

# Utilization of Buttressing Effects for Comparing Ring Inversion and $\pi$ Bond Shifting Transition State Geometries in Cyclooctatetraenes<sup>1</sup>

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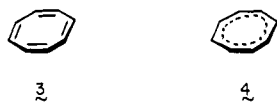
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**Abstract:** The free energies of activation for ring inversion and bond shifting in 1,8-di-, 1,2,3-tri-, and 1,2,3,4-tetramethyl substituted cyclooctatetraenes are compared and analyzed in terms of  $\Delta\Delta G^\ddagger$ . The incremental increases in the barriers are somewhat larger for ring inversion than for bond shifting, in accordance with the steric demands of the planar alternate and planar delocalized transition states. The possible involvement of highly puckered or bicyclic structures for the activated complex is ruled out. Therefore, for cyclooctatetraene an unfavorable delocalization energy of 3.5–4 kcal/mol is seen to be operative.

Because [4n]annulenes play a central role in our understanding of conjugated, nonaromatic  $\pi$  systems, they have commanded substantial theoretical and experimental attention in the last decade. Each member of this class can be represented by two Kekulé formulas in which the single and double bonds are site exchanged. Recent major advances in synthetic methodology have enabled several *shelf-stable* pairs of cyclooctatetraene bond shift isomers such as **1** and **2** to be isolated.<sup>1,3-7</sup> These valence tau-



tomers are the first of their kind to become available and exemplify the very sort of isomerism vainly sought by pre-Kekulé chemists in ortho-disubstituted benzenes. Several elegant experiments designed to define the mechanism of interconversion of [8]annulene bond shift isomers and to establish the geometry and electronic nature of the mediating transition states have been carried out.<sup>8,9</sup> Although the inference has been advanced repeatedly that planar delocalized species of the general type **4** are involved, direct



evidence is (as usual in such circumstances) not available, and the situation is sufficiently complicated that alternative schemes can be imagined. A nonplanar "crown" structure has, for example, been postulated on theoretical grounds.<sup>10</sup>

Structure **4**, with its  $D_{4h}$  symmetry and equal bond lengths, must be viewed as a species with an orbitally degenerate  $\pi$ -electron

system. In accordance with the Jahn–Teller theorem,<sup>11</sup> this symmetrical molecular arrangement will likely be geometrically unstable with respect to some displacement of atoms which removes the degeneracy. A distortion to make the C–C bonds alternately longer and shorter or to buckle the ring could consequently lead to enhanced stabilization by reduction of the induced paramagnetic ring current to a finite value. A key question is whether such distortions will still allow for the interconversion of bond-shift isomers. At the moment, it is clear that the extent of bond alternation cannot be so accentuated as to compare to the  $D_{4h}$  symmetric **3**, since it is already well established that **3** and its substituted analogues are the transition states involved in the energetically less demanding tub-to-tub ring inversion of cyclooctatetraenes.

In simple Hückel terms, the free-energy difference between **3** and **4**, if both are indeed planar, would correspond largely to the delocalization energy of [8]annulene, a quantity of considerable theoretical importance. Since quantitative information concerning this issue has been limited, further detailed comparative analysis of theory and experiment remained to be made.<sup>12</sup>

In the preceding two papers,<sup>1,13</sup> studies intended to provide additional kinetic and thermodynamic evidence on these questions have been described. With the present analysis of these results, we believe that the weight of evidence has become sufficient to justify the acceptance of **3** and **4** as reasonably accurate descriptors of the ring inversion (RI) and bond shifting (BS) transition states associated with cyclooctatetraene automerization.

**Effect of Incremental Peripheral Strain on the Ring Inversion Barrier.** From the results of calculations due chiefly to Allinger,<sup>12</sup> Dewar,<sup>10</sup> and Wipff,<sup>14</sup> mechanical inversion in unsubstituted cyclooctatetraene (COT) is seen to be disfavored by increases in the van der Waals and angular bending energies of the molecule. A decrease in torsional energy accompanies conversion to **3**, but this effect compensates for only about 40% of the destabilization arising from the two causes above. A total energy increase of 15.1 kcal/mol is computed for flattening the [8]annulene frame into the optimized  $D_{4h}$  planar geometry. These facts do not mean that **3** is necessarily characterized by destabilizing  $\pi$ -electronic energy. This conclusion would demand that **3** be less stable than a corresponding open-chain polyene with the same number and types of bonds. However, such a structure is not one of the options available to COT, which has only a choice of being flat or puckered in some fashion. The point of significance, then, is to what degree the angle bending and van der Waals forces which tend to pucker the eight-membered ring are counterbalanced by the delocalization

(1) Bond Fixation in Annulenes. 10. For part 9, see: Paquette, L. A.; Gardlik, J. M.; Johnson, L. K.; McCullough, K. J. *J. Am. Chem. Soc.* preceding paper in this issue.

