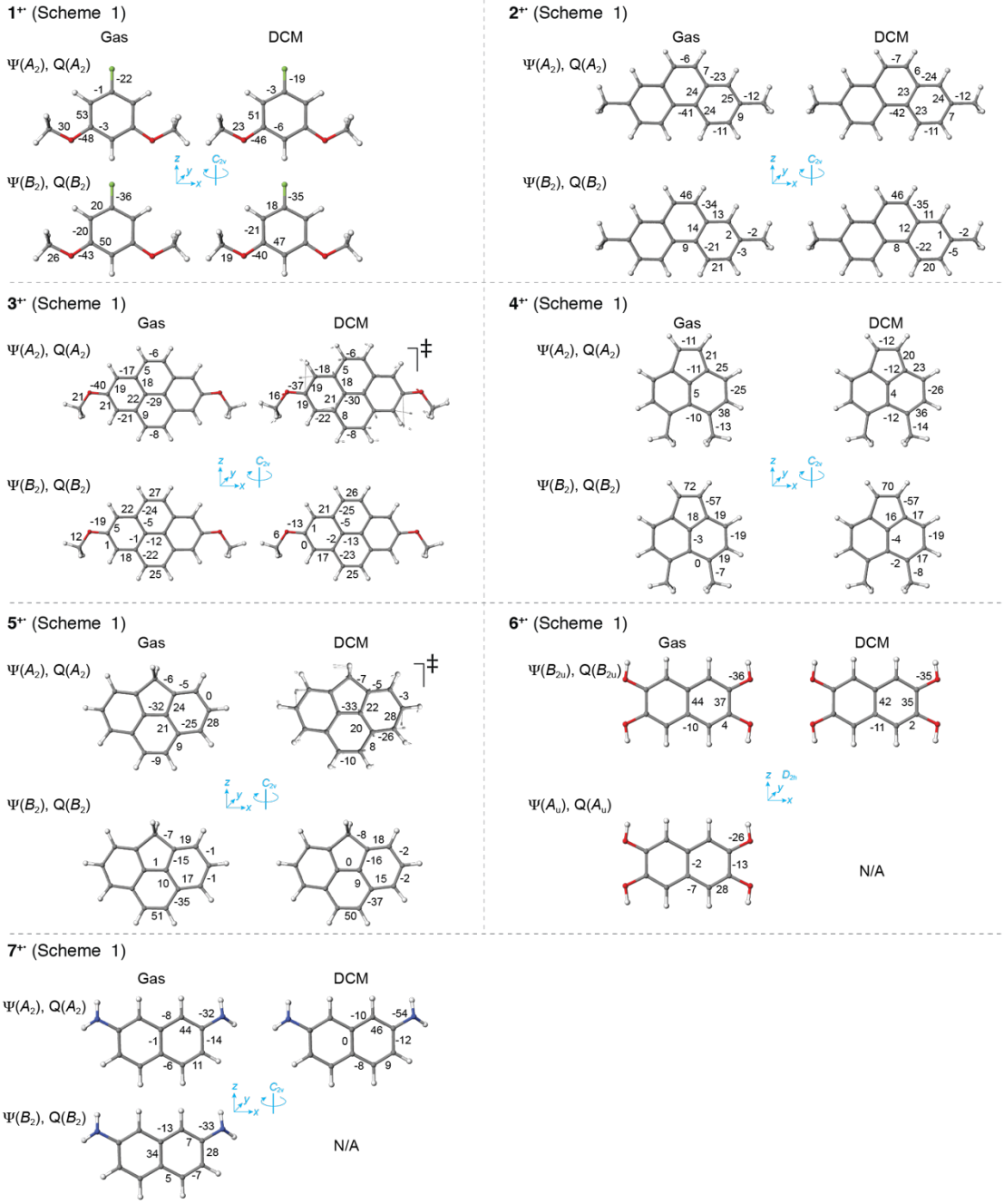


Figure S1. Equilibrium geometries [B1LYP40/6-31G(d)] of the electronic isomers of (**1**-**7**)$^{+\bullet}$ without and with the implicit solvation model, as denoted. The values near the bonds in indicate the bond length displacement due to the oxidation (in milli-Å). The wavefunction symmetry is denoted as Ψ(sym) while the geometry used for the single-point calculation is denoted as *Q*(sym). For example, Ψ(A_2), *Q*(B_2) denotes that the geometry optimization for the cation radical state with symmetry B_2 was followed by a single-point calculation for a cation radical state with symmetry A_2. Double-dagger symbols in **3**$^{+\bullet}$ and **5**$^{+\bullet}$ indicate the presence of imaginary frequency in the vibrational Hessian, and the corresponding displacement vectors are shown using arrows.

Cation Radical Electronic Structures

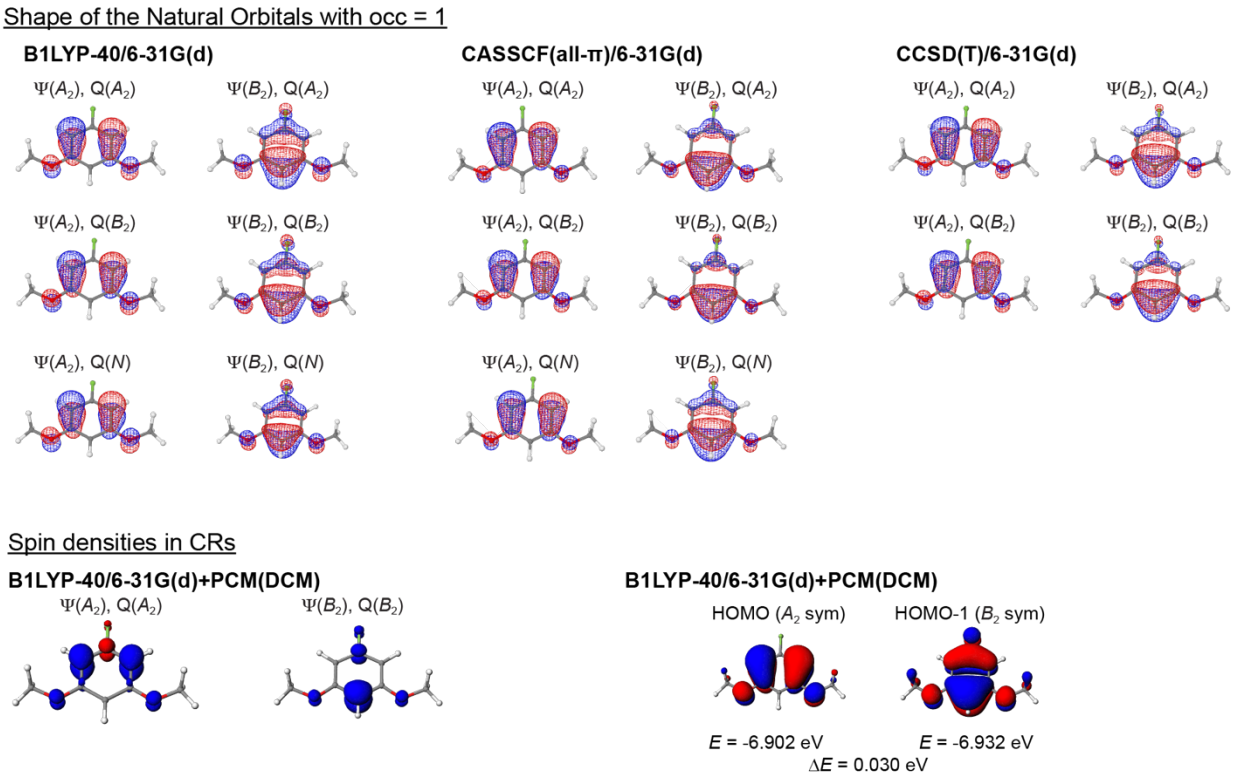


Figure S2. Spin density distribution in $\mathbf{1}^{+\bullet}$ represented as the singly-occupied natural orbital isovalue (0.03 a.u.) plots, isovalue (0.03 a.u.) plots of the HOMO and HOMO-1 of **1**, and spin density ($\rho_\alpha - \rho_\beta$) plots (0.001 a.u.) for the electronic isomers of $\mathbf{1}^{+\bullet}$, as denoted.

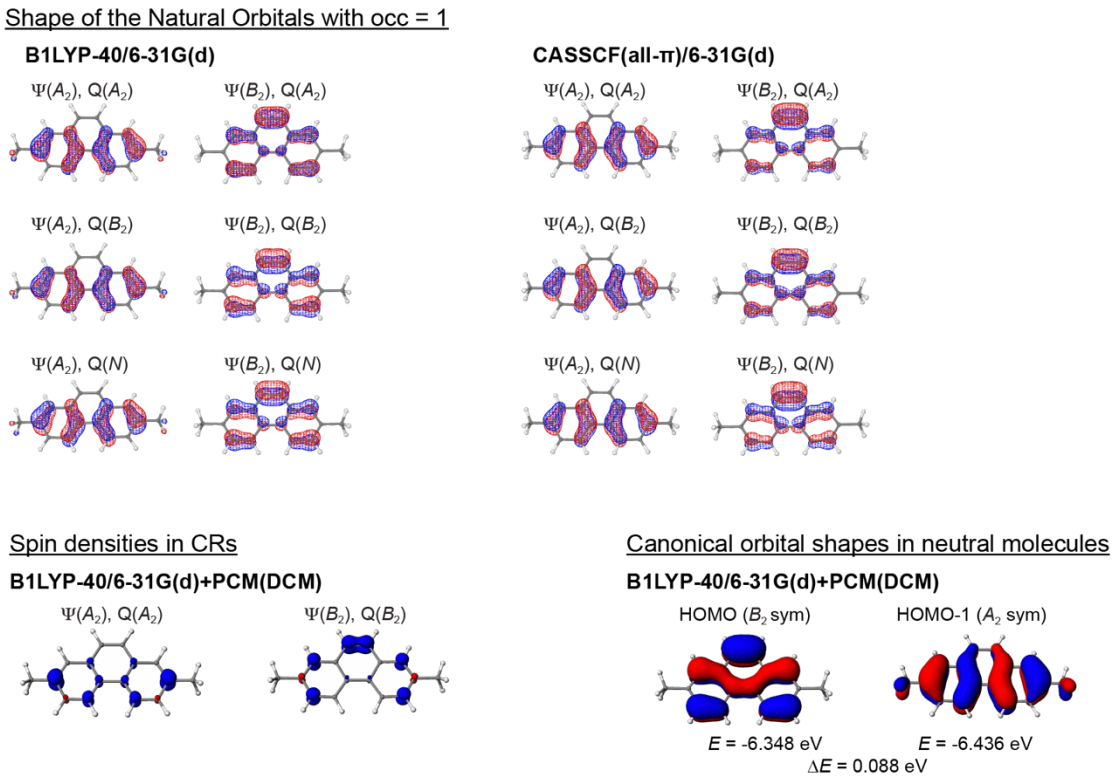


Figure S3. Spin density distribution in $\mathbf{2}^{+\bullet}$ represented as the singly-occupied natural orbital isovalue (0.03 a.u.) plots, isovalue (0.03 a.u.) plots of the HOMO and HOMO-1 of **2**, and spin density ($\rho_\alpha - \rho_\beta$) plots (0.001 a.u.) for the electronic isomers of $\mathbf{2}^{+\bullet}$, as denoted.

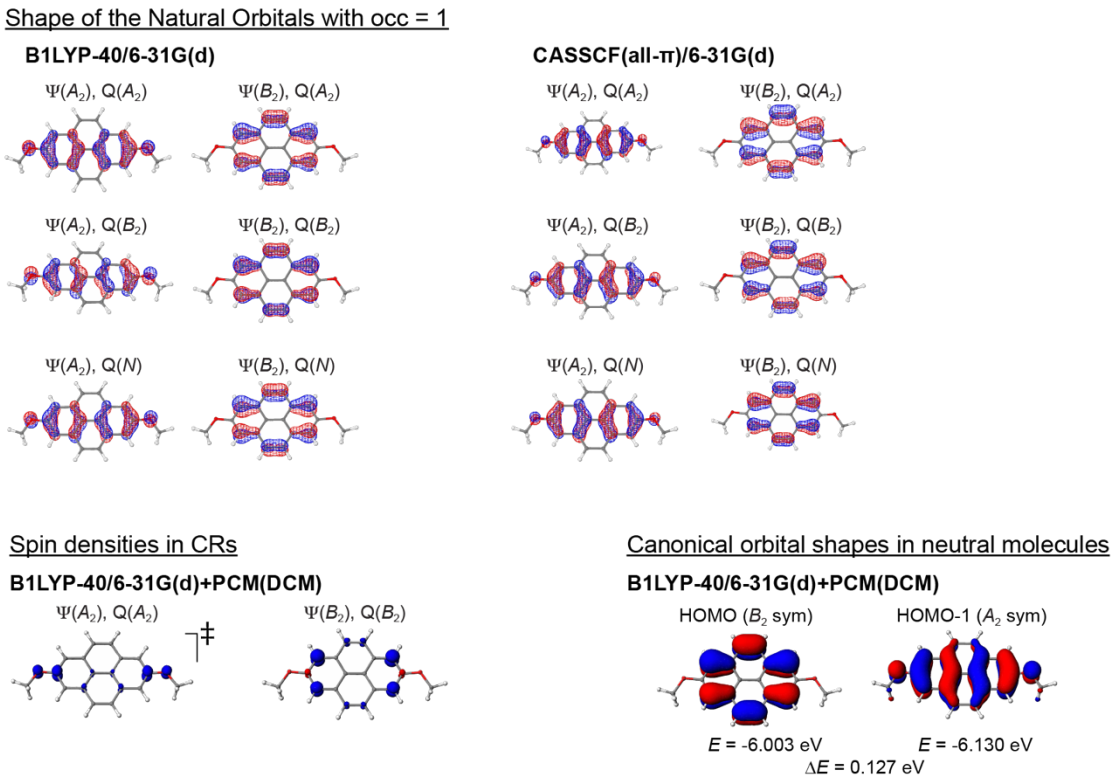


Figure S4. Spin density distribution in $\mathbf{3}^{+\bullet}$ represented as the singly-occupied natural orbital isovalue (0.03 a.u.) plots, isovalue (0.03 a.u.) plots of the HOMO and HOMO-1 of **3**, and spin density ($\rho_\alpha - \rho_\beta$) plots (0.001 a.u.) for the electronic isomers of $\mathbf{3}^{+\bullet}$, as denoted.

