A computational study of sulfur bridged cyclooctatetraenophanes

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Abstract

Calculations of several thiacyclooctatetraenophanes predicted, as part of their overall geometry, substantial flattening of the cyclooctatetraene (COT) structures relative to the tub conformation generally associated with the COT molecule. The COT structures were approximately parallel to each other and the interplanar distances were predicted to be within 2.787–2.803 Å at the DFT/UB3YLP level of calculation. DFT/UB3LYP optimized geometries afforded significant delocalization of the COT structures in each of the thiacyclooctatetraenophanes. Hartree–Fock (HF) methods and the semi-empirical Austin Model 1 (AM1) method deviated significantly from the DFT/UB3LYP optimized geometries. Cyclooctatetraenes can undergo reversible sizing by oxidation and reduction reactions to form the aromatic dication and aromatic dianion, respectively, which could then be used to prepare molecular backbones for polymeric organometallic molecular wires. The number of bridges and the introduction of the sulfur atom have been investigated to provide disparate synthetic routes.
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1. Introduction

The ground state geometry for COT is a D_{2d} tub-shaped conformer with alternating single (1.43 Å) and double bonds (1.33 Å) [1]. It undergoes a variety of dynamic processes such as ring inversion, bond shifting and a plethora of isomerizations [2]. These processes make COT a mechanistically interesting molecule to study. The commonly recognized transition state for the process of ring inversion is a planar localized structure with D_{4h} symmetry [3–6] while the bond shifting mechanism passes through a transition state with D_{8h} symmetry [4–7].

A great deal of interest has been recently reported concerning 8π cyclic systems [8–13] and planar cyclooctatetraenes [3,14–16]. Isolation and characterization of perfluorotetracyclobuta-cyclo-octatetraene [17a–c] and Komatsu et al. synthesis of a planar cyclooctatetraene annelated with bicycle[2.1.1]hex-2-ene [18,19] are the best synthetic examples of proposed [20,21] planar delocalized diradicaloid cyclooctatetraenes. However, these synthesized cyclooctatetraenes utilize small annelating rings [18] to advance planarity. Although some delocalization

occurs as shown by X-ray analysis [17a] of its bond lengths, small ring effects inhibit bond shifting in the planar COT derivatives. Therefore, it would be advantageous to construct a molecule with a geometry that has the propensity to be planar but does not suffer from these ring effects. We previously investigated the annelating effects on 4π cyclic systems [22] and herein extend these tools to 8π cyclic systems.

The thiacyclooctatetraenophanes **1–5** (Fig. 1) were investigated for the flattening and delocalization of their COT rings and interplanar distances between these rings. Several two-deck systems have been previously synthesized to investigate cyclophanes. Paquette and Kesselmayer [23] two-deck [2_2](1,5)cyclooctatetraenophane was synthesized from [6.3.3]-propellenediones and as expected, the COT units were in tub conformations. Two additional two-deck systems by Garbe and Boeckelheide [24] [2_2](1,6)cyclooctatetraenyl(1,4)cyclophane and [2_4](1,2,5,6)cyclooctatetraenyl(1,2,4,5)cyclophane, were found to have the familiar tub conformation as well.

