About the Antiaromaticity of Planar Cyclooctatetraene**

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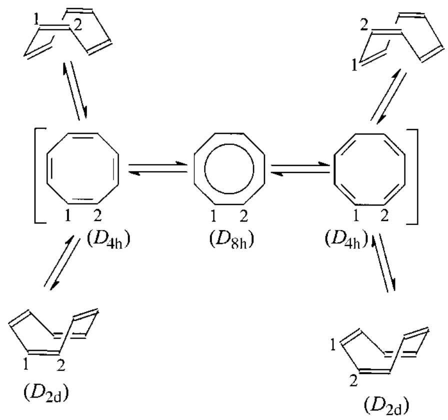
Aromaticity is one of the most important concepts in chemistry. Recently, special issues of *Chemical Reviews*[1] and *Tetrahedron Symposium in Print*[2] (May 2001) highlighted the current interest in this field, even though it is now 176 years since Faraday[3] discovered benzene and 136 years since Kekulé[4] made his famous proposal for the structure of benzene. It was 70 years ago that E. Hückel first explained why cyclic delocalized π systems that have $[4n+2]$ π electrons are unusually stable, for example, benzene ($n=1$, 6 π electrons). Based on his molecular orbital theory (HMO), these systems were classified as aromatic. Today, structural, magnetic, and energy properties, which result from the cyclic π-bond delocalization,[11] such as the equal lengths of formal C–C and C=C bonds,[7] the resonance energy,[8] the nucleus-independent chemical shift (NICS),[9] and the increased magnetic susceptibility[10] are used as criteria for aromaticity.[11] HMO theory predicts that the cyclic delocalization of the $[4n]$ π electrons should lead to open-shell systems with triplet ground states. Based on the extremely low acidity of substituted cyclopropenes, Breslow concluded that the cyclic conjugation of $[4n]$ π electrons leads to the destabilization of the system which he described as antiaromatic[12]. This review was prompted by the current interest in 1,3,5,7-cyclooctatetraene (COT),[13] the higher vinylogue of benzene. COT is an 8π-electon system ($[4n]$, $n=2$) and is predicted by HMO theory to have a triplet ground state, provided that the π electrons are delocalized. It is essential that the system is planar for an optimum conjugation interaction of the π electrons.

COT, however, adopts a nonplanar boat conformation (D_{2d}) with alternating single and double bonds, and behaves as a polyolefin (Scheme 1). The dihedral angle between vicinal double bonds is 56° (single-crystal X-ray structure analysis)[14] so that the conjugation interaction between the π bonds is small. This is confirmed inter alia by the good agreement between the experimental and the calculated standard enthalpy of formation of COT (ΔH_f° [kcal mol^{-1}] = 71.13 (exp.), 71.56 (calcd)). This value was calculated by using an extended MM2 force field (MM2ERW),[15] which was parametrized with 1,3-butadiene as a model for conjugated polyenes, and led directly to the resonance energy, which is now standardized for 1,3-butadiene ($E_{res} = \Delta H_f^\circ(\text{calcd}) - \Delta H_f^\circ(\text{exp.})$) and is negligible in the case of COT (D_{2d}; $E_{res} = < 0.5$ kcal mol^{-1}).[16]



Scheme 1. Ring inversion and π-bond shift.

The dynamic processes (ring inversion and π-bond shift) observed in the variable-temperature NMR spectra of substituted COT derivatives are particularly significant in the antiaromaticity of the cyclic 8-π systems.[17] Accordingly, the activation energy for the ring inversion (10–11 kcal mol^{-1}) is about 3–4 kcal mol^{-1} lower than that for the π-bond shift. Planar COT conformations were proposed to be the transition states of these two processes: the D_{4h} conformation with alternating single and double bonds for the ring inversion, and the D_{8h} conformation with delocalized π bonds for the π-bond shift. The activation barrier for the π-bond shift, which is 3–4 kcal mol^{-1} higher than that for the ring inversion, was taken as evidence for the antiaromatic destabilization of the delocalized 8-π-electron system. A similar value was calculated for the resonance energy of the delocalized D_{8h} conformation ($E_{res} = 4.6$ kcal mol^{-1}) by using the MM2ERW force field. In contrast, the corresponding force-field calculations for the localized D_{4h} conformation result in a small, almost insignificant destabilization as a result of the cyclic interactions of the π electrons ($E_{res} = \approx -1$ kcal mol^{-1}).[16] The planar D_{4h} conformation is generally accepted to be the transition state of the ring inversion, whereas the D_{8h}

