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Directing Power of Cyclobutenoid Annelations on the Double Bonds of Planar Cyclooctatetraenes

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Abstract: Ab initio and hybrid density functional quantum mechanical computations are applied to the structure and energetics of a series of two-atom-bridge annelated cyclooctatetraenes. The contribution of each annelation to the exo/endo relative energy is estimated. Key directing factors for a given type of annelation, such as strain, electronegativity, or cyclic electron count, can be sorted out by comparison of various bridge compositions. Overall, electron count and the essential components of the Clar/Robinson rule work well to predict the exo/endo preferences. Specifically, three 4-e$^-$ Hückel systems (CH−CH, NH−BH and NH−C(O)) display dominant exo forms whereas the three $4n + 2$ Hückel counterparts (C(O)−C(O), BH−BH, and planar NH−NH) display a common preference for endo. These endo systems act like four independent four-membered "aromatic" rings linked by "single" bonds. An analysis based on the effective hybridization of carbon atoms in the annulene (Bent's rule) provides a rationale for subtle trends in their specific annulene geometry.

Introduction

The design of planar cyclooctatetraenes with small annelations has been a "stand alone" research goal.[1−13] In these planar forms the relative energy of COT valence tautomers has provided useful information about annelations and the control conjugated structure. [1] Similar information can be derived from the induced bond-length alternation in multiply annelated benzenes,[14−16] or related Hückel [$4n + 2$] annulenes,[17,18] especially those with benzocyclobutadieno or bicyclo[2.1.1]hexeno fragments. The direction and magnitude of these structural or energy differences can been rationalized in terms of strain[19,20] and/or resonance effects.[21,22] For COT, cyclobuteno and bicyclo[2.1.1]hexeno annelation induces a planar conformation and a preferred valence-bond isomer with double bonds exo to the ring fusion.[1,2] The difference in energy between "exo" and "endo" valence bond forms can be described as a "directing power" of the annelation, and the magnitude and origins of these directing powers for cyclobutenoid annelations form the basis of this work. Our interpretation of these effects indicates that classical π-orbital interactions (Hückel) are predictive and indicate that the π system in annulenes can be altered to create well-defined changes in the annulene structure.

Computational Considerations

All calculations have been carried out using the GAMESS[23] and Gaussian98[24] software packages, running on the hardware facilities at the San Diego Supercomputer Center, including a generous amount of time donated by SUN computers. The molecular 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 described here include Hartree−Fock (HF) and second-order Møller−Plesset perturbation

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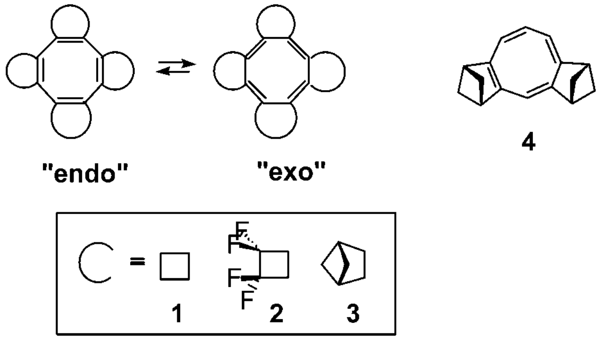

Figure 1. Endo/exo isomers for annelated COT's.

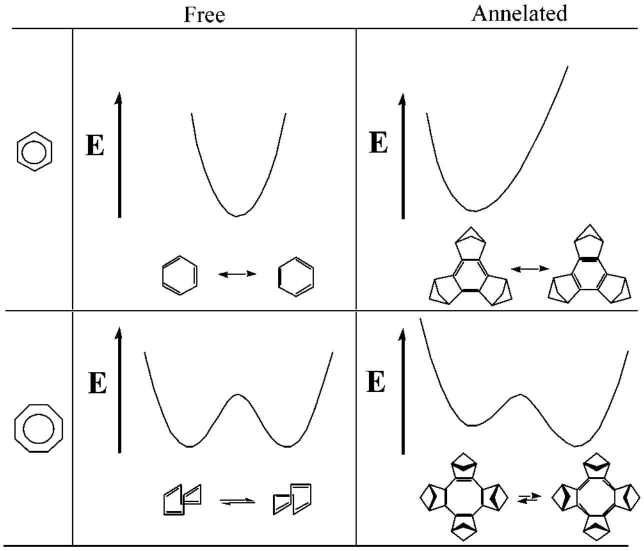

Figure 2. Potential energy diagrams for parent and annelated benzene and COT.

theory.[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 3 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)[8] 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.[1] 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.[30,31] 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.[32]

Discussion

Benzene is well-known to adopt a flat and delocalized D_{6h} structure. Selective annelation of benzene can shift the minimum energy structure significantly toward a D_{3h} bond localized form.[16] In contrast, even after idealizing the tub form to a flat annulene, COT exists as two bond-localized tautomers of D_{4h} symmetry separated by about a 4 kcal/mol barrier.[33−35] In *sym*-tetrakis-annelated COTs one can define these tautomers as exo or endo on the basis of the location of the double bonds relative to the annelation (Figure 1). The annelations on COT alter not only the geometry of each tautomer but also their relative energy, something not possible for benzenoid systems (Figure 2).[1] This energy difference between exo and endo forms is a measure of the "directing power" of an annelation to control the position of double bonds.