The electron-rich cyclooctatetraenophanes molecules proposed herein will provide COT moieties with a high degree of flattening and delocalization. The purpose of this study is to find synthetically viable cyclooctatetraenophanes to be used as molecular wire backbones. Sansores and co-workers [25,26] provided several theoretical examples of superphanes with ring sizes
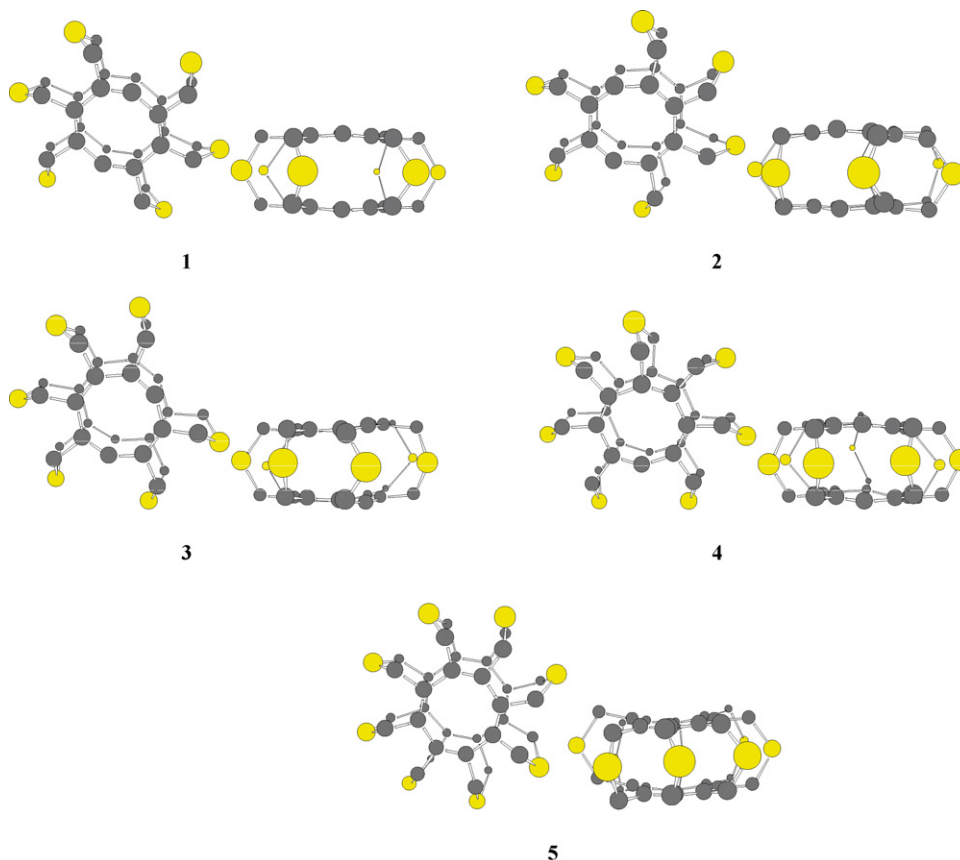
Fig. 1. Top and side views of DFT/B3LYP (6-31G(d,p)) optimized geometries for the thiacyclooctatetraenophanes (**1–5**).

from 3 to 7 adapting symmetric geometries and suggested their use as molecular wires. However, these superphanes are all synthetically difficult to prepare [25,26]. The cyclooctatetraenophanes investigated in this article possess sulfur bridges that provide an accessible entry to their assemblage. $[3_6](1,2,3,5,6,7)$-Hexathiacyclooctatetraenophane **1**, exo-$[3_6](1,2,3,4,6,7)$-hexathiacyclooctatetraenophane **2**, endo-$[3_6](1,2,3,4,6,7)$-hexathiacyclooctatetraenophane **3**, $[3_7](1,2,3,4,5,6,7)$-heptathiacyclooctatetraenophane **4** and $[3_8](1,2,3,4,5,6,7,8)$-octathiacyclooctatetraenophane **5** vary in respect to the number and location of these sulfur bridges.

2. Methodology

The relative flattening (F_r) of each individual COT structure with respect to the tub conformation was calculated by first summing the absolute values of each bonded dihedral angle in the ring. Each bonded dihedral angle in the COT structures for **1–5** was measured and assigned to the variable D_{phane_i}, where $i = 1, 2, \ldots, 8$ and corresponds to the first carbon atom in the four carbons involved in the dihedral angle. The summation of the absolute values of the bonded dihedral angles was then:

$$\sum_{i=1}^{8}|D_{phane_i}| = D_{phane}$$

The same procedure was also performed on a COT molecule such that:

$$\sum_{i=1}^{8}|D_{cot_i}| = D_{cot}$$

The relative flattening could then be defined as:

$$F_r = \frac{D_{phane}}{D_{cot}}$$

Arithmetic mean values for the interplanar distance for each structure were calculated by averaging the distances between the corresponding atoms in the upper and lower rings. Standard deviations were calculated utilizing the biased standard deviation formula. The standard deviation of the interplanar distances for each compound gave an indication of the planarity of stacking since the individual rings were ostensibly flattened.

