Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Analysis of Bonding Motifs in Unusual Molecules: Planar Hexacoordinated Carbon and Infinitene

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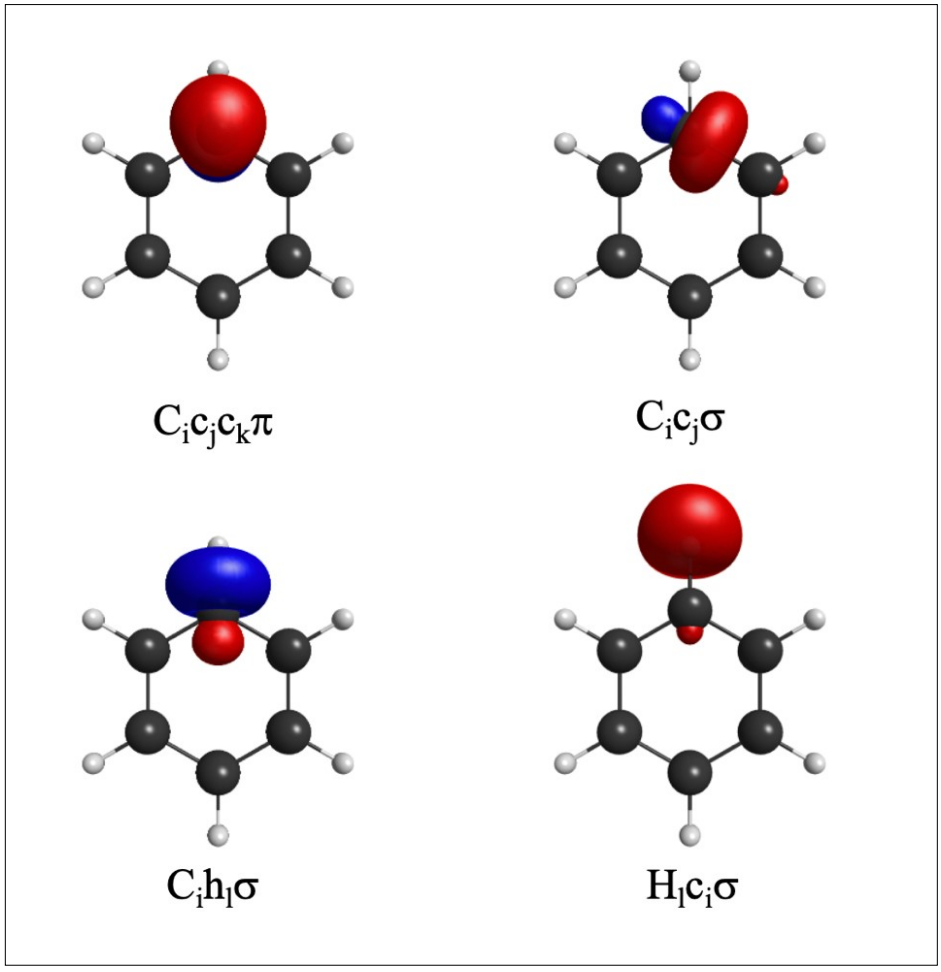
Supporting Information

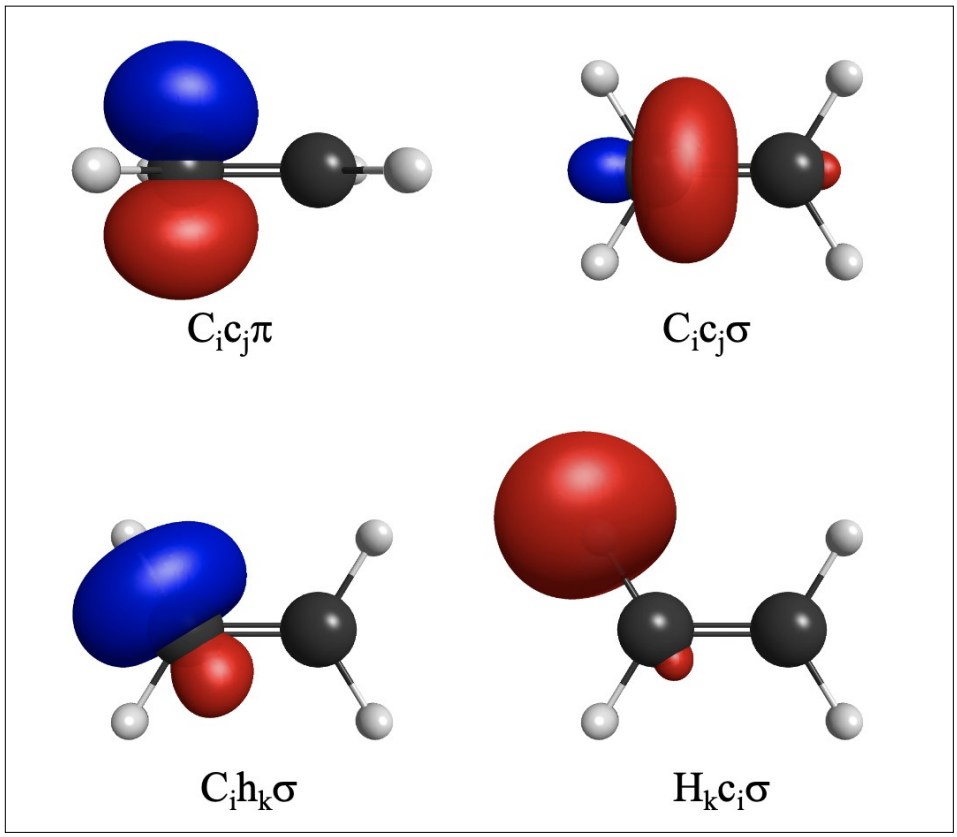
Optimized geometries of all relevant molecules are given in .xyz format in a .zip folder.

Benzene



SI Figure SI:1. Symmetric unique σ and π- QUAOs in benzene. Subscripted letters, i,j,k, and l correspond to different atoms. The structure of benzene was optimized at the RHF/6-31G(d) level of theory. Bond lengths for CC = 1.39 Å and CH= 1.08 Å.

Ethene



SI Figure SI:2. Symmetric unique σ and π- QUAOs in ethene. Subscripted letters, i,j, and k correspond to different atoms. The structure of ethene was optimized at the RHF/6-31G(d) level of theory. Bond lengths for CC = 1.34 Å and CH= 1.09 Å.

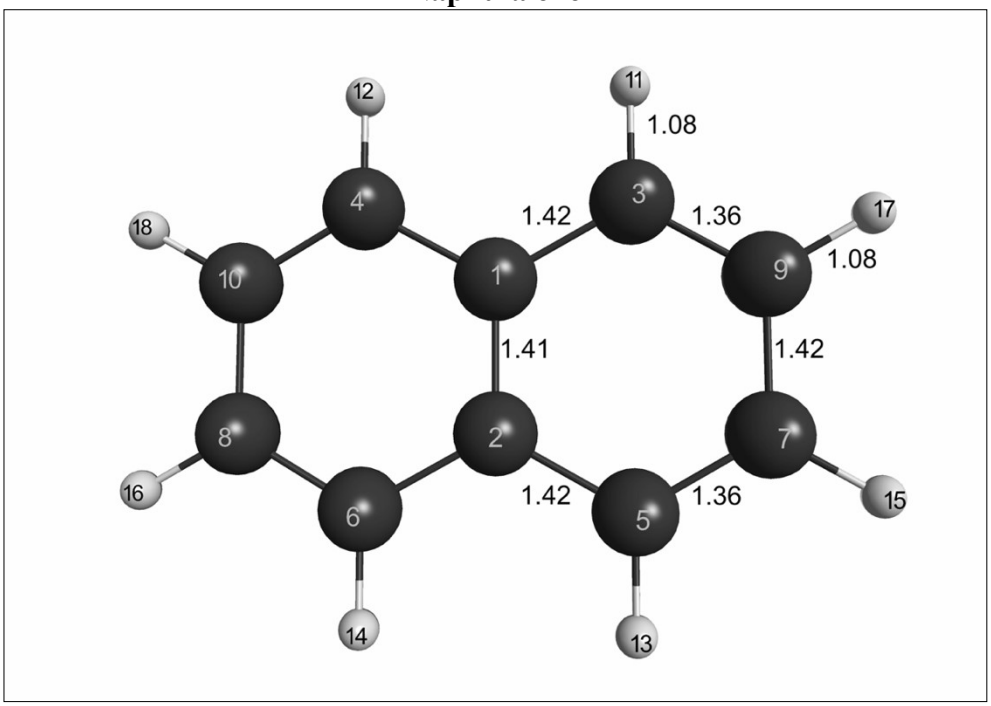
SI Table SI:1: Symmetric unique σ and π- Bonding interactions in ethene. Orbital occupations, bond occupation totals, bond orders, and KBOs (kcal/mol) are shown for non-repetitive interactions. The structure of ethene was optimized at the RHF/6-31G(d) level of theory. Bond lengths for CC = 1.34 Å and CH= 1.09 Å.

