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Quantum Mechanical Designs toward Planar Delocalized Cyclooctatetraene: A New Target for Synthesis

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Abstract: Ab initio and hybrid density functional quantum mechanical computation are applied to the structure and energetics of a series of annelated cyclooctatetraenes. Tetrakis-cyclobuteno, perfluorocyclobuteno or bicyclo-[2.1.1]hexeno annelations result in planar structures with distinct exo and endo valence tautomers of the double bonded cycle. The contribution of each basic annelation to the exo/endo relative energy is estimated. An additivity scheme for approximating the energy of a mixed system is developed and compared to the quantum mechanical prediction. Bis bicyclic annelation to the a and d positions creates "valence tautomeric frustration" and strongly perturbs the molecular structure. This phenomenon leads to a general design for a planar cyclooctatetraenes where the "delocalized" diradicaloid state is the minimum energy form. These compounds are seen as excellent targets for chemical synthesis.

The standard view of cyclooctatetraene (**1**) is that of a molecule with a tub shape undergoing two dynamic processes: (I) tub-inversion and (II) valence-bond shifting (Figure 1).[1−4] Colloquially, the bond-localized nonplanar structure of **1** is ascribed to "anti-aromatic" character of [4*n*]-annulenes in general. Given our recent success in using bicyclic annelations to create a bond-length alternate benzene,[5,6] and related [4*n*+2]-annulenes,[7,8] it seemed worthy to apply similar annelation strategies in pursuit of planar symmetric cyclooctatetraene.[9,10]

The energy hypersurface of **1** is a double-welled potential in the tub-inversion, as well as in the bond-shift coordinate.[11] The bond-localized nonplanar "tub" form (D_{2d}) is the global minimum, and the planar delocalized D_{8h} form is a saddle-point of relatively high energy (∼14 kcal/mol).[12,13] In addition, the tub (D_{2d}) or localized-flat (D_{4h}) forms adopt a closed-shell singlet electronic configuration. The flat delocalized D_{8h} form could be viewed as "triplet-aromatic;"[14,15] however, a general phenomenon in "disjoint" singlet diradicals has been shown to stabilize the open-shell singlet in **1**.[16−18] On the basis of these characteristic electronic states and the perturbations induced by bicyclic annelations, it is our contention that it should be possible to create a planar delocalized diradicaloid cyclooctatetraene.

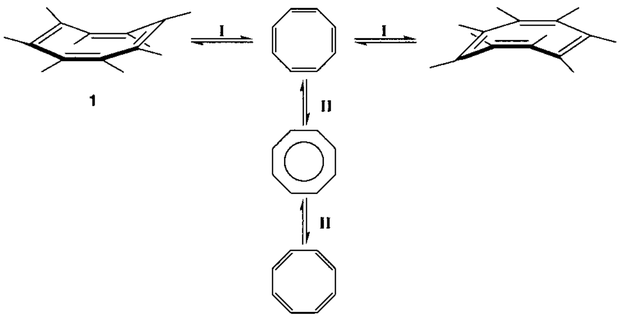

Figure 1. The tub-inversion (I) and valance-bond shift (II) processes in **1**.

Computational Considerations

All calculations have been carried out using the GAMESS,[19] Gaussian98,[20] and MOLPRO[21] software packages, running on the hardware facilities at the San Diego Supercomputer Center, including a generous amount of time donated by Compaq Inc. The molecular

