

ON THE INVERSION BARRIER IN TETRABENZOCYCLOOCTATETRAENE

C. J. Finder, D. Chung, and N. L. Allinger

Department of Chemistry, University of Georgia, Athens, Georgia 30601

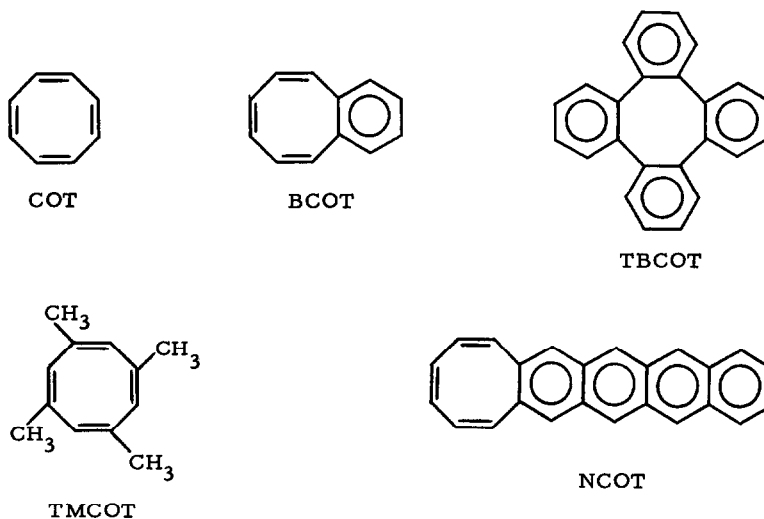
(Received in USA 28 August 1972; received in UK for publication 10 October 1972)

Recently Figeys and Dralants¹ reported that the barrier to inversion of tetrabenzocyclooctatetraene (TBCOT) was 5 kcal/mol, using the nmr decoalescence of two diastereomeric methyl groups in a substituted derivative. Other cyclooctatetraene derivatives show much higher barriers to inversion than this (see Table 1), in the range 13 - 23 kcal/mol. The very low barrier in the tetrabenz derivative was interpreted by Figeys and Dralants¹ as a result of the decrease in the anti-aromaticity of the eight-membered ring in the transition state relative to cyclooctatetraene (COT), by a delocalization of the π electrons from the eight-membered ring into the benzene rings.

A model of TBCOT suggests that the ortho hydrogens on adjacent benzene rings must necessarily come very close to one another (0.8 \AA)¹ if the transition state is planar,^{1,2} and it is difficult to see how the transition state can be other than planar.

Models and preliminary force field calculations³ suggest that the repulsion between the ortho hydrogens in the transition state in fact must be very serious; sufficiently large so that the inversion would not occur at room temperature. Since our force field calculations for such systems are not yet finalized, we sought some other confirmation of this idea, and turned to a CNDO/2 calculation⁴ for further information. Such a calculation would be expected to give good results in a case like this, and any results arising from "anti-aromaticity" should be clearly discernible. For comparison purposes, similar calculations were simultaneously carried out on the tub and planar forms of a number of other cyclooctatetraenes, and the results are summarized in Table 1. The geometry in each case was determined by force field calculations, and should be sufficiently accurate for comparison purposes. Actually, when the calculated and observed inversion barriers are compared in Table 1 for cyclooctatetraene (COT), benzocyclooctatetraene (BCOT), and 1,3,5,7-tetramethylcyclooctatetraene (TMCOT), it is seen that the difference between the experimental and

calculated values ranges from about 0 - 10 kcal/mol. In tetrabenzocyclooctatetraene, the calculations predict a barrier of 222.4 kcal/mol!



We considered the possibility that round-off error in the calculations would become more serious with increasing molecular size, although our error estimate was ± 0.1 Hartree for TBCOT. As a check the barrier in naphthacenocyclooctatetraene (NCOT) was calculated, and again found to be small, not really different from benzocyclooctatetraene. The large calculated barrier in TBCOT is therefore believed to be a real result, and not an artifact of some kind.

