JOC Article

Dicyclobuta[*de*,*ij*]naphthalene and Dicyclopenta[*cd*,*gh*]pentalene: A Theoretical Study

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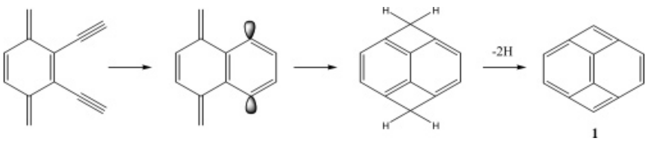
The structures, energetics, and aromatic character of dicyclobuta[*de*,*ij*]naphthalene, **1**, dicyclopenta[*cd*,*gh*]pentalene, **2**, dihydrodicyclobuta[*de*,*ij*]naphthalene, **3**, and dihydrocyclopenta[*cd*,*gh*]pentalene, **4**, have been examined at the B3LYP/6-311++G**//B3LYP/6-31G* level of theory. All molecules are bowl-shaped, and the pentalene isomers, **2** and **4**, are most stable. A comparison with other $C_{12}H_6$ and $C_{12}H_8$ isomers indicates that **2** is ~25 kcal/mol less stable than 1,5,9-tridehydro[12]-annulene and **4** is ~100 kcal/mol higher in energy than acenaphthylene, both of which are synthetically accessible. The transition state structure for bowl-to-bowl inversion of **1** is planar (D_{2h}) and lies 30.9 kcal/mol higher in energy than the ground state; the transition state for inversion of **2** is C_{2h} and lies 46.6 kcal/mol higher in energy. Symmetry considerations, bond length alternations, and NICS values (a magnetic criterion) all indicate that the ground states of **1**, **3**, and **4** are very aromatic; however, HOMA values (a measure of bond delocalization) indicate that **3S** and **4S** are aromatic but that **1S** is less so. NICS values for the ground state of **2** strongly indicate aromaticity; however, bond localization, symmetry, and HOMA values argue otherwise.

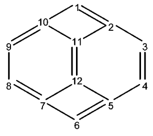
Introduction

This report describes the geometries and energetics of a series of unusual geodesic polyarenes **1**−**4**. We came to compound **1** by thinking about the hypothetical Bergman cyclization in Scheme 1.

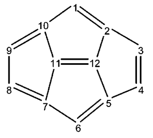
SCHEME 1



Compound **2** is an obvious isomer; calculations on **3** and **4** came to mind as we thought about whether **1** and **2** could be stabilized by alleviating the strain on the interior carbon atoms. These $C_{12}H_6$ and $C_{12}H_8$ molecules are isomers of such previously studied systems as benzotricyclobutadiene, **5**, and biphenylene, **6**. To our knowledge, **1**−**4** have not been isolated; however, **2** has been the subject of previous theoretical analysis.[1] We were interested in these molecules due to their unusual structure and their potential aromatic character; highly strained as **1**−**4** are, they contain a peripheral 10 π-electron system.[2]



1



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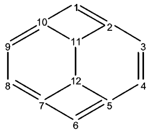

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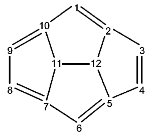

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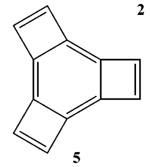
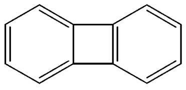


5



6

Computational Methods

The structures were obtained by geometry optimization, without symmetry constraint, using the BLYP and B3LYP density functional with the 6-31G* basis set as implemented in the Gaussian 03[3] program. The B3LYP/6-31G* treatment has been shown to adequately describe similar systems.[1] The restricted B3LYP wave functions were tested for stability with respect to becoming unrestricted using the "stable" keyword. Stability was further tested by reoptimizing the RB3LYP

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(1) Zywietz, T. K.; Jiao, H.; Schleyer, P. v. R.; de Meijere, A. *J. Org. Chem.* **1998**, *63*, 3417.

(2) Myers, A. G.; Sogi, M.; Lewis, M. A.; Arvedson, S. P. *J. Org. Chem.* **2004**, *69*, 2516.

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TABLE 1. The Total Energies[6] Calculated for the Singlet Ground States of 1−4

	E^a B3LYP/ 6-31G*	E^a B3LYP/ 6-311+G*	E^a B3LYP/ 6-311++G**	ΔE^b B3LYP/ 6-31G*	ΔE^b B3LYP/ 6-311++G**
1S ($C_{12}H_6$, C_{2v})	−460.614	−460.712	−460.723	12.1^c	12.5^c
2S ($C_{12}H_6$, C_s)	−460.633	−460.732	−460.743	[0.0]	[0.0]
3S ($C_{12}H_8$, C_{2v})	−461.876	−461.974	−461.988	26.7^d	27.9^d
4S ($C_{12}H_8$, C_{2v})	−461.918	−462.019	−462.032	[0.0]	[0.0]

[a] In au. [b] In kcal/mol. [c] With respect to **2S**. [d] With respect to **4S**.

TABLE 2. The Total Energies Calculated for the Triplet, Dication, and Dianion of 1−4[a]

	ΔE (B3LYP/6-31G*)	ΔE (B3LYP/6-311++G**)
1T ($C_{12}H_6$, C_{2v})	22.3	23.1
$\mathbf{1}^{2-}$ ($C_{12}H_6^{2-}$, C_{2v})	90.0	53.3
$\mathbf{1}^{2+}$ ($C_{12}H_6^{2+}$, C_{2v})	437.9	448.8
2T ($C_{12}H_6$, C_s)	6.4	6.1
$\mathbf{2}^{2-}$ ($C_{12}H_6^{2-}$, C_{2v})	60.7	18.0
$\mathbf{2}^{2+}$ ($C_{12}H_6^{2+}$, C_s)	445.0	455.5
3T ($C_{12}H_8$, C_{2v})	26.2	26.5
$\mathbf{3}^{2-}$ ($C_{12}H_8^{2-}$, C_{2v})	115.0	77.0
$\mathbf{3}^{2+}$ ($C_{12}H_8^{2+}$, C_{2v})	397.2	408.2
4T ($C_{12}H_8$, C_{2v})	17.7	18.6
$\mathbf{4}^{2-}$ ($C_{12}H_8^{2-}$, C_{2v})	120.6	75.3
$\mathbf{4}^{2+}$ ($C_{12}H_8^{2+}$, C_{2v})	402.6	414.1

[a] In each case, the energies are given in kcal/mol relative to the corresponding ground-state energies (**1S**−**4S**) shown in Table 1.

solutions with UB3LYP and the “guess=(mix,always)” option. Harmonic frequency analysis was used to confirm all structures as stationary points on the B3LYP/6-31G* and BLYP/6-31G* potential energy surfaces. Single-point energetic analysis was performed with the B3LYP/6-311+G* and B3LYP/6-311++G** basis sets using the B3LYP/6-31G* geometries. The nucleus-independent chemical shifts were calculated at the ring centers (NICS(0)) and 1 Å away from the ring centers (NICS(1)) on the inside and the outside of each geodesic polyarene. This was done using the GIAO method[4,5] and the 6-311++G** basis set.