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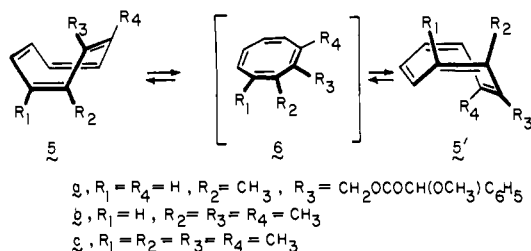
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energy which is striving to flatten the system. Theoreticians agree that the first factors are the more dominant. Accordingly, in terms of its  $\pi$  component, planarity within COT is energetically advantageous. Therefore, any equation of the concept of "anti-aromaticity" with a tendency for nonplanarity generates an erroneous impression of the prevailing energetics and has been a source of confusion in the past literature.<sup>15</sup>

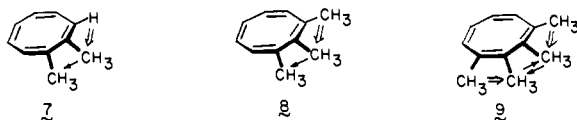
The purpose of our study was quantitative assessment of the energetic impact caused by incremental methyl substitution of contiguous carbon atoms comprising the COT ring. In this fashion, the gradual onset of nonbonded interactions and butressing contributions on the ring inversion barrier could be compared directly with those exerted during  $\pi$ -bond shifting (see subsequent section). Analysis of the differences or similarities in steric interaction at the respective transition states would then provide an independent probe of the geometries of **3** and **4**.

Although rates and activation parameters for ring inversion in 1,8-Me<sub>2</sub>COT are unavailable, Anet and Bock were successful in determining by <sup>1</sup>H NMR spectroscopy the free energy of ring inversion for 8-methylcyclooctatetraenylmethyl *O*-methylmandelate (**5a**  $\rightleftharpoons$  **5'a**) at 70 °C. Extrapolation of their data to

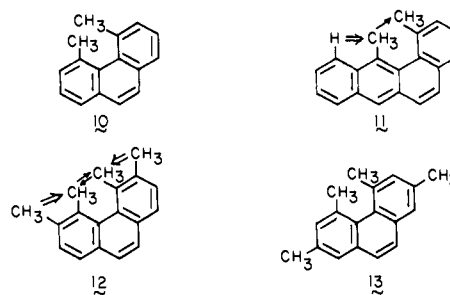


122 °C shows  $\Delta G_{\text{RI}}^{\ddagger}(122^\circ\text{C}) = 18.4$  kcal/mol. Thus, the rate of ring inversion is expectedly somewhat decreased by 1,8 disubstitution. The 1,2,3-Me<sub>3</sub> substitution plan (**5b**  $\rightleftharpoons$  **5'b**) further impedes ring flattening ( $\Delta G_{k_1}^{\ddagger}(122^\circ\text{C}) = 25.5$  kcal/mol)<sup>6a,13</sup> and to a substantial degree ( $\Delta\Delta G^\ddagger = 7.1$  kcal/mol). Introduction of a fourth methyl group as in **5c** enhances the barrier to ring inversion still further ( $\Delta G_{k_1}^{\ddagger}(122^\circ\text{C}) = 32.9$  kcal/mol).<sup>1,8</sup> The striking feature of this experimental result is the additional large impedance to flattening which the fourth methyl group introduces relative to **5b** ( $\Delta\Delta G^\ddagger = 7.4$  kcal/mol).

The differences in free energies of activation realized above might be regarded as the standard values for steric strain due to intramolecular crowding in the planar alternate [8]annulene structure **6**. Certainly, **6** is the simplest reference point which can be selected in which the pertinent steric features are accommodated. Viewed in this way, the degree of added strain which develops in the transition state attained during flattening of **5a** can be considered to arise in large part because of the CH<sub>3</sub>/CH<sub>2</sub>OR interaction. For the present discussion, the intramolecular strain in **6a** is considered to closely approximate that present in the dimethyl derivative **7**. The third and fourth methyl groups in **8** and **9** introduce added strain, including Me-Me butressing effects, not present in **7**.



There does not exist a wealth of information concerning methyl butressing effects (MBE). However, a line of investigation pursued by Newman and Margrave several years ago is relevant.<sup>16</sup> Heats of combustion measurements performed on **10**–**13** and additional reference compounds established a number of interesting points. In comparing **12** and **13**, which both contain the same



4,5-methyl group interaction, but with methyl butressing groups in **12** instead of hydrogen atoms, a 7.2 kcal/mol difference in stability was noted (3.6 kcal/mol per CH<sub>3</sub> group). Also, **11** was found to be 3.0 kcal/mol less stable than **10**, indicating that the additional fused aromatic ring sterically approximates a methyl group located at the same position.