Orbital I	Occupation I	Orbital J	Occupation J	Bond Total	BO	KBO (kcal/mol)
$C_ic_j\sigma$	1.00	$C_jc_i\sigma$	1.00	2.00	0.99	-53.3
$H_kc_j\sigma$	0.86	$C_jh_k\sigma$	1.14	2.00	0.98	-38.0
$C_ic_j\pi$	1.00	$C_jc_i\pi$	1.00	2.00	1.00	-23.0

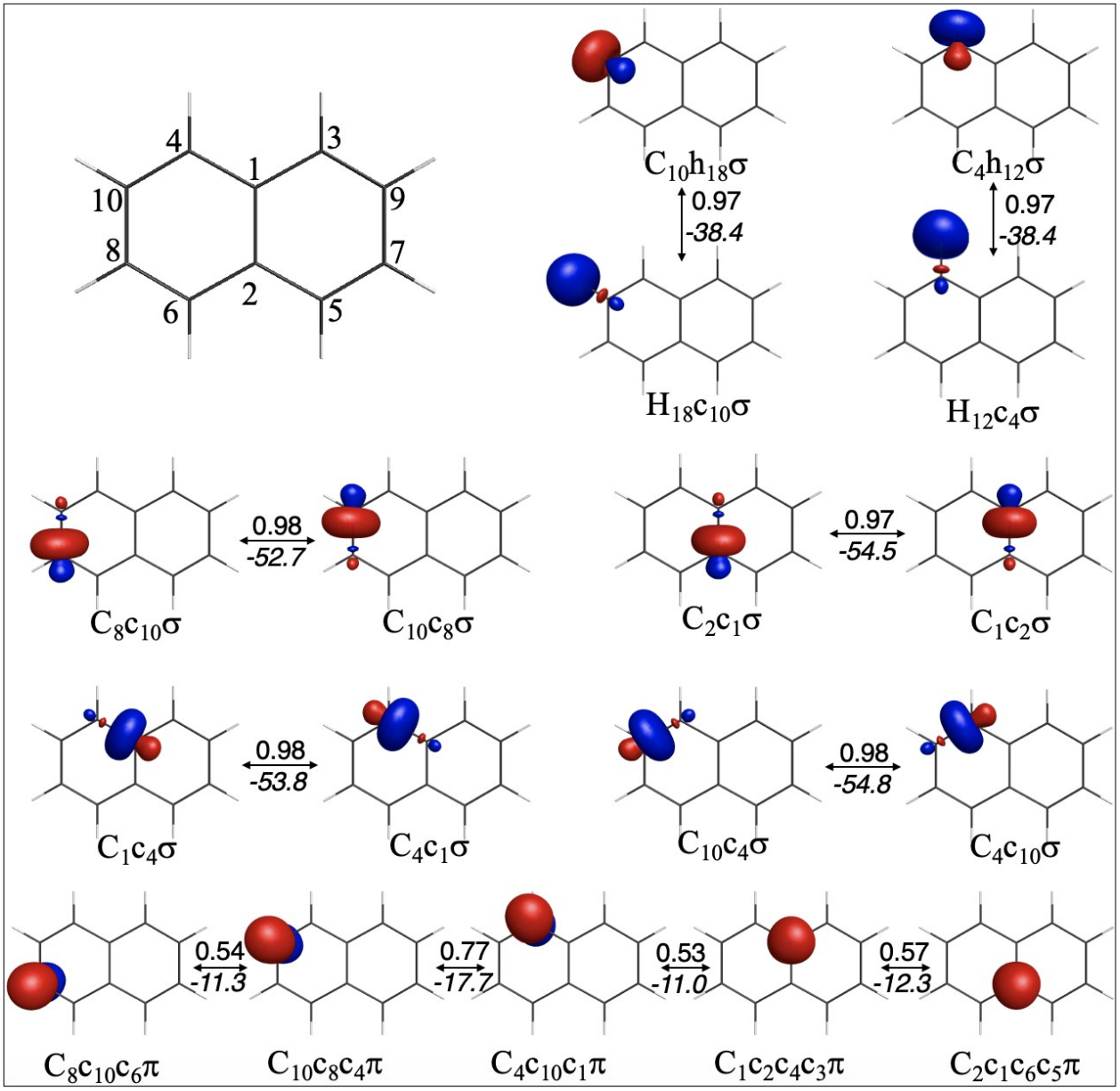
SI Table SI:2: Orbital hybridization fraction, s- and p-character, in ethene. SI Figure X3. Non-repetitive σ and π- bonding interactions in naphthalene. Bond orders (above arrow), and KBOs (below arrow) in kcal/mol are shown between pairs of bonding QUAOs.

Orbital	s-fraction	p-fraction
$C_ic_j\sigma$	0.34	0.66
$C_ih_k\sigma$	0.27	0.73
$C_ic_j\pi$	0.00	1.00
$H_kc_i\sigma$	1.00	0.00

Naphthalene



SI Figure SI:3: Optimized structure of naphthalene at the RHF/6-31G(d) level of theory. Carbon-carbon and carbon-hydrogen bond lengths are shown in angstrom.