Results and Discussion

Energetics. The ground-state singlet energies of **1**−**4** are shown in Table 1, while the corresponding triplet, dianion, and dication energies are shown in Table 2. We studied systems with two more and two less electrons to explore perturbations of aromaticity by electron count. In most cases, the results with the smaller 6-31G* basis set are in agreement with the calculations using larger basis sets; however, the energetics of the dianion systems are quite dependent on the theoretical treatment. As noted in Tables 1 and 2, increasing the diffuseness and polarizability of the basis set leads to a greater stabilization of the dianion relative to the ground-state singlet in each case, leading to a decrease in the energetic differences upon basis set expansion. The discussions that follow will utilize the B3LYP/6-311++G**//B3LYP/6-31G* energies unless otherwise noted.

Dicyclopenta[*cd*,*gh*]pentalene **2** is 12.5 kcal/mol more stable than dicyclobuta[*de*,*ij*]naphthalene **1**; dihydrocyclopenta[*cd*,*gh*]pentalene **4** is 27.9 kcal/mol more stable than dihydrodicyclobuta[*de*,*ij*]naphthalene **3** at this level of theory. In all cases (**1**−**4**), the singlet lies lower in energy than the triplet, as expected. The singlet−triplet energy gaps for the naphthalene-based systems are 23.1 kcal/mol for **1** and 26.5 kcal/mol for **3**, while the corresponding gaps for the pentalene systems are smaller, 6.1 kcal/mol for **2** and 18.6 kcal/mol for **4**. These small singlet−triplet splittings, especially that in **2**, are similar to those reported theoretically for pentalene (7.7 kcal/mol) and acepentalene (2.5 kcal/mol).[1]

Isomers. The ground-state singlet energies for a variety of other isomers of $C_{12}H_6$ and $C_{12}H_8$ were also computed (Tables 3 and 4). (In the discussion that follows, all energies are reported in kcal/mol.) Of the $C_{12}H_6$ isomers studied, the experimentally elusive[7] acenaphthyne is the most stable structure, followed by 1,5,9-tridehydro[12]annulene which lies 26.2 higher in energy. The first successful synthesis of this molecule was reported in 1966.[8,9] Next in stability is the dicyclobuta[*a*,*f*]pentalene (49.2), which, to the best of our knowledge, has not yet been synthesized. The energies of **3** (50.1) and **1** (62.5 kcal) bracket the energy of the so far synthetically inaccessible[10] benzotricyclobutadiene **5** (53.7). The [3]circulene lies highest in energy, 87.0 less stable than acenaphthyne.

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(3) Frisch, M. J.; T., G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2003.

(4) Wolinski, K.; Hilton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251.

(5) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317.

(6) The energies calculated using the 6-311+G* basis set are not reported. In most cases, they were within 1 kcal/mol of the energies calculated with the 6-311++G** basis set; in all cases, they were within 5 kcal/mol.

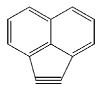
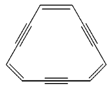
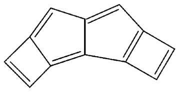
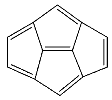
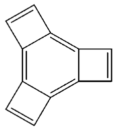
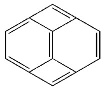
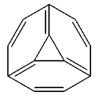
(7) The spectra of matrix-isolated acenaphthyne was first reported by Chapman et al. in 1981 (Chapman,O. L.; Gano, J.; West, P. R. *J. Am. Chem. Soc.* **1981**, *103*, 7033). The radical anion was recently synthesized by Broadus and Kass (Broadus, K. M.; Kass, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 4189.)

(8) Sondheimer, F.; Wolovsky, R.; Garratt, P. J.; Calder, I. C. *J. Am. Chem. Soc.* **1966**, *88*, 2610.

(9) Untch, K. G.; Wysocki, D. C. *J. Am. Chem. Soc.* **1966**, *88*, 2608.

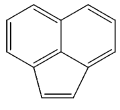
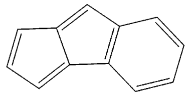
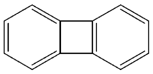
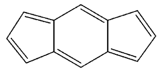
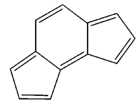
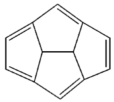
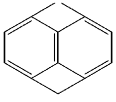
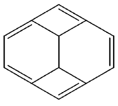
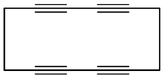
(10) The closest known compound is tris(benzocyclobutadieno)-benzene, first synthesized by Diercks and Vollhardt (*J. Am. Chem. Soc.* **1986**, *108*, 3150). Thummel's group synthesized the saturated tricyclobutabenzene in 1979 (Nutakul, W.; Thummel, R. P.; Taggart, A. D. *J. Am. Chem. Soc.* **1979**, *101*, 770).

TABLE 3. Energetic Comparisons of $C_{12}H_6$ Isomers Calculated at the B3LYP/6-311+G*//B3LYP/6-31G* Level of Theory

Structure		Relative Energy (kcal/mol)
	acenaphthyne	[0.0] [a]
	1,5,9-tridehydro[12]annulene	26.2
	dicyclobuta[*a,f*]pentalene	49.2
	dihydrodicyclobuta[*de,ij*]naphthalene **3**	50.1
	benzotricyclobutadiene **5**	53.7
	dicyclobuta[*de,ij*]naphthalene **1**	62.5
	[3]circulene	87.0

[a] The B3LYP/6-311+G*//B3LYP/6-31G* energy of this molecule is −460.812 10 au.