Semi-empirical Austin Model 1 (AM1) [27] and ab initio calculations at the levels RHF/6-31G(d) and RHF/6-31G(d,p) were performed using Spartan '04 Windows [28] and Gaussian '03 [29]. Density functional theory (DFT) [30] calculations employed the B3LYP method [31,32] with the 6-31G(d,p) basis set. All cyclooctatetraenophanes were optimized beginning from tub-shaped COT conformers. All structures were determined to be energetic minima from frequency calculations.
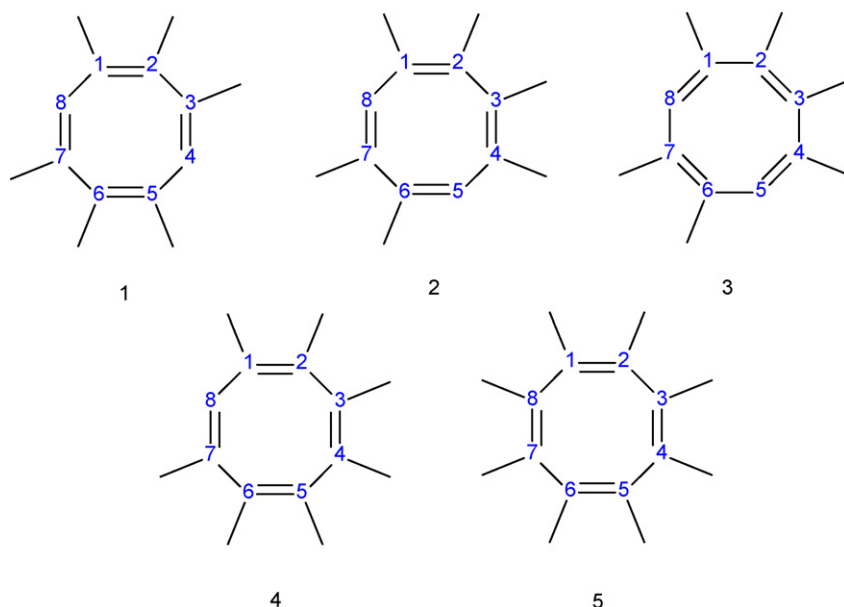
Fig. 2. Top view of COT structures (upper ring) in **1**–**5** with carbons labeled and positions of sulfur bridges shown.

All initial geometries of the structures were tested for their wavefunction stability and showed a slight RHF/UHF instability (ca. 2–3 kcal/mol). Upon further optimization at the UB3LYP level using the unrestricted wavefunction new optimized geometries were obtained that had a significantly lower energy (ca. 20–25 kcal/mol). These structures had no net spin, so that the B3LYP and UB3LYP methods yielded the same energy and the stability test was passed. The main change in the geometries was a closer approach of the two eight-membered rings (in the range of 2.80 Å compared with 3.00 Å for the initial structures) and a disappearance of bond alternation.

3. Results and discussion

Fig. 1 shows the DFT/B3LYP (6-31G(d,p)) optimized geometries of the five thiacyclophanes **1**–**5**. The pinwheel or spiral galaxy-shaped molecules possessed a high degree of symmetry due to the flattening of the individual COT rings. There were both endo and exo tautomers for the $[3_6](1,2,3,4,6,7)$-hexathiacyclooctatetraenophane except for the DFT/UB3LYP optimized geometries as the two structures merged at this level of theory due to the delocalization of their bond lengths. Studies were not undertaken to account for the possibility of endo/exo geometry combinations which should have a negligible effect on overall planarity of the molecule. Fig. 2 shows the labeling scheme for the carbon atoms found in the COT substructures as well as the locations of the sulfur bridges attached to these rings for **1**–**5**.

There was significant delocalization of the DFT/UB3LYP predicted bond lengths in all structures. **1** was the most delocalized as evident from the standard deviation of the mean of the carbon–carbon bonds in the COT substructures found within the molecule (Tables 1 and 2). This delocalization was not predicted by any of the other levels of theory including the DFT/B3LYP method. Table 3 shows the large disparities

between the geometries predicted for **5** by each level of calculation as well as the bond alternation predicted by semi-empirical AM1, RHF/6-31G(d), RHF/6-31G(d,p) and DFT/B3LYP calculations. While the geometry of **5** is explicitly

Table 1
DFT/UB3LYP optimized average bond lengths for upper and lower COT rings for **1**–**5**

	Upper ring average bond length (Å)	Lower ring average bond length (Å)
1	1.421 (0.008)	1.423 (0.007)
2/3	1.424 (0.017)	1.424 (0.017)
4	1.435 (0.027)	1.436 (0.023)
5	1.453 (0.011)	1.456 (0.012)

Standard deviations are shown in parentheses.