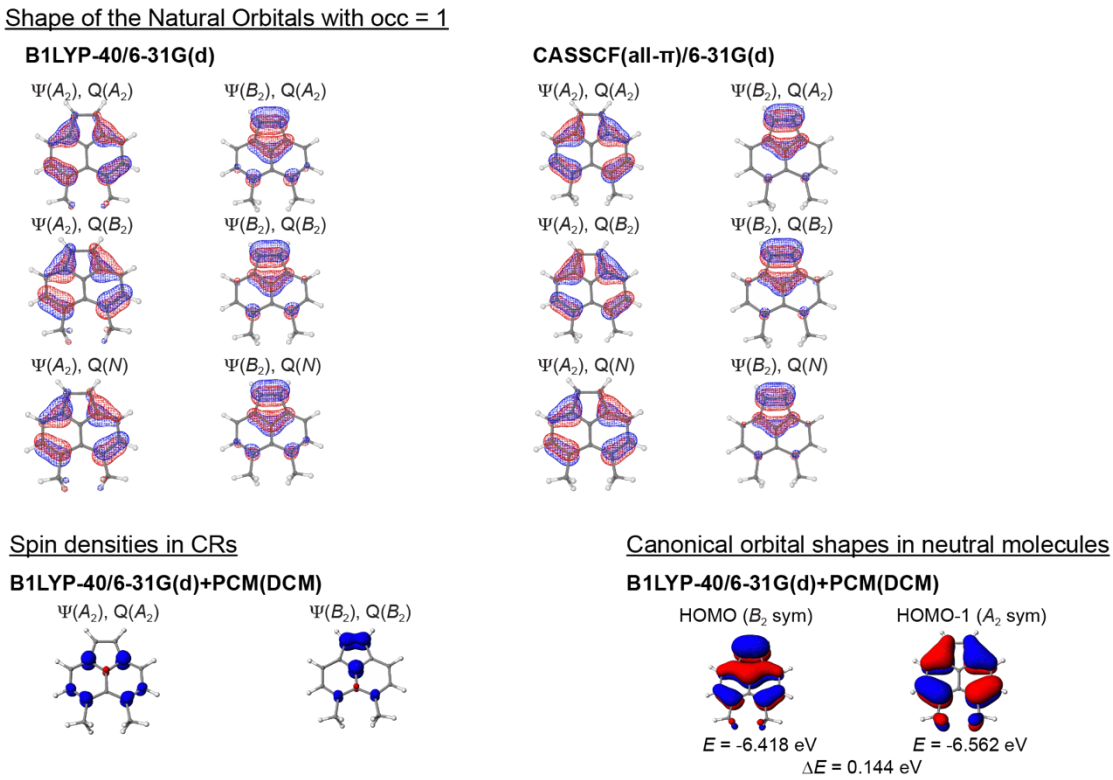


Figure S5. Spin density distribution in $\mathbf{4}^{+\bullet}$ represented as the singly-occupied natural orbital isovalue (0.03 a.u.) plots, isovalue (0.03 a.u.) plots of the HOMO and HOMO-1 of **4**, and spin density ($\rho_\alpha - \rho_\beta$) plots (0.001 a.u.) for the electronic isomers of $\mathbf{4}^{+\bullet}$, as denoted.

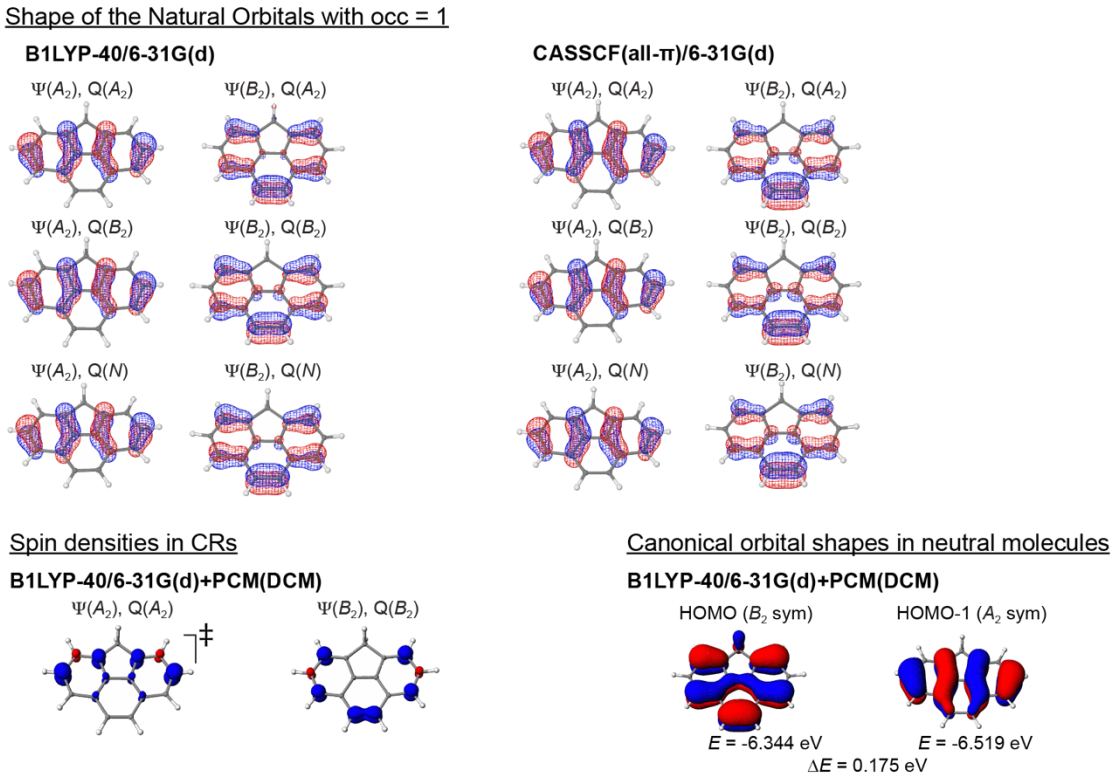


Figure S6. Spin density distribution in $\mathbf{5}^{+\bullet}$ represented as the singly-occupied natural orbital isovalue (0.03 a.u.) plots, isovalue (0.03 a.u.) plots of the HOMO and HOMO-1 of **5**, and spin density ($\rho_\alpha - \rho_\beta$) plots (0.001 a.u.) for the electronic isomers of $\mathbf{5}^{+\bullet}$, as denoted.

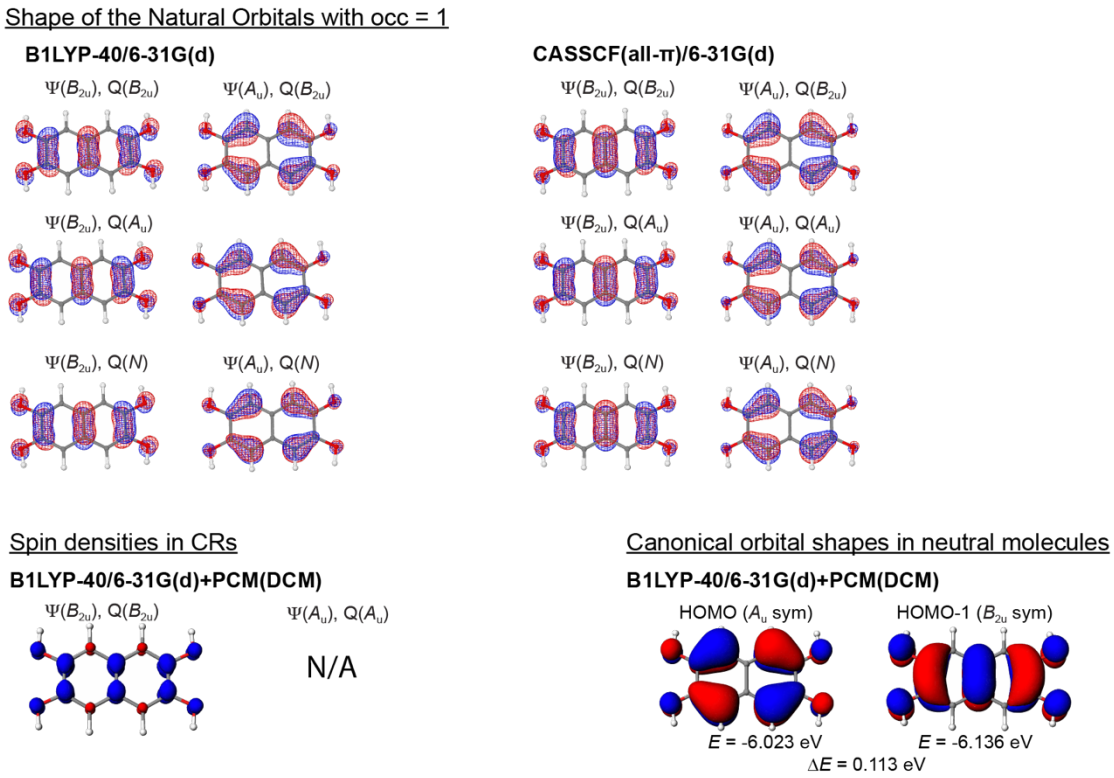


Figure S7. Spin density distribution in $\mathbf{6}^{+\bullet}$ represented as the singly-occupied natural orbital isovalue (0.03 a.u.) plots, isovalue (0.03 a.u.) plots of the HOMO and HOMO-1 of **6**, and spin density ($\rho_\alpha - \rho_\beta$) plots (0.001 a.u.) for the electronic isomers of $\mathbf{6}^{+\bullet}$, as denoted.

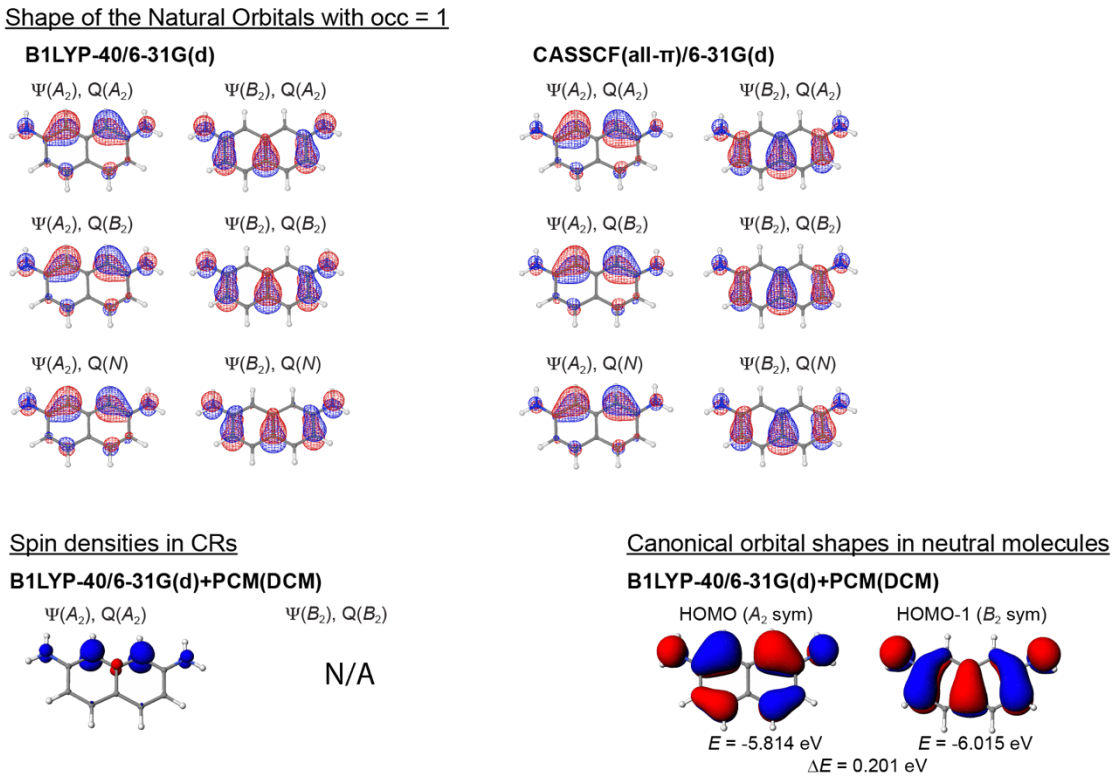


Figure S8. Spin density distribution in $\mathbf{7}^{+\bullet}$ represented as the singly-occupied natural orbital isovalue (0.03 a.u.) plots, isovalue (0.03 a.u.) plots of the HOMO and HOMO-1 of **7**, and spin density ($\rho_\alpha - \rho_\beta$) plots (0.001 a.u.) for the electronic isomers of $\mathbf{7}^{+\bullet}$, as denoted.