TABLE 4. Energetic Comparisons of $C_{12}H_8$ Isomers Calculated at the B3LYP/6-311+G*//B3LYP/6-31G* Level

Structure		Relative Energy (kcal/mol)
	acenaphthylene	[0.0] [a]
	cyclopent[*a*]indene	30.0
	biphenylene	35.2
	*s*-indacene	36.8
	*as*-indacene	43.6
	dihydrocyclopenta[*cd,gh*]pentalene **4**	104.0
	dicyclobuta[*de,ij*]naphthalene	112.3
	dihydrodicyclobuta[*de,ij*]naphthalene **3**	131.9
	1,3,7,9-cyclododecatetrayne	149.6

[a] The B3LYP/6-311+G*//B3LYP/6-31G* energy of this molecule is −462.184 38 au.

Of the $C_{12}H_8$ isomers studied, the saturated form of acenaphthyne, acenaphthylene, is the most stable isomer on the B3LYP/6-311+G*//B3LYP/6-31G* surface. The synthesis of this molecule was first reported in 1873.[11] Next in stability is cyclopent[*a*]indene (benzopentalene) (30.0) followed by biphenylene (35.2), *s*-indacene (36.8), and *as*-indacene (43.6). Benzopentalene and biphenylene are both known experimentally,[12,13] while *s*-indacene has been isolated only in the solid state when protected from reaction by bulky substituents.[14] *as*-Indacene was once thought to have been generated as an intermediate,[15] but the evidence was later found to have been erroneous,[13] and the compound has never been isolated. Dihydrocyclopenta[*cd,gh*]pentalene **4** is next in the energetic ordering and is very unstable relative to the isomers discussed above (104.0), as is dicyclobuta[*de,ij*]naphthalene (112.3) and dihydrodicyclobuta[*de,ij*]naphthalene **3** (131.9). To the best of our knowledge, these three molecules have not been synthesized even as transient species, but, surprisingly, the highly strained and less energetically feasible 1,3,7,9-cyclododecatetrayne (149.6) has been detected as a reactive intermediate,[16] and its octamethyl derivative is a stable crystalline compound.[17]

Bond Localization. The geometry-optimized structures for **1**−**4** are shown in Figures 1−6. The Figures showing the geometries are grouped in the following way: Figure 1 compares the ground states of **1**−**4**, Figure 2 shows transition states for bowl inversions, and Figures 3−6 show the triplet and charged species. The structures of **1**, **3**, and **4** are nonplanar, bowl-shaped systems possessing C_{2v} symmetry. The various forms of **2** are also bowl-shaped; however, **2**, **2T**, and $\mathbf{2}^{2+}$ adopt C_s symmetry, while the $\mathbf{2}^{2-}$ geometry minimizes to the more symmetric C_{2v} shape.

Molecules **1**−**4** feature a peripheral 10 π Huckel system. The calculated structure of **1** reflects this in two ways. First, the central $C_{11}-C_{12}$ bond is clearly an isolated double bond; second, the peripheral π system shows a reasonable degree of delocalization (range of CC

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[11] Behr, A.; van Dorp, W. A. *Ber.* **1873**, *6*, 753.

[12] Wittig, G.; Herwig, W. *Chem. Ber.* **1954**, *87*, 1511.

[13] Brown, R. F. C.; Choi, N.; Coulston, K. J.; Eastwood, F. W.; Wiersum, U. E.; Jenneskens, L. W. *Tetrahedron Lett.* **1994**, *35*, 4405.

[14] Hafner, K.; Stowasser, B.; Krimmer, H. P.; Fisher, S.; Bohm, M. C.; Lindner, H. J. *Angew. Chem.* **1986**, *25*, 630.

[15] Wiersum, U. E.; Jenneskens, L. W. *Tetrahedron Lett.* **1993**, *34*, 6615.

[16] Wolovsky, R.; Sondheimer, F. *J. Am. Chem. Soc.* **1965**, *87*, 5720.

[17] Santiago, C.; Houk, K. N.; DeCicco, G. J.; Scott, L. T. *J. Am. Chem. Soc.* **1978**, *100*, 692.

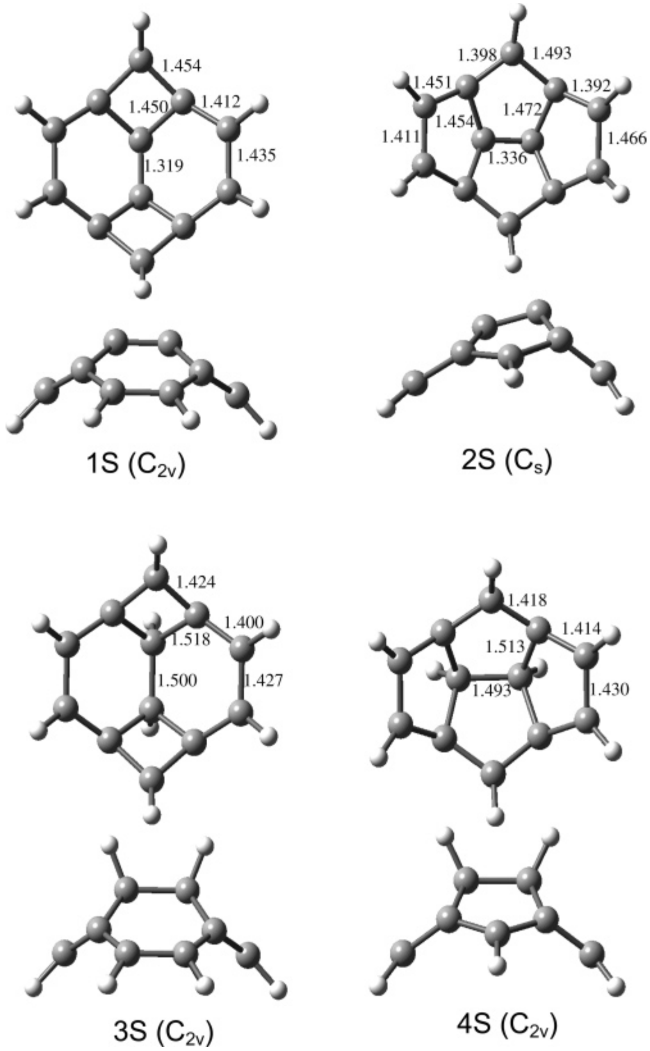

FIGURE 1. B3LYP/6-31G* structures of the ground-state singlets of **1**−**4**.

distances computed is 1.412−1.454 Å). The $C_{11}-C_{12}$ saturated analogue **3** is similar (CC range 1.400−1.427 Å). In **2** again, there is an isolated central double bond; now there is somewhat more localization in the periphery, emphasized in the C_s geometry. The C_{2v} centrally saturated relative, **4**, is quite delocalized in the periphery.

We will return to a discussion of the aromaticity in these systems, including a metric of bond delocalization, after a detailed discussion of each molecule below.