Table 2
DFT/UB3LYP optimized bond lengths (Å) of COT rings in **1**–**5**

	1	**2/3**[a]	**4**	**5**
C_1–C_2	1.43	1.44	1.43	1.45
C_2–C_3	1.42	1.45	1.46	1.47
C_3–C_4	1.41	1.44	1.44	1.46
C_4–C_5	1.41	1.42	1.48	1.45
C_5–C_6	1.43	1.41	1.45	1.45
C_6–C_7	1.43	1.41	1.42	1.46
C_7–C_8	1.42	1.40	1.39	1.45
C_8–C_1	1.42	1.42	1.41	1.43
C_{11}–C_{12}	1.42	1.45	1.43	1.45
C_{12}–C_{13}	1.43	1.44	1.44	1.45
C_{13}–C_{14}	1.42	1.42	1.48	1.47
C_{14}–C_{15}	1.42	1.41	1.46	1.47
C_{15}–C_{16}	1.41	1.41	1.44	1.46
C_{16}–C_{17}	1.43	1.40	1.42	1.43
C_{17}–C_{18}	1.43	1.42	1.42	1.46
C_{18}–C_{11}	1.42	1.44	1.40	1.46

[a] DFT/UB3LYP optimized endo and exo tautomers merged into the same structure.

Table 3
[3$_8$](1,2,3,4,5,6,7,8)Octathiacyclooctatetraenophane bond lengths (Å)/bond angles (°) from geometries predicted by five different levels of calculation

	AM1	6-31G*	6-31G**	B3LYP (6-31G**)	UB3LYP (6-31G**)
C$_1$–C$_2$	1.37	1.36	1.36	1.39	1.45
C$_2$–C$_3$	1.47	1.52	1.52	1.51	1.47
C$_3$–C$_4$	1.37	1.36	1.36	1.38	1.46
C$_4$–C$_5$	1.48	1.56	1.56	1.55	1.45
C$_5$–C$_6$	1.37	1.36	1.36	1.39	1.45
C$_6$–C$_7$	1.48	1.56	1.56	1.54	1.46
C$_7$–C$_8$	1.37	1.36	1.36	1.39	1.45
C$_8$–C$_1$	1.47	1.55	1.55	1.53	1.43
C$_1$–C$_2$–C$_3$	132.36	130.44	130.57	130.34	132.56
C$_2$–C$_3$–C$_4$	134.51	134.64	134.59	134.20	135.78
C$_3$–C$_4$–C$_5$	134.82	136.21	136.23	136.30	137.25
C$_4$–C$_5$–C$_6$	135.38	132.40	132.49	131.82	132.19
C$_5$–C$_6$–C$_7$	134.84	133.62	133.68	133.84	132.47
C$_6$–C$_7$–C$_8$	134.07	135.20	135.16	134.88	135.00
C$_7$–C$_8$–C$_1$	134.41	135.04	135.04	135.26	137.47
C$_8$–C$_1$–C$_2$	135.62	134.75	134.77	134.68	131.04

shown as an example of these differences, similar trends were found in all structures (**1–5**). The DFT/UB3LYP carbon–carbon bond lengths of structures **1–5** ranged between 1.39 and 1.46 Å (Table 2). The thiacyclophanes **2** and **3** geometries merged due to delocalization at this level of theory and their bond lengths ranged between 1.40 and 1.45 Å.

The relative flattening of the COT structures in the cyclooctatetraenophanes were calculated (Table 4) with respect to the tub conformation typically associated with the COT molecule. **2/3** was the closest to planar with an average relative flattening of 0.018 (Table 4) at the UB3YLP(6-31G**) level of calculation. The average of the relative flattening refers to an average taken between the two COT rings present in each thiacyclophane. This very small average relative flattening value meant that **2/3** was almost completely flat as it possessed dihedral angles with a magnitude of $1.34°$ or less. **1** possessed the next smallest average relative flattening ($F_{\mathrm{r,ave}} = 0.021$) followed by **4** ($F_{\mathrm{r,ave}} = 0.354$) and then **5** ($F_{\mathrm{r,ave}} = 0.454$). As evident from Table 4, the Hartree–Fock, semi-empirical AM1 and DFT/B3LYP methods predicted less flattened cyclooctatetraenophane geometries.

