Preferred Conformations and Inversion Barriers in 1,2:5,6-Dibenzocyclo-octadienones

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CYCLO-OCTA-1,5-DIENE and its annellated homologues could adopt either chair or flexible conformations;[1] the energy barrier separating these is likely to be higher than in the case of cyclohexane,[2] and likely also to be further increased by annellation with aromatic rings.[3] We have therefore examined 1,2 : 5,6-dibenzocyclo-octadien-3-one (I)[4], and its methylated homologue, (II). The ^{1}H n.m.r. spectrum of (I)† shows a sharp singlet for 4-H (τ 5·9, 2H) and similarly for the

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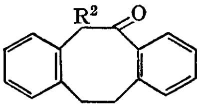
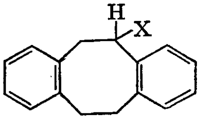
remaining benzylic protons (τ 6·8, 4H): these signals remain unchanged down to −90°. In contrast the spectrum of (II) at ordinary temperatures, and below, shows two methyl singlets (τ 8·33 and τ 8·48, 3H each) and the signal for the benzylic protons is complex (τ 6·8—τ 7·2, 4H); the methyl signals coalesce at 66°. Since the signals are sharp, and the interconversion is between conformers of the same energy, the rate of inversion may be estimated; $k_{60°} = 12{\cdot}57$ sec.$^{-1}$ and $k_{66°} = 19{\cdot}99$ sec.$^{-1}$, hence $E_{\text{rac}} \sim 17$ kcal./mol. In view of the short temperature range over which the measurements could be made this value for the energy barrier to inversion (which is also the barrier to the chair–twist tub isomerisation) is only very approximate, but it does confirm that the barrier is substantially higher than in the cases of cyclohexane[3] and cycloheptene.[5]

The simplicity of the ^{1}H n.m.r. spectrum of (II) in the region of τ 8 shows that only one conformation is populated to a significant amount, and the large discrepancy between (I) and (II) as regards the height of the inversion barrier can only mean that this is a twist-tub conformation. An energetically inexpensive pseudo-rotation, which would interconvert mirror image twist-tubs, is possible for (I) only. [Pseudo-rotation of (II) involves intolerably close approach of a methyl and the C_8-methylene.] The infrared spectra of (I) and its monobromination product [ν(C=O) 1685 and 1718 cm.$^{-1}$ respectively] support this view, as they imply considerable conjugation between the carbonyl and the aromatic ring in the first instance, and substantial alignment of the two dipoles in the second: neither is possible in a chair conformation.

Dibenzocyclo-octadiene, (III; X = H), is reported to possess the chair conformation in the crystalline state;[1] however the ^{1}H n.m.r. spectrum of the 3-ol, (III; X = OH), is more readily reconciled with a twist-tub than with a chair conformation as the 3-H signal is a triplet (J = 7 c./sec.). A twist-tub conformation has also been suggested for *trans*-3,4-dicyano-1,2 : 5,6-dibenzocyclo-octadiene,[6] and in view of the reported temperature independence of its ^{1}H n.m.r. spectrum,[7] now seems probable for 1,5-cyclo-octadiene itself.



(I) R=H
(II) R=Me



(III)

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