Dicyclobuta[*de*,*ij*]naphthalene, 1. The geometry-optimized structures of **1** are shown in Figures 1−3. The singlet, triplet, dianion, and dication of **1** are bowl-shaped and possess C_{2v} symmetry. The singlet ground state (**1S**) (Figure 1) has a reasonably delocalized structure along the peripheral atoms with the central carbon atoms the only ones with a "classical" double bond structure. The triplet (**1T**) (Figure 3) exhibits more bond length differences along the perimeter bonds and a lengthening of the interior bond. The maximum bond difference (0.1 Å) in the triplet occurs between the cyclobutene ($r_{1-2} = 1.507$ Å) and perimeter naphthyl ring bonds ($r_{2-3} = 1.399$ Å).

The transition state (**1TS**) for ring inversion of the ground-state singlet of **1** (Figure 2) is planar and lies 30.9 kcal/mol higher in energy than the ground state. As

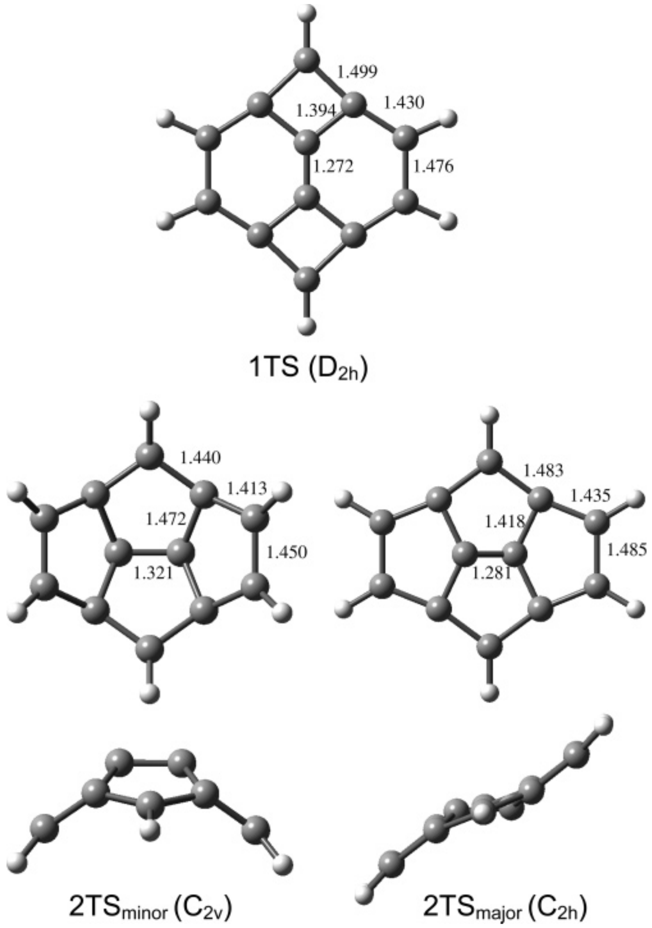

FIGURE 2. B3LYP/6-31G* transition state structures for ring inversion of dicyclobuta[*de*,*ij*]naphthalene (**1TS**), $C_s \leftrightarrow C_s$ interconversion (**2TS**$_{\mathrm{minor}}$), and ring interconversion (**2TS**$_{\mathrm{major}}$) of dicyclopenta[*cd*,*gh*]pentalene.

shown in Figure 2, the electronic structure of the transition state is D_{2h} and delocalized. During ring inversion, all of the interior bonds shorten significantly, while all of the exterior bonds simultaneously lengthen. This is similar to the geometric changes associated with the bowl-to-bowl transition state in corannulene.[18−20]

The dication and the dianion are rather localized structures with maximum bond differences of 0.095 Å between r_{2-3} and r_{3-4} in the six-membered ring for $\mathbf{1}^{2+}$ and 0.160 Å between r_{1-2} in cyclobutene and r_{2-3} in the six-membered ring of $\mathbf{1}^{2-}$. This is expected of 8 and 12 π electron peripheries; in each case, the molecule has an isolated central double bond.

The structure of $\mathbf{1}^{2-}$ indicates significant pyramidalization at the cyclobutane CH units. One commonly used[21−24] measure of hydrocarbon pyramidalization is the π-orbital axis vector (POAV) method proposed by Haddon.[25,26] In this method, the degree of pyramidalization

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[18] Sygula, A.; Rabideau, P. W. *J. Mol. Struct.* **1995**, *333*, 215.

[19] Unpublished results; at the B3LYP/6-31G* level, the interior bonds of corannulene shorten by 0.017 and 0.020 Å at the TS, while the exterior bonds lengthen by 0.014 and 0.015 Å.

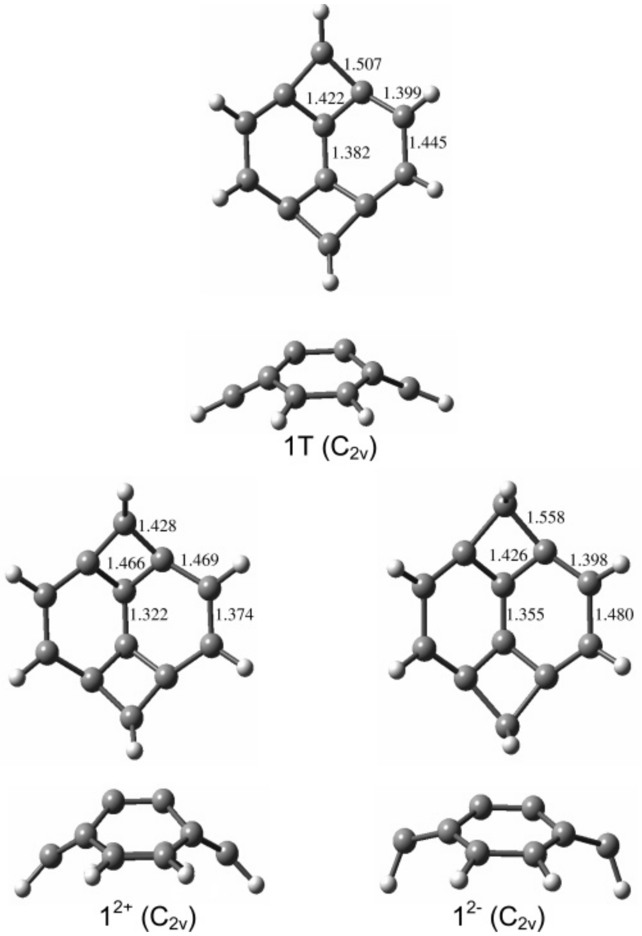
[20] Seiders, T. J.; Baldridge, K. K.; Grube, G. H.; Siegel, J. S. *J. Am. Chem. Soc.* **2001**, *123*, 517 and references therein.