Another important parameter in our study was the interplanar distance between the two COT rings found in each molecule. The interplanar distances for the five thiacyclooctatetraenophanes ranged between 2.798 and 2.803 Å (Table 5) at the UB3YLP level of calculation. This distance is significantly shorter than the van der Waals radii [33] for two carbon atoms of 3.4 Å and could

allow for electronic communication between the rings. This communication would be required for these cyclooctatetraenophanes to serve as backbones for molecular wires. Since the COT structures were reasonably close to planar and the standard deviations were very small (especially at the UB3LYP level) with respect to the mean interplanar distances, the COT planes were approximately parallel to each other. This is also evident in Fig. 1. As with the other properties measured, the DFT/UB3LYP predicted interplanar distances deviated significantly from the interplanar distances predicted by the other levels of calculation (Table 5).

COT can undergo two-electron oxidation to form the aromatic dication or undergo a two-electron reduction to form the aromatic dianion [34]. Therefore, since the thiacyclooctatetraenophanes **1–5** have short interplanar distances and substantially flattened 8π systems, the resulting aromatic materials should result in transannular interactions [23] and therefore would be candidates to prepare polymeric organometallic molecular wires (Fig. 3).

We are currently investigating the syntheses of **1–5** as molecular wire backbones. These cyclophanes have ligands of three atoms in length bridging the two COT planes. Therefore, they form 10-membered dithiaether annelating rings. This is a very large ring size to impart any constraining effects on the COT structures. Perfluorotetracyclobutacyclo-octatetraene is reported [17b] to be planar however, tetrakis(perfluorocyclopenta)cyclooctatetraene) is reported as a tub conformer.

Table 4
Average relative flattening^a (F_r)

Molecule	AM1	6-31G*	6-31G**	B3LYP (6-31G**)	UB3LYP (6-31G**)
1	0.619	0.257	0.257	0.266	0.021
2	0.693	0.410	0.402	0.376	0.018^b
3	0.725	0.464	0.443	0.397	0.018^b
4	0.743	0.467	0.455	0.472	0.354
5	0.456	0.524	0.518	0.578	0.454

^{a} Average taken between the two COT rings present in each molecule.
^{b} DFT/UB3LYP optimized exo and endo tautomers merged into the same structure.

Table 5
Mean interplanar distances (Å)

Molecule	AM1	6-31G*	6-31G**	B3LYP (6-31G**)	UB3LYP (6-31G**)
1	3.326 (0.222)	3.242 (0.103)	3.238 (0.102)	3.233 (0.105)	2.793 (0.010)
2	3.282 (0.185)	3.235 (0.095)	3.238 (0.097)	3.218 (0.096)	2.798 (0.008)[a]
3	3.416 (0.277)	3.245 (0.141)	3.246 (0.140)	3.218 (0.128)	2.798 (0.008)[a]
4	3.268 (0.274)	3.151 (0.143)	3.177 (0.131)	3.171 (0.138)	2.803 (0.008)
5	3.089 (0.047)	3.060 (0.019)	3.057 (0.017)	3.047 (0.020)	2.787 (0.006)

Standard deviations are shown in parentheses.

[a] DFT/UB3LYP optimized exo and endo tautomers merged into the same structure.
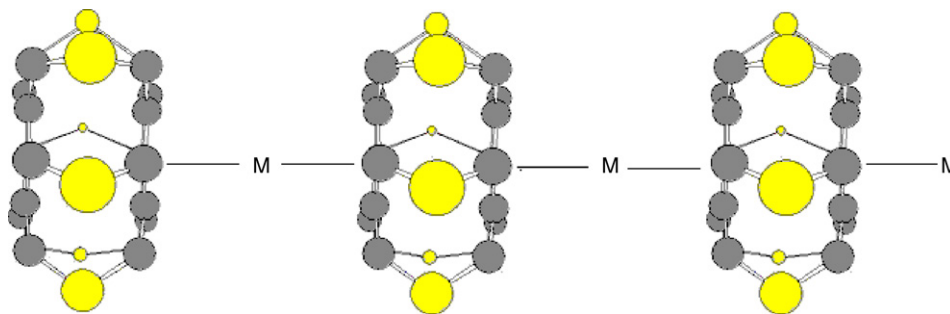

Fig. 3. Polymeric organometallic molecular wire made from the proposed thiacyclophanes.