We have considered the possibility of various kinds of deformations of the transition state in an effort to lower its energy, but can find no way that will bring the calculated energy anywhere near into agreement with the reported experimental value. We therefore suggest that the experimental quantity measured does not correspond to an inversion of this molecule, although it is not completely clear just what has been measured. We note that the experimental measurements merely showed a broadening of the nmr peak in question at -116° . It is possible that this broadening is simply due to a viscosity effect, or to the onset of precipitation, for example. In any case, we believe that the above calculations provide strong evidence that it does not correspond to inversion of the cyclooctatetraene ring.

It might be pointed out that the concept of anti-aromaticity is one which readily lends itself to misunderstanding. "Anti-aromatic" does not necessarily indicate a destabilization of a molecule. It only indicates that the molecule is less stable than the

TABLE 1.

Compound	Energy (Hartrees) ^a	calc. ΔH^\ddagger kcal/mol	obs. ΔH^\ddagger ^b kcal/mol
COT - tub	-62.6802	7.82	13.7 ⁵
COT - planar	-62.6677		
BCOT - tub	-92.7008	13.76	13.4 \pm .2 ²
BCOT - planar	-92.6788		
TMCOT - tub	-97.4722	33.16	22.5 \pm 2 ⁶
TMCOT - planar	-97.4192		
TBCOT - tub	-182.3621	222.4	5.7 \pm 1 ¹
TBCOT - planar	-182.0066		
NCOT - tub	-182.2559	17.45	----- ^c
NCOT - planar	-182.2280		

(a) 1 Hartree = 625.6 kcal.

(b) The quantity usually measured was ΔG^\ddagger , sometimes on substituted systems. It has been found that ΔS^\ddagger for ring inversion in related systems is negligible (see ref. 4 in ref. 2), and it is assumed ΔG^\ddagger and ΔH^\ddagger are the same to a good approximation. The effects of substituents are assumed negligible.

(c) This barrier has not been measured but it would be expected to be similar to the barrier for BCOT.

corresponding linear polyene.⁷ In the case of cyclooctatetraene, the molecule is anti-aromatic be it planar or otherwise.* The planar form has a lower pi energy, however, and the pi resonance is tending to stabilize the planar form of a cyclooctatetraene molecule.⁸ Making it non-planar makes it still less stable; in other words, non-planarity does not improve the anti-aromaticity with respect to a planar conjugated polyene, but rather makes it worse. (The tub form is more stable only because of the contributions from the sigma system.) Thus any delocalization of the electrons out of the pi system

*It should be pointed out that an alternative definition of aromaticity in terms of ring current exists.¹ We are concerned here with the thermodynamic definition, however.

destabilizes the planar form, relative to the tub form. As far as the pi system alone is concerned, fusion of benzene rings onto the cyclooctatetraene ring system should lead to an increase in the barrier height, not to a decrease.

ACKNOWLEDEMENT: The authors are grateful to Eli Lilly and Company for support of this research.

REFERENCES

1. H. P. Figeys and A. Dralants, Tetrahedron Letters, 1971, 3901.
2. G. W. Buchanan, Tetrahedron Letters, 1972, 665.
3. N. L. Allinger and J. T. Sprague, J. Amer. Chem. Soc., 94, 5734 (1972); N. L. Allinger, M. A. Miller, M. T. Tribble, and D. A. Wertz, J. Amer. Chem. Soc., 93, 1637 (1971).
4. The program used was QCPE 91, CNDO/2 by G. A. Segal. The program received was written for 38 atoms and 72 basis functions. Arrays were enlarged as necessary to handle the larger system. The program was used on the IBM 360/65. Calculation times ranged up to approximately one hour of cpu time per run for the large molecules.
5. F. A. L. Anet, A. J. R. Bourn, and Y. S. Lin, J. Amer. Chem. Soc., 86, 3576 (1964).
6. P. Ganis, A. Musco, and P. A. Temussi, J. Phys. Chem., 73, 3201 (1969).
7. R. Breslow, J. Brown, and J. J. Gajewski, J. Amer. Chem. Soc., 89, 4383 (1967); M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, 1969, pp 179, 212.
8. R. Breslow and E. Mahacsi, J. Amer. Chem. Soc., 85, 431 (1963); N. L. Allinger, M. A. Miller, L. W. Chow, R. A. Ford, and J. C. Graham, J. Amer. Chem. Soc., 87, 3430 (1965).