[21] Dinadayalane, T. C.; Sastry, G. N. *J. Org. Chem.* **2002**, *67*, 4605.

[22] Haddon, R. C. *J. Am. Chem. Soc.* **1990**, *112*, 3385.

[23] Scott, L. T.; Bratcher, M. S.; Hagen, S. *J. Am. Chem. Soc.* **1996**, *118*, 8743.

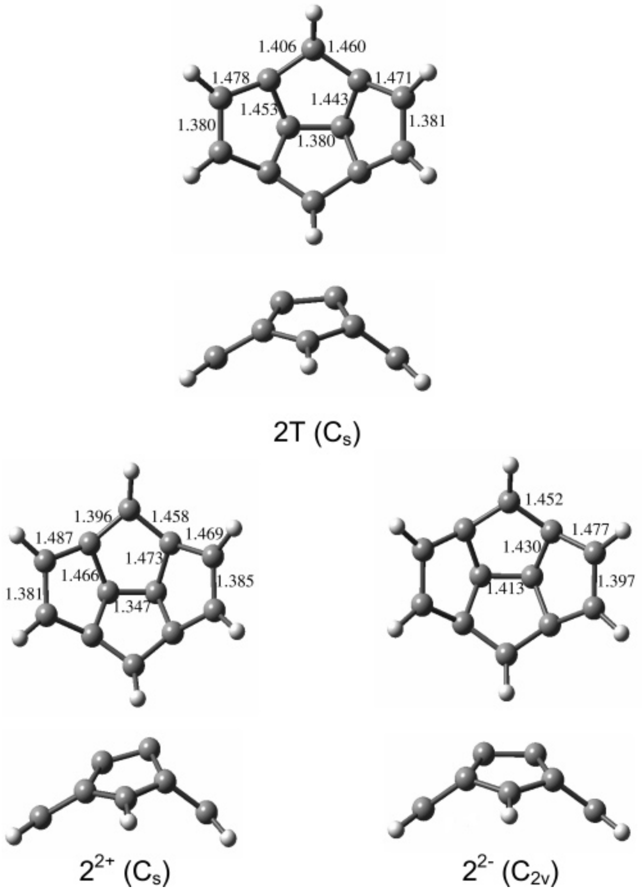
[24] Ferrer, S. M.; Molina, J. M. *J. Comput. Chem.* **1999**, *20*, 1412.



$1T\ (C_{2v})$

$1^{2+}\ (C_{2v})$ $1^{2-}\ (C_{2v})$

FIGURE 3. B3LYP/6-31G* structures of the triplet, dication, and dianion of dicyclobuta[*de*,*ij*]naphthalene, **1**.

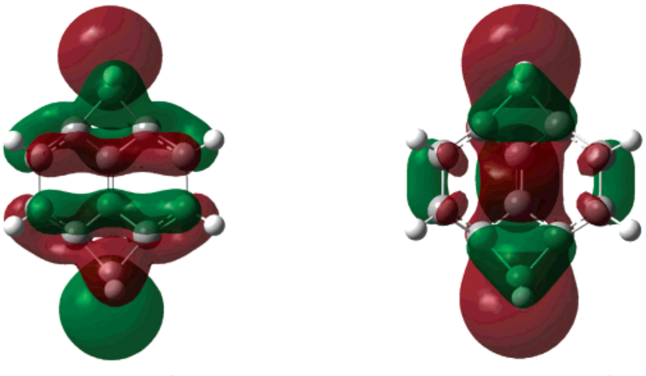


$2T\ (C_s)$

$2^{2+}\ (C_s)$ $2^{2-}\ (C_{2v})$

FIGURE 4. B3LYP/6-31G* structures of the triplet, dication, and dianion of dicyclopenta[*cd*,*gh*]pentalene, **2**.

SCHEME 2. HOMO and HOMO−1 for $\mathbf{1}^{2-}$


HOMO of $\mathbf{1}^{2-}$ HOMO − 1 of $\mathbf{1}^{2-}$

is measured by orienting the π-orbital axis vector so as to form equal angles, $\theta_{\sigma\pi}$, with each of the three σ-bonds. The POAV pyramidalization angle is then defined as POAV = $(\theta_{\sigma\pi} - 90)°$; for a planar conjugated molecule, $\theta_{\sigma\pi} = 90°$ and POAV = 0°. In $\mathbf{1}^{2-}$, the cyclobutene hydrogen atoms are bent downward with a POAV angle of 24.1° (relative to 6.5°, 0.1°, and 7.7° for **1S**, **1T**, and $\mathbf{1}^{2+}$.) An examination of the HOMO and HOMO−1 for $\mathbf{1}^{2-}$ (Scheme 2), along with the long bond (i.e., r_{1-2}) that connects the cyclobutene CH units to the naphthalene core, suggests a localization of the negative charge onto the CH units, resulting in significant carbanion character on the two cyclobutene carbon atoms.

Dicyclopenta[*cd*,*gh*]pentalene, 2. This isomer adopts an asymmetric, bowl-shaped C_s structure in the singlet ground state on both the B3LYP/6-31G* and the BLYP/6-31G* surfaces, in agreement with previously reported theoretical treatments of this system.[1] The C_{2v} transition state for $C_s \leftrightarrow C_s$ interconversion shown in Figure 2 is only 1.9 kcal/mol higher in energy; obviously, there is a relatively flat potential energy surface near the minimum. The asymmetry of the singlet ground state shown in Figure 1 results in some localization with a bond alternation of 0.095 Å between atoms 1−2 and 1−10. The asymmetry of **2S** seems to be caused by the desire to lessen the pyramidalization of one interior carbon atom while simultaneously introducing strain into the other interior carbon atom. The POAV angles for the interior carbon atoms in **2S** are 23.4° and 12.2°, reflecting the differences in interior carbon atom strain in this asymmetrical molecule.

The C_{2h} transition state to ring inversion, shown in Figure 2, lies 46.6 kcal/mol higher in energy than the singlet ground state; thus the barrier here is more than 50% higher than the barrier for ring inversion of **1**. The triplet state **2T** is also C_s and has shorter C3−C4 and C8−C9 bonds along the sides and longer bonds along the top of the molecule, relative to the orientation shown in Figure 4. The asymmetry of the triplet is less than for the singlet, as the side-on views in Figure 4 and the

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(25) Haddon, R. C.; Raghavachari, K. *Tetrahedron* **1996**, *52*, 5207.
(26) Haddon, R. C. *J. Phys. Chem. A* **2001**, *105*, 4164.