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[**] I thank Jens Panitzky for the additional DFT calculations, and Professor Jay Siegel, La Jolla, CA, and Professor Otto Ermer, Cologne, for helpful comments.

conformation suggested to be the transition state of the π-bond shift has been questioned. Nonplanar crown-[18] and saddle-like COT conformations[19] have been discussed as alternative transition states. Especially the finding that substituents in COT derivatives bring about a decrease in the difference between the measured Gibbs enthalpy of activation of the π-bond shift and of the ring inversion (e.g. 1,2,3,4-tetramethyl-COT: $\Delta\Delta G^{\neq} = 32.0 - 31.8 = 0.2\,\text{kcal mol}^{-1}$) suggests a nonplanar geometry of the transition state of the π-bond shift.[20]

According to quantum mechanical ab initio calculations, both transition states should be planar in the parent COT system.[21] Although the triplet state of the delocalized $D_{8\text{h}}$ structure can be regarded as aromatic,[22] the calculations show that in this case the open-shell singlet state is more stable than the triplet state, contrary to the predictions of simple HMO theory. The violation of Hund's rule is explained here by the phenomenon of the "disjoint diradicals".[23] The localized $D_{4\text{h}}$ structure, however, exists in a closed-shell singlet state, which results from a second-order Jahn–Teller distortion, comparable to a polyolefin. The photoelectron spectrum of the planar cyclooctatetraene radical anion ($\text{COT}^{\bullet-}$) (used as transition-state spectroscopy) shows two transitions to two electronic states of COT: the first corresponds to the singlet $D_{4\text{h}}$ ($^1A_{1g}$) state and the second to the triplet $D_{8\text{h}}$ ($^3A_{2u}$) state.[24] The difference in energy between these two states, which is determined from the electron-binding energies, amounts to about $12\,\text{kcal mol}^{-1}$ and is in good agreement with the ab initio calculations. The results of the spectroscopic measurements and quantum mechanical calculations are summarized in Figure 1.

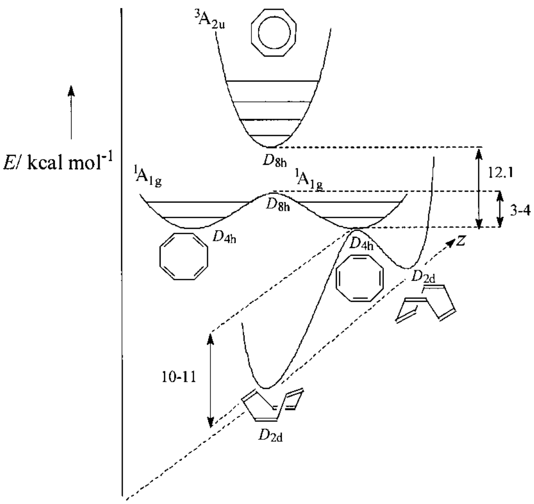
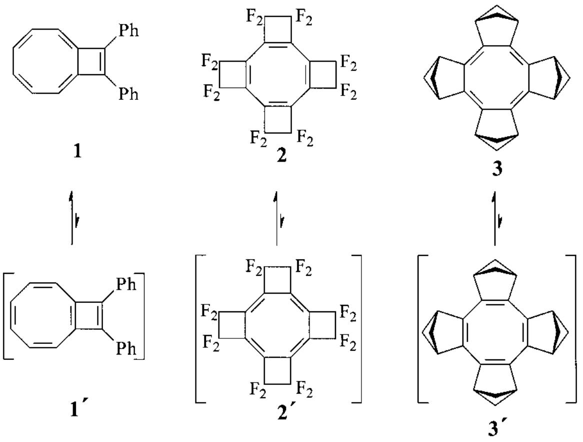


Figure 1. Schematic representation of the potential energy for singlet and triplet COT. The x axis represents the change in bond length, and the y axis reflects the change in the dihedral angle between vicinal double bonds.