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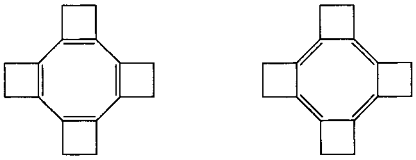
structures were determined using a variety of levels of theory to establish self-consistency in terms of basis sets as well as effects of dynamic correlation. Wave function-based methods were considered, specifically Hartree−Fock (HF), second-order Møller−Plesset perturbation theory,[22] coupled cluster theory with all single and double substitutions augmented by a quasi-perturbative accounting of triple excitations (CCSD(T)),[23] and conventional multiconfigurational SCF (MCSCF).[24,25] Hybrid density functional theory (HDFT) methods, which constitute a known improvement over “pure” DFT methods via inclusion of the exact HF exchange based on Kohn−Sham orbitals,[26] were also considered. The HDFT methods employed Becke’s three parameter hybrid exchange functional[27] in combination with the Perdew and Wang 1991 gradient-corrected nonlocal correlation functional, B3PW91.[28,29] The DZV(2d,p), DZ(2d,p), and DZV(2df,pd)[30] double-ζ valence quality basis sets were employed. These basis sets include 2d (2df) polarization functions on all heavy atoms, and p (pd) polarization functions on hydrogen atoms. These levels of theory have been previously shown by us to be reliable for structural determination in these types of compounds.[8] The nature of each stationary point was uniquely characterized by calculating and diagonalizing the matrix of energy second derivatives (Hessian) to determine the number of imaginary frequencies. This Hessian also provided the zero-point energy corrections used in the evaluation of the energetics. Stability checks were performed on the HF and HDFT wave functions.[31,32] Molecular orbital contour plots, used as an aid in the discussion of the results, were generated using the program 3D-PLTORB (San Diego, 3D version: 1997), and depicted using QMView.[33]

The multiconfigurational self-consistent-field wave function (CASSCF) computations were used to investigate several of the analogues studied. These MCSCF computations[24,25] were carried out using GAMESS, with the DZV(2d,p) basis set. An 8-electron-8-orbital active space was chosen [CASSCF(8,8)]. A modified virtual orbital computation[34] was performed for improved starting orbitals. The multiconfiguration quasi-degenerate perturbation theory (MCQDPT) method[35] was performed on top of the MCSCF for second order perturbation correction. This method is a multistate, as well as multireference perturbation theory. MCQDPT will recover dynamic correlation energy comparable to that of the CASPT2 methodology, and is thought to be potentially better for the prediction of singlet−triplet splittings. This latter point is a result of slightly different definition of the high-spin zeroth order functions.

Discussion

Table 1. HDFT Comparison of the Tautomeric (**I**/**II**) Structures and Energies for **2**, **3**, **4**, **5**, and **6**[a]

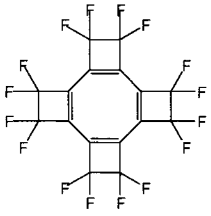


I **II**

	I			II			
cmpd	C−C$_{exo}$	C−C$_{endo}$	E$_{I}$	C−C$_{exo}$	C−C$_{endo}$	E_{II}	$E_{annelation}$
2	1.449	1.356	0	1.331	1.484	17.2	4.3
3	1.453	1.365	2.3	1.335	1.487	0	0.6
4	1.487/1.484	1.334	0	1.358/1.361	1.449	7.2	
5	1.449	1.355	32.7	1.339	1.496	0	8.2
6	1.446	1.364	13.6	1.336	1.493/1.479	0	

[a] Bond lengths are in Å and energies in kcal/mol.

Arguably, the nonplanarity of the tub conformation of cyclooctatetraene could come solely from angle strain, as a planar localized structure need not suffer antiaromatic destabilization. Opening the interior CCC angle to 135° from 120° would then result in a planar structure. Indeed, the crystal structure of perfluorotetracyclobutenocyclooctatetraene (**2**) has been reported as a flat molecule of ∼D_{4h} symmetry.[36] Our HDFT computations (B3PW91/DZ(2d,p)) of **2** and its parent hydrocarbon (**3**) also predict the minimum energy structure to be flat and D_{4h} symmetric (Table 1), thus, demonstrating that modulation of bond angles by annelations can be used to control the planarity (structure coordinate I) of derivatives of **1**.