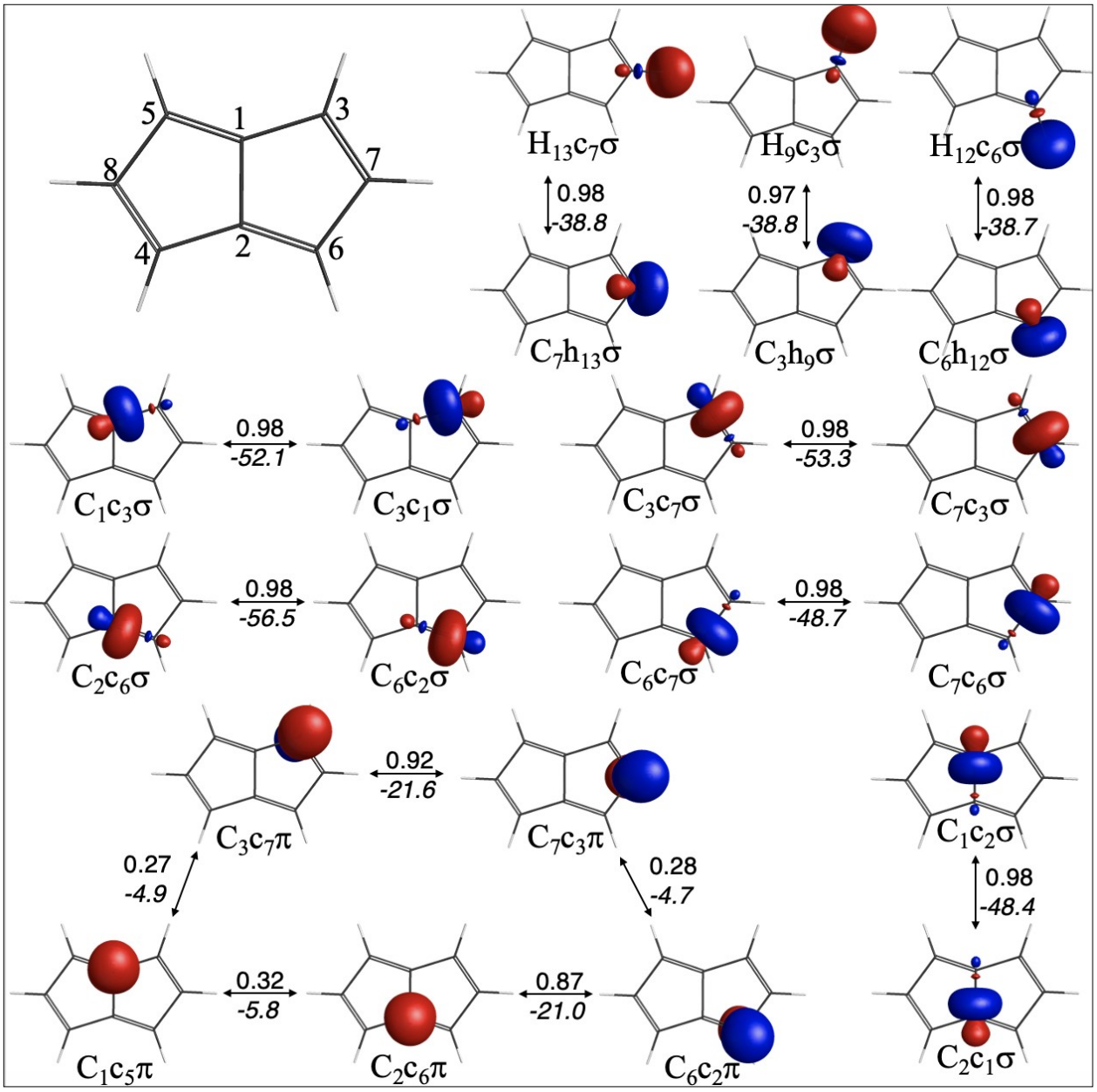
SI Figure SI:4. Non-repetitive σ and π- bonding interactions in naphthalene. Bond orders (above arrow), and KBOs (below arrow) in kcal/mol are shown between pairs of bonding QUAOs.

SI Table SI:3: σ and π- Bonding interactions in naphthalene. Orbital occupations, bond occupation totals, bond orders, and KBOs (kcal/mol) are shown for non-repetitive interactions. Numbers display in table reference the atom numbered on SI Figure X3.

Orbital I	Occupation I	Orbital J	Occupation J	Bond Total	BO	KBO (kcal/mol)
$C_8c_6\sigma$	1.00	$C_6c_8\sigma$	1.00	2.00	0.98	-54.8
$C_1c_2\sigma$	1.00	$C_2c_1\sigma$	1.00	2.00	0.97	-54.5
$C_1c_4\sigma$	1.00	$C_4c_1\sigma$	1.00	2.00	0.98	-53.8
$C_8c_{10}\sigma$	1.00	$C_{10}c_8\sigma$	1.00	2.00	0.98	-52.7
$H_{12}c_4\sigma$	0.86	$C_4h_{12}\sigma$	1.14	2.00	0.97	-38.4

$C_4c_{10}c_1\pi$	1.00	$C_{10}c_8c_4\pi$	1.00	2.00	0.77	-17.7
$C_2c_1c_6c_5\pi$	1.00	$C_1c_2c_4c_3\pi$	1.00	2.00	0.57	-12.3
$C_8c_{10}c_6\pi$	1.00	$C_{10}c_8c_4\pi$	1.00	2.00	0.54	-11.3
$C_4c_{10}c_1\pi$	1.00	$C_1c_2c_4c_3\pi$	1.00	2.00	0.53	-11.0

Pentalene

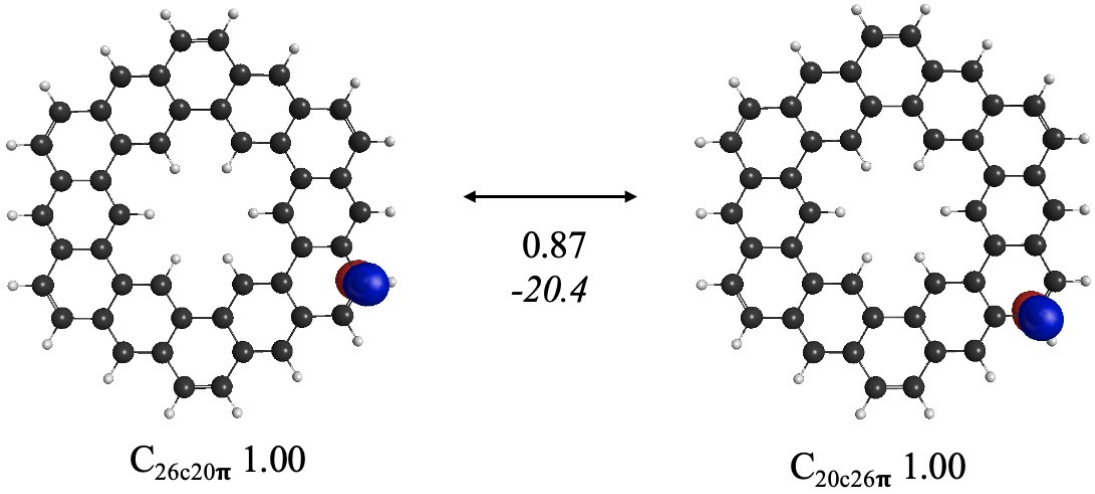


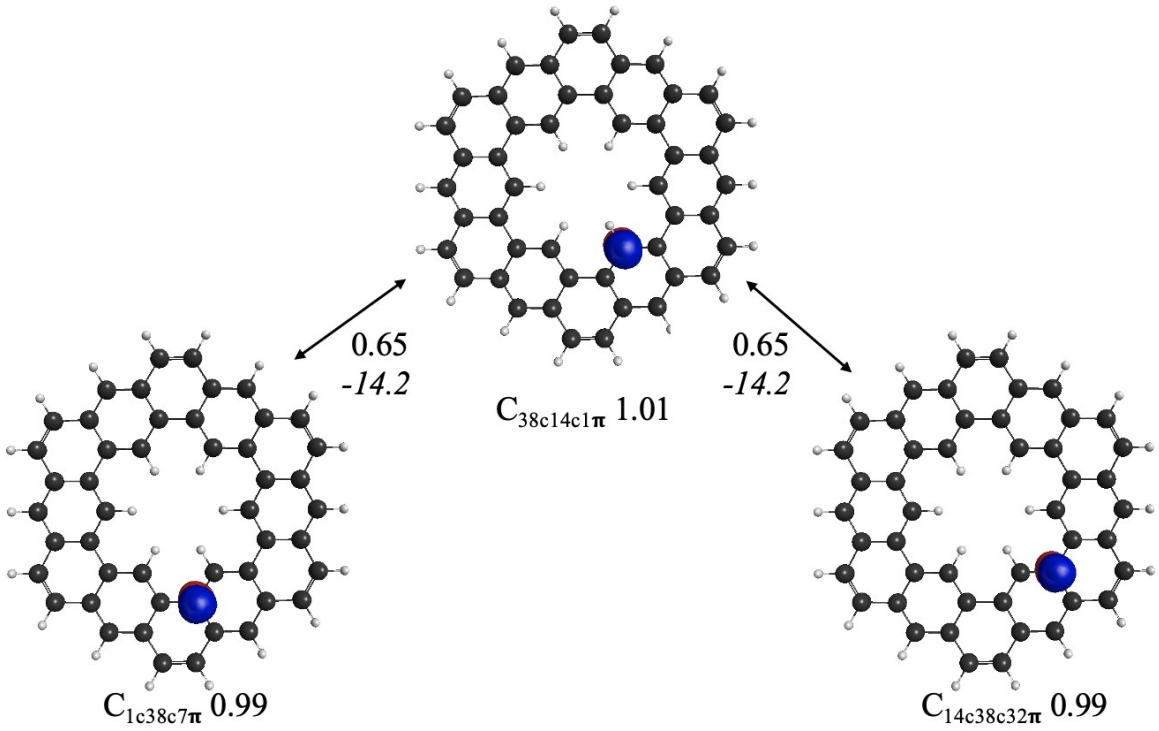
SI Figure SI:5. Non-repetitive σ and π- bonding interactions in pentalene. Bond orders (above arrow), and KBOs (below arrow) in kcal/mol are shown between pairs of bonding QUAOs.