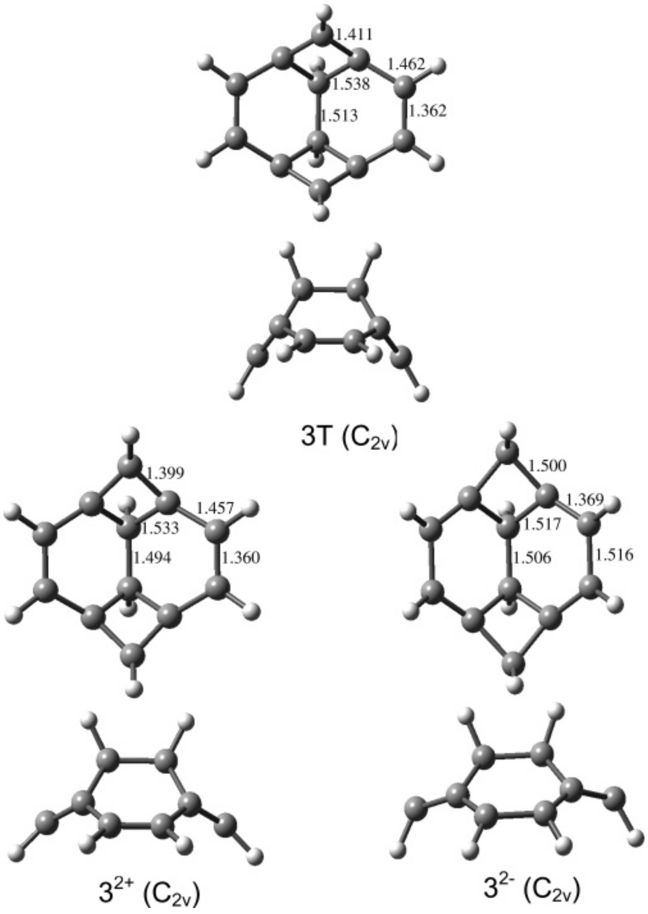
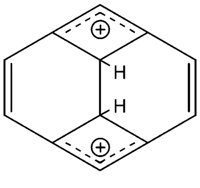


FIGURE 5. B3LYP/6-31G* structures of the triplet, dication, and dianion of dihydrodicyclobuta[*de*,*ij*]naphthalene, **3**.

POAV angles around the interior carbon atoms (18.5° and 22.8°) indicate. The dication is quite asymmetric, with POAV angles of 28.0° and 15.7°; it displays peripheral bond lengths similar to those of the triplet. The dianion adopts a more symmetrical C_{2v} structure that flattens out somewhat (the POAV angle of interior carbon atoms is 18.4°) as shown in Figure 4. There is significant bond lengthening of the interior C−C bond in the dianion.

Dihydrodicyclobuta[*de*,*ij*]naphthalene, 3. Adding hydrogens to the C11−C12 bond of **1** and **2** lessens the strain at the interior carbon atoms. As expected, the interior bond lengths are longer in the saturated systems, and the ground-state singlet structures are delocalized along the exterior. The singlet (Figure 1), triplet, dication, and dianion (Figure 5) all assume C_{2v} structures for **3**. The singlet is more delocalized than the triplet, particularly along the perimeter. (The largest bond alternation of **3S** is 0.027 Å, while for **3T** it is 0.100 Å.) The triplet, **3T**, lies 26.5 kcal/mol higher in energy than the singlet. The high energy dication is probably best represented as:



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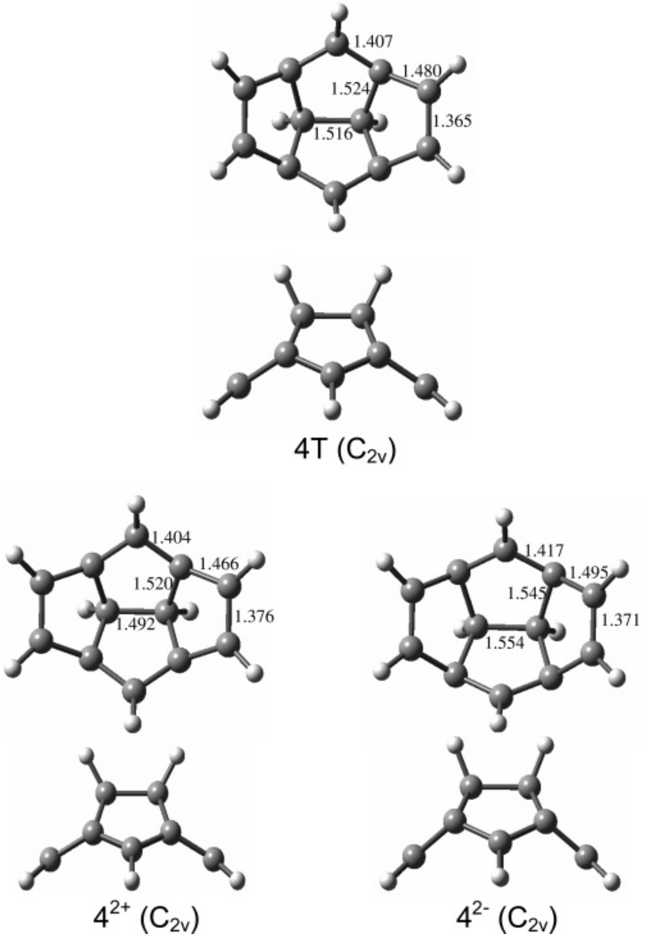
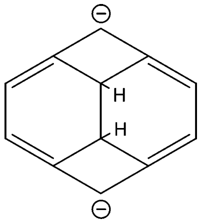


FIGURE 6. B3LYP/6-31G* structures of the triplet, dication, and dianion of dihydrocyclopenta[*cd*,*gh*]pentalene, **4**.

The dianion, with long cyclobutene bond lengths (1.500) and alternating long and short six-membered ring bond lengths (1.369/1.516), is best represented as:



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The cyclobutene hydrogens are bent downward in 3^{2-} with a POAV angle of 20.5° (relative to 5.4°, 3.1°, and 6.9° for **3S**, **3T**, and 3^{2+}).