The directing power of an annelation on COT provides insight to questions of resonance and strain effects on annulene electronic structure in general. Previously,[1] we found for **1**−**3** that tetrakis cyclobuteno (exo), perfluorocyclobuteno (endo), and [2.1.1]bicyclohexeno (exo) annelations displayed preferences of 4, 17, and >30 kcal/mol, respectively; all of the preferred structures were flat in the eight-membered ring.[7,11,12,36] It was possible to show that the directing powers are approximately additive and this led us to design a valence-bond frustrated system, **4**.[37]

The concepts we used as the basis for our understanding of the structural distortions in annelated benzenes stem from orbital interactions with the π system, e.g. delocalization effects such as Hückel electron counting (4n + 2 is favored, 4*n* is avoided), $\sigma-\pi$ conjugation, and an extension of Bent's rule.[38,39] Applied to the previously computed annelated COT's, these schemes correctly predict the preferred valence-bond isomers of **1**−**3** and motivate the design of **4**. Outside of a polyaza and polybora annelated benzene calculated by Stanger,[20] this mnemonic has been faithful in predicting the preferred structural form in a variety of annelated benzenes.[21,22] Still, a more stringent test would then be to look at a series of annelations wherein the σ-strain vs π-orbital interaction can be directly tested. Such is the focus of the present work.

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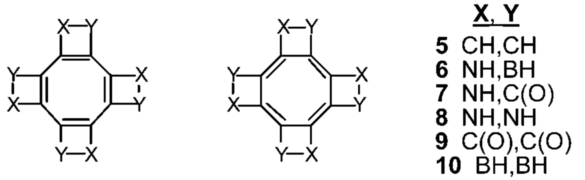

5-10-*endo* **5-10-*exo***

Figure 3. Table legend for compounds **5**−**10**.

Table 1. Structures and Relative Energies (kcal/mol) for **5**−**10**

compd	"exo" bond	"endo" bond	$\delta_{(en-ex)}$	$Q_{(en+ex)/2}$	rel energy[a]
5-*exo*	1.337	1.498	16.1	1.418	0.0 (0.0)
6-*exo*	1.344	1.485	14.1	1.415	0.0 (0.0)
7-*exo*	1.343	1.470	12.7	1.407	0.0 (0.0)
8-*exo* (D_{4h})[b]	1.338	1.494	15.6	1.416	12.7 (11.9)
8-*endo* (D_{4h})[b]	1.430	1.388	−4.2	1.409	0.0 (0.0)
8-I-*exo* (D_4)[b]	1.334	1.470	13.6	1.403	0.0 (0.0)
8-I-*endo* (D_4)[b]	1.436	1.361	−7.5	1.395	2.8 (2.7)
9-*exo*[b]	1.361	1.439	7.8	1.400	5.0 (4.0)
9-*endo*[b]	1.442	1.373	−6.9	1.407	0.0 (0.0)
10-*endo*[b]	1.475	1.402	−7.3	1.439	0.0 (0.0)

[a] B3PW91/DZ(2d,p) and (B3PW91/DZ(2df,pd)//B3PW91/DZ(2d,p) single point). [b] Optimized within symmetry constraints. Negative eigenvalues are for out-of-plane motions.

Consider a set of tetrakis annelated COT's with two-atom-bridge annelations (X−Y; Figure 3) where X and Y can be CH, NH, BH, and C═O equivalently (X = Y, symmetrical case), or in combination (X ≠ Y, unsymmetrical case). In the archetypal anti-Hückel situation, X = Y = CH (**5**). Computations readily produce a flat exo isomer with exo/endo bond lengths of 1.337 and 1.498 Å, respectively (Table 1). The difference in endo and exo bond lengths is roughly 16 pm and the specific bond lengths correspond to a typical C(sp^2)−C(sp^2) double and single bond, respectively.[40] The average carbon−carbon bond length in the central ring, $Q_{((en+ex)/2)}$, is 1.418 Å, slightly longer than the roughly 1.40 Å one would expect from a sterically analogous aromatic system like hexamethylbenzene;[40] this slight lengthening is consistent with a loss of bond order between aromatic and nonaromatic conjugated annulenes.[41,42]