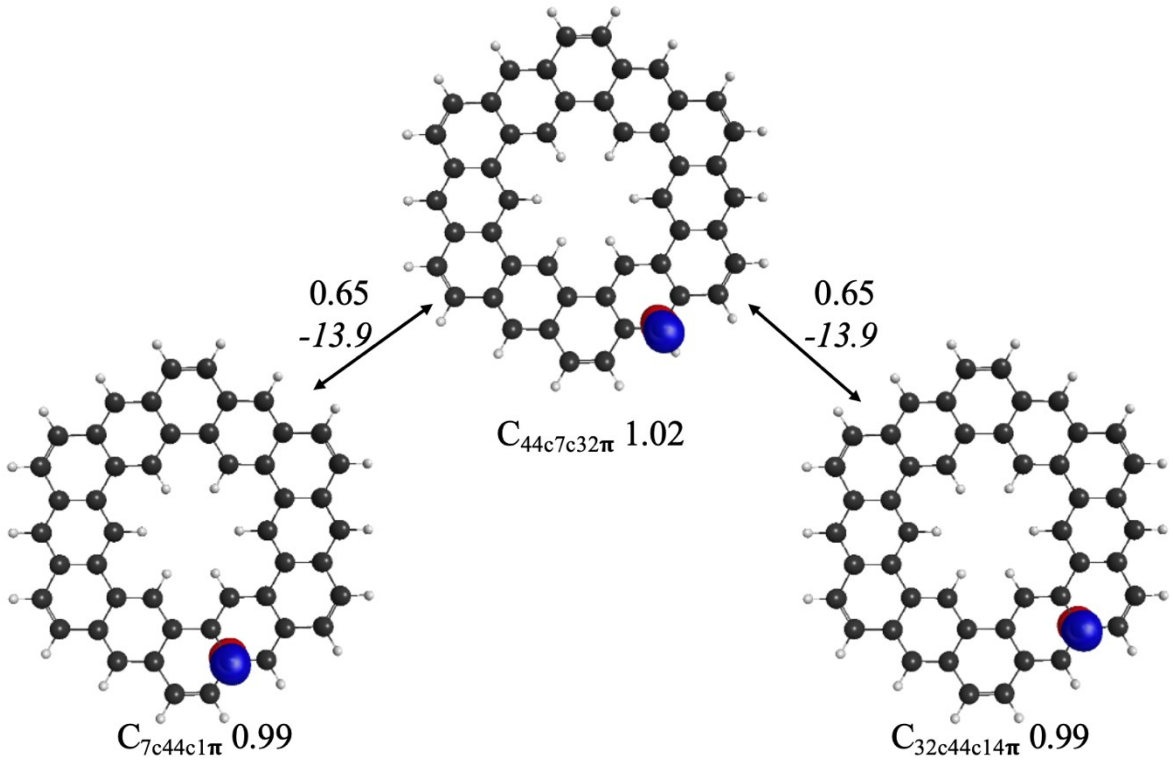
SI Table SI:4: σ and π- Bonding interactions in pentalene. Orbital occupations, bond occupation totals, bond orders, and KBOs (kcal/mol) are shown for non-repetitive interactions. Numbers display in table reference the atom numbered in Figure 3.

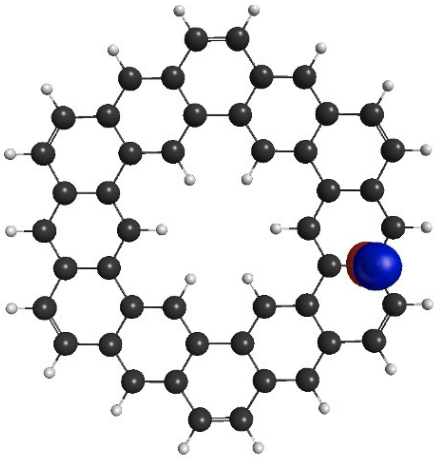
Orbital I	Occupation I	Orbital J	Occupation J	Bond Total	BO	KBO (kcal/mol)
$C_6c_2\sigma$	1.00	$C_2c_6\sigma$	1.00	2.00	0.98	-56.5
$C_3c_7\sigma$	1.00	$C_7c_3\sigma$	0.99	1.99	0.98	-53.3
$C_1c_3\sigma$	1.01	$C_3c_1\sigma$	0.99	2.00	0.98	-52.1
$C_7c_6\sigma$	0.98	$C_6c_7\sigma$	1.01	1.99	0.98	-48.7
$C_1c_2\sigma$	0.99	$C_2c_1\sigma$	0.99	1.98	0.98	-48.4
$H_{13}c_7\sigma$	0.86	$C_7h_7\sigma$	1.15	2.01	0.98	-38.8
$H_9c_3\sigma$	0.85	$C_3h_9\sigma$	1.16	2.01	0.97	-38.8
$H_{12}c_6\sigma$	0.85	$C_6h_{12}\sigma$	1.16	2.01	0.98	-38.7
$C_7c_3\pi$	1.03	$C_3c_7\pi$	1.00	2.03	0.92	-21.6
$C_2c_6\pi$	1.03	$C_6c_2\pi$	0.94	1.97	0.87	-21.0
$C_1c_5\pi$	1.03	$C_2c_6\pi$	1.03	2.06	0.32	-5.8
$C_3c_7\pi$	1.00	$C_1c_5\pi$	1.03	2.03	0.27	-4.9
$C_7c_3\pi$	1.03	$C_6c_2\pi$	0.94	1.97	0.28	-4.7

Kekulene

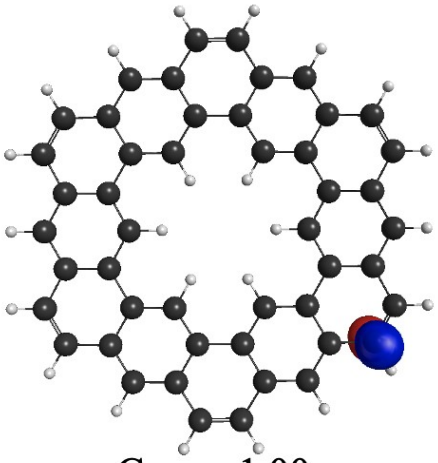



0.65
-14.2
0.65
-14.2
$C_{38c14c1\pi}$ 1.01
$C_{1c38c7\pi}$ 0.99
$C_{14c38c32\pi}$ 0.99


0.65
-13.9
0.65
-13.9
$C_{44c7c32\pi}$ 1.02
$C_{7c44c1\pi}$ 0.99
$C_{32c44c14\pi}$ 0.99