These values are considered to be lower MBE limits, since phenanthrene itself is slightly nonplanar owing to interference between H-4 and H-5. Furthermore, the angle at which the methyl groups are projected toward each other in **10**–**13** surely differs from than in **7**–**9**. The question can now be posed concerning the extent to which the magnitudes of the MBEs will differ in the two systems. As matters turn out, the values are remarkably similar within the limits of confidence imposed by certain necessary assumptions.

Comparison of the  $\Delta G_{\text{RI}}^{\ddagger}(122^\circ\text{C})$  of **5a** to experimentally determined free energies of activation for several monosubstituted COTs (adjusted to the same temperature)<sup>9b,17</sup> shows 1,2-dialkyl substitution as in **7** to add approximately 3.5 kcal/mol to the RI barrier. This is as expected on the basis of increased van der Waals and bending repulsions generated between these substituents as the eight-membered ring strives to attain planarity. In the 1,2,3-Me<sub>3</sub> example, a second Me-Me interaction across a C=C bond is added (cf. **8**). Furthermore, the central methyl group is now caught in between the two other methyls. Additional steric impedance is therefore introduced in the form of methyl butressing effects. If it is assumed in general terms that Me-Me single bond interactions ( $\Delta G_{\text{Me-Me}(-)}$ ) destabilize the planar alternate transition state by 3.5 kcal/mol while Me-Me double bond interactions ( $\Delta G_{\text{Me-Me}(=)}$ ) contribute approximately 4 kcal/mol of strain, then the MBE contributions in the 1,2,3-Me<sub>3</sub> and 1,2,3,4-Me<sub>4</sub> derivatives can be calculated as follows:

$$\Delta\Delta G^\ddagger = \Delta\Delta G_{\text{Me-Me}(-)} + \Delta\Delta G_{\text{Me-Me}(=)} + \Delta G_{\text{MBE}} \quad (1)$$

where all values except  $\Delta G_{\text{MBE}}$  deal with increments relative to the next lower homologue. Solution of this simple expression reveals the methyl butressing effects to be 3.1 and 3.4 kcal/mol, respectively.

The same calculation can be used to approximate the magnitude of  $\Delta G_{\text{MBE}}$  for the exhaustively substituted Me<sub>6</sub>COT molecule. To do this, we apply Allinger's computed barrier to ring inversion for this hydrocarbon (93.7 kcal/mol),<sup>12</sup> relate matters to the 1,8-Me<sub>2</sub> derivative, and obtain a  $\Delta\Delta G^\ddagger$  of 75.2 kcal/mol. Substitution into eq 1 gives

$$\Delta G_{\text{MBE}} = 75.2 - +(3.5) - 4(4) = 45.2 \text{ kcal/mol}$$

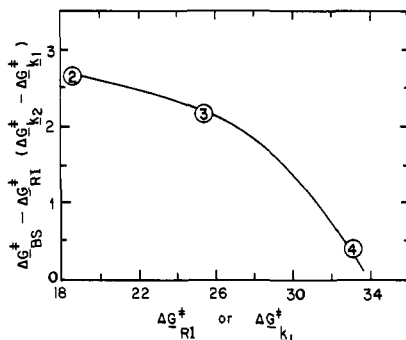
Since in this example each methyl group exerts a butressing influence, the  $\Delta G_{\text{MBE}}$  value must be divided by the total number of such interactions, i.e., 8. The resulting value is then 5.6 kcal/mol. This finding is as expected, since  $\Delta G_{\text{MBE}}$  is not a real constant but should increase with increasing congestion. The general trend of 3.1 (trimethyl), 3.4 (tetramethyl), and 5.6 (octamethyl) conforms nicely to this hypothesis.

The observed range of values (3.1–5.6 kcal/mol) is cogently accommodated by the planar *D*<sub>4h</sub> structures identified above, although it is also possible that in the highly congested systems

(15) This problem has been pointed out previously; see, for example, Gy-gax, R.; Wirz, J.; Sprague, J. T.; Allinger, N. L. *Helv. Chim. Acta* **1977**, *60*, 2522.