Efforts to find an endo isomer that is computationally stable were carried out, but none were revealed. Initial geometries with flat endo conformations swiftly reverted to the exo isomer during optimization; initial tub-shaped endo conformations flatten and revert to the exo isomer. Various other starting geometries also revert to the exo isomer. Although this does not preclude our having missed the endo potential well, it is our best estimate that **5** prefers an exo geometry and has shifted from a double-well to a single-well potential surface! Although this was surprising at first, one possible explanation for the switch from double- to single-welled potential is that the directing power against the cyclobutadiene form is so great that it overwhelms the 4 kcal/mol intrinsic barrier between planar valence tautomeric forms and creates a single-welled surface. It is noteworthy that such changes in the energy hypersurface are possible.

The preference in **5** could in principle be explained by either strain or Hückel π-electron count. To investigate this further two additional annelated COTs with 4*n* Hückel π-electron counts were studied: (BH−NH), **6**, and (C═O−NH), **7**. For each of these 4-electron Hückel cycles, a clear preference for the exo isomer was found and $\delta_{(en-ex)}$ values of 14.1 and 12.7 pm were computed for **6** and **7**, respectively. The average annulene bond length, $Q_{((en+ex)/2)}$, in each case was ca. 1.41 Å, indicating that all three systems (**5**−**7**) are behaving similarly and in a normal manner compared to general structure correlations. As in the case of **5**, no endo form could be found computationally for **6** or **7**. Even after considering numerous endo starting geometries, each one reverted uniformly to a common exo isomer upon structural optimization. Again, this does not preclude our having missed such an endo form, but given our efforts, it is our best estimation that these systems are controlled by single-well potentials, with their minima at the exo valence-bond form. The common feature among the three structures is the 4-electron count for the annelation in the endo form; the apparent absence of such a form is thus consistent with avoidance of 4*n* electron cycles.

Turning our attention to 4*n* + 2 systems, three annelations were investigated: (NH−NH), **8**; (BH−BH), **10**; and (C═O−C═O), **9**, *n* = 1, 0, and 0, respectively. Compound **8** was first fully optimized within D_{4h} symmetry to study the rigorously planar forms. In the planar form there is a forced interaction between the COT π system and the lone pairs on the nitrogens of the annelations. There is a clear preference for the endo form by 12 kcal/mol. Although **8**-*endo* and **8**-*exo* possess normal average annulene bond lengths ($Q_{((en+ex)/2)}$ = 1.409 and 1.416 Å, respectively), the bond lengths in the preferred endo form (1.430 and 1.388 Å, $\delta_{(en-ex)}$ = −4.2 pm) are much more similar than that seen for exo-favored isomers. The exo tautomer of planar **8** displays the expected geometry of 1.338 (exo) and 1.494 Å (endo) with a substantial difference between formally single and double bonds, $\delta_{(en-ex)}$ = 15.6 pm. The origin of such structural behavior seems a bit obscure at first, but may be viewed as analogous to the structure of triphenylene, a cyclic trimer of independent aromatic rings.

In triphenylene, the central ring has bond lengths such that the endo bond length resembles that of a normal C(ar)−C(ar) and the exo bond length resembles that of the single bond between two benzenes in biphenyl. As such, triphenylene is best modeled as three benzenes forming a cycle with single bonds pairwise between them. This behavior is expected if each annelation were an energetically favored independent unit, like an aromatic ring. To study this for **8**, the structure of one four-membered ring (**8′**) was computed. The C−C, C−N, and N−N bonds of the isolated cycle closely match the analogous structural parameters in the complete COT, $\delta(\text{bond length})_{\mathbf{8}-\mathbf{8'}}$ of 0.1, 0.9, and 0.9 pm, respectively. The only bond in **8** not present in **8′** is the one holding the four four-membered rings together. At 1.430 Å this bond length is clearly too long to be a standard C═C; however, at first glance it may appear to be short enough to betray a strong interaction among the annelations. Careful examination of standard bond lengths reveals that this bond length is intermediate between that expected for a C(sp^2)−C(sp^2) and a C(sp)−C(sp) single bond length, 1.46 vs 1.38 Å. Considering the ring strain and electronegativity effect on the carbon atoms by being in a four-membered ring and attached to nitrogen, one would expect the effective hybridization at carbon also to be intermediate between C(sp^2) and

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C(sp);[38,39,43] thus, the bond length is well rationalized as a single bond between two of the four-membered rings.