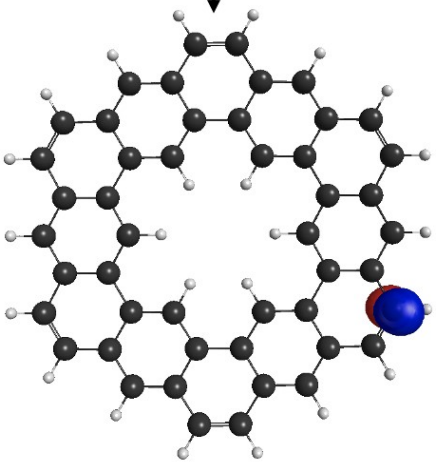


$C_{8c45c2\pi}$ 0.99



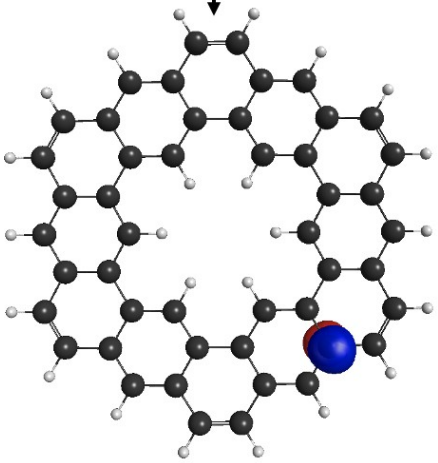
$C_{26c20\pi}$ 1.00

0.38
-7.2

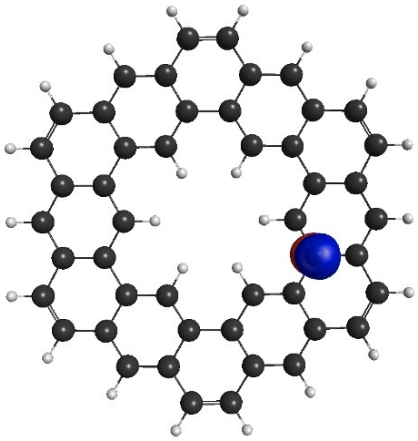


$C_{20c26\pi}$ 1.00

0.38
-7.2

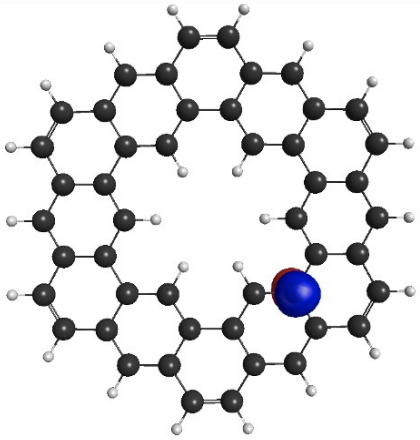


$C_{32c44c14\pi}$ 0.99

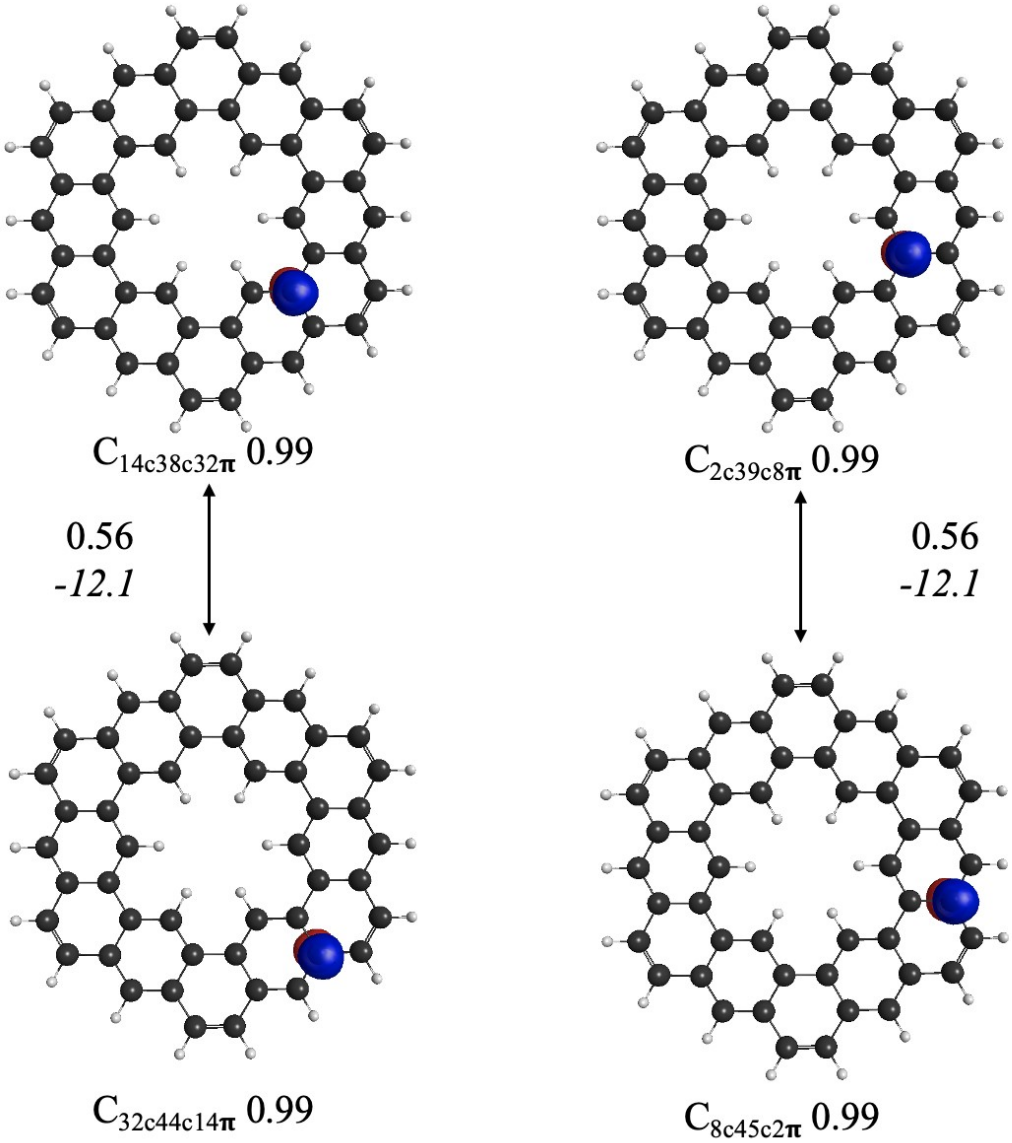


$C_{2c39c8\pi}$ 0.99

0.36
-6.9

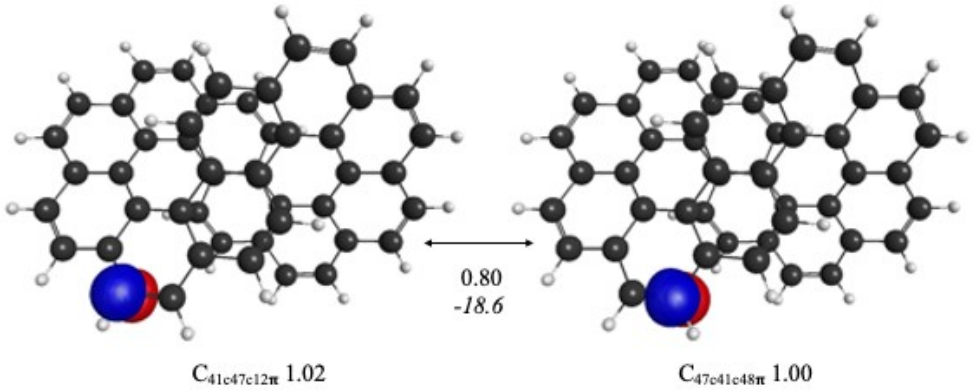