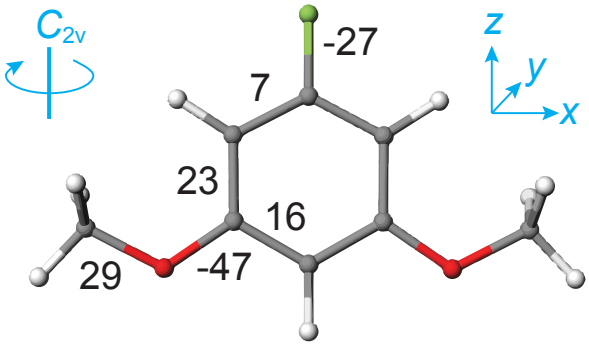


Figure S9. The structure of the conical intersection [CASSCF(3;2)/6-31G(d)] of the interconversion of $\mathbf{1}^{+\bullet}$ isomers. The values near the bonds in indicate the bond length displacement due to the oxidation (in milli-Å).

Cation Radical Spectral Properties

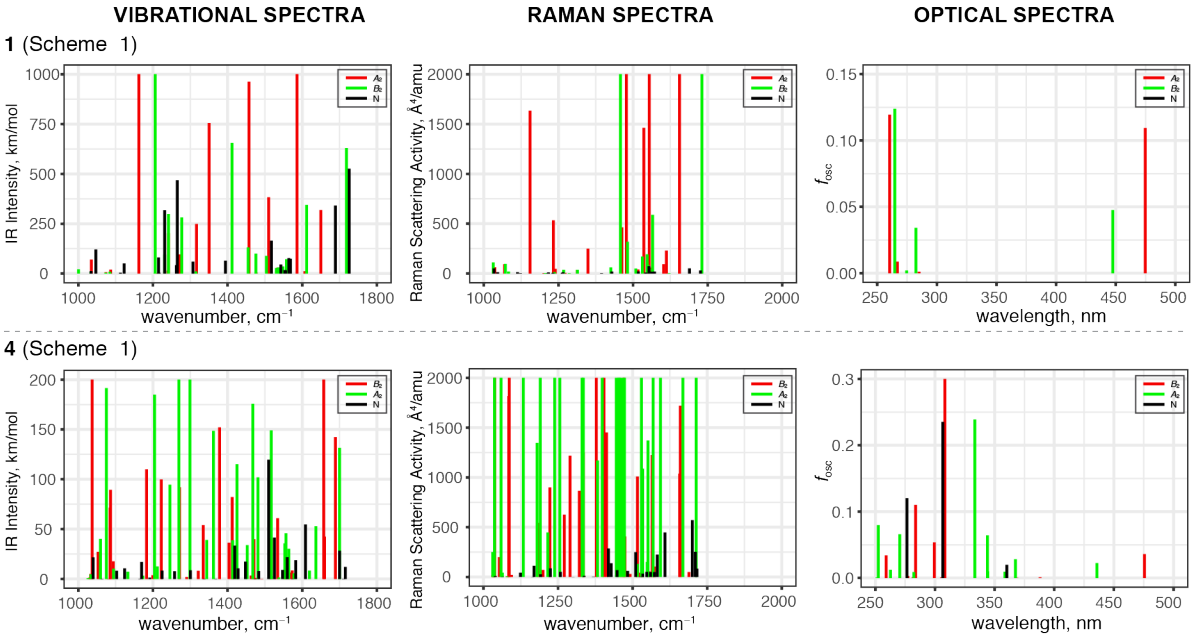


Figure S10. Infrared and Raman stick spectra of $\mathbf{1}^{+\bullet}$ and $\mathbf{4}^{+\bullet}$ obtained from the harmonic frequency analysis (left, central panels). Stick spectra of the optical absorption of $\mathbf{1}^{+\bullet}$ and $\mathbf{4}^{+\bullet}$ obtained from the time-dependent calculations [B1LYP40/6-31G(d)+PCM(DCM)]. Green and red sticks denote the pick positions/intensities for the electronic isomers with the A_2 and B_2 symmetry, respectively, while black line denotes the corresponding peaks for neutral state.

Modeling of the single-molecule conductance through phenanthrene

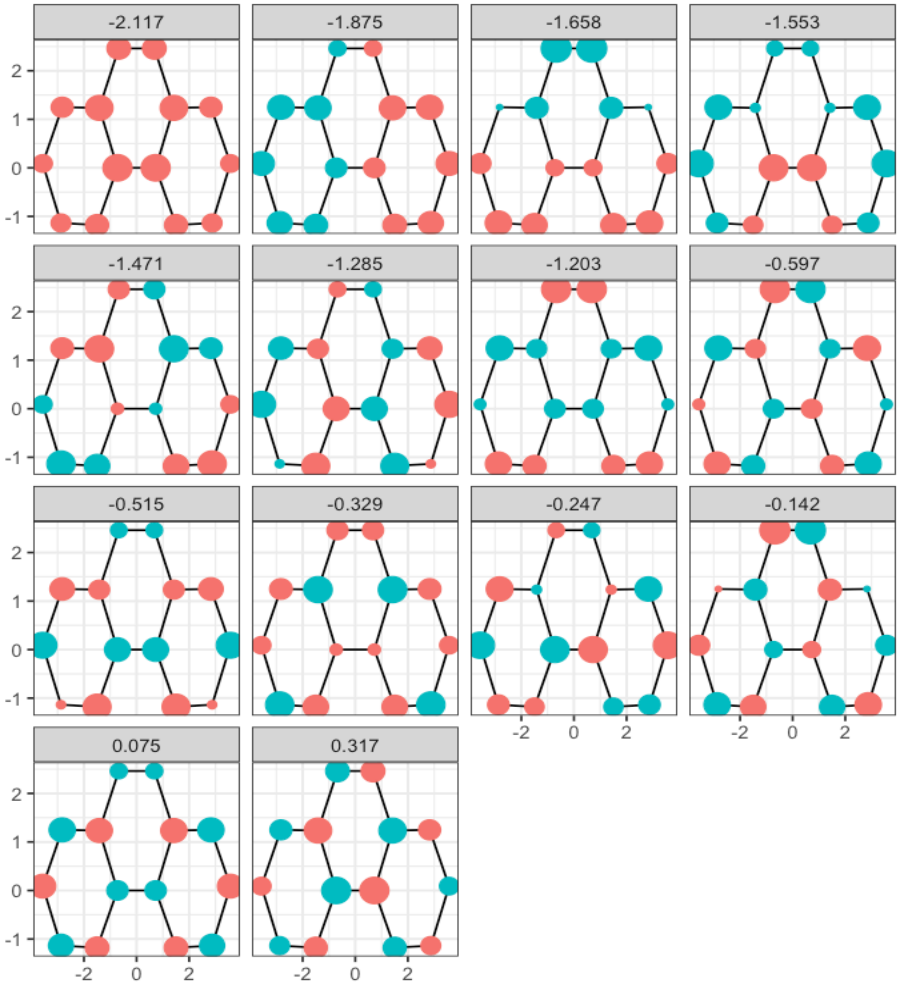


Figure S11. Eigenvectors (which represent shapes of molecular orbitals) and eigenvalues (which represent the orbital energies) of the topological Hamiltonian for phenanthrene (HOMO is the orbital with index 7). Each panel represents one molecular orbital juxtaposed with phenanthrene molecule, which is shown in the XY-plane without hydrogen atoms. Colored circles, centered at carbon atoms, show the sign and magnitude of the corresponding p_z atomic orbital into the molecular orbital.

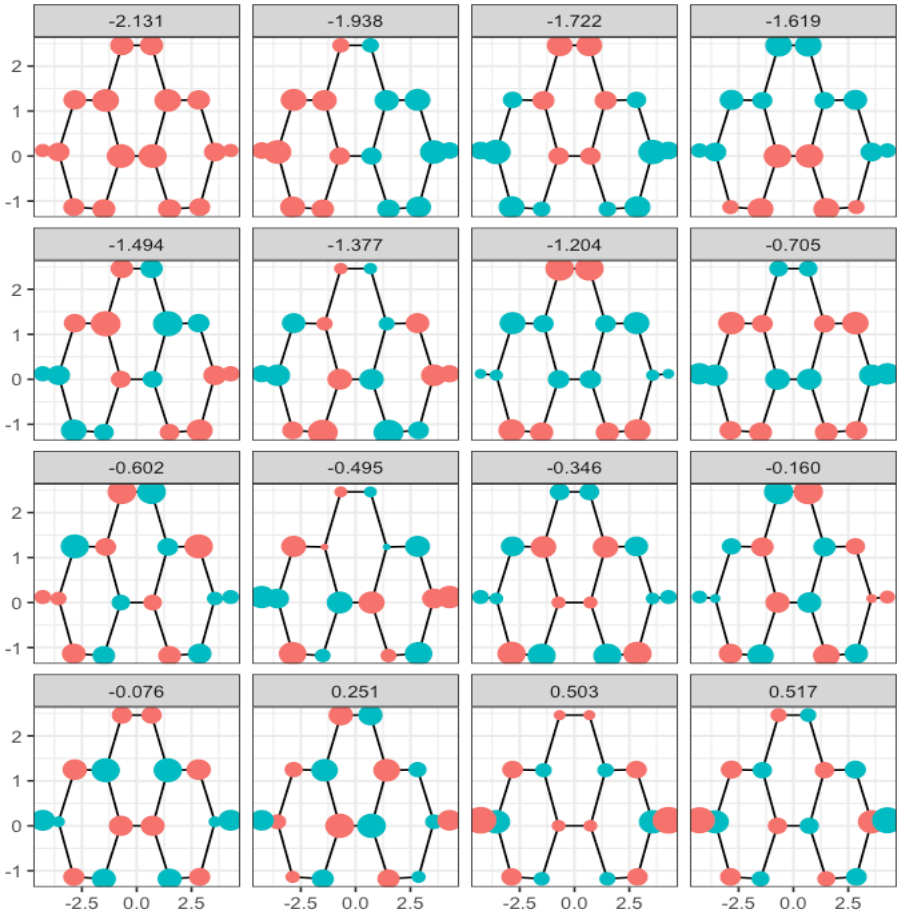


Figure S12. Eigenvectors (which represent shapes of molecular orbitals) and eigenvalues (which represent the orbital energies) of the topological Hamiltonian for phenanthrene with two electrodes connected at the 2,7-positions (HOMO is the orbital with index 7). Each panel represents one molecular orbital juxtaposed with phenanthrene molecule, which is shown in the XY-plane without hydrogen atoms. Colored circles, centered at carbon atoms, show the sign and magnitude of the corresponding p_z atomic orbital into the molecular orbital.

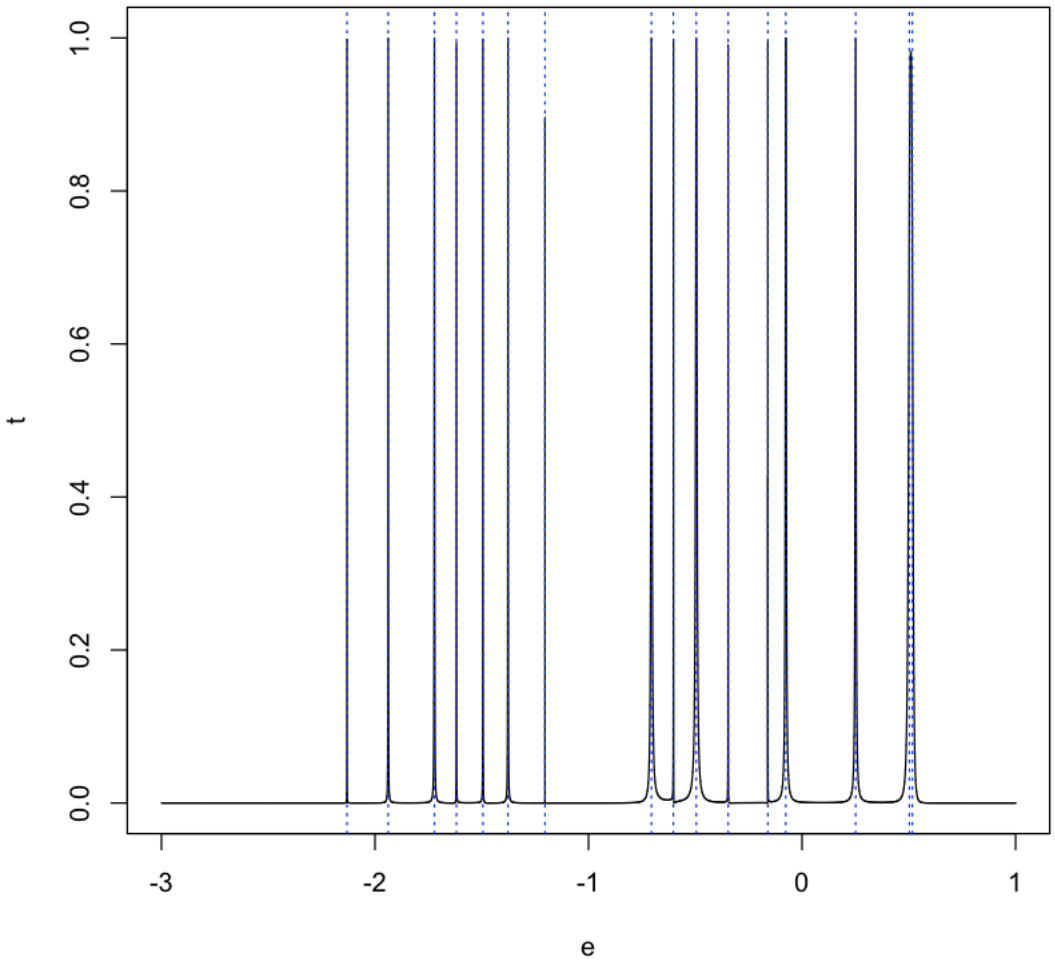


Figure S13. Transmission as function of energy for phenanthrene with electrodes connected at the 2,7-positions. Dash lines represent the molecular orbital energies obtained from the Hamiltonian *H*.