Small ring effect mechanisms from perfluorotetracyclobutacyclo-octatetraene that would prohibit bond shifting should not be evident in the proposed cyclophanes.

4. Conclusion

The cyclooctatetraenophanes herein are found to consist of rings that exhibit substantial flattening and delocalization. Structures **1** and **2/3** exhibit these properties to the greatest degree and will be good candidates for molecular wire building blocks. Further studies will investigate the communication between the rings and molecular strain in these molecules.

References

[1] M. Traetteberg, The molecular structure of 1,3,5,7-cyclo-octatetraene, Acta Chem. Scand. 20 (1966) 1724–1726.

[2] L. Paquette, The current view of dynamic change within cyclooctatetraenes, Acc. Chem. Res. 26 (1993) 57–62.

[3] F. Klärner, About the antiaromaticity of planar cyclooctatetraene, Angew. Chem. Int. Ed. 40 (2001) 3977–3981.

[4] D.A. Hrovat, W.T. Borden, CASSCF calculations find that a D8h geometry is the transition state for double bond shifting in cyclooctatetraene, J. Am. Chem. Soc. 114 (1992) 5879–5881.

[5] P.G. Wenthold, D.A. Hrovat, W.T. Borden, W.C. Lineberger, Transition-state spectroscopy of cyclooctatetraene, Science 272 (1996) 1456–1459.

[6] F.A.L. Anet, J.R. Bourn, Y.S. Lin, Ring inversion and bond shift in cyclooctatetraene derivatives, J. Am. Chem. Soc. 86 (1964) 3576–3577.

[7] F.A.L. Anet, The rate of bond change in cyclooctatetraene, J. Am. Chem. Soc. 84 (1962) 671–672.

[8] L.E. Sansores, R. Salcedo, L. Fomina, P. Guadarrama, Electronic structure study of planar conjugated eight-membered ring compounds, J. Mol. Struct.-Theochem 389 (1997) 217–226.

[9] R. Salcedo, L.E. Sansores, L. Fomina, Theoretical study about the radical and anions of [8]annulenes, J. Mol. Struct.-Theochem 397 (1997) 159–166.

[10] H.N. Wong, P. Garratt, F. Sondheimer, Unsaturated eight-membered ring compounds. XI. Synthesis of *sym*-dibenzo-1,5-cyclooctadiene-3,7-diyne and *sym*-dibenzo-1,3,5-cyclooctatrien-7-yne, presumably planar conjugated eight-membered ring compounds, J. Am. Chem. Soc. 96 (1974) 5604–5605.

[11] R. Destro, T. Pilati, M. Simonetta, The structure and electron density of *sym*-dibenzo-1,5-cyclooctadiene-3,7-diyne by X-ray analysis at three different temperatures, Acta Crystallogr. Sect. B B33 (1977) 447–456.

[12] R. Destro, T. Pilati, M. Simonetta, Crystal structure of 5,6,11,12-tetradehydrodibenzo[*a,e*]cyclooctene (*sym*-dibenzo-1,5-cyclooctadiene-3,7-diyne), J. Am. Chem. Soc. 97 (1975) 658–659.

[13] R. de Graaf, S. Gorter, C. Romers, H. Wong, F. Sondheimer, Crystal structure of 5,6-didehydrodibenzo[*a,e*]cyclo-octene, J. Chem. Soc., Perkin Trans. 2 3 (1985) 478–480.

[14] K. Takashi, Challenge of antiaromatic cyclooctatetraene, Kagaku 57 (2002) 64–65.

[15] O. Ermer, F.G. Klarner, M. Wette, Planarization of unsaturated rings: cycloheptatriene with a planar seven-membered ring, J. Am. Chem. Soc. 108 (1986) 4908–4911.

[16] P. Schleyer, H. Jiao, H. Sulzbach, H. Schaefer, Highly aromatic planar *all-cis*-[10]annulene derivatives, J. Am. Chem. Soc. 118 (1996) 2093–2094.