COT derivatives that have planar ground states are of great interest to gain further insight into the electronic properties of cyclic conjugated 8-π-electron systems. Such derivatives can be produced by the annelation of strained three- or four-membered rings to the COT skeleton or by the replacement of endocyclic double bonds with triple bonds.[25–28] These structural modifications cause an expansion of the endocyclic bond angles and hence the planarization of the COT skeleton. Compounds **1**–**3** are discussed as examples (Scheme 2).



Bond lengths in the eight-membered ring			
endo:	1.53 Å	1.35 Å	1.50 Å
exo:	1.34 Å	1.43 Å	1.33 Å
Bond angles in the eight-membered ring			
	135°	135°	135°

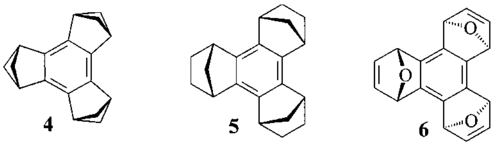
Scheme 2. Bond lengths and angles in the eight-membered rings of substituted COT derivatives **1**—**3**.

According to the single-crystal X-ray structure analysis, 9,10-diphenylbicyclo[6.2.0]decapentaene (**1**) possesses a nearly planar COT substructure with localized single and double bonds.[25] The diphenylcyclobutene unit not only results in the increase in the bond angle mentioned above, but also fixes one of the dihedral angles in the COT substructure at 0° and hence results in the planarization of the eight-membered ring. The π-bond fixation can be explained by the π-bond shift leading to valence-bond isomers, e.g. **1′**, which are less stable than the observed structure **1** as a result of the antiaromatic cyclobutadiene substructure. The valence-bond isomer **1** can be considered formally as a cyclic 10-π-electron system, which should be aromatic according to the Hückel rule. However, the positive resonance energy of $0.3\,\text{kcal mol}^{-1}$, derived from the enthalpy of hydrogenation measured for the parent bicyclo[6.2.0]decapentaene,[29] is very small. Thus, the resonance energy gives no further insight into the electronic properties of the planar COT substructure of **1**.

Single-crystal X-ray structure analysis shows that perfluorotetracyclobutacyclooctatetraene (**2**) is also planar.[26] The surprising localization of the π bonds inside the annelated four-membered rings can be explained by the unique electronic effect of the fluoro substituents.[30] Compound **2** is $17.2\,\text{kcal mol}^{-1}$ more stable than its valence tautomer **2′**, as calculated by using the HDFT (Hybrid-Density Functional Theory) method[31]. Corresponding calculations for unsubstituted tetracyclobutacyclooctatetraene predict that the valence isomer with the double bonds outside the annelated four-membered ring is about $3.2\,\text{kcal mol}^{-1}$ more stable.

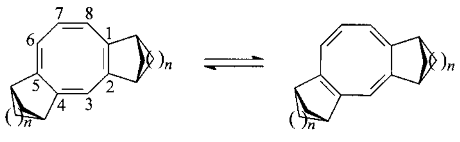
Single-crystal X-ray structure analysis shows that tetrakis(bicyclo[2.1.1]hexeno)cyclooctatetraene (**3**) possesses an entirely planar 8-π-electron system with alternating bond lengths.[28] The alternation of the bond lengths can be explained by the distortions of the bond angles which result from the annelated bicyclohexene subunits. Furthermore, the unusually high enthalpy of formation for bicyclo[2.1.1]hexene, which can be attributed to steric and electronic effects, is evidently also important for the fixation of the π bonds in **3** outside the bicyclic subunits.[32] According to quantum mechanical calculations, **3** is about 32.7 kcal mol^{-1} more stable than the valence isomer **3′**, which contains four bicyclo[2.1.1]-hexene substructures.[31]