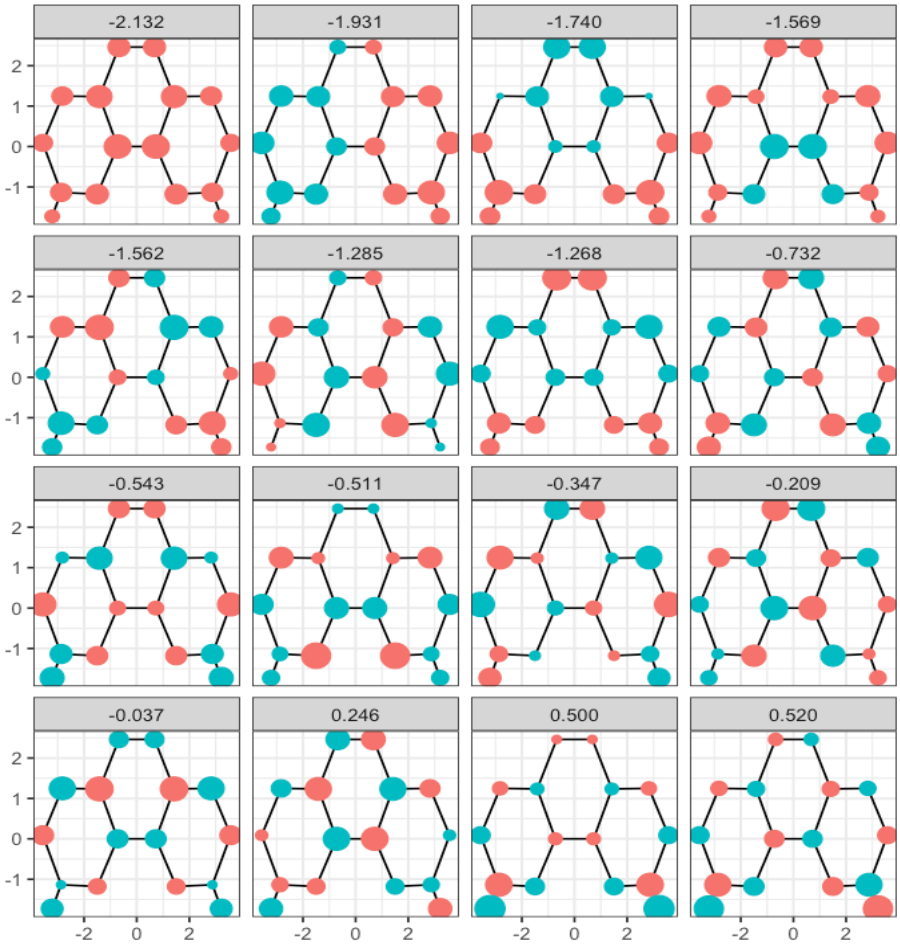


Figure S14. Eigenvectors (which represent shapes of molecular orbitals) and eigenvalues (which represent the orbital energies) of the topological Hamiltonian for phenanthrene with two electrodes connected at the 3,6-positions (HOMO is the orbital with index 7). Each panel represents one molecular orbital juxtaposed with phenanthrene molecule, which is shown in the XY-plane without hydrogen atoms. Colored circles, centered at carbon atoms, show the sign and magnitude of the corresponding p_z atomic orbital into the molecular orbital.

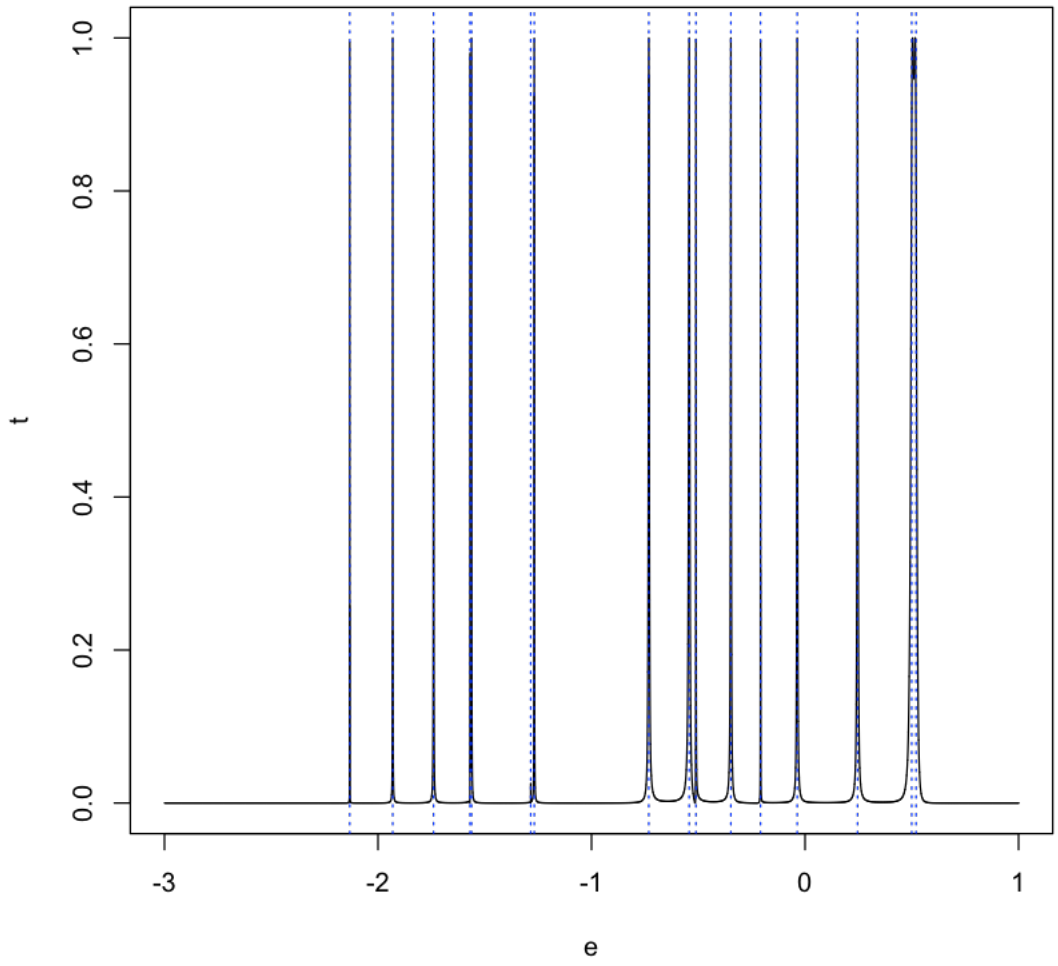


Figure S15. Transmission as function of energy for phenanthrene with electrodes connected at the 2,7-positions. Dash lines represent the molecular orbital energies obtained from the Hamiltonian *H*.

Table S2. Orbital-associated transmissions evaluated as described in the Computational Details

Orbital Index	2,7	3,6
1	0.006	0.006
2	0.028	0.023
3	0.042	0.034
4	0.011	0.006
5	0.017	0.030
6 (HOMO-1)	**0.034**	**0.001**
7 (HOMO)	**0.001**	**0.025**
8	0.124	0.088
9	0.015	0.106
10	0.156	0.022
11	0.011	0.070
12	0.007	0.013
13	0.110	0.068
14	0.103	0.093
15	0.182	0.223
16	0.154	0.194

Cartesian Coordinates of the Optimized Structures

1 (Scheme 1)

B1LYP-40/6-31G(d) NEUTRAL; gas (Molpro)

C	0.0000000000	0.0000000000	-2.7355738471
C	1.2047115427	0.0000000000	-2.0410956228
C	1.2200754599	0.0000000000	-0.6443635433
C	0.0000000000	0.0000000000	0.0040719016
C	-1.2200754599	0.0000000000	-0.6443635433
C	-1.2047115427	0.0000000000	-2.0410956228
H	2.1255669806	0.0000000000	-0.0628922192
H	-2.1255669806	0.0000000000	-0.0628922192
O	2.3223101048	0.0000000000	-2.8040593216
H	0.0000000000	0.0000000000	-3.8135042887
O	-2.3223101048	0.0000000000	-2.8040593216
C	3.5777762794	0.0000000000	-2.1646754165
H	4.3181369877	0.0000000000	-2.9587103782
H	3.7125169808	-0.8900747870	-1.5470770014
H	3.7125169808	0.8900747870	-1.5470770014
C	-3.5777762794	0.0000000000	-2.1646754165
H	-4.3181369877	0.0000000000	-2.9587103782
H	-3.7125169808	0.8900747870	-1.5470770014
H	-3.7125169808	-0.8900747870	-1.5470770014
F	0.0000000000	0.0000000000	1.3456372430

B1LYP-40/6-31G(d) Cation Radical A2-SYM; gas (Molpro)

C	0.0000000000	0.0000000000	-2.7628972981
C	1.1975535415	0.0000000000	-2.0623938191
C	1.2069261714	0.0000000000	-0.6121661555
C	0.0000000000	0.0000000000	0.0591003650
C	-1.2069261714	0.0000000000	-0.6121661555
C	-1.1975535415	0.0000000000	-2.0623938191
H	2.1265020134	0.0000000000	-0.0504818347
H	-2.1265020134	0.0000000000	-0.0504818347
O	2.2998886991	0.0000000000	-2.7604238685
H	0.0000000000	0.0000000000	-3.8403741146
O	-2.2998886991	0.0000000000	-2.7604238685
C	3.6090561748	0.0000000000	-2.1639733595
H	4.2942656543	0.0000000000	-3.0018470118
H	3.7512113082	-0.8980129344	-1.5678747417
H	3.7512113082	0.8980129344	-1.5678747417
C	-3.6090561748	0.0000000000	-2.1639733595
H	-4.2942656543	0.0000000000	-3.0018470118
H	-3.7512113082	0.8980129344	-1.5678747417
H	-3.7512113082	-0.8980129344	-1.5678747417
F	0.0000000000	0.0000000000	1.3789721125

B1LYP-40/6-31G(d) Cation Radical B2-SYM; gas (Molpro)

C	0.0000000000	0.0000000000	-2.6912260248
C	1.2531500801	0.0000000000	-1.9813168261
C	1.2489528205	0.0000000000	-0.6040282063
C	0.0000000000	0.0000000000	0.0320190821
C	-1.2489528205	0.0000000000	-0.6040282063
C	-1.2531500801	0.0000000000	-1.9813168261
H	2.1410800290	0.0000000000	-0.0016419059
H	-2.1410800290	0.0000000000	-0.0016419059
O	2.3009724002	0.0000000000	-2.7679784471
H	0.0000000000	0.0000000000	-3.7708314588
O	-2.3009724002	0.0000000000	-2.7679784471
C	3.6211725881	0.0000000000	-2.2050395231
H	4.2937361746	0.0000000000	-3.0530120080
H	3.7681059681	-0.8959655399	-1.6051389609
H	3.7681059681	0.8959655399	-1.6051389609
C	-3.6211725881	0.0000000000	-2.2050395231
H	-4.2937361746	0.0000000000	-3.0530120080
H	-3.7681059681	0.8959655399	-1.6051389609
H	-3.7681059681	-0.8959655399	-1.6051389609
F	0.0000000000	0.0000000000	1.3373580781

B1LYP-40/6-31G(d) NEUTRAL; PCM(DCM) (Gaussian 09)

C	0.00004	-1.23115	-0.00022
C	-1.20609	-0.53723	-0.00021
C	-1.22160	0.85971	-0.00019
C	-0.00001	1.50464	-0.00018
C	1.22160	0.85976	-0.00019
C	1.20614	-0.53718	-0.00020
H	-2.12812	1.43968	-0.00019
H	2.12810	1.43975	-0.00018
O	-2.32296	-1.29977	-0.00022
H	0.00006	-2.30969	-0.00023
O	2.32303	-1.29968	-0.00021
C	-3.58439	-0.65742	-0.00022
H	-4.32331	-1.45198	-0.00024
H	-3.71559	-0.04154	-0.89045
H	-3.71561	-0.04156	0.89002
C	3.58445	-0.65729	-0.00021
H	4.32340	-1.45182	-0.00022
H	3.71563	-0.04142	0.89003
H	3.71563	-0.04140	-0.89043
F	-0.00004	2.84913	-0.00017