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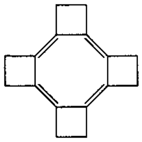

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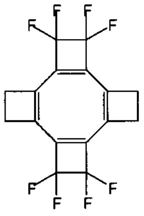

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Although **2** and **3** are planar, they remain D$_{4h}$ symmetric with strong bond length alternation ($|\delta_{exo-endo}| = 9.3$ and 15.2 pm, respectively) and leave open the question of the double-welled bond-shift coordinate (structure coordinate II). For these types of molecules, we can have two isomers differing only by the position of the double bonds with respect to the annelations (exo vs endo valence tautomers).[37] The X-ray crystal structure of **2** displays the double bonds within the four-membered ring annelations, contrary to classical strain arguments,[38] but consistent with our predictions on the basis of the electronic perturbations induced by such perfluorinations.[39]

Computations reveal two minima of D_{4h} symmetry for **2** and **3**. In accord with the experimental structures, tautomer **I** is lower in energy for **2**, by 17.2 kcal/mol, and tautomer **II** is lower for **3**, by 2.3 kcal/mol (cf. Table 1). Thus, the hydrocarbon shows a small preference to having the π bonds localized outside the annelations, whereas the energetic requirements for the fluorocarbon are substantially reversed. Assuming an equal contribution to the energy from each annelation, one would predict that each hydrocarbon annelation prefers exo double bonds by

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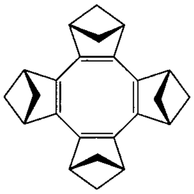
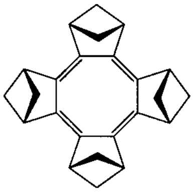
~0.6 kcal/mol, whereas the fluorocarbon annelations prefer endo double bonds by ~4.3 kcal/mol. Applying a simple additivity scheme to **4**, a mixed system with two hydrocarbon annelations and two fluorocarbon annelations, one finds two annelations favoring the exo tautomer by 0.6 kcal/mol and two favoring the endo isomer by 4.3 kcal/mol for an exo−endo energy difference of 7.4 kcal/mol in favor of the endo tautomer. These results, which come very close to those obtained from the computations for **4**, show that the fluorocarbon annelations are dominant and encourage the use of this additivity scheme in future designs.

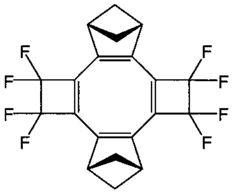
Previously, we had touted the special character of bicycloannelations, especially the bicyclo[2.1.1]hexeno fragment, for controlling bond length alternation in annulenes.[7,39] Computations on tetrakisbicyclo[2.1.1]hexenocyclooctatetraene (**5**) also predict a planar structure of D_{4h} symmetry. In **5**, the bond length alternation is more extreme than in **2** or **3**, and the lower energy tautomer is of form **II**, paralleling the chemistry of **3**. The energy difference between **5-I** and **5-II** (32.7 kcal/mol, or roughly 8−9 kcal/mol/annelation) is much greater than that for **3**. As in test compound **4**, we also calculated compound **6** in which the bicyclohexeno annelation is competed against the perflurocyclobuteno annelations. Here the additivity predicts the exo tautomer (**6-I**) in favor of the endo tautomer (**6-II**) by approximately 8−9 kcal/mol. The QM calculations indeed predict the exo form (**6-I**) as the favored tautomer, but by 13.6 kcal/mol.



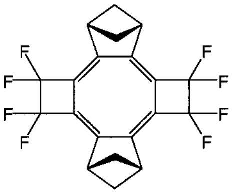
5-I (D_{2d})



5-II (D_{4h})



6-I (D_{2h})



6-II (D_{2h})

It would seem from these results that the bicycloannelation is able to induce a planar structure through angle deformations,[40] but these annelations should also interact strongly with the π orbitals in the central ring.[41−43] This supposition led us to ask whether bicyclic annelations could be placed so as to "frustrate" the valence tautomers and lead to a delocalized annulene (more precisely, could bicyclic annelation at bonds a and d result in a planar cyclooctatetraene ring with a single-well potential in the bond-shift coordinate). The design principle is clear, and the target is [*a*,*d*]bisbicyclo[2.1.1]hexenocyclooctatetraene (**7**) or a cognate (for example, **8**).