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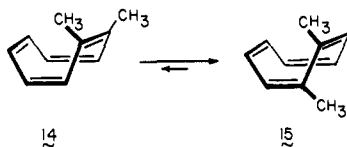


**Figure 1.** Plot of  $\Delta G_{\text{BS}}^{\ddagger}(122^{\circ}\text{C}) - \Delta G_{\text{RI}}^{\ddagger}(122^{\circ}\text{C})$  vs.  $\Delta G_{\text{RI}}^{\ddagger}(122^{\circ}\text{C})$  as a function of the level of alkyl substitution. The encircled number relates to the number of pendant groups.

the situation is somewhat less simple. For example, the possibility remains that the 1-, 3-, 5-, and 7-methyl groups in  $\text{Me}_8\text{COT}$  may go through the developing plane of the ring carbons first, then the ring may go planar, and finally the other four methyls may pass through to the other side.

**Analysis of Methyl Steric Effects on  $\pi$  Bond Shifting Energetics.** Although  $\pi$ -bond shifting in [8]annulenes can be viewed as a symmetry-allowed pericyclic reaction, migration of the single and double bonds cannot transpire while the molecule still retains its tub geometry. The vital issue concerns whether this process requires passage through planar transition states related to the  $C_{8h}$  symmetry **4** or to some quasi-planar modification of this structure.

Earlier work by Meisinger demonstrated the  $\Delta G_{\text{BS}}^{\ddagger}(122^{\circ}\text{C})$  for bond exchange in 1,2-MeCOT (**14**) to be 21.1 kcal/mol.<sup>18</sup> As in the case of other 1,2-disubstitution plans,<sup>8c,19-21</sup> the "skew" structure present in the 1,8 isomer (**15**) is energetically favored



because of lessened crowding between the alkyl groups. The free energies of activation for  $k_2$  in 1,2,3-Me<sub>3</sub>COT and 1,2,3,4-Me<sub>4</sub>COT at the same temperature were previously determined to be 27.7 and 33.3 kcal/mol, respectively.<sup>1,13</sup> Thus, the incre-

mental increases in free energy ( $\Delta\Delta G^{\ddagger}$ ) witnessed in this series are 6.6 and 5.6 kcal/mol, values somewhat smaller in magnitude than those observed for RI. These effects, which are considered to be beyond the limits of experimental uncertainty, are best viewed by plotting  $\Delta G_{\text{BS}}^{\ddagger} - \Delta G_{\text{RI}}^{\ddagger}$  vs.  $\Delta G_{\text{RI}}^{\ddagger}$  (Figure 1). At a glance, it is seen that the  $\Delta\Delta G^{\ddagger}$  differences decrease as the quantities themselves increase.

The steadily increasing barriers to BS and RI can without any doubt be ascribed to the existence of greater repulsive interactions in the transition states relative to the ground states. If BS transition states were highly puckered or of crown geometry (see **16**) as suggested by Dewar,<sup>10</sup> the reverse ordering would be expected. Furthermore, crown conformation **16** cannot pseudorotate with the tub (or boat) form, as models clearly show. If the geometry of this transition state were puckered, its geometry should be analogous to the boat-boat form of cyclooctane.<sup>22</sup> However, this point is rendered moot by the present experimental evidence. Identical deductive reasoning rules out the possible intervention of bicyclo[3.3.0]octadienediyl intermediates (**17**).<sup>23</sup> As with the



entropies of activation for ring inversion, the negative  $\Delta S_{\text{BS}}^{\ddagger}$  values are in agreement with flattening of the ring. However, does it follow that equalized bond lengths prevail? Symmetry effects would at the most give a few entropy unit contributions to  $\Delta S^{\ddagger}$ . The major portions of the negative  $\Delta S^{\ddagger}$  terms found for BS and RI probably arise not directly because of ring planarity but rather because of strongly restricted methyl rotations in the transition states. Effectively planar delocalized structures accommodate best the requisite steric compression of these peripheral substituents.

In light of this conclusion, the energy ( $E_R$ ) required to delocalize  $8\pi$  electrons about a planar  $C_8$  perimeter

$$E_R = \Delta H_{\text{RI}}^{\ddagger} - \Delta H_{\text{BS}}^{\ddagger} \quad (2)$$

appears to be somewhat destabilizing (3.5–4 kcal/mol) for the parent hydrocarbon, i.e., **3** vs. **4**. This value is in excellent agreement with the early PPP and SPO MO calculations of Dewar and Gleicher<sup>24</sup> for an  $8\pi$ -electron system on a  $D_{8h}$  perimeter (4 kcal/mol) and at wide variance with a more recent value of 15.4 kcal/mol.<sup>10</sup>

**Acknowledgments.** This investigation was supported in part by the National Science Foundation (Grant CHE-7608764). Enlightening exchanges of information were had with Professors N. L. Allinger, F. A. L. Anet, and J. Hine.

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