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THE LOW BARRIER OF INVERSION OF TETRAPHENYLENE : AN EXPERIMENTAL PROOF OF THE ANTI-AROMATICITY OF THE PLANAR 8-π ELECTRON RING SYSTEM.

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Some years ago, Anet et al.(1) and Oth(2) showed by careful analysis of the evolution of the NMR spectra of suitably substituted cyclooctatetraene derivatives as a function of the temperature, that the eight-membered ring undergoes ring-inversion at room temperature. Line-shape analysis of the temperature dependence of the signals of the methyl groups led to a value of $\Delta G^{\ddagger}$ = 14.7 Kcal/M for 1-(1-hydroxy-1-methylethyl)-cyclooctatetraene-2,3,4,5,6,7-d_6(1) at -2° and $\Delta G^{\ddagger}$ = 12.7 Kcal/M for isopropoxycyclooctatetraene at 0°(2). Oth(2) was also able to show that entropy variations $\Delta S^{\ddagger}$ may be neglected in this process.

From the vast experience which has been accumulated in recent years by several investigators, it has become clear that the magnitude of the barrier to ring-inversion may be discussed in the light of at least two general rules(3): an increase in angle strain and (or) steric compression in the transition state, as compared to the molecule in its equilibrium configuration, produces a significant increase in the barrier height ; on the other hand, for rings containing 4n+2 π-electrons, extended π-delocalisation in the transition state enhances considerably the rate of inversion. Such a case has been described recently by Mislow et al.(3). The barrier ($\Delta G^{\ddagger}_{25}$) for pyramidal inversion at phosphorus in 1-isopropyl-2-methyl-5-phenylphosphole

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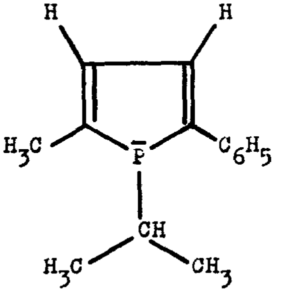
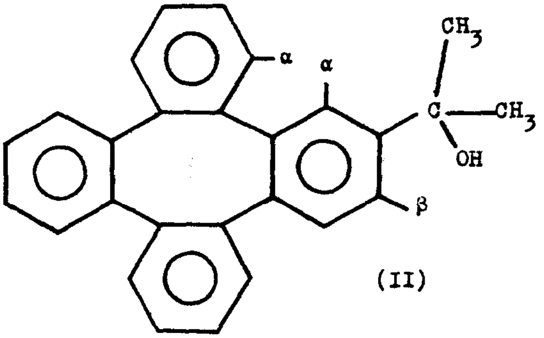
(I) has a value of 16 Kcal/M, i.e. some 25 Kcal/M less than the corresponding saturated ring compounds.



(I)



(II)

Some years ago, Karle and Brockway$^{(4)}$ showed by electron diffraction study that the eight-membered ring of tetraphenylene has a non-planar "tub" form with bonds alternating in length around the ring. The shorter bonds (1.39 $\pm$ 0.02 A) are common to the six-membered rings, while the bonds joining the benzene rings have a length of 1.52 $\pm$ 0.04 A ; all the angles in the benzene rings, which are alternatively above and below the average plane of the molecule, are near 120°. Scale drawings show that, if these geometrical features are maintained in the hypothetical planar transition state for ring-inversion of the eight-membered ring$^{(5)}$, the α-hydrogen atoms on two adjacent benzene rings are as close as 0.8 A.

We wish to report that, in spite of this strong steric interaction, the barrier for ring-inversion (E_a) in 2-(1-hydroxy-1-methylethyl)-tetraphenylene (II) has the extraordinarily low value of 5.7 $\pm$ 1 Kcal/M (as compared to the value of $\Delta G^{\ddagger}_{-2}$ = 14.7 Kcal/M for the corresponding cyclooctatetraene derivative $^{(1)}$).

The synthesis of (II) was accomplished by acetylation of tetraphenylene (obtained by sealed-tube pyrolysis of biphenylene at 400°/1 Torr$^{(6)}$) using acetyl chloride in sym-tetrachlorethane (1 hour at -15°); the mono-acetylated compound was easily separated by column chromatography (alumina, 60-70° petroleum ether, yield 72%) and engaged in a Grignard reaction with methyl magnesium iodide in ether/benzene to give (II) in 94% yield. The NMR spectrum at 60 MHz of the monoacetylated compound provides convincing evidence that the substitution occurred at a β-position : 2 protons deshielded by ortho-substituent effect, H_β (ortho- and meta-couplings) centered at 471 Hz and H_α (meta- and para-couplings) centered at 464 Hz ; other aromatic protons as a complex multiplet centered at 433 Hz (internal TMS=0).

The aliphatic part of the spectrum of (II) shows at 35° a very intense singlet (6H, $\Delta\nu_{1/2}$ = 1 Hz, δ = 85 Hz) in a solvent mixture CS_2/perdeutero-tetrahydrofuran in the ratio 20/80) assigned to the two diastereotopic methyl groups ; the multiplicity and $\Delta\nu_{1/2}$-value are unaffected in different solvents (C_6H_6, C_2Cl_4, $CHCl_3$). As the temperature decreases, important broadening occurs together with a slight high-field shift. At -116°, $\Delta\nu_{1/2}$ = 24 Hz and δ = 84 Hz (even at this temperature, $\Delta\nu_{1/2}$ for the TMS-peak used as internal standard shows no broadening). This situation is characteristic of rapid exchange of the two methyl groups above the coalescence temperature ; when the theory of Piette and Anderson(7) is applied to this evolution, a value of 5.7 ± 1 Kcal/M for the barrier of ring-inversion is obtained.

This surprising result may be ascribed to the decreased anti-aromaticity (as compared to cyclooctatetraene itself) of the eight-membered ring in the postulated planar transition state of the inversion. Calculation of the ring-current of the eight-membered ring for the whole series of benzocyclooctenes by McWeeny's LCAO-perturbation theory(8), using the iterative LCAO-BETA method(9), shows indeed that the successive addition of fused benzene rings produces a decrease of the paramagnetic ring-current in the [8]-π electron system.

Table 1 : Ring-current intensity in the eight-membered ring of benzocyclooctenes (benzene = +1.0).

Cyclooctatetraene	-0.882	Dibenzo-[a,c]-cyclooctene	-0.159
Benzocyclooctene	-0.331	Tribenzocyclooctene	-0.090
Dibenzo-[a,e]-cyclooctene	-0.159	Tetraphenylene	-0.053

If we accept that the intensity of the paramagnetic ring-current is a criterion of anti-aromaticity(10,11), i.e. a measure of destabilisation of the planar eight-membered ring, and if we assume that, in the "tub" form, the eight-membered ring is non-aromatic(12), then we should observe a lowering of the barrier of inversion along the series of compounds listed in table 1. Our results on tetraphenylene should thus constitute the first experimental evidence of the anti-aromaticity of planar [8]annulene. The study of the barrier to ring-inversion for other benzocyclooctenes is in progress, together with all valence electron calculations(13, 14) on these molecules in the equilibrium configuration and in the transition state.

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