Table 2. MCSCF and HDFT Structures for Singlet and Triplet **7** and **8**[a]

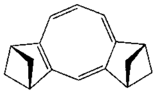
	singlet		triplet
cmpd	C_s	C_{2v}	C_{2v}
7 B3PW91/DZ(2d,p)	1.454, **1.360**, 1.451, 1.351, 1.470, 1.341, **1.508**, 1.340	1.393, **1.435**, 1.389, 1.410	1.390, **1.439**, 1.383, 1.410
7 MCSCF/DZV(2d,p)	1.467, **1.357**, 1.463, 1.350, 1.478, 1.343, **1.506**, 1.322	1.396, **1.434**, 1.393, 1.414	1.389, **1.454**, 1.377, 1.419
8 B3PW91/DZ(2d,p)	1.454, **1.365**, 1.439, 1.366, 1.482, 1.336, **1.508**, 1.346	1.396, **1.439**, 1.380, 1.425	1.393, **1.443**, 1.373, **1.427**

[a] Lengths are in Å starting from bond a−h; bold bond lengths are for the endo bonds.

Table 3. MCQDPT and HDFT Computed Relative (kcal/mol) Energetics for Structure **7**

method	singlet C_s	singlet C_{2v}	triplet C_{2v}
B3PW91/DZ(2d,p)	2.25	0.0	4.59
B3PW91/DZ(2d,p)+ZPE	4.29	0.0	6.09
B3PW91/DZV(2df,pd)//B3PW91/DZ(2d,p)	2.29	0.0	4.59
MCSCF/DZV(2d,p)	8.77	0.0	13.5
MCQDPT/DZV(2d,p)[a]	5.47	0.0	5.81

[a] MCQDPT/DZV(2d,p)//MCSCF/DZV(2d,p).



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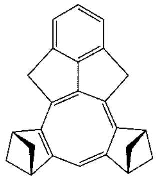

8

Computationally, localized singlet **7** and **8** are predicted to be essentially planar with a large HOMO/LUMO gap; the precise planar form with C_s symmetry is roughly 0.6 kcal/mol higher in energy than the corresponding nonplanar C_1 form.[44] In the C_{2v} "bond delocalized" structures the HOMO and LUMO converge, allowing three possible singlet configurations to exist, with electron populations of (2,0), (0,2), and (1,1), respectively. The configuration with both electrons occupying the same orbital lies ~17 kcal/mol higher than the C_s structure; however, the disjoint nature of the orbitals allows for the (1,1) configuration of the singlet to relieve electron repulsion and benefit from "dynamic spin polarization".[45] *In **7**, this stabilization is sufficient enough to drop the relative energy of the C_{2v} (1,1) singlet to lower than that of the C_s singlet, thus predicting singlet **7** to be a planar delocalized cyclooctatetraene (Tables 2 and 3).* Although hybrid DFT methods have been noted for their success in predicting singlet−triplet gaps, for example in substituted carbenes,[46−49] the method remains controversial. Multireference perturbation theory provides an important computational comparison. In particular, the method used here, MCQDPT/DZV(2d,p), is known to give quantitatively accurate singlet−triplet energy splittings and the algorithm ensures that avoided crossings of states of the same symmetry are treated correctly.

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[40] The synthesis of **5** has been recently accomplished by Matsuura and Komatsu. Their crystallographically determined structure agrees well with our computational prediction, see: Matsuura, A.; Komatsu, K. *J Am. Chem. Soc.* **2001**, *123*, 1768−1769.

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[44] A small out of plane mode indicates that the C_s structure sits on a flat hill. Optimization along that out of plane coordinate produces a minimum energy C_1 structure 0.6 kcal/mol lower than the C_s structure.