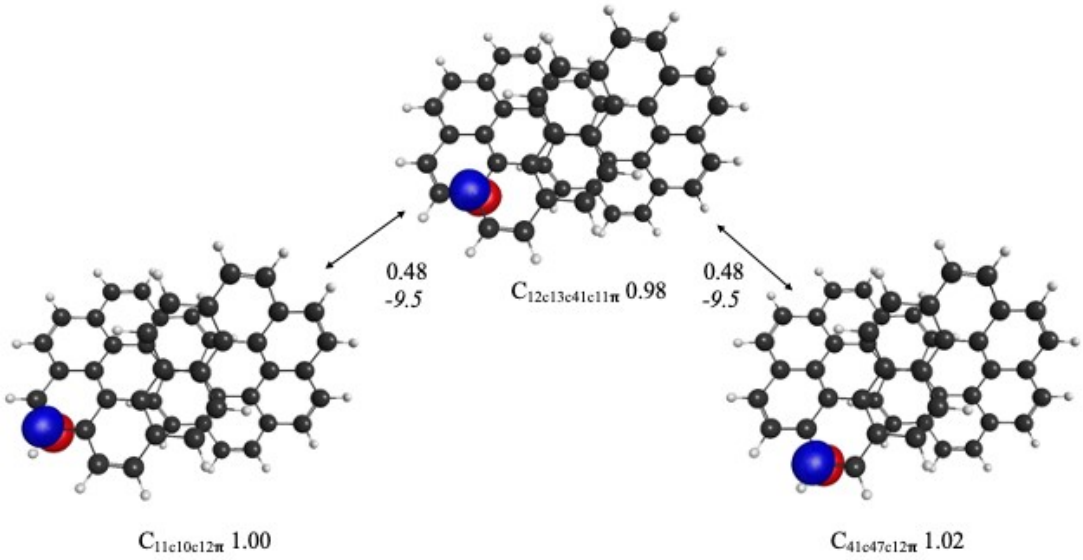
$C_{14c38c32\pi}$ 0.99

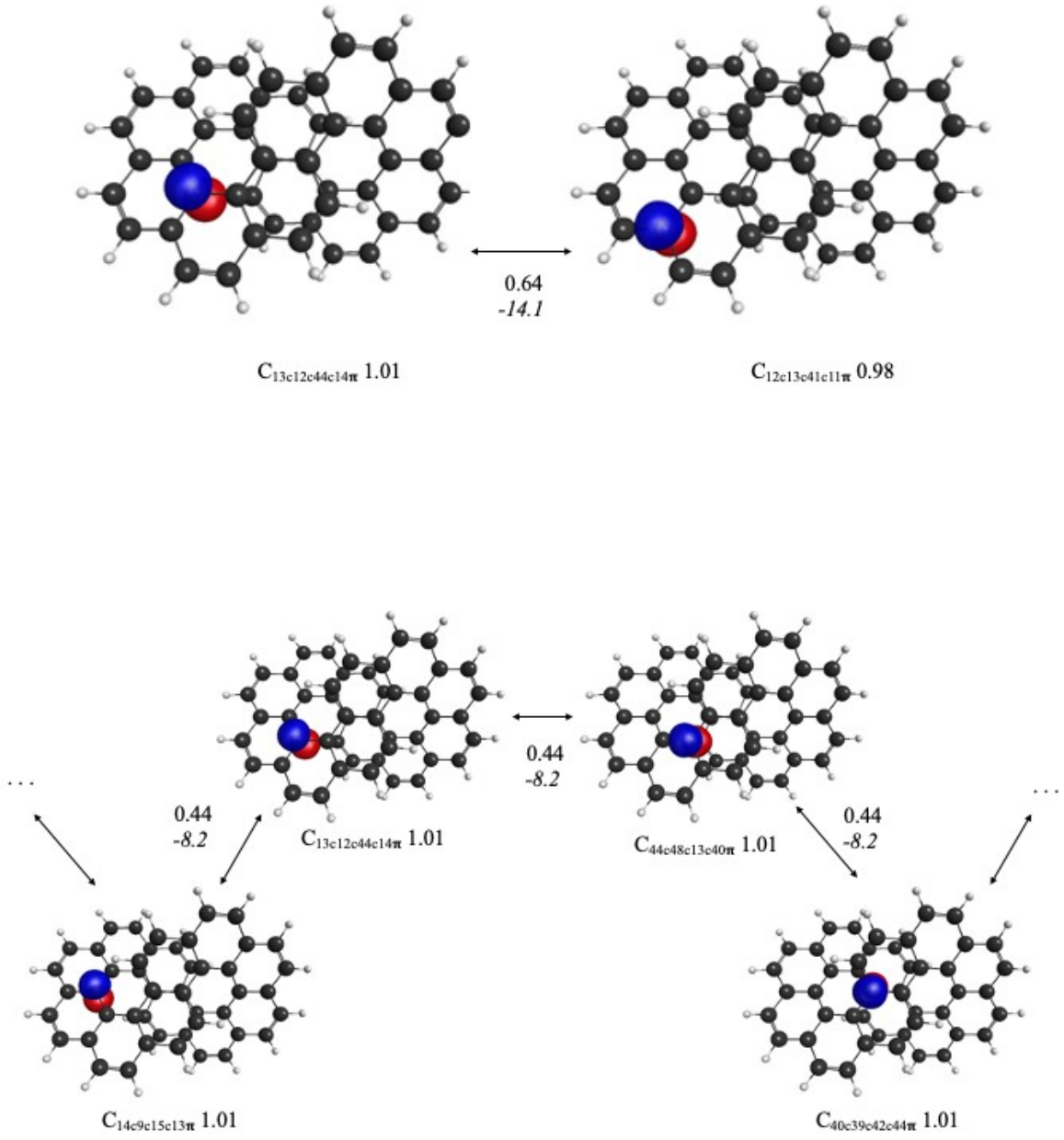


SI Figure SI:6. Non-repetitive σ and π- bonding interactions in kekulene. Bond orders (below arrow), and KBOs (in italics) in kcal/mol are shown between pairs of bonding QUAOs. Each QUAO label is given below each QUAO representation along with the QUAO population.