B1LYP-40/6-31G(d) Cation Radical A2-SYM; PCM(DCM) (Gaussian 09)

C	0.00017	-1.26289	-0.00020
C	-1.19585	-0.56252	-0.00022
C	-1.20660	0.88591	-0.00022
C	0.00017	1.55278	-0.00021
C	1.20693	0.88592	-0.00020
C	1.19620	-0.56251	-0.00019

H	-2.12613	1.44590	-0.00023
H	2.12646	1.44591	-0.00020
O	-2.29958	-1.26118	-0.00022
H	0.00018	-2.33971	-0.00020
O	2.29993	-1.26117	-0.00019
C	-3.60227	-0.65033	-0.00024
H	-4.29607	-1.48071	-0.00025
H	-3.73661	-0.05225	-0.89712
H	-3.73664	-0.05225	0.89663
C	3.60261	-0.65030	-0.00016
H	4.29642	-1.48068	-0.00014
H	3.73694	-0.05223	0.89672
H	3.73698	-0.05222	-0.89703
F	0.00016	2.87794	-0.00022

B1LYP-40/6-31G(d) Cation Radical B2-SYM; PCM(DCM) (Gaussian 09)

C	0.00004	-1.19945	-0.00023
C	-1.25049	-0.48909	-0.00023
C	-1.24780	0.88666	-0.00023
C	-0.00001	1.52018	-0.00021
C	1.24780	0.88672	-0.00022
C	1.25054	-0.48903	-0.00023
H	-2.14125	1.48557	-0.00022
H	2.14123	1.48566	-0.00021
O	-2.30402	-1.27174	-0.00023
H	0.00006	-2.27785	-0.00024
O	2.30409	-1.27165	-0.00022
C	-3.61386	-0.68756	-0.00022
H	-4.30046	-1.52394	-0.00032
H	-3.75120	-0.08427	-0.89481
H	-3.75125	-0.08443	0.89447
C	3.61392	-0.68743	-0.00020
H	4.30054	-1.52379	-0.00030
H	3.75129	-0.08430	0.89449
H	3.75125	-0.08413	-0.89479
F	-0.00005	2.82999	-0.00023

2 (Scheme 1)

B1LYP-40/6-31G(d) NEUTRAL; gas (Molpro)

C	0.6760413960	0.0000000000	2.4608509655
C	0.7255340067	0.0000000000	0.0003820061
C	-1.4169847788	0.0000000000	1.2354822838
C	-0.6760413960	0.0000000000	2.4608509655
C	1.4169847788	0.0000000000	1.2354822838
H	1.2254310576	0.0000000000	3.3925671043
C	-0.7255340067	0.0000000000	0.0003820061
C	2.8265592907	0.0000000000	1.2489542395
C	3.5680378774	0.0000000000	0.0897179532

C	2.8724386237	0.0000000000	-1.1358157067
H	3.3297128023	0.0000000000	2.2075585482
C	1.4995765912	0.0000000000	-1.1786695940
H	1.0140535018	0.0000000000	-2.1423513073
C	-1.4995765912	0.0000000000	-1.1786695940
C	-3.5680378774	0.0000000000	0.0897179532
C	-2.8265592907	0.0000000000	1.2489542395
H	-3.3297128023	0.0000000000	2.2075585482
H	-1.2254310576	0.0000000000	3.3925671043
H	3.4328904602	0.0000000000	-2.0615753617
C	-2.8724386237	0.0000000000	-1.1358157067
H	-1.0140535018	0.0000000000	-2.1423513073
H	-3.4328904602	0.0000000000	-2.0615753617
C	5.0729928795	0.0000000000	0.1100624196
C	-5.0729928795	0.0000000000	0.1100624196
H	5.4761707899	-0.8779306204	-0.3983988532
H	5.4761707899	0.8779306204	-0.3983988532
H	5.4561309093	0.0000000000	1.1293641557
H	-5.4761707899	-0.8779306204	-0.3983988532
H	-5.4561309093	0.0000000000	1.1293641557
H	-5.4761707899	0.8779306204	-0.3983988532

B1LYP-40/6-31G(d) Cation Radical A2-SYM; gas (Molpro)

C	0.6729061684	0.0000000000	2.5016570529
C	0.7051400851	0.0000000000	0.0090159689
C	-1.4090690966	0.0000000000	1.2647628183
C	-0.6729061684	0.0000000000	2.5016570529
C	1.4090690966	0.0000000000	1.2647628183
H	1.2287683296	0.0000000000	3.4275753305
C	-0.7051400851	0.0000000000	0.0090159689
C	2.7956456895	0.0000000000	1.2671989531
C	3.5413131004	0.0000000000	0.0812187803
C	2.8482022379	0.0000000000	-1.1559455427
H	3.3173798997	0.0000000000	2.2136530941
C	1.4861164218	0.0000000000	-1.1943726219
H	0.9949618927	0.0000000000	-2.1530725779
C	-1.4861164218	0.0000000000	-1.1943726219
C	-3.5413131004	0.0000000000	0.0812187803
C	-2.7956456895	0.0000000000	1.2671989531
H	-3.3173798997	0.0000000000	2.2136530941
H	-1.2287683296	0.0000000000	3.4275753305
H	3.4139676535	0.0000000000	-2.0760902610
C	-2.8482022379	0.0000000000	-1.1559455427
H	-0.9949618927	0.0000000000	-2.1530725779
H	-3.4139676535	0.0000000000	-2.0760902610
C	5.0342636559	0.0000000000	0.1026396442
C	-5.0342636559	0.0000000000	0.1026396442
H	5.4223958344	-0.8758666777	-0.4217046218
H	5.4223958344	0.8758666777	-0.4217046218
H	5.4295043839	0.0000000000	1.1148986049

H	-5.4223958344	-0.8758666777	-0.4217046218
H	-5.4295043839	0.0000000000	1.1148986049
H	-5.4223958344	0.8758666777	-0.4217046218

B1LYP-40/6-31G(d) Cation Radical B2-SYM; gas (Molpro)

C	0.6991138613	0.0000000000	2.4218501388
C	0.7298279237	0.0000000000	-0.0210379299
C	-1.4257713673	0.0000000000	1.2273024033
C	-0.6991138613	0.0000000000	2.4218501388
C	1.4257713673	0.0000000000	1.2273024033
H	1.2276516747	0.0000000000	3.3644539862
C	-0.7298279237	0.0000000000	-0.0210379299
C	2.8482135123	0.0000000000	1.2573038138
C	3.5991838428	0.0000000000	0.1016419606
C	2.8946351110	0.0000000000	-1.1150821956
H	3.3382397312	0.0000000000	2.2210877062
C	1.5012321793	0.0000000000	-1.1767291978
H	1.0374634530	0.0000000000	-2.1502503257
C	-1.5012321793	0.0000000000	-1.1767291978
C	-3.5991838428	0.0000000000	0.1016419606
C	-2.8482135123	0.0000000000	1.2573038138
H	-3.3382397312	0.0000000000	2.2210877062
H	-1.2276516747	0.0000000000	3.3644539862
H	3.4509650794	0.0000000000	-2.0423359139
C	-2.8946351110	0.0000000000	-1.1150821956
H	-1.0374634530	0.0000000000	-2.1502503257
H	-3.4509650794	0.0000000000	-2.0423359139
C	5.1020259446	0.0000000000	0.1187961859
C	-5.1020259446	0.0000000000	0.1187961859
H	5.4973266495	-0.8787360730	-0.3915500671
H	5.4973266495	0.8787360730	-0.3915500671
H	5.4873044714	0.0000000000	1.1358295021
H	-5.4973266495	-0.8787360730	-0.3915500671
H	-5.4873044714	0.0000000000	1.1358295021
H	-5.4973266495	0.8787360730	-0.3915500671

B1LYP-40/6-31G(d) NEUTRAL; PCM(DCM) (Gaussian 09)

C	0.67627	2.11766	0.00008
C	0.72588	-0.34407	-0.00002
C	-1.41736	0.89160	0.00004
C	-0.67627	2.11766	0.00008
C	1.41736	0.89160	0.00003
H	1.22545	3.04940	0.00012
C	-0.72588	-0.34407	-0.00001
C	2.82753	0.90589	0.00003
C	3.56933	-0.25386	-0.00002
C	2.87338	-1.47992	-0.00007
H	3.33039	1.86453	0.00006
C	1.50005	-1.52374	-0.00007
H	1.01585	-2.48810	-0.00011

C	-1.50005	-1.52374	-0.00006
C	-3.56933	-0.25386	-0.00000
C	-2.82752	0.90589	0.00004
H	-3.33038	1.86453	0.00008
H	-1.22544	3.04940	0.00012
H	3.43374	-2.40551	-0.00011
C	-2.87338	-1.47991	-0.00006
H	-1.01585	-2.48810	-0.00010
H	-3.43374	-2.40550	-0.00009
C	5.07415	-0.23352	-0.00003
C	-5.07414	-0.23351	0.00000
H	5.47584	-0.74363	-0.87734
H	5.47584	-0.74369	0.87725
H	5.45689	0.78564	0.00001
H	-5.47584	-0.74362	-0.87731
H	-5.45689	0.78564	0.00004
H	-5.47584	-0.74368	0.87728

B1LYP-40/6-31G(d) Cation Radical A2-SYM; PCM(DCM) (Gaussian 09)

C	0.67280	2.15713	0.00166
C	0.70476	-0.33513	-0.00489
C	-1.40822	0.92026	-0.00042
C	-0.67269	2.15717	-0.00226
C	1.40826	0.92017	0.00007
H	1.22943	3.08223	0.00368
C	-0.70478	-0.33510	0.00478
C	2.79412	0.92255	0.00323
C	3.53751	-0.26414	-0.00329
C	2.84601	-1.50048	-0.01933
H	3.31670	1.86797	0.01079
C	1.48395	-1.53909	-0.02079
H	0.99215	-2.49682	-0.03891
C	-1.48404	-1.53901	0.02091
C	-3.53753	-0.26392	0.00318
C	-2.79409	0.92271	-0.00357
H	-3.31661	1.86816	-0.01130
H	-1.22927	3.08230	-0.00446
H	3.41152	-2.42022	-0.03115
C	-2.84609	-1.50031	0.01945
H	-0.99229	-2.49676	0.03921
H	-3.41165	-2.42001	0.03144
C	5.03011	-0.24124	0.00555
C	-5.03013	-0.24097	-0.00566
H	5.42295	-0.77179	-0.86371
H	5.41033	-0.75996	0.88779
H	5.42117	0.77250	0.00241
H	-5.41036	-0.75974	-0.88787
H	-5.42115	0.77279	-0.00261
H	-5.42299	-0.77144	0.86364

B1LYP-40/6-31G(d) Cation Radical B2-SYM; PCM(DCM) (Gaussian 09)

C	0.69900	2.07710	0.00009
C	0.72977	-0.36601	-0.00001
C	-1.42445	0.88198	0.00004
C	-0.69905	2.07709	0.00009
C	1.42441	0.88200	0.00004
H	1.22722	3.01886	0.00013
C	-0.72980	-0.36602	-0.00001
C	2.84570	0.91318	0.00004
C	3.59443	-0.24327	-0.00001
C	2.89225	-1.46033	-0.00006
H	3.33471	1.87709	0.00007
C	1.49972	-1.52250	-0.00006
H	1.03657	-2.49586	-0.00010
C	-1.49973	-1.52252	-0.00005
C	-3.59445	-0.24333	0.00000
C	-2.84574	0.91314	0.00005
H	-3.33476	1.87704	0.00008
H	-1.22729	3.01884	0.00013
H	3.44824	-2.38727	-0.00010
C	-2.89226	-1.46037	-0.00004
H	-1.03656	-2.49588	-0.00009
H	-3.44824	-2.38732	-0.00008
C	5.09706	-0.22433	-0.00001
C	-5.09709	-0.22440	0.00001
H	5.49196	-0.73540	-0.87839
H	5.49196	-0.73544	0.87835
H	5.47822	0.79428	0.00001
H	-5.49198	-0.73547	-0.87837
H	-5.47826	0.79420	0.00003
H	-5.49198	-0.73551	0.87836

3 (Scheme 1)

B1LYP-40/6-31G(d) NEUTRAL; gas (Molpro)

C	0.6755411901	4.9004594601	0.0000000000
C	-0.6755411901	4.9004594601	0.0000000000
C	-1.4267139855	3.6726295764	0.0000000000
C	-0.7103436901	2.4445977784	0.0000000000
C	0.7103436901	2.4445977784	0.0000000000
C	1.4267139855	3.6726295764	0.0000000000
H	-1.2219837776	5.8337341889	0.0000000000
H	1.2219837776	5.8337341889	0.0000000000
C	-2.8154220410	3.6521420535	0.0000000000
C	-3.5140488975	2.4433971020	0.0000000000
C	-2.8264871245	1.2367280422	0.0000000000
C	-1.4252074053	1.2228052404	0.0000000000
H	-3.3823981713	4.5717211301	0.0000000000
H	-3.3540057690	0.2957101065	0.0000000000