	X, Y
8′	NH,NH
9′	C(O),C(O)
10′	BH,BH

Neither the **8**-*endo* nor the **8**-*exo* flat structure is an absolute minimum (i.e., not positive definite in the Hessian matrix), as each has multiple negative eigenvalues associated with pyramidalization at nitrogen. When the symmetry constraints are relaxed to D_4 from D_{4h}, the (NH−NH) isomers pyramidalize at nitrogen in an up−down fashion around the perimeter of the ring. These isomers, in which the lone pairs are much less interactive with the COT π system, display energy characteristics similar to the (CH_2-CH_2) forms previously discussed.[1] In the relaxed versions the exo isomer is 2.8 kcal/mol more stable than endo and $\delta_{(\mathrm{en-ex})}$ for **8-I**-*endo* and **8-I**-*exo* are −7.5 and 13.6, respectively. In **8-I**-*endo* the "single" bond between four-membered rings elongates slightly compared to that in **8**-*endo*, which is consistent with the pyramidal nitrogen having a smaller strain effect on the carbons than the planar nitrogen. All of these variations fit with our notions of hybridization, strain, and electronegativity. For us, these findings demonstrate how the effect of strain-induced perturbation of electronegativity (ala Cremer)[44] alters details of annulene structure but not necessarily the sign of $\delta_{(\mathrm{en-ex})}$ as concluded by Stanger. [20]

In the case of **9** (C═O, C═O) in D_{4h} symmetry the endo isomer is found to be lower in energy than the exo isomer by 5.0 kcal/mol. Both structures optimize well in the plane but have negative eigenvalues in the Hessian matrix corresponding to the out-of-plane motion. The average annulene bond lengths are in the range expected, $Q_{((\mathrm{en+ex})/2)} = 1.407$ (**9**-*endo*) and 1.400 Å (**9**-*exo*), and values for $\delta_{(\mathrm{en-ex})}$ in **9**-*endo* and **9**-*exo* are −6.9 and 7.8 pm, respectively. Computation of the analogous four-membered-ring fragment, **9′**, and a comparison as described above for **8** and **8′** also shows that the bond lengths of the isolated four-membered ring match the annulene within 1 pm. The "single" bond between the fragments in **9**-*endo*, 1.442 Å, is longer than that in **8**-*endo*, further supporting the relationship between this bond length and the effective electronegativity of the annulene carbons. A minimum energy structure with corresponding positive definite Hessian was found; however, the structure was not a fully planar structure, but instead has slightly twisted annelations. The endo and exo bond lengths for this structure are 1.391 and 1.416 Å, respectively.

Computations on the D_{4h} structure of **10** (BH−BH) yield an endo isomer but no exo isomer; all starting structures reverted back to the endo isomer. As in the above cases of **5**−**7**, we cannot exclude the possibility of having missed the exo structure but our efforts lead us to conclude that such a structure does not exist.[45] The average annulene bond length in **10** is 1.439 Å and as such is outside what one would expect from normal perturbations. The value of −7.3 pm for $\delta_{(\mathrm{en-ex})}$ is a bit more difficult to interpret given that the "short" bond in the annulene is 1.402 Å, i.e., more like a normal aromatic C−C bond length. Here the computations on the four-membered-ring fragment (**10′**) are very helpful in evaluating the structure. The C−C, C−B, and B−B bond lengths for **10** vs **10′** differ by 1.6, 0.5, and 1.3 pm, respectively. The "single" bond between the four-membered rings in **10** is 1.475 Å, which is slightly longer than the normal $C(sp^2)-C(sp^2)$ bond length, but given the fact that boron is less electronegative than carbon, this result fits well with our expectations for structural patterns in these systems. Thus, taken on the whole, the structure of **10** follows the same pattern observed for **8** and **9**: the planar annulene is best seen as four isolated aromatic fragments connected together in a cycle by single bonds. Thus, the π-electron count consistently provides a predictive picture in these systems much as the sextet rule of Clar and Robinson works for polynuclear aromatic hydrocarbons such as triphenylene or kekulene.[46,47] The aza and bora systems studied here can be related to Stanger's benzene studies.[20]

Conclusions

Overall, we find the comparison of structure and energies in the exo and endo valence bond forms in annelated COT's to be a powerful way to investigate the relative effects of σ-strain and Hückel-π electron count. The data reinforce our opinion that one simple way to understand and predict the preferred tautomer of these systems is through Hückel-π-electron counting in the annulene. More subtle aspects of the molecular geometry can be explained by using electronegativity and strain-induced hybridization changes a la Bent's rule. The results taken in whole also indicate to us that, no matter what term (σ or π) contributes the most to determining the overall D_{6h} structure of benzene, the variations in structures among annulenes is well rationalized by Hückel-π orbital arguments.[48−50] Indeed, it remains an effective and rewarding enterprise to design materials based on π-modified annulene structures.

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

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