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THE RING INVERSION IN TETRABENZOCYCLOOCTATETRAENE: A CORRECTION

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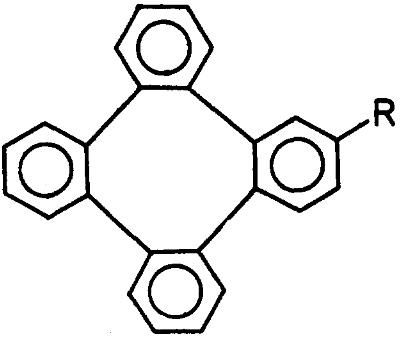
In a recent note, Figeys and Dralants (1) have reported on the temperature-dependent ^{1}H-NMR spectrum of 2-(1-hydroxy-1-methylethyl)-tetrabenzocyclooctatetraene (Ib). The methyl groups gave a singlet, but a strong broadening at low temperature was interpreted as being due to a slow inversion of the eight-membered ring with a barrier of 5.7 ± 1 kcal/mol. The authors point out the very close approach of the neighbouring hydrogen atoms on adjacent rings in a



I; a, R = H
b, R = $C(CH_3)_2OH$
c, R = $COCH_3$
d, R = $CH_2CSN(CH_2CH_2)_2O$
e, R = $CH_2CSN(CH_2CD_2)_2O$
f, R = $COCH(CH_3)_2$

planar transition state, but they contend that this unfavourable interaction is more than balanced by the decease in antiaromaticity of the planar cyclooctatetraene ring caused by the annellation of the benzene rings. The reality of such an effect has recently been demonstrated by Buchanan (2) for benzocyclooctatetraene, but it is fairly small, diminishing the barrier to ring inversion from 14.7-14.8 kcal/mol (2,3) for cyclooctatetraene to 13.4 kcal/mol for the benzo derivative (2). Westheimer-type calculations on the strain energy in a transition state with all carbon atoms in one plane have been performed, allowing for C-H in plane and out of plane bending, deformation of the benzene rings, stretching of the inter-benzene ring bonds, and compression of the C-H bonds. When the energy is minimzed with respect to these parameters, utilizing a Lennard-Jones type non-bonded potential function and the harmonic approximation, with current force constants for bond bending, stretching and compression, a minimum energy of about 120 kcal/mol is obtained. To this should be added π-electron stabilization (energy lowering) and angle deflection in the eight-membered ring (energy raising). It is possible that the strain energy is somewhat exaggerated since the harmonic approximation might not be valid with the large deflections obtained (C-H in plane 10.3°, out of plane 27.7°). However, the strain energy was considered too large to be compensated by the π-electron effect of the benzene rings. Therefore, the CH_3 singlet observed in the room temperature NMR spectrum of Ib was assumed to be due to accidental equivalence of the diastereotopic methyl groups.

Repetition of the preparations and spectra described in Ref. (1) gave identical results. Not even in the presence of the shift reagent $Eu(fod)_3$ (4) was a doubling of the methyl signal observed. The investigation was therefore continued with other prochiral groups.

Willgerodt-Kindler reaction with Ic, sulphur, and morpholine in a sealed tube at $150^{\circ}C$ gave a 43 % yield of Id. The 100 MHz spectrum of this compound showed non-equivalence of the benzylic protons with a small shift difference. The spectrum of the morpholine protons was much more complex than that of thiophenylacetmorpholide, which shows two AA'BB' spectra due to slow rotation around the N-C(S) bond. The greater complexity of the spectrum of Id was assumed to arise from non-equivalence of the protons in at least two of the methylene groups. In order to obtain simpler spectra, the reaction was repeated with 2,2,6,6-morpholine-d_4 (5). The resulting labelled thiomorpholide (Ie) showed an AB spectrum for the benzylic protons (ν_A = 435.2 Hz, ν_B = 427.8 Hz, J_{AB} = 15.5 Hz), and one for the morpholine CH_2 group Z to the thiocarbonyl group (ν_A = 435.6 Hz, ν_B = 412.6 Hz, J_{AB} = 13.5 Hz). The E morpholine CH_2 group gave a singlet at 343.0 Hz. All data were obtained at 100 MHz in $CDCl_3$ solution with TMS as internal lock signal. In hexachlorobutadiene solution, the spectrum showed the same general appearance up to about + 100°C, but at higher temperatures exchange broadening, due to the rotation around the N-C(S) bond becoming fast, obscured the spectrum, and the fast exchange limit was not reached at + 190°C. Therefore, this compound gives a lower limit to the barrier to inversion of the eight-membered ring in Ie of ca. 18 kcal/mol.

Acylation of Ia with isobutyryl chloride gave If, and the NMR spectrum of this compound showed a doublet of doublets for the methyl protons with splittings of 7.2 and 1.6 Hz. These splittings persisted up to 190°C in hexachlorobutadiene solution.

Evidently, the apparent equivalence of the methyl protons in Ib is due to a low asymmetry in the region close to position 2. In more distant prochiral groups the effect of anisotropy increases, since then the nuclei reside at least part of the time closer to the more strongly anisotropic and asymmetrically disposed neighbouring benzene rings.

The spectrum of If at 190°C gives a lower limit to the barrier to ring inversion in If and also in Ia of about 26 kcal/mol. It is likely that the barrier is considerably higher, though the assumption of a planar transition state may not be quite justified. This investigation will be continued with attempts to prepare optically active derivatives of Ia and to study their racemization in order to determine the true barrier.

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All compounds Ia-f gave satisfactory mass and NMR spectra and elemental analysis data.