Dihydrocyclopenta[*cd*,*gh*]pentalene, 4. All of the structures of **4** are of C_{2v} symmetry, and the interior bond length, while a little short, is that of a single bond

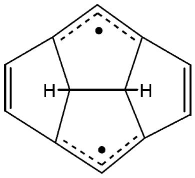

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TABLE 5. HOMA Values for 1−4 Computed along the Peripheral Bonds Using the B3LYP/6-31G* Optimized Structures[a]

	sym	GEO	EN	HOMA
1S	C_{2v}	0.091	0.522	0.387
2S	C_s	0.392	0.557	0.051
3S	C_{2v}	0.039	0.188	0.773
4S	C_{2v}	0.009	0.244	0.747

[a] Peripheral HOMA values for triplets, dications, and dianions can be found in the Supporting Information, along with HOMA values calculated using all bonds.

(Figures 1 and 6). The perimeter bonds are quite delocalized in **4S**, while the structure of **4T** is best viewed as:

$\mathbf{4}^{2-}$ may be similarly represented; however, the extra electron density in the dianion causes the perimeter bonds to be 0.006−0.150 Å longer than in the triplet and dication perimeter.

Aromaticity. Are these molecules aromatic? There are many measures of aromaticity;[27] no single measure will define this wonderfully fuzzy and elastic, but useful, quality. One criterion for judging the aromatic nature of a molecule is bond length delocalization or alternation. This may be gauged by the harmonic oscillator measure of aromaticity (HOMA),[28−30] defined as

$$\mathrm{HOMA} = 1 - \frac{\alpha}{n}\sum_{i=1}^{n}(R_{\mathrm{opt}} - R_i)^2$$

where R_i are the "n" bond lengths in each molecule and α is an empirical constant that forces HOMA = 0 in a nonaromatic (bond localized) system and HOMA = 1 in a fully aromatic system with all bonds equal to R_{opt}. For CC bonds, $\alpha = 257.7$ Å^{-2} and $R_{\mathrm{opt}} = 1.388$ Å. This equation can be separated into two terms:[31] a geometric term that emphasizes bond alternation (GEO), and an energetic term that reflects the change in energy caused by changes in the average bond length (EN).

$$\mathrm{HOMA} = 1 - \mathrm{EN} - \mathrm{GEO} = 1 - \alpha(R_{\mathrm{opt}} - R_{\mathrm{av}})^2 - \frac{\alpha}{n}\sum_{i=1}^{n}(R_{\mathrm{av}} - R_i)^2$$

For calibration, the HOMA values in benzene and naphthalene are 0.979 and 0.802, respectively,[30] and in antiaromatic cyclooctatetraene, HOMA is −0.21.[32] The HOMA, GEO, and EN values calculated along the peripheral bonds for **1S**−**4S** are shown in Table 5. The corresponding values for the triplets, dications, and dianions can be found in the Supporting Information along with the HOMA values determined using the perimeter and interior bond lengths. The GEO component of HOMA is a measure of bond length alternation; GEO for benzene is 0.000, 0.121 in naphthalene, and 1.12 in cyclooctatetraene.[32] GEO values for **1S**, **3S**, and **4S** indicate significant delocalization, while the corresponding triplets, dianions, and dications display larger GEO values, indicative of more localized structures. For **2**, the ground-state singlet, triplet, and dication display larger GEO values, while the dianion is more delocalized with a bond alternation (0.220) closer to that of naphthalene.[30]

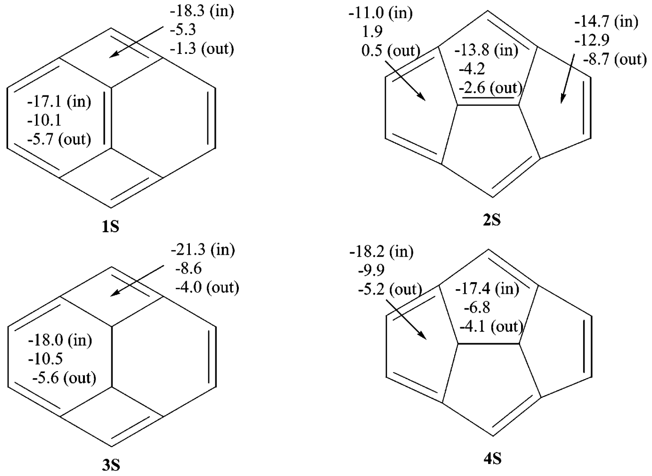

FIGURE 7. GIAO-B3LYP/6-311++G**//B3LYP/6-31G* computed NICS values for the ground-state singlets of **1**−**4**. NICS(0), NICS (in), and NICS (out) are computed, as suggested by Schleyer and co-workers,[1] at the distance-averaged center of each ring and at the point 1.0 Å inside and outside of each bowl-shaped molecule, respectively. NICS values for the triplets, dianions, and dications can be found in the Supporting Information.

Another useful probe of aromaticity is the nucleus-independent chemical shift values (NICS), first introduced by Schleyer et al. in 1996.[5] While not without controversy,[33] NICS is routinely employed for probing the aromatic character of polycyclic molecules.[1,24,34−45] NICS values at the center of each ring, and 1.0 Å inside and outside of each ground-state, bowl-shaped molecule, are shown in Figure 7. Large negative and large positive NICS values indicate aromaticity and antiaromaticity, respectively. For calibration, the NICS value at the ring center in benzene is −11.5, and in antiaromatic planar cyclooctatetraene the NICS value is 29.2.[5] In another polycyclic bowl-shaped molecule, $C_{30}H_{12}$, the sum of the NICS values are −38.3 inside and −11.8 outside of the bowl.[24]