C	-0.6774372204	-0.0005858042	0.0000000000
C	0.6774372204	-0.0005858042	0.0000000000
C	1.4252074053	1.2228052404	0.0000000000
H	-1.2212975086	-0.9356687797	0.0000000000
H	1.2212975086	-0.9356687797	0.0000000000
C	2.8154220410	3.6521420535	0.0000000000
C	3.5140488975	2.4433971020	0.0000000000
C	2.8264871245	1.2367280422	0.0000000000
H	3.3540057690	0.2957101065	0.0000000000
H	3.3823981713	4.5717211301	0.0000000000
O	4.8676264369	2.5542746402	0.0000000000
O	-4.8676264369	2.5542746402	0.0000000000
C	5.6397287169	1.3780238868	0.0000000000
H	6.6771516838	1.6988714275	0.0000000000
H	5.4508560596	0.7733249755	-0.8897293193
H	5.4508560596	0.7733249755	0.8897293193
C	-5.6397287169	1.3780238868	0.0000000000
H	-6.6771516838	1.6988714275	0.0000000000
H	-5.4508560596	0.7733249755	0.8897293193
H	-5.4508560596	0.7733249755	-0.8897293193

B1LYP-40/6-31G(d) Cation Radical A2-SYM; gas (Molpro)

C	0.6727854442	4.9200738167	0.0000000000
C	-0.6727854442	4.9200738167	0.0000000000
C	-1.4203100908	3.6838305775	0.0000000000
C	-0.6959236046	2.4392903611	0.0000000000
C	0.6959236046	2.4392903611	0.0000000000
C	1.4203100908	3.6838305775	0.0000000000
H	-1.2242492131	5.8487265184	0.0000000000
H	1.2242492131	5.8487265184	0.0000000000
C	-2.7923064364	3.6631482516	0.0000000000
C	-3.4946659747	2.4343130412	0.0000000000
C	-2.8000029719	1.2073309638	0.0000000000
C	-1.4199841105	1.1974657135	0.0000000000
H	-3.3713581278	4.5740023345	0.0000000000
H	-3.3388740881	0.2738055388	0.0000000000
C	-0.6734505054	-0.0372784848	0.0000000000
C	0.6734505054	-0.0372784848	0.0000000000
C	1.4199841105	1.1974657135	0.0000000000
H	-1.2228726447	-0.9672837699	0.0000000000
H	1.2228726447	-0.9672837699	0.0000000000
C	2.7923064364	3.6631482516	0.0000000000
C	3.4946659747	2.4343130412	0.0000000000
C	2.8000029719	1.2073309638	0.0000000000
H	3.3388740881	0.2738055388	0.0000000000
H	3.3713581278	4.5740023345	0.0000000000
O	4.8085237115	2.5428579372	0.0000000000
O	-4.8085237115	2.5428579372	0.0000000000
C	5.6464930164	1.3861326098	0.0000000000
H	6.6603078049	1.7671695715	0.0000000000

H	5.4743592594	0.7909525094	-0.8947815621
H	5.4743592594	0.7909525094	0.8947815621
C	-5.6464930164	1.3861326098	0.0000000000
H	-6.6603078049	1.7671695715	0.0000000000
H	-5.4743592594	0.7909525094	0.8947815621
H	-5.4743592594	0.7909525094	-0.8947815621

B1LYP-40/6-31G(d) Cation Radical B2-SYM; gas (Molpro)

C	0.6888480797	4.8788511122	0.0000000000
C	-0.6888480797	4.8788511122	0.0000000000
C	-1.4153475046	3.6645415110	0.0000000000
C	-0.7043455134	2.4387496097	0.0000000000
C	0.7043455134	2.4387496097	0.0000000000
C	1.4153475046	3.6645415110	0.0000000000
H	-1.2268841634	5.8156532690	0.0000000000
H	1.2268841634	5.8156532690	0.0000000000
C	-2.8259625344	3.6418398570	0.0000000000
C	-3.5381643382	2.4358104103	0.0000000000
C	-2.8389243457	1.2345588274	0.0000000000
C	-1.4198760774	1.2182641266	0.0000000000
H	-3.3880806421	4.5643391567	0.0000000000
H	-3.3638326482	0.2923791152	0.0000000000
C	-0.6898171106	0.0096106945	0.0000000000
C	0.6898171106	0.0096106945	0.0000000000
C	1.4198760774	1.2182641266	0.0000000000
H	-1.2235684117	-0.9298106633	0.0000000000
H	1.2235684117	-0.9298106633	0.0000000000
C	2.8259625344	3.6418398570	0.0000000000
C	3.5381643382	2.4358104103	0.0000000000
C	2.8389243457	1.2345588274	0.0000000000
H	3.3638326482	0.2923791152	0.0000000000
H	3.3880806421	4.5643391567	0.0000000000
O	4.8715135940	2.5552535154	0.0000000000
O	-4.8715135940	2.5552535154	0.0000000000
C	5.6757342765	1.3857563751	0.0000000000
H	6.7015128991	1.7354352099	0.0000000000
H	5.4955287222	0.7871289368	-0.8935430971
H	5.4955287222	0.7871289368	0.8935430971
C	-5.6757342765	1.3857563751	0.0000000000
H	-6.7015128991	1.7354352099	0.0000000000
H	-5.4955287222	0.7871289368	0.8935430971
H	-5.4955287222	0.7871289368	-0.8935430971

B1LYP-40/6-31G(d) NEUTRAL; PCM(DCM) (Gaussian 09)

C	0.67582	2.59506	0.00002
C	-0.67582	2.59506	0.00010
C	-1.42684	1.36662	0.00021
C	-0.71062	0.13846	0.00023
C	0.71062	0.13846	0.00015
C	1.42684	1.36662	0.00004

H	-1.22168	3.52856	0.00009
H	1.22168	3.52856	-0.00006
C	-2.81627	1.34591	0.00030
C	-3.51474	0.13644	0.00040
C	-2.82694	-1.07099	0.00042
C	-1.42570	-1.08387	0.00034
H	-3.38004	2.26774	0.00028
H	-3.35486	-2.01151	0.00050
C	-0.67756	-2.30825	0.00036
C	0.67756	-2.30825	0.00027
C	1.42570	-1.08387	0.00017
H	-1.22131	-3.24310	0.00044
H	1.22131	-3.24310	0.00029
C	2.81627	1.34591	-0.00004
C	3.51474	0.13644	-0.00002
C	2.82693	-1.07099	0.00008
H	3.35486	-2.01151	0.00010
H	3.38004	2.26774	-0.00012
O	4.86784	0.24551	-0.00011
O	-4.86784	0.24551	0.00047
C	5.64200	-0.93732	-0.00010
H	6.67890	-0.61680	-0.00017
H	5.45021	-1.53866	-0.88985
H	5.45032	-1.53857	0.88974
C	-5.64200	-0.93732	0.00057
H	-6.67890	-0.61680	0.00061
H	-5.45022	-1.53858	0.89038
H	-5.45032	-1.53866	-0.88921

B1LYP-40/6-31G(d) Cation Radical A2-SYM; PCM(DCM) (Gaussian 09)
This structure is a transition state.

C	0.67272	2.61564	0.00003
C	-0.67271	2.61564	0.00010
C	-1.41980	1.37931	0.00021
C	-0.69567	0.13524	0.00023
C	0.69568	0.13524	0.00015
C	1.41981	1.37932	0.00005
H	-1.22452	3.54390	0.00009
H	1.22452	3.54391	-0.00006
C	-2.79155	1.35855	0.00029
C	-3.49187	0.12948	0.00039
C	-2.79867	-1.09725	0.00042
C	-1.41934	-1.10645	0.00034
H	-3.36810	2.27070	0.00028
H	-3.33728	-2.03040	0.00049
C	-0.67334	-2.34141	0.00036
C	0.67334	-2.34140	0.00029
C	1.41934	-1.10644	0.00018
H	-1.22372	-3.27048	0.00044
H	1.22372	-3.27047	0.00030

C	2.79157	1.35857	-0.00004
C	3.49188	0.12953	-0.00002
C	2.79865	-1.09722	0.00009
H	3.33727	-2.03037	0.00011
H	3.36811	2.27073	-0.00012
O	4.80782	0.23485	-0.00011
O	-4.80781	0.23485	0.00046
C	5.63399	-0.93245	-0.00010
H	6.65170	-0.56244	-0.00019
H	5.45360	-1.52531	-0.89378
H	5.45372	-1.52523	0.89365
C	-5.63400	-0.93244	0.00056
H	-6.65171	-0.56240	0.00061
H	-5.45362	-1.52522	0.89430
H	-5.45374	-1.52530	-0.89314

B1LYP-40/6-31G(d) Cation Radical B2-SYM; PCM(DCM) (Gaussian 09)

C	0.68897	2.57531	-0.00001
C	-0.68839	2.57544	0.00007
C	-1.41432	1.36134	0.00019
C	-0.70413	0.13585	0.00023
C	0.70422	0.13571	0.00016
C	1.41465	1.36106	0.00004
H	-1.22601	3.51191	0.00004
H	1.22677	3.51166	-0.00010
C	-2.82485	1.33860	0.00026
C	-3.53308	0.13312	0.00038
C	-2.83671	-1.06896	0.00042
C	-1.41829	-1.08482	0.00035
H	-3.38279	2.26312	0.00023
H	-3.36041	-2.01128	0.00052
C	-0.68991	-2.29422	0.00039
C	0.68950	-2.29435	0.00032
C	1.41813	-1.08510	0.00020
H	-1.22435	-3.23264	0.00049
H	1.22376	-3.23288	0.00036
C	2.82518	1.33803	-0.00004
C	3.53317	0.13241	0.00000
C	2.83656	-1.06954	0.00012
H	3.36006	-2.01196	0.00016
H	3.38331	2.26244	-0.00014
O	4.87286	0.24596	-0.00007
O	-4.87275	0.24694	0.00044
C	5.66077	-0.93547	-0.00013
H	6.69196	-0.60119	-0.00025
H	5.47127	-1.53248	-0.89208
H	5.47147	-1.53244	0.89189
C	-5.66090	-0.93433	0.00045
H	-6.69203	-0.59985	0.00043
H	-5.47163	-1.53134	0.89246

```
H          -5.47160       -1.53138       -0.89152
```

4 (Scheme 1)

B1LYP-40/6-31G(d) NEUTRAL; gas (Molpro)

```
 C          -0.8224933887        0.0000000000        1.1503758701
 C           1.3983450730        0.0000000000        0.0000000000
 C           1.1996258466        0.0000000000        2.4203457238
 C          -0.2139057623        0.0000000000        2.3760352178
 C           0.0003716593        0.0000000000        0.0000000000
 C           2.0148756946        0.0000000000        1.3029506202
 C          -0.8224933887        0.0000000000       -1.1503758701
 C          -0.2139057623        0.0000000000       -2.3760352178
 C           1.1996258466        0.0000000000       -2.4203457238
 C           2.0148756946        0.0000000000       -1.3029506202
 C          -2.2101423710        0.0000000000        0.6765265259
 C          -2.2101423710        0.0000000000       -0.6765265259
 H          -3.0796281477        0.0000000000        1.3145033619
 H          -3.0796281477        0.0000000000       -1.3145033619
 H           1.6733894104        0.0000000000        3.3924769532
 H           1.6733894104        0.0000000000       -3.3924769532
 H          -0.7763641852        0.0000000000        3.2999858781
 H          -0.7763641852        0.0000000000       -3.2999858781
 C           3.5058574531        0.0000000000        1.5294356492
 H           3.9888768700       -0.8772065470        1.0993731445
 H           3.9888768700        0.8772065470        1.0993731445
 H           3.7206783439        0.0000000000        2.5964438106
 C           3.5058574531        0.0000000000       -1.5294356492
 H           3.7206783439        0.0000000000       -2.5964438106
 H           3.9888768700        0.8772065470       -1.0993731445
 H           3.9888768700       -0.8772065470       -1.0993731445
```

B1LYP-40/6-31G(d) Cation Radical A2-SYM; gas (Molpro)

```
 C          -0.8124954468        0.0000000000        1.1400174656
 C           1.4096484721        0.0000000000        0.0000000000
 C           1.1870420979        0.0000000000        2.4360195961
 C          -0.2010444681        0.0000000000        2.3918255511
 C           0.0064505206        0.0000000000        0.0000000000
 C           2.0277480251        0.0000000000        1.2907335457
 C          -0.8124954468        0.0000000000       -1.1400174656
 C          -0.2010444681        0.0000000000       -2.3918255511
 C           1.1870420979        0.0000000000       -2.4360195961
 C           2.0277480251        0.0000000000       -1.2907335457
 C          -2.2234691458        0.0000000000        0.6711606840
 C          -2.2234691458        0.0000000000       -0.6711606840
 H          -3.0840211693        0.0000000000        1.3187332963
 H          -3.0840211693        0.0000000000       -1.3187332963
 H           1.6690395022        0.0000000000        3.4023449241
 H           1.6690395022        0.0000000000       -3.4023449241
 H          -0.7716146834        0.0000000000        3.3088371950
 H          -0.7716146834        0.0000000000       -3.3088371950
```

C	3.5040014230	0.0000000000	1.5293910476
H	3.9811257393	-0.8766153527	1.0890243079
H	3.9811257393	0.8766153527	1.0890243079
H	3.7235178902	0.0000000000	2.5931012488
C	3.5040014230	0.0000000000	-1.5293910476
H	3.7235178902	0.0000000000	-2.5931012488
H	3.9811257393	0.8766153527	-1.0890243079
H	3.9811257393	-0.8766153527	-1.0890243079

B1LYP-40/6-31G(d) Cation Radical B2-SYM; gas (Molpro)