Bicyclo[2.1.1]hexene has the same effect on the benzene structure. The single-crystal X-ray structure analysis shows that tris(bicyclo[2.1.1]hexeno)benzene has the cyclohexatriene structure **4** with alternating bond lengths (Scheme 3).[33] The annelation of strained norbornene and oxanorbornadiene units also leads to the benzene structures **5** and **6** with alternating bond lengths.[34, 35] The difference in the bond lengths is, however, smaller in the structures **5** and **6** than in **4**. To estimate the influence of the bicyclo[2.1.1]hexene subunits on the aromaticity and antiaromaticity of **3** and **4**, respectively, the nucleus-independent chemical shift (NICS), the increase in magnetic susceptibility (Λ), and the resonance energies of the pairs benzene/**4** and D_{4h}-COT/**3** were calculated by quantum mechanical methods and compared with each other. Whereas the NICS value calculated for **4** is similar to that for benzene (GIAO-HF/6-31+G*: benzene: $\delta = -9.7$, **4**: $\delta = -8.0$) thus indicating that a substantial degree of aromaticity is retained in **4**,[36] the antiaromaticity of **3** is substantially lower than that of D_{4h}-COT (from NICS: $\delta = +10.6$ and $+27.2$, respectively). The values of the increase in magnetic susceptibility calculated for these systems show a similar trend. According to the calculated resonance energies, the bicyclo[2.1.1]hexene units should not have a considerable effect either on the antiaromaticity of **3** or on the aromaticity of **4**.[28] Dia- and paramagnetic ring-current effects induce shifts of the signals in the ^{1}H NMR spectra, which are frequently employed to characterize aromatic or antiaromatic systems qualitatively.[37] The ^{1}H NMR signals of bicyclohexene bridgehead protons of **3** and **4**, which are located in the plane of the eight- and six-membered rings, respectively, differ only by $\delta = 0.18$ ppm and therefore do not provide evidence for a ring-current effect in one or the other direction.



	4	**5**	**6**
endo:	1.438	1.417 (1.423)	1.425
exo:	1.349	1.379 (1.380)	1.353

Scheme 3. Bond lengths in the benzene rings of substituted derivatives **4**–**6**.

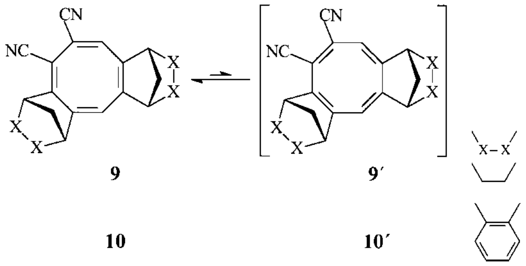


$n = 1$: **7** **7′**

$n = 2$: **8** **8′**

Scheme 4. Substituted COT derivatives **7** and **8**.

Another possibility to planarize cyclooctatetraene consists of the annelation of two bicyclo[2.1.1]hexene or bicyclo[2.2.1]-heptene units at positions C1,C2 and C4,C5 of the eight-membered ring to give **7** and **8**, respectively (Scheme 4).[19] In these compounds, the planarization could essentially be achieved by fixing the dihedral angle C3-C4-C5-C6 at 0° as a result of the bicyclic subunit. The dinitriles **9** and **10** were the first derivatives with such a substitution pattern to be synthesized (Scheme 5).[38] However, the single-crystal X-ray structure analysis of **9** shows a nonplanar eight-membered ring with alternating bond lengths (Figure 2). The experimentally determined structural parameters agree well with PM3 and DFT calculations (BP/DN**//pBP/DN).[38] According to the DFT calculations, the energies of the nonplanar valence isomers **9** and **9′** differ only by $\Delta E = 1$ kcal mol^{-1}. The difference in energy between the planar and the nonplanar structure is, accordingly, lowered from the value calculated for 1,8-dicyano-COT (15 kcal mol^{-1}) to that calculated for **9** (10 kcal mol^{-1}) and should be even lower in the case of **10** because the rigidity of the annelated bicyclic unit is increased by the additional benzene rings. For the comparison of the parent cyclooctatetraene with **7** and **8**, the difference in energy between the planar and the corresponding nonplanar COT structure was calculated by the same DFT method; a decrease from 12 kcal mol^{-1} to 3 and 5 kcal mol^{-1}, respectively,



9 **9′**

10 **10′**

Scheme 5. Nitrile-substituted COT derivatives **9** and **10**.