[17] (a) F.W.B. Einstein, A.C. Willis, W.R. Cullen, R.L. Soulen, Perfluorotetracyclobutacyclo-octatetraene; a planar eight-membered ring system; X-ray crystal structure, J. Chem. Soc. Chem. Commun. 11 (1981) 526–528;
(b) F. Gerson, W. Huber, P. Merstetter, G. Persy, R.L. Soulen, C. Spondlin, J. Wirz, Powerful oxidizing properties of a planar [8]annulene: tetrakis(perfluorocyclobuta)cyclooctatetraene and its radical anion, Helv. Chim. Acta 82 (1999) 1434–1444;

(c) R.L. Soulen, S.K. Choi, J.D. Park, Copper coupling of I-chloro-2-iodo- and 1,2-di-iodo-perfluorocycloalkenes, J. Fluorine Chem. 3 (1973/1974) 141–150.

[18] K. Komatsu, T. Uto, T. Nishinaga, Novel cyclooctatetraene radical cation planarized by full annelation with bicyclo[2.1.1]hexene units, Org. Lett. 6 (2004) 4611–4613.

[19] K. Komatsu, A. Matsuura, Efficient synthesis of benzene and planar cyclooctatetraene fully annelated with bicyclo[2.1.1]hex-2-ene, J. Am. Chem. Soc. 123 (2001) 1768–1769.

[20] K. Baldridge, J. Siegel, Directing power of cyclobutenoid annelations on the double bonds of planar cyclooctatetraene, J. Am. Chem. Soc. 124 (2002) 5514–5517.

[21] K. Baldridge, J. Siegel, Quantum mechanical designs toward planar delocalized cyclooctatetraene: a new target for synthesis, J. Am. Chem. Soc. 123 (2001) 1755–1759.

[22] S.E. McKay, P. Kiprof, A.B. Brown, The effects of annulation on cyclobutadiene bond alternation: a comparative study of semi-empirical and ab initio methods, J. Mol. Struct.-Theochem 368 (1996) 197–204.

[23] L.A. Paquette, M.A. Kesselmayer, $[2_2](1,5)$Cyclooctatetraenophane, J. Am. Chem. Soc. 112 (1990) 1258–1259.

[24] J.E. Garbe, V. Boeckelheide, A study of the syntheses and properties of $[2_2](1,6)$cyclooctatetraenyl(1,4)cyclophane and $[2_4](1,2,5,6)$cyclooctatetraenyl(1,2,4,5)cyclophane, J. Am. Chem. Soc. 105 (1983) 7384–7388.

[25] N. Mireles, R. Salcedo, L. Sansores, A. Martínez, Theoretical description of aromaticity in superphane cages, Int. J. Quantum Chem. 80 (2000) 258–263.

[26] N. Mireles, L. Sansores, A. Martínez, R. Salcedo, Theoretical study of 4-, 5-, 6-, and 7-member ring superphane cages with a metal inside, Int. J. Quantum Chem. 94 (2003) 51–56.

[27] M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, J.J.P. Stewart, Development and use of quantum mechanical molecular models. 76. AM1: a new general purpose quantum mechanical molecular model, J. Am. Chem. Soc. 107 (1985) 3902–3909.

[28] Spartan '04 Windows, Version 1.0.1, Wavefunction Inc., Irvine, CA, 2004

[29] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision C.02, Gaussian Inc., Wallingford, CT, 2004.

[30] W. Kohn, L.J. Sham, Self-consistent equations including exchange and correlation effects, Phys. Rev. 140 (1965) A1133–A1138.

[31] A.D. Becke, Density-functional thermochemistry. III. The role of exact exchange, J. Chem. Phys. 98 (1993) 5648–5652.

[32] C. Lee, W. Yang, R.G. Parr, Development of the Colle–Salvetti correlation-energy formula into a functional of the electron density, Phys. Rev. B 37 (1988) 785–789.

[33] A. Bondi, van der Waals volumes and radii, J. Phys. Chem. 68 (1964) 441–451.

[34] G.A. Olah, J.S. Staral, G. Liang, L.A. Paquette, W.P. Melega, M.J. Carmody, Novel aromatic systems. 8. Cyclooctatetraene dications, J. Am. Chem. Soc. 99 (1977) 3349–3355.