C	-0.8255286255	0.0000000000	1.1671639983
C	1.3992578889	0.0000000000	0.0000000000
C	1.1865590117	0.0000000000	2.4422394749
C	-0.2078585830	0.0000000000	2.4096823474
C	0.0041730856	0.0000000000	0.0000000000
C	2.0083263578	0.0000000000	1.3060229788
C	-0.8255286255	0.0000000000	-1.1671639983
C	-0.2078585830	0.0000000000	-2.4096823474
C	1.1865590117	0.0000000000	-2.4422394749
C	2.0083263578	0.0000000000	-1.3060229788
C	-2.1596312398	0.0000000000	0.7125658675
C	-2.1596312398	0.0000000000	-0.7125658675
H	-3.0455264937	0.0000000000	1.3275037334
H	-3.0455264937	0.0000000000	-1.3275037334
H	1.6714509357	0.0000000000	3.4065673073
H	1.6714509357	0.0000000000	-3.4065673073
H	-0.7734554847	0.0000000000	3.3299830124
H	-0.7734554847	0.0000000000	-3.3299830124
C	3.4912209441	0.0000000000	1.5364729809
H	3.9652106019	-0.8780705385	1.0993281821
H	3.9652106019	0.8780705385	1.0993281821
H	3.7113114862	0.0000000000	2.6001531471
C	3.4912209441	0.0000000000	-1.5364729809
H	3.7113114862	0.0000000000	-2.6001531471
H	3.9652106019	0.8780705385	-1.0993281821
H	3.9652106019	-0.8780705385	-1.0993281821

B1LYP-40/6-31G(d) NEUTRAL; PCM(DCM) (Gaussian 09)

C	1.53233	-1.17513	-0.04362
C	-0.67354	0.00489	0.00171
C	-0.50771	-2.41744	-0.07179
C	0.90651	-2.39262	-0.07719
C	0.72515	-0.01396	-0.00525
C	-1.30849	-1.28912	-0.03450
C	1.56364	1.12506	0.02500
C	0.97122	2.35898	0.06458
C	-0.44178	2.42188	0.07324
C	-1.27297	1.31553	0.04406
C	2.92649	-0.72042	-0.03630
C	2.94492	0.63297	0.00404

H	3.78680	-1.37053	-0.05954
H	3.82262	1.25967	0.01878
H	-0.99437	-3.38262	-0.09861
H	-0.90201	3.39979	0.10478
H	1.45591	-3.32378	-0.10736
H	1.54575	3.27501	0.08912
C	-2.80215	-1.49442	-0.03508
H	-3.28048	-1.03125	-0.89758
H	-3.27466	-1.08138	0.85555
H	-3.03182	-2.55757	-0.06474
C	-2.76046	1.56104	0.05941
H	-2.96103	2.63000	0.09128
H	-3.24254	1.11076	0.92663
H	-3.25269	1.16108	-0.82650

B1LYP-40/6-31G(d) Cation Radical A2-SYM; PCM(DCM) (Gaussian 09)

C	1.51962	-1.16420	-0.04103
C	-0.68485	0.00481	0.00102
C	-0.49570	-2.43208	-0.07076
C	0.89221	-2.40665	-0.07345
C	0.71766	-0.01399	-0.00564
C	-1.31988	-1.27557	-0.03597
C	1.55050	1.11430	0.02235
C	0.95688	2.37308	0.05964
C	-0.42973	2.43573	0.07038
C	-1.28489	1.30180	0.04434
C	2.93614	-0.71471	-0.03373
C	2.95439	0.62702	0.00316
H	3.78541	-1.37625	-0.05504
H	3.82127	1.26547	0.01727
H	-0.99120	-3.39062	-0.09700
H	-0.89910	3.40718	0.10113
H	1.45150	-3.32945	-0.10055
H	1.54058	3.28078	0.08068
C	-2.79803	-1.49120	-0.04515
H	-3.26159	-1.02179	-0.91376
H	-3.26972	-1.06132	0.83882
H	-3.03135	-2.55127	-0.07053
C	-2.75643	1.55775	0.06939
H	-2.96002	2.62390	0.09711
H	-3.22306	1.10135	0.94323
H	-3.24955	1.14115	-0.80914

B1LYP-40/6-31G(d) Cation Radical B2-SYM; PCM(DCM) (Gaussian 09)

C	1.53249	-1.19055	-0.04120
C	-0.67466	0.00479	0.00127
C	-0.49557	-2.43716	-0.06973
C	0.89964	-2.42317	-0.07211
C	0.71960	-0.01394	-0.00563
C	-1.30062	-1.29133	-0.03650

C	1.56424	1.14046	0.02217
C	0.96501	2.38967	0.05892
C	-0.42919	2.44111	0.07040
C	-1.26505	1.31728	0.04546
C	2.87324	-0.75476	-0.03480
C	2.89262	0.66880	0.00385
H	3.74879	-1.38269	-0.05500
H	3.78496	1.27279	0.01640
H	-0.99326	-3.39434	-0.09608
H	-0.90082	3.41123	0.10178
H	1.45472	-3.34868	-0.09822
H	1.54490	3.30003	0.07936
C	-2.78634	-1.49870	-0.04797
H	-3.24582	-1.03482	-0.91993
H	-3.25794	-1.07129	0.83549
H	-3.01999	-2.55913	-0.07203
C	-2.74439	1.56496	0.07278
H	-2.94866	2.63141	0.09877
H	-3.20670	1.11409	0.95002
H	-3.23719	1.15031	-0.80512

5 (Scheme 1)

B1LYP-40/6-31G(d) NEUTRAL; gas (Molpro)

C	0.6842871460	0.0000000000	4.6549017350
C	0.7025548659	0.0000000000	2.2617706053
C	-1.4523561541	0.0000000000	3.4330687079
C	-0.6842871460	0.0000000000	4.6549017350
C	1.4523561541	0.0000000000	3.4330687079
H	1.2101684391	0.0000000000	5.6003704506
C	-0.7025548659	0.0000000000	2.2617706053
C	2.8507661272	0.0000000000	3.2483985347
C	3.3725752895	0.0000000000	1.9648711675
C	2.5658081337	0.0000000000	0.8014376372
H	3.5181346690	0.0000000000	4.0996380579
H	4.4468663327	0.0000000000	1.8420586104
C	1.1980139547	0.0000000000	0.9541742679
H	3.0373388689	0.0000000000	-0.1718522150
H	-1.2101684391	0.0000000000	5.6003704506
C	-1.1980139547	0.0000000000	0.9541742679
C	-2.5658081337	0.0000000000	0.8014376372
C	-3.3725752895	0.0000000000	1.9648711675
C	-2.8507661272	0.0000000000	3.2483985347
H	-4.4468663327	0.0000000000	1.8420586104
H	-3.5181346690	0.0000000000	4.0996380579
H	-3.0373388689	0.0000000000	-0.1718522150
C	0.0000000000	0.0000000000	0.0008396814
H	0.0000000000	-0.8758488150	-0.6516474000
H	0.0000000000	0.8758488150	-0.6516474000

B1LYP-40/6-31G(d) Cation Radical A2-SYM; gas (Molpro)

C	0.6798436970	0.0000000000	4.6883320316
C	0.6865999787	0.0000000000	2.2610638017
C	-1.4435488708	0.0000000000	3.4530582045
C	-0.6798436970	0.0000000000	4.6883320316
C	1.4435488708	0.0000000000	3.4530582045
H	1.2149075008	0.0000000000	5.6265561958
C	-0.6865999787	0.0000000000	2.2610638017
C	2.8169858969	0.0000000000	3.2665559087
C	3.3428099422	0.0000000000	1.9542749253
C	2.5534048232	0.0000000000	0.7795355983
H	3.4983794616	0.0000000000	4.1046455619
H	4.4177328935	0.0000000000	1.8436410698
C	1.1902956844	0.0000000000	0.9312713495
H	3.0346980003	0.0000000000	-0.1866813121
H	-1.2149075008	0.0000000000	5.6265561958
C	-1.1902956844	0.0000000000	0.9312713495
C	-2.5534048232	0.0000000000	0.7795355983
C	-3.3428099422	0.0000000000	1.9542749253
C	-2.8169858969	0.0000000000	3.2665559087
H	-4.4177328935	0.0000000000	1.8436410698
H	-3.4983794616	0.0000000000	4.1046455619
H	-3.0346980003	0.0000000000	-0.1866813121
C	0.0000000000	0.0000000000	-0.0228410977
H	0.0000000000	-0.8763115583	-0.6732227862
H	0.0000000000	0.8763115583	-0.6732227862

B1LYP-40/6-31G(d) Cation Radical B2-SYM; gas (Molpro)

C	0.7095509515	0.0000000000	4.6258296079
C	0.7029146819	0.0000000000	2.2546069666
C	-1.4586866428	0.0000000000	3.4338816632
C	-0.7095509515	0.0000000000	4.6258296079
C	1.4586866428	0.0000000000	3.4338816632
H	1.2159630948	0.0000000000	5.5808918965
C	-0.7029146819	0.0000000000	2.2546069666
C	2.8744483681	0.0000000000	3.2539752221
C	3.3925951378	0.0000000000	1.9705620618
C	2.5775720828	0.0000000000	0.8138710311
H	3.5371565342	0.0000000000	4.1070313435
H	4.4641197893	0.0000000000	1.8403132482
C	1.1894736555	0.0000000000	0.9599517192
H	3.0458407820	0.0000000000	-0.1600646751
H	-1.2159630948	0.0000000000	5.5808918965
C	-1.1894736555	0.0000000000	0.9599517192
C	-2.5775720828	0.0000000000	0.8138710311
C	-3.3925951378	0.0000000000	1.9705620618
C	-2.8744483681	0.0000000000	3.2539752221
H	-4.4641197893	0.0000000000	1.8403132482
H	-3.5371565342	0.0000000000	4.1070313435
H	-3.0458407820	0.0000000000	-0.1600646751
C	0.0000000000	0.0000000000	0.0070977622

```
 H          0.0000000000       -0.8754029199       -0.6467889660
 H          0.0000000000        0.8754029199       -0.6467889660
```

B1LYP-40/6-31G(d) NEUTRAL; PCM(DCM) (Gaussian 09)

```
C          0.68451        2.36346       -0.00008
C          0.70264       -0.03094       -0.00006
C         -1.45254        1.14079       -0.00007
C         -0.68451        2.36346       -0.00008
C          1.45254        1.14079       -0.00007
H          1.21054        3.30872       -0.00009
C         -0.70264       -0.03094       -0.00006
C          2.85155        0.95661       -0.00007
C          3.37263       -0.32791       -0.00007
C          2.56567       -1.49188       -0.00006
H          3.51888        1.80777       -0.00008
H          4.44681       -0.45126       -0.00007
C          1.19745       -1.33928       -0.00005
H          3.03700       -2.46507       -0.00006
H         -1.21054        3.30872       -0.00009
C         -1.19745       -1.33928       -0.00005
C         -2.56567       -1.49188       -0.00006
C         -3.37263       -0.32791       -0.00007
C         -2.85155        0.95661       -0.00007
H         -4.44681       -0.45126       -0.00007
H         -3.51888        1.80777       -0.00008
H         -3.03700       -2.46507       -0.00006
C          0.00000       -2.29269       -0.00004
H          0.00000       -2.94567        0.87494
H          0.00000       -2.94569       -0.87500
```

B1LYP-40/6-31G(d) Cation Radical A2-SYM; PCM(DCM) (Gaussian 09)
This structure is a transition state.

```
C          0.67963        2.39456       -0.00008
C          0.68631       -0.03120       -0.00006
C         -1.44328        1.15982       -0.00007
C         -0.67963        2.39456       -0.00008
C          1.44328        1.15982       -0.00007
H          1.21593        3.33161       -0.00009
C         -0.68631       -0.03120       -0.00006
C          2.81577        0.97371       -0.00007
C          3.34068       -0.33894       -0.00006
C          2.55204       -1.51229       -0.00005
H          3.49659        1.81180       -0.00008
H          4.41504       -0.44956       -0.00006
C          1.18889       -1.36062       -0.00006
H          3.03174       -2.47880       -0.00005
H         -1.21593        3.33161       -0.00009
C         -1.18889       -1.36062       -0.00006
C         -2.55204       -1.51229       -0.00005
C         -3.34068       -0.33894       -0.00006
```

C	-2.81577	0.97371	-0.00007
H	-4.41504	-0.44956	-0.00006
H	-3.49659	1.81180	-0.00008
H	-3.03174	-2.47880	-0.00005
C	0.00000	-2.31345	-0.00005
H	0.00000	-2.96265	0.87618
H	0.00000	-2.96266	-0.87626

B1LYP-40/6-31G(d) Cation Radical B2-SYM; PCM(DCM) (Gaussian 09)