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(27) Schleyer, P. v. R. *Chem. Rev.* **2001**, *101*, 1115.
(28) Kruszewski, J.; Krygowski, T. M. *Tetrahedron Lett.* **1972**, *36*, 3839.
(29) Krygowski, T. M. *J. Chem. Inf. Comput. Sci.* **1993**, *33*, 70.
(30) Krygowski, T. M.; Cyranski, M. K. *Chem. Rev.* **2001**, *101*, 1385.
(31) Krygowski, T. M.; Cyranski, M. K. *Tetrahedron* **1996**, *52*, 1713.
(32) Krygowski, T. M.; Cyranski, M. K. *Tetrahedron* **1999**, *55*, 11143.
(33) Aihara, J.-i. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 101.
(34) Pogodin, S.; Agranat, I.; Fetzer, J. C. *Polycyclic Aromat. Compd.* **2004**, *24*, 151.
(35) De Proft, F.; Fowler, P. W.; Havenith, R. W. A.; Schylener, P. v. R.; Lier, G. V.; Geerlings, P. *Chem.-Eur. J.* **2004**, *10*, 940.
(36) Cyranski, M. K.; Krygowski, T. M.; Katritzky, A. R.; Schleyer, P. v. R. *J. Org. Chem.* **2002**, *67*, 1333.
(37) Alkorta, I.; Rozas, I.; Elguero, J. *Tetrahedron* **2001**, *57*, 6043.
(38) Juselius, J.; Sundholm, D. *Phys. Chem. Chem. Phys.* **2001**, *3*, 2433.
(39) Schulman, J. M.; Disch, R. L.; Jiao, H.; Schleyer, P. v. R. *J. Phys. Chem. A* **1998**, *102*, 8051.
(40) Tantillo, D. J.; Hoffmann, R.; Houk, K. N.; Warner, P. M.; Brown, E. C.; Henze, D. K. *J. Am. Chem. Soc.* **2004**, *126*, 4256.
(41) Bong, D. T.-Y.; Chan, E. W. L.; Diercks, R.; Dosa, P. I.; Haley, M. M.; Matzger, A. J.; Miljanic, O. S.; Vollhardt, K. P. C. *Org. Lett.* **2004**, *6*, 2249.
(42) Zhao, Y.; Li, S.; Xu, W.-G.; Li, Q.-S. *J. Phys. Chem. A* **2004**, *108*, 4887.
(43) Lee, V. Y.; Takanashi, K.; Matsuno, T.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2004**, *126*, 4758.
(44) Bui, B. H.; Schreiner, P. R. *Org. Lett.* **2003**, *5*, 4871.
(45) Havenith, R. W. A.; Jiao, H.; Jenneskens, L. W.; Lenthe, J. H. v.; Sarobe, M.; Schleyer, P. v. R.; Kataoka, M.; Necula, A.; Scott, L. T. *J. Am. Chem. Soc.* **2002**, *124*, 2363.

Symmetry considerations, bond length alternations, and NICS values all indicate that the ground states of **1**, **3**, and **4** are very aromatic; however, HOMA values determined using peripheral bonds indicate that **3S** and **4S** are aromatic but that **1S** is less aromatic. NICS values for the ground state of **2** strongly indicate aromaticity; however, bond localization, symmetry, and HOMA values argue otherwise. As shown in Table 5, the HOMA values for **3S** and **4S** are close to that of naphthalene; the HOMA of **1S** is much smaller (0.387), while that of **2S** is so close to zero to be considered nonaromatic. HOMA values typically correlate well with NICS measures of aromaticity;[46] however, for these bowl-shaped molecules, only the values for the ground-state singlets show reasonably good correlation with ∑NICS (for **1S**−**4S**; $R^2 = 0.844$; for ∑NICS(in)).

Why this disagreement? It is quite likely that the bowl-shaped geometries of these systems reduce the utility of the HOMA index for gauging aromaticity, mainly because the average bond length differs so much from the R_{opt} value of 1.388. One of the ways to lessen strain and improve π overlap in bowl-shaped molecules is to lengthen perimeter bonds and shorten interior bonds, thereby flattening the molecule. As shown in Figure 1, the perimeter bonds in **1S**−**4S** are considerably longer than the HOMA R_{opt} value of 1.388. This leads to large EN values that overestimate the deviation from an "ideal" aromatic geometry. However, the index has been applied to other bowl-shaped molecules with some success.[30,47−49] The GEO term may be more applicable in these systems; Table 5 shows the GEO values for **1S**, **3S**, and **4S** are all smaller than that in naphthalene. There is a strong correlation between GEO and ∑NICS (for **1S**−**4S**; $R^2 = 0.996$; for ∑NICS(in)).

For **1** and **2**, removing two electrons "turns off" aromaticity, as indicated by an increase in bond length alternation (larger GEO values) and large positive NICS values (given in the Supporting Information). Saturation of the interior bond of **1** does not change the aromatic character significantly, as judged by the NICS values. Saturation of the interior bond of **2** decreases the NICS values and the bond alternation along the periphery, indicating an increase in aromaticity along the 10 π periphery. The HOMA values for the dianions indicate antiaromaticity, while the NICS values indicate some aromaticity for $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$. The dication of **3** shows unusually large negative NICS values inside the bowl-shaped molecule, and this, along with the structure, indicates significant homocyclopropenium ion character in the cyclobutyl rings.[50]

Conclusions

We have determined that molecules **1**−**4** are stable, bowl-shaped molecules on the B3LYP/6-311++G**//B3LYP/6-31G* surface. The ground-state pentalene isomers, **2** and **4**, are more stable than the naphthalene isomers, **1** and **3**, by 13 and 28 kcal/mol, respectively. Singlets, triplets, dications, and dianions of **1**, **3**, and **4** adopt C_{2v} structures, while the dianion is the only form of **2** to adopt a C_{2v} structure; all others adopt C_s symmetry. We have identified the transition states for ring inversion of **1** and **2**; **1TS** is planar and lies 30.9 kcal/mol higher in energy than the ground state, while **2TS** is nonplanar and lies 46.6 kcal/mol higher in energy than **2S**. NICS values for **1S**, **3S**, and **4S** point to aromaticity in these molecules; however, bond length alternations and symmetry considerations for **2S** do not indicate aromaticity.

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Supporting Information Available: Tables of HOMA values for **1**−**4** calculated (1) including only periphery bonds, (2) including all bonds, and (3) for each individual ring; POAV for interior atoms of **1** and **2**; NICS information for **1**−**4**, and Cartesian coordinates and absolute energies for all optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(46) Krygowski, T. M.; Cyranski, M. K.; Czarnocki, Z.; Hafelinger, G.; Katritzky, A. R. *Tetrahedron* **2000**, *56*, 1783.

(47) Bodwell, G. J.; Bridson, J. N.; Cyranski, M. K.; Kennedy, J. W. J.; Krygowski, T. M.; Mannion, M. R.; Miller, D. O. *J. Org. Chem.* **2003**, *68*, 2089.

(48) Salcedo, R.; Sansores, L. E.; Picazo, A.; Sanson, L. *J. Mol. Struct.* **2004**, *678*, 211.

(49) Poater, J.; Fradera, X.; Duran, M.; Sola, M. *Chem.-Eur. J.* **2003**, *9*, 1113.

(50) The 10−1−2 angle in **3S** is 91°, and in $\mathbf{3}^{2+}$ it is 83°, consistent with this idea.