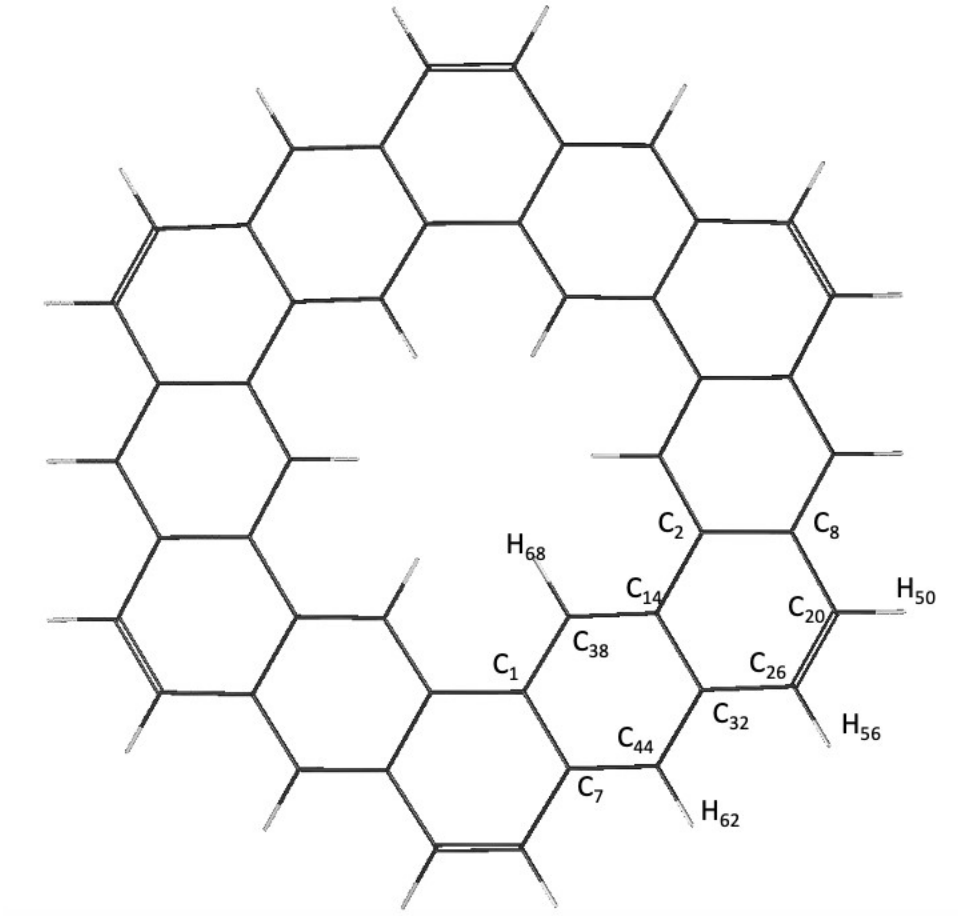
Infinitene


0.80
-18.6
C41c47c12π 1.02
C47c41c48π 1.00


0.48
-9.5
C12c13c41c11π 0.98
0.48
-9.5
C11c10c12π 1.00
C41c47c12π 1.02



SI Figure SI:7. Non-repetitive σ and π- bonding interactions in infinitene. Bond orders (below arrow), and KBOs (in italics) in kcal/mol are shown between pairs of bonding QUAOs. Each QUAO label is given below each QUAO representation along with the QUAO population.



SI Figure SI:8: Atom labels for non-repetitive and symmetric portion of kekulene. The atom numbers shown here were generated by GAMESS

SI Table SI:5: C-H σ-bonding QUAOs for non-repetitive and symmetric portion of kekulene with orbital occupations, bond occupation totals, bond orders, and KBOs (kcal/mol). The atom numbers shown here were generated by GAMESS.

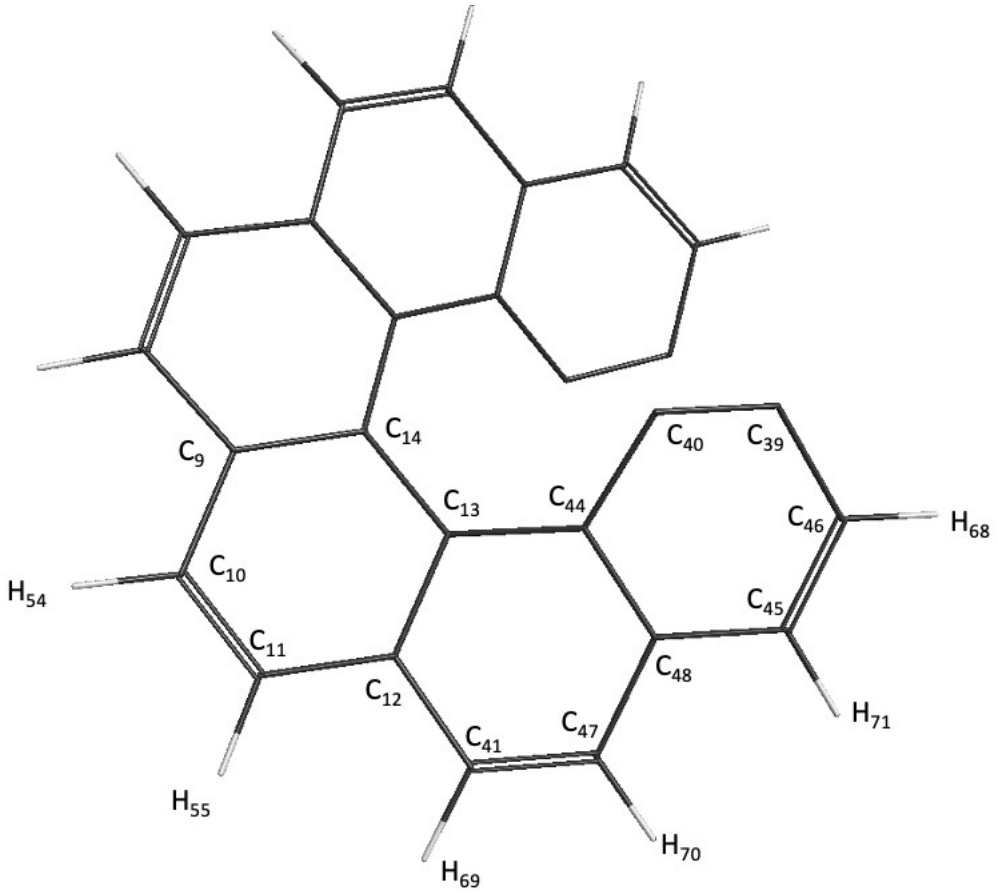
Kekulene C-H Sigma Bonds						
Orbital I	Occupation I	Orbital J	Occupation J	Bond Total	BO	KBO (kcal/mol)
$H_{68}c_{38}\sigma$	0.87	$C_{38}h_{68}\sigma$	1.13	2.00	-0.97	-41.68
$H_{62}c_{44}\sigma$	0.87	$C_{44}h_{62}\sigma$	1.13	2.00	0.98	-39.08
$H_{50}c_{20}\sigma$	0.86	$C_{20}h_{50}\sigma$	1.14	2.00	-0.97	-38.94
$H_{56}c_{26}\sigma$	0.86	$C_{26}h_{56}\sigma$	1.14	2.00	-0.97	-38.94

SI Table SI:6: C-C π-bonding QUAOs for non-repetitive and symmetric portion of kekulene with orbital occupations, bond occupation totals, bond orders, and KBOs (kcal/mol). The atom numbers shown here were generated by GAMESS.

Kekulene C-C Pi Bonds						
Orbital I	Occupation I	Orbital J	Occupation J	Bond Total	BO	KBO (kcal/mol)
$C_{26}c_{20}\pi$	1.00	$C_{20}c_{26}\pi$	1.00	2.01	0.87	-20.4
$C_{38}c_{14}c_{1}\pi$	1.01	$C_{14}c_{38}c_{32}\pi$	0.99	2.00	0.65	-14.2
$C_{38}c_{14}c_{1}\pi$	1.01	$C_{1}c_{38}c_{7}\pi$	0.99	2.00	0.65	-14.2
$C_{44}c_{7}c_{32}\pi$	1.02	$C_{7}c_{44}c_{1}\pi$	0.99	2.01	-0.64	-13.9
$C_{32}c_{44}c_{14}\pi$	0.99	$C_{14}c_{38}c_{32}\pi$	0.99	1.98	0.56	-12.1
$C_{8}c_{45}c_{2}\pi$	0.99	$C_{2}c_{39}c_{8}\pi$	0.99	1.98	0.56	-12.1
$C_{20}c_{26}\pi$	1.00	$C_{8}c_{45}c_{2}\pi$	0.99	1.99	0.38	-7.2
$C_{14}c_{32}c_{38}\pi$	0.99	$C_{2}c_{39}c_{8}\pi$	0.99	1.99	0.36	-6.9

SI Table SI:7: C-C σ-bonding QUAOs for symmetric quarter of kekulene with orbital occupations, bond occupation totals, bond orders, and KBOs (kcal/mol). The atom numbers shown here were generated by GAMESS.