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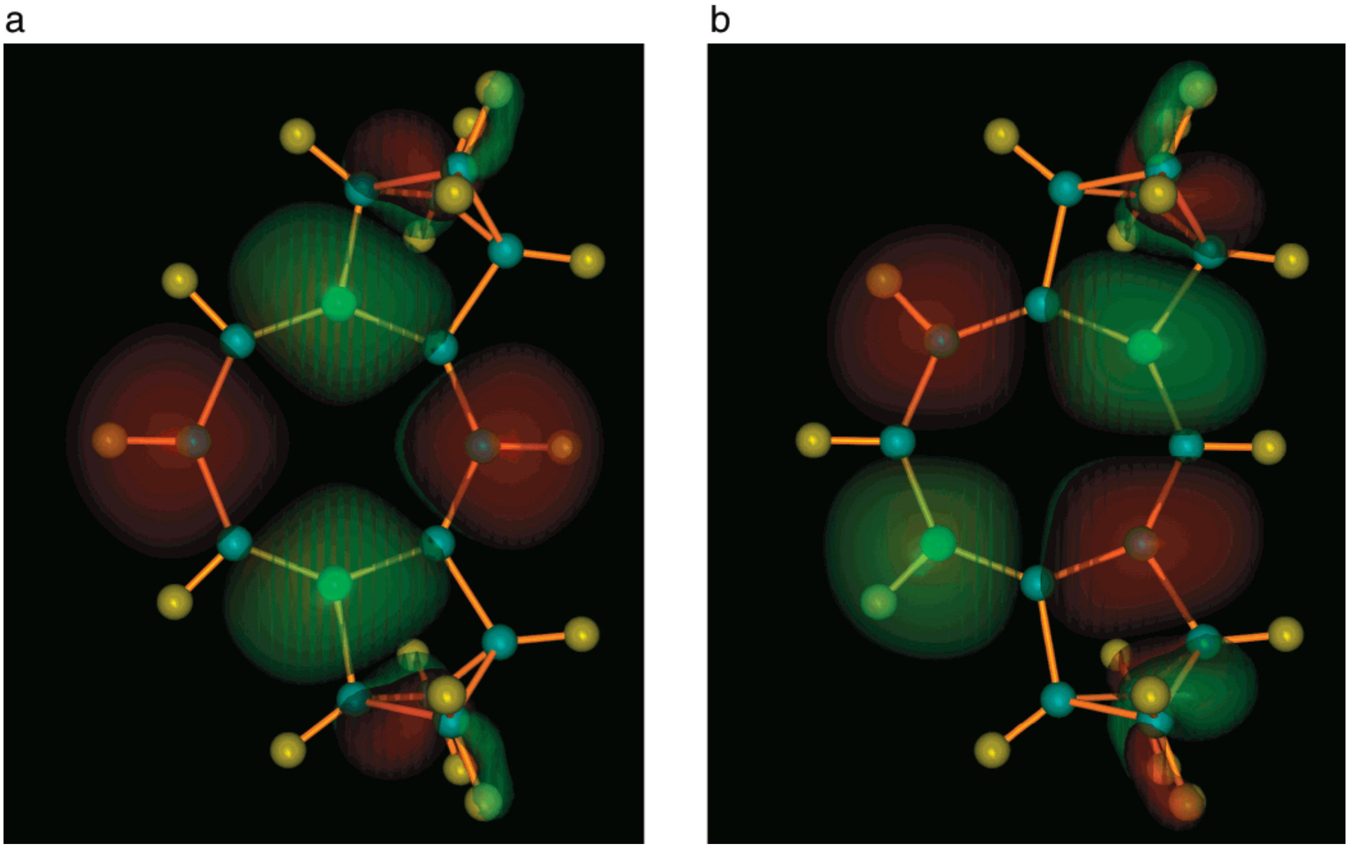
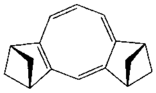
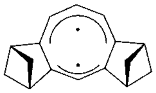


Figure 2. Disjoint singly occupied orbitals of **7**.