C	0.70946	2.33205	-0.00004
C	0.70268	-0.03864	-0.00005
C	-1.45761	1.14010	-0.00005
C	-0.70946	2.33205	-0.00004
C	1.45761	1.14010	-0.00005
H	1.21609	3.28603	-0.00004
C	-0.70268	-0.03864	-0.00005
C	2.87240	0.96093	-0.00007
C	3.38975	-0.32255	-0.00009
C	2.57525	-1.47942	-0.00010
H	3.53289	1.81523	-0.00006
H	4.46101	-0.45320	-0.00011
C	1.18826	-1.33332	-0.00008
H	3.04197	-2.45358	-0.00013
H	-1.21609	3.28603	-0.00004
C	-1.18826	-1.33332	-0.00008
C	-2.57525	-1.47942	-0.00010
C	-3.38975	-0.32255	-0.00009
C	-2.87240	0.96093	-0.00007
H	-4.46101	-0.45320	-0.00011
H	-3.53289	1.81523	-0.00006
H	-3.04197	-2.45358	-0.00013
C	0.00000	-2.28523	-0.00009
H	0.00000	-2.93824	0.87505
H	0.00000	-2.93827	-0.87519

6 (Scheme 1)

B1LYP-40/6-31G(d) NEUTRAL; gas (Molpro)

C	-1.2412389232	0.0000000000	-1.3896950027
C	0.0000000000	0.0000000000	0.7085794251
C	-2.4294592005	0.0000000000	0.7110522389
C	-2.4294592005	0.0000000000	-0.7110522389
C	0.0000000000	0.0000000000	-0.7085794251
H	-1.2474052594	0.0000000000	-2.4731114342
C	-1.2412389232	0.0000000000	1.3896950027
H	-1.2474052594	0.0000000000	2.4731114342
C	1.2412389232	0.0000000000	-1.3896950027
C	2.4294592005	0.0000000000	-0.7110522389
C	2.4294592005	0.0000000000	0.7110522389
H	1.2474052594	0.0000000000	-2.4731114342
C	1.2412389232	0.0000000000	1.3896950027

H	1.2474052594	0.0000000000	2.4731114342
O	-3.6470674099	0.0000000000	-1.3110140851
O	-3.6470674099	0.0000000000	1.3110140851
O	3.6470674099	0.0000000000	1.3110140851
H	-3.5235517503	0.0000000000	2.2647897134
H	-3.5235517503	0.0000000000	-2.2647897134
O	3.6470674099	0.0000000000	-1.3110140851
H	3.5235517503	0.0000000000	-2.2647897134
H	3.5235517503	0.0000000000	2.2647897134

B1LYP-40/6-31G(d) Cation Radical Au-SYM; gas (Molpro)

C	-1.2326553968	0.0000000000	-1.3891309842
C	0.0000000000	0.0000000000	0.7074685450
C	-2.4497584291	0.0000000000	0.7046882397
C	-2.4497584291	0.0000000000	-0.7046882397
C	0.0000000000	0.0000000000	-0.7074685450
H	-1.2417886549	0.0000000000	-2.4711387929
C	-1.2326553968	0.0000000000	1.3891309842
H	-1.2417886549	0.0000000000	2.4711387929
C	1.2326553968	0.0000000000	-1.3891309842
C	2.4497584291	0.0000000000	-0.7046882397
C	2.4497584291	0.0000000000	0.7046882397
H	1.2417886549	0.0000000000	-2.4711387929
C	1.2326553968	0.0000000000	1.3891309842
H	1.2417886549	0.0000000000	2.4711387929
O	-3.6408880847	0.0000000000	-1.2985344140
O	-3.6408880847	0.0000000000	1.2985344140
O	3.6408880847	0.0000000000	1.2985344140
H	-3.5663313419	0.0000000000	2.2596665721
H	-3.5663313419	0.0000000000	-2.2596665721
O	3.6408880847	0.0000000000	-1.2985344140
H	3.5663313419	0.0000000000	-2.2596665721
H	3.5663313419	0.0000000000	2.2596665721

B1LYP-40/6-31G(d) Cation Radical B2u-SYM; gas (Molpro)

C	-1.2272248432	0.0000000000	-1.4159339354
C	0.0000000000	0.0000000000	0.7304874484
C	-2.4154504940	0.0000000000	0.7295458965
C	-2.4154504940	0.0000000000	-0.7295458965
C	0.0000000000	0.0000000000	-0.7304874484
H	-1.2324177086	0.0000000000	-2.4967894952
C	-1.2272248432	0.0000000000	1.4159339354
H	-1.2324177086	0.0000000000	2.4967894952
C	1.2272248432	0.0000000000	-1.4159339354
C	2.4154504940	0.0000000000	-0.7295458965
C	2.4154504940	0.0000000000	0.7295458965
H	1.2324177086	0.0000000000	-2.4967894952
C	1.2272248432	0.0000000000	1.4159339354
H	1.2324177086	0.0000000000	2.4967894952
O	-3.6170435466	0.0000000000	-1.2787352287

O	-3.6170435466	0.0000000000	1.2787352287
O	3.6170435466	0.0000000000	1.2787352287
H	-3.5703236022	0.0000000000	2.2434518780
H	-3.5703236022	0.0000000000	-2.2434518780
O	3.6170435466	0.0000000000	-1.2787352287
H	3.5703236022	0.0000000000	-2.2434518780
H	3.5703236022	0.0000000000	2.2434518780

B1LYP-40/6-31G(d) NEUTRAL; PCM(DCM) (Gaussian 09)

C	1.24055	-1.39272	0.00002
C	0.00000	0.70908	-0.00000
C	2.42716	0.71115	-0.00000
C	2.42716	-0.71115	0.00003
C	0.00000	-0.70908	-0.00001
H	1.24778	-2.47528	0.00003
C	1.24055	1.39272	-0.00001
H	1.24778	2.47527	-0.00003
C	-1.24055	-1.39272	-0.00005
C	-2.42716	-0.71115	-0.00006
C	-2.42716	0.71115	-0.00000
H	-1.24778	-2.47527	-0.00008
C	-1.24055	1.39272	0.00001
H	-1.24777	2.47528	0.00004
O	3.64760	-1.30985	0.00008
O	3.64760	1.30985	-0.00003
O	-3.64759	1.30985	0.00004
H	3.52996	2.26566	0.00002
H	3.52996	-2.26566	0.00003
O	-3.64760	-1.30985	-0.00011
H	-3.52996	-2.26566	-0.00009
H	-3.52996	2.26566	-0.00001

B1LYP-40/6-31G(d) Cation Radical B2u-SYM; PCM(DCM) (Gaussian 09)

C	1.22607	-1.41687	-0.00001
C	-0.00002	0.73032	-0.00000
C	2.41154	0.72860	0.00002
C	2.41161	-0.72886	0.00001
C	0.00002	-0.73032	-0.00001
H	1.23222	-2.49687	-0.00001
C	1.22589	1.41675	0.00001
H	1.23219	2.49675	0.00002
C	-1.22589	-1.41675	-0.00003
C	-2.41155	-0.72860	-0.00004
C	-2.41162	0.72886	-0.00003
H	-1.23219	-2.49675	-0.00004
C	-1.22607	1.41687	-0.00001
H	-1.23223	2.49687	-0.00001
O	3.61437	-1.28422	0.00002
O	3.61414	1.28411	0.00003
O	-3.61438	1.28422	-0.00003

H	3.55207	2.24865	0.00004
H	3.55236	-2.24875	0.00001
O	-3.61415	-1.28411	-0.00005
H	-3.55207	-2.24865	-0.00005
H	-3.55237	2.24875	-0.00003

7 (Scheme 1)

B1LYP-40/6-31G(d) NEUTRAL; gas (Molpro)

C	1.2370752951	0.0000000000	-0.6926219845
C	0.0000000000	0.0000000000	1.4162128533
C	2.4253496571	0.0000000000	1.4130942366
C	2.4362927920	0.0000000000	-0.0093845955
C	0.0000000000	0.0000000000	-0.0089883957
H	1.2370273332	0.0000000000	-1.7754537391
C	1.2410532139	0.0000000000	2.0928972250
H	1.2438919762	0.0000000000	3.1752945097
C	-1.2370752951	0.0000000000	-0.6926219845
C	-2.4362927920	0.0000000000	-0.0093845955
C	-2.4253496571	0.0000000000	1.4130942366
H	-1.2370273332	0.0000000000	-1.7754537391
C	-1.2410532139	0.0000000000	2.0928972250
H	-1.2438919762	0.0000000000	3.1752945097
N	3.6429269769	0.0000000000	-0.6669739433
H	4.5057677705	0.0000000000	-0.1621413758
H	3.6855895759	0.0000000000	-1.6661490377
N	-3.6429269769	0.0000000000	-0.6669739433
H	-3.6855895759	0.0000000000	-1.6661490377
H	-4.5057677705	0.0000000000	-0.1621413758
H	3.3657686911	0.0000000000	1.9480464759
H	-3.3657686911	0.0000000000	1.9480464759

B1LYP-40/6-31G(d) Cation Radical A2-SYM; gas (Molpro)

C	1.2229815423	0.0000000000	-0.6922529224
C	0.0000000000	0.0000000000	1.4242127051
C	2.4383976930	0.0000000000	1.4205193388
C	2.4604101198	0.0000000000	0.0124239064
C	0.0000000000	0.0000000000	0.0003170317
H	1.2293398346	0.0000000000	-1.7734692909
C	1.2379486001	0.0000000000	2.0941045504
H	1.2448051698	0.0000000000	3.1752384714
C	-1.2229815423	0.0000000000	-0.6922529224
C	-2.4604101198	0.0000000000	0.0124239064
C	-2.4383976930	0.0000000000	1.4205193388
H	-1.2293398346	0.0000000000	-1.7734692909
C	-1.2379486001	0.0000000000	2.0941045504
H	-1.2448051698	0.0000000000	3.1752384714
N	3.6138011379	0.0000000000	-0.6745593577
H	4.5006843725	0.0000000000	-0.2025496457
H	3.6319191968	0.0000000000	-1.6784672667

N	-3.6138011379	0.0000000000	-0.6745593577
H	-3.6319191968	0.0000000000	-1.6784672667
H	-4.5006843725	0.0000000000	-0.2025496457
H	3.3697392901	0.0000000000	1.9669673480
H	-3.3697392901	0.0000000000	1.9669673480

B1LYP-40/6-31G(d) Cation Radical B2-SYM; gas (Molpro)

C	1.2274968074	0.0000000000	-0.7296443789
C	0.0000000000	0.0000000000	1.4034435039
C	2.4126782824	0.0000000000	1.4226130609
C	2.4239378493	0.0000000000	-0.0283066986
C	0.0000000000	0.0000000000	-0.0561508529
H	1.2394369151	0.0000000000	-1.8099153265
C	1.2353144116	0.0000000000	2.0999628866
H	1.2289850226	0.0000000000	3.1799355864
C	-1.2274968074	0.0000000000	-0.7296443789
C	-2.4239378493	0.0000000000	-0.0283066986
C	-2.4126782824	0.0000000000	1.4226130609
H	-1.2394369151	0.0000000000	-1.8099153265
C	-1.2353144116	0.0000000000	2.0999628866
H	-1.2289850226	0.0000000000	3.1799355864
N	3.6181461246	0.0000000000	-0.6393926327
H	4.4771633152	0.0000000000	-0.1185662649
H	3.6926001461	0.0000000000	-1.6420042480
N	-3.6181461246	0.0000000000	-0.6393926327
H	-3.6926001461	0.0000000000	-1.6420042480
H	-4.4771633152	0.0000000000	-0.1185662649
H	3.3547002013	0.0000000000	1.9518916902
H	-3.3547002013	0.0000000000	1.9518916902

B1LYP-40/6-31G(d) NEUTRAL; PCM(DCM) (Gaussian 09)

C	1.23816	-1.11543	-0.01616
C	0.00000	0.99420	-0.00812
C	2.42550	0.98855	-0.00777
C	2.43586	-0.43320	-0.01437
C	0.00000	-0.43023	-0.01743
H	1.23767	-2.19808	-0.01983
C	1.24225	1.67182	-0.00243
H	1.24585	2.75393	0.00607
C	-1.23816	-1.11543	-0.01616
C	-2.43586	-0.43320	-0.01437
C	-2.42550	0.98855	-0.00777
H	-1.23767	-2.19808	-0.01983
C	-1.24225	1.67182	-0.00243
H	-1.24585	2.75393	0.00607
N	3.65833	-1.09912	-0.08045
H	4.42504	-0.60556	0.34802
H	3.62928	-2.05450	0.23812
N	-3.65833	-1.09912	-0.08046
H	-3.62928	-2.05450	0.23812

H	-4.42504	-0.60556	0.34801
H	3.36669	1.52154	-0.01072
H	-3.36669	1.52154	-0.01072

B1LYP-40/6-31G(d) Cation Radical A2-SYM; PCM(DCM) (Gaussian 09)

C	1.22155	-1.11607	0.06527
C	-0.00021	1.00181	0.01761
C	2.43700	0.99880	0.01707
C	2.45839	-0.41065	0.04813
C	-0.00018	-0.42252	0.04992
H	1.22882	-2.19660	0.08987
C	1.23762	1.67156	0.00245
H	1.24321	2.75226	-0.02180
C	-1.22188	-1.11613	0.06519
C	-2.45875	-0.41078	0.04796
C	-2.43741	0.99867	0.01691
H	-1.22909	-2.19666	0.08981
C	-1.23806	1.67150	0.00236
H	-1.24371	2.75219	-0.02188
N	3.60923	-1.09581	0.06242
H	4.49606	-0.62422	0.04520
H	3.62489	-2.09959	0.07927
N	-3.60957	-1.09598	0.06221
H	-3.62519	-2.09977	0.07887
H	-4.49641	-0.62443	0.04480
H	3.36986	1.54204	0.00476
H	-3.37030	1.54188	0.00454