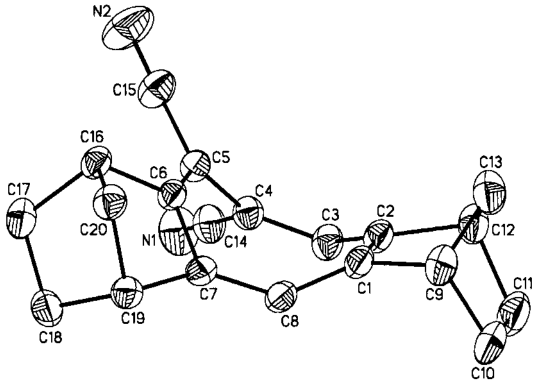
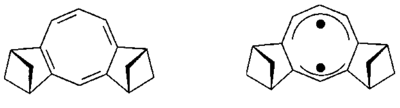


Figure 2. Crystal structure of **9** (single-crystal X-ray analysis).

was found. The DFT calculations clearly show that the nitrile groups have a considerable effect on the COT structure, which disfavors the planarization of the eight-membered ring.

According to the most recent quantum mechanical calculations (MCQDPT/DZV-(2d,p)), the planar structure **7** (C_s symmetry; Scheme 6 left) with localized bonds and a relatively large HOMO/LUMO gap is only 0.6 kcal mol^{-1} less stable than the nonplanar C_1 structure.[31] In the C_{2v} structure of **7** with delocalized π bonds, the highest occupied molecular orbital (HOMO) and the lowest occupied molecular orbital (LUMO) converge, thus allowing three possible singlet states to exist with electron populations of (2,0), (0,2),and (1,1). The configurations (2,0) and (0,2) (both electrons occupy the same orbital) lie ~17 kcal mol^{-1} higher than the localized C_s structure. According to the calculations, the delocalized singlet C_{2v} structure **7″** (Scheme 6, right) with the electron configuration (1,1) is the ground state, and was calculated to be 5.5 and 5.8 kcal mol^{-1} lower than the localized C_s and the delocalized triplet C_{2v} structures, respectively. The structure **7″** is an example of a "disjoint diradical"[23] in which the (1,1) singlet state is favored over the other possible singlet and triplet states because it benefits from the relief of electron repulsion in the half-occupied orbitals as well as from dynamic-spin polarization.



7 **7′′**

Scheme 6. The C_s-symmetric COT derivative **7** with localized bonds and the C_{2v}-symmetric (1,1) diradical **7″**.

The question concerning the antiaromaticity of the planar COT system has certainly been answered for the parent cyclooctatetraene. Contrary to 1,3-cyclobutadiene in which the cyclic interaction of the π bonds leads to a substantial destabilization even in the localized structure (E_{res} = 71.9 (MM2ERW) − 114 = − 42.1 kcal mol^{-1},[39] this effect of the π bonds in the localized D_{4h} COT structure is negligible. The additional destabilization of the planar delocalized D_{8h} COT structure (3–4 kcal mol^{-1}) is also relatively small according to the experimental results as well as theoretical calculations. Substituents have a substantial effect on the COT structure. For future work it would certainly be interesting to verify experimentally the prediction resulting from quantum mechanical calculations[31] that the ground state of compound **7** is the planar singlet diradical **7″** with C_{2v} geometry.

Received: July 5, 2001 [M 1524]

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[39] K. B. Wiberg[6] uses homoisodesmic reactions, for example, the H_2 transfer from *n*-butane to benzene or 1,3-cyclobutadiene (to form *cis*-2-butene, 1,3-cyclohexadiene and cyclobutene, respectively) as thermochemical criterion for aromaticity and antiaromaticity, respectively. In the case of benzene, this reaction is highly endothermic ($\Delta H \approx +34$ kcal mol^{-1}) and in the case of 1,3-cyclobutadiene highly exothermic ($\Delta H = -49$ kcal mol^{-1}). The enthalpy of formation of cyclobutadiene ($\Delta H_\mathrm{f}^\circ = 114 \pm 11$ kcal mol^{-1}) obtained from photoacoustic calorimetric measurements was used for the calculation of the reaction enthalpy.

1433-7851/01/4021-3981 $ 17.50+.50/0