Kekulene C-C sigma Bonds						
Orbital I	Occupation I	Orbital J	Occupation J	Bond Total	BO	KBO (kcal/mol)
$C_{26}c_{20}\sigma$	1.00	$C_{20}c_{26}\sigma$	1.00	2.00	0.99	-55.7
$C_{14}c_{38}\sigma$	1.00	$C_{38}c_{14}\sigma$	1.00	2.00	0.98	-55.4
$C_{38}c_{1}\sigma$	1.00	$C_{1}c_{38}\sigma$	1.00	2.00	0.98	-55.4
$C_{44}c_{32}\sigma$	1.00	$C_{32}c_{44}\sigma$	1.00	2.00	0.98	-54.9
$C_{7}c_{44}\sigma$	1.00	$C_{44}c_{7}\sigma$	1.00	2.00	0.98	-54.9
$C_{1}c_{7}\sigma$	1.00	$C_{7}c_{1}\sigma$	1.00	2.00	0.97	-54.3
$C_{32}c_{14}\sigma$	1.00	$C_{14}c_{32}\sigma$	1.00	2.00	0.97	-54.3
$C_{8}c_{2}\sigma$	1.00	$C_{2}c_{8}\sigma$	1.00	2.00	0.97	-54.3
$C_{2}c_{14}\sigma$	1.00	$C_{14}c_{2}\sigma$	1.00	2.00	0.98	-53.5
$C_{32}c_{26}\sigma$	1.00	$C_{26}c_{32}\sigma$	1.00	2.00	0.98	-52.5
$C_{20}c_{8}\sigma$	1.00	$C_{8}c_{20}\sigma$	1.00	2.00	0.98	-52.5



SI Figure SI:9: Atom labels for symmetric quarter of infinitene. The atom numbers shown here were generated by GAMESS.

SI Table SI:8: C-H σ-bonding QUAOs for symmetric quarter of infinitene with orbital occupations, bond occupation totals, bond orders, and KBOs (kcal/mol). The atom numbers shown here were generated by GAMESS.

Infinitene C-H Sigma Bonds						
Orbital I	Occupation I	Orbital J	Occupation J	Bond Total	BO	KBO (kcal/mol)
$H_{54}c_{10}\sigma$	0.86	$C_{10}h_{54}\sigma$	1.14	2.00	-0.97	-38.19
$H_{55}c_{11}\sigma$	0.86	$C_{11}h_{55}\sigma$	1.14	2.00	-0.97	-38.20
$H_{68}c_{46}\sigma$	0.85	$C_{46}h_{68}\sigma$	1.15	2.00	0.97	-38.22
$H_{69}c_{41}\sigma$	0.86	$C_{41}h_{69}\sigma$	1.14	2.00	0.97	-38.19
$H_{70}c_{47}\sigma$	0.86	$C_{47}h_{70}\sigma$	1.14	2.00	-0.97	-38.20
$H_{71}c_{45}\sigma$	0.86	$C_{45}h_{71}\sigma$	1.14	2.00	0.97	-38.18

SI Table SI:9: C-C π-bonding QUAOs for symmetric quarter of infinitene with orbital occupations, bond occupation totals, bond orders, and KBOs (kcal/mol). The atom numbers shown here were generated by GAMESS.

Infinitene C-C Pi Bonds						
Orbital I	Occupation I	Orbital J	Occupation J	Bond Total	BO	KBO (kcal/mol)
$C_{11}c_{10}c_{12}\pi$	1.00	$C_{10}c_{11}c_{9}\pi$	1.01	2.01	0.81	-18.7
$C_{46}c_{45}c_{39}\pi$	0.99	$C_{45}c_{46}c_{48}\pi$	1.02	2.01	0.80	-18.6
$C_{47}c_{41}c_{48}\pi$	1.00	$C_{41}c_{47}c_{12}\pi$	1.02	2.01	-0.80	-18.5
$C_{14}c_{9}c_{13}c_{15}\pi$	1.01	$C_{9}c_{14}c_{8}c_{10}\pi$	0.98	2.00	0.65	-14.3
$C_{48}c_{44}c_{47}c_{45}\pi$	0.98	$C_{44}c_{48}c_{13}c_{40}\pi$	1.01	1.99	-0.64	-14.1
$C_{40}c_{39}c_{42}c_{44}\pi$	0.99	$C_{39}c_{40}c_{46}c_{34}\pi$	0.99	1.97	0.65	-14
$C_{47}c_{41}c_{48}\pi$	1.00	$C_{48}c_{44}c_{47}c_{45}\pi$	0.98	1.98	0.48	-9.7
$C_{41}c_{47}c_{12}\pi$	1.02	$C_{12}c_{13}c_{41}c_{11}\pi$	0.98	2.00	0.48	-9.6
$C_{46}c_{45}c_{39}\pi$	0.99	$C_{39}c_{40}c_{46}c_{34}\pi$	0.99	1.98	0.48	-9.5
$C_{11}c_{10}c_{12}\pi$	1.00	$C_{12}c_{13}c_{41}c_{11}\pi$	0.98	1.99	0.47	-9.4
$C_{10}c_{11}c_{9}\pi$	1.01	$C_{9}c_{14}c_{8}c_{10}\pi$	0.98	1.99	-0.47	-9.4
$C_{45}c_{46}c_{48}\pi$	1.02	$C_{48}c_{44}c_{47}c_{45}\pi$	0.98	2.01	-0.47	-9.3
$C_{44}c_{48}c_{13}c_{40}\pi$	1.01	$C_{13}c_{12}c_{44}c_{14}\pi$	1.01	2.01	0.46	-8.7
$C_{44}c_{48}c_{13}c_{40}\pi$	1.01	$C_{40}c_{39}c_{42}c_{44}\pi$	0.99	1.99	0.44	-8.3
$C_{14}c_{9}c_{13}c_{15}\pi$	1.01	$C_{13}c_{12}c_{44}c_{14}\pi$	1.01	2.02	-0.44	-8.0

SI Table SI:10: C-C σ-bonding QUAOs for symmetric quarter of infinitene with orbital occupations, bond occupation totals, bond orders, and KBOs (kcal/mol). The atom numbers shown here were generated by GAMESS.

Infinitene C-C sigma Bonds						
Orbital I	Occupation I	Orbital J	Occupation J	Bond Total	BO	KBO (kcal/mol)
$C_{10}c_{11}\sigma$	1.00	$C_{11}c_{10}\sigma$	1.00	2.00	0.98	-55.8
$C_{41}c_{47}\sigma$	1.00	$C_{47}c_{41}\sigma$	1.00	2.00	0.98	-55.6
$C_{45}c_{46}\sigma$	1.00	$C_{46}c_{45}\sigma$	1.00	2.00	0.98	-55.6
$C_{48}c_{44}\sigma$	1.00	$C_{44}c_{48}\sigma$	1.00	2.00	0.98	-54.7
$C_{39}c_{40}\sigma$	1.00	$C_{40}c_{39}\sigma$	1.00	2.00	0.98	-54.7
$C_{12}c_{13}\sigma$	1.00	$C_{13}c_{12}\sigma$	1.00	2.00	0.98	-54.4
$C_{9}c_{14}\sigma$	1.00	$C_{14}c_{9}\sigma$	1.00	2.00	0.98	-54.3
$C_{40}c_{44}\sigma$	1.00	$C_{44}c_{40}\sigma$	1.00	2.00	0.98	-53.9
$C_{44}c_{13}\sigma$	1.00	$C_{13}c_{44}\sigma$	1.01	2.00	0.98	-53.7
$C_{47}c_{48}\sigma$	1.00	$C_{48}c_{47}\sigma$	1.00	2.00	0.98	-53.3
$C_{48}c_{45}\sigma$	1.01	$C_{45}c_{48}\sigma$	0.99	2.00	0.98	-53.1
$C_{46}c_{39}\sigma$	0.99	$C_{39}c_{46}\sigma$	1.01	2.00	0.98	-53.1
$C_{11}c_{12}\sigma$	1.00	$C_{12}c_{11}\sigma$	1.00	2.00	0.98	-53.0
$C_{13}c_{14}\sigma$	1.00	$C_{14}c_{13}\sigma$	1.00	2.00	0.98	-53.0
$C_{12}c_{41}\sigma$	1.00	$C_{41}c_{12}\sigma$	0.99	2.00	0.98	-53.0
$C_{9}c_{10}\sigma$	1.00	$C_{10}c_{9}\sigma$	1.00	2.00	0.98	-52.9