We have performed MCSCF[(8,8)] computations followed by MCQDPT corrections on **7** to evaluate the relative ordering of states. In the case of **7**, the relatively low energy of the diradical C_{2v} form persists.



localized C_s



diradical C_{2v}

Stabilization due to dynamic spin polarization is at the core of violations of Hund's rule,[50] as pointed out by Borden.[45] If applicable in the case of **7**, this would mean that the triplet structure should be higher in energy than the singlet. Turning our attention to the triplet configuration of **7**, computations at all levels predict a C_{2v} symmetric structure to be the minimum energy form. Distortion along the "bond shift" coordinate reoptimizes to the C_{2v} structure, supporting a single-well potential for the triplet surface. The bond lengths in **7** are close to the standard C(aromatic)−C(aromatic) length. Comparing the singlet and triplet C_{2v} energies, one finds that, consistent with Hrovat and Borden's computations on the parent cyclooctatetraene,[16] the triplet structure is significantly lower in energy than the (2,0) singlet of same symmetry ($\Delta E = 14.6$ kcal/mol), but still higher in energy than the (1,1) singlet configuration (~5 kcal/mol). The two singly occupied orbitals of **7** display disjoint nodal structures, one of the key elements in the Borden model (Figure 2). Even though the triplet C_{2v} structure is higher than the singlet C_{2v} for **7**, it remains only 2.3 kcal/mol higher than the bond-localized C_s singlet, at the B3PW91/DZ(2d,p) level of theory.[51] In the case of **8**, the trends in energy among the respective triplet and singlet forms parallels that seen for **7**.

As a model for pure strain-induced effects, one can look to the structures and properties of **1** restricted in its CCH angles. From this procedure a control structure for **5-I**, **5-II**, and **7** (C_{2v}) is developed by replacing the annelations with hydrogens and fixing the CCH angle to that of the CCC angle in the annelated species. Computations on this series showed that the differential energetics between exo and endo forms of **5** is not substantiated by σ-angle distortion alone (~ 0.7 kcal/mol for the control versus 32.4 kcal/mol for **5-I** − **5-II**). Furthermore, in the control structure versus **7** the special stabilization of the C_{2v} diradical is not reproduced. Both of these comparisons support the model wherein the bicyclic annelation interacts directly with the π-system and acts more than to simply constrict angles. It is our contention that this is in general true for the bicyclic annelated compounds we have studied and contradicts ideas that strain-induced bond localization dominates these systems.[38] Additional support for the direct π interaction can be seen in the experimental and theoretical work on model bicyclo[2.1.1]hexene and 2,3-dimethylenebicyclo[2.1.1]hexane.[41−43]

In conclusion, this work demonstrates that planar localized cyclooctatetraene is a reasonable structure once the issue of angle strain is removed. The comparison of **2**, **3**, and **5** with distorted COT conformers reinforces our model that bicyclic[2.1.1]hexeno annelations strongly perturb the electronic structure and bond length alternation in annulenes. This especially strong perturbation of the electronic structure by bicyclo[2.1.1]hexeno annelation makes feasible the idea of "valance bond

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(50) Hund, F. *Zeitschrift Physik* **1925**, *33*, 855.

(51) Single-point computations performed on **7** at B3PW91/DZV(2df, pd)//B3PW91/DZ(2dp) showed no change in the relative energy profile of the singlet and triplet states.

frustration” in the design of **7** and **8**. The delocalized diradicaloid state of **7** and **8** are predicted to be lower in energy than the localized closed-shell state. On the basis of these predictions, we anticipate the synthesis and isolation of a planar “delocalized” cyclooctatetraene in the image of **7**.

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Supporting Information Available: Optimized coordinates for all the molecules calculated (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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