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BARRIERS TO EIGHT-MEMBERED RING INVERSION IN BENZOCYCLOOCTATETRAENE AND A BENZOCYCLOOCTATRIENE

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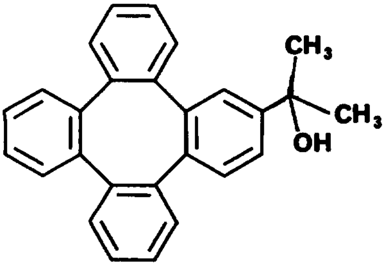
Recently, Figeys and Dralants(1) have presented evidence for the anti-aromaticity(2) of a planar eight-membered ring containing [8]- π electrons in the substituted tetraphenylene I.

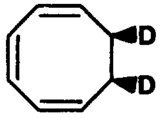


I

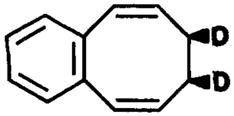
LCAO calculations indicate that successive addition of fused benzene rings to [8]-π electron systems decrease the anti-aromaticity, i.e. increase the stability(2) of these moieties. Since cyclooctatetraene ring inversion is generally accepted to occur via a planar transition state(3,4) the low barrier observed for I (5.7 kcal/mole) relative to cyclooctatetraene (ca. 15 kcal/mole) is thus rationalized.

We herein report results for ring inversion in benzo-substituted cyclooctatetraene and cyclooctatriene which support the concept of an increase in the electronic stabilization of a planar [8]-π electron eight-membered ring, on addition of a fused benzene function. Inclusion of the triene allows assessment of the effect of benzene fusion when no paramagnetic ring current can exist in the eight-membered ring.

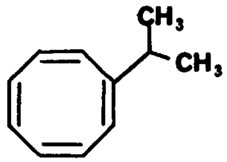
The compounds employed for the present study are shown below.



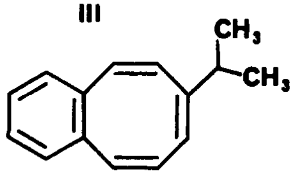
II



III



IV



V

In the table are listed coalescence data obtained from low temperature ^1H NMR experiments which permit calculation of the barriers to eight-membered ring inversion using the Eyring equation. Neglect of entropy terms is not deemed serious, Oth(4) having found that changes in $\Delta S^{\neq}$ are negligible for ring inversion in related systems.

TABLE

Compound	T_c ($^\circ C$) ± 2[d]	ΔV (Hz)[a]	$\Delta G^{\neq}$ (kcal/mole)
II[b]	-136	29.5	6.7 ± 0.2
III[b]	-98	26.0	9.2 ± 0.2
IV[c]	-25	0.7	14.8 ± 0.2
V[c]	-30	1.9	13.4 ± 0.2

[a] At 100 MHz (Varian HA-100 and XL-100 Spectrometers)

[b] 1:1 $CClF_2H$: CH_2CHCl solution

[c] CS_2 solution

[d] Temperatures calibrated with a copper-constantan thermocouple

The barrier for II agrees with that of 6.2 ± 0.5 kcal/mole recently reported by St.-Jacques *et al.*(5) Compound III was synthesized via deuterio diimide reduction of benzocyclooctatetraene.(6) In a typical reduction, the tetraene was dissolved in methanol-d and mixed with a solution of potassium ferricyanide in D_2O. To this was added hydrazine hydrate-d_6 dropwise over a period of 90 minutes at room temperature. On column chromatography (alumina, impregnated with 5% by weight $AgNO_3$ in H_2O, 30-60° petroleum ether solvent), the products were separated. The isomeric 1,2-benzo-cis-7,8-dideuterio-1,3,5-cyclooctatriene was eluted first, followed by 1,2-benzo-cis-5,6-dideuterio-1,3,7-cyclooctatriene III and then starting material. Compound III shows low resolution mass spectral parent ion at m/e 158 and an NMR spectrum characteristic of its symmetry.

At room temperature the cis-methylene protons of II and III appear as broad singlets near $\delta = 2.5$. On cooling these singlets separate into broad doublets below -136 and -98°C respectively, indicating slow eight-membered ring inversion on the NMR time scale.

The 2.5 kcal/mole higher barrier in III than in II can be attributed to an increase in the angle strain in the transition state for inversion of III, due to the fusion of the benzene ring. A transition state for cyclooctatriene inversion has been proposed,(5) in which the three double bonds approach planarity. This being the case, the internal bond angles in the eight-membered ring must expand in the transition state.(7) Clearly fusion of a benzene ring will render this expansion more difficult and will increase the barrier.

Barriers for IV and V were determined from the temperature dependence of the ^1H NMR spectra of the diastereotopic methyl groups. At room temperature a doublet is seen for the isopropyl methyls in each compound. On cooling below the coalescence temperature a pair of doublets of equal intensity appears in each spectrum due to slow ring inversion.

It is interesting that the barrier for 1,2-benzo-5-isopropyl-1,3,5,7-cyclooctatetraene V is 1.4 kcal/mole lower than that for isopropyl cyclooctatetraene IV. Presumably the barrier-enhancing steric effect of benzene fusion observed in the triene will be at least as great in the tetraene. In a planar transition state for cyclooctatetraene ring inversion the internal bond angles must open to 135°, a process which will be retarded by benzene ring fusion.

Accordingly we attribute the lower barrier in V than in IV to increased electronic stabilization in the planar transition state for inversion in the benzo- substituted tetraene. To offset an angle strain effect of ca. 2.5 kcal/mole by 1.4 kcal/mole, this electronic stabilization must be of the order of 4 kcal/mole. By analogy with I, it is tempting to attribute this stabilizing effect to a decrease in the anti-aromaticity of the planar eight-membered ring transition state caused by fusion to the benzene ring.

Detailed lineshape analyses are in progress on these and related compounds to more precisely define the magnitude of the observed phenomena.

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REFERENCES

1. H. P. Figeys and A. Dralants, Tetrahedron Letters, 3901 (1971).
2. F. Sondheimer, I. C. Calder, J. A. Elix, Y. Gaoni, P. J. Garratt, K. Grohmann, G. di Maio, J. Mayer, M. V. Sargent and R. Wolonsky, in "Aromaticity," Special Publication No. 21 of the Chemical Society, London, 1967, p. 75.
3. F. A. L. Anet, A. J. R. Bourn and Y. S. Lin, J. Amer. Chem. Soc. 86, 3576 (1964).
4. J. F. M. Oth in D. Lloyd, "Topics in Carbocyclic Chemistry," Vol. 1, Chapt. 5, Logos Press, London, 1969.
5. M. St.-Jacques and R. Prud'homme, Tetrahedron Letters, 4833 (1970).
6. H. E. Zimmerman, R. S. Givens and R. M. Pagni, J. Amer. Chem. Soc. 90, 6096 (1968).
7. The ground state conformation of cyclooctatriene is similar to the "tub" form which has been verified by electron diffraction for cyclooctatetraene and for the eight-membered ring of tetraphenylene. See reference (5) and I. L. Karle and L. O. Brockway, J. Amer. Chem. Soc. 66, 1974 (1944). .Accordingly, ring inversion in these systems constitutes a "tub-tub" interconversion.