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A COMMENT ON THE MAGNITUDE OF HOMOALLYLIC COUPLING AND THE CONFORMATION OF 1,4-CYCLOHEXADIENE

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Considerable effort has been directed towards identification of the preferred conformation of the 1,4-cyclohexadiene ring. The most recent information comes from an electron diffraction study of the gaseous diene, and demonstrates that the ring adopts a boat conformation with a dihedral angle α, (figure 1), of 159.3°.(1) This is in marked contrast with the conclusions drawn from an elegant nmr investigation by Garbisch and Griffith, whose results suggested that the ring is planar ($\alpha = 180^{\circ}$), or nearly so.(2)

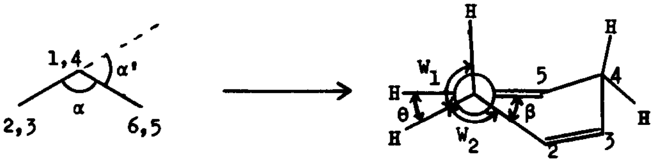
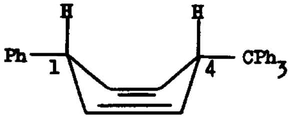
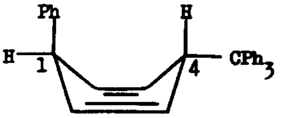


Fig. 1

When we first noted long-range homoallylic coupling in the nmr spectra of 1,4-cyclohexadienes, we reported that cis- and trans-1,4-dihydro-4-tritylbiphenyl (I and II) exhibited 1,4-couplings of ca. 11 and 7.5Hz respectively.(3)



(I)



(II)

A slight doubt remained, however, as to the correctness of our configurational assignments. These have now been substantiated both by equilibration of the tetrahydro-derivatives of (I) and (II),(4) and by an X-ray structure analysis of a crystalline bromo-derivative of (II).(8)

In the light of our new structural information, we wish to indicate how Garbisch and Griffith's results might be reconciled with the electron diffraction data, and, more significantly, to point out a discrepancy between the experimental results and the existing theory of homoallylic coupling due to Karplus.(11)

Garbisch and Griffith assumed a rapid (on the nmr time scale) inversion of the unsubstituted cyclohexadiene boat, and, following Karplus,(11) derived the expression:

$$\frac{J_{1,4\underline{cis}}}{J_{1,4\underline{trans}}} = \frac{(\sin^2\theta)^2 \quad + \quad [\sin^2(W_1-\theta)]^2}{2\sin^2\theta \quad x \quad \sin^2(W_1-\theta)} \qquad \text{(i)}$$

where W_1 and θ are the angles depicted in figure 1. The experimental value for $J_{\underline{cis}}/J_{\underline{trans}}$ was found to be 1.2. Assuming $W_1 = 120^\circ$, this gives $\theta \hat{=} 45^\circ$ (or 75°), and, using the relationship:

$$\alpha \hat{=} 180^\circ - \tfrac{1}{2}\left|60^\circ - \theta\right| \qquad \text{(ii)}$$

α was calculated to be *ca*. 172.5°.

No derivation of equations (i) or (ii) was presented, and it appears to us that (ii) is in error and should be replaced by(12)

$$\alpha \hat{=} 180^\circ - \left|60^\circ - \theta\right| \qquad \text{(iii)}$$

This leads to $\alpha \hat{=} 165^\circ$, already in fair agreement with the electron diffraction study. However, as Garbisch and Griffith point out, it is implicit in Karplus's analysis, and hence in eq . (i), that for a planar cyclohexadiene $J_{\underline{cis}} = J_{\underline{trans}}$. It is our present purpose to show that $J_{\underline{cis}}$ may be appreciably smaller than $J_{\underline{trans}}$ for the planar conformation, and that even better agreement with the electron diffraction data may consequently be obtained.

Because of the bulk of the trityl group, it is impossible to construct space-filling models of (I) and (II) unless the cyclohexadiene ring is puckered into a boat conformation with the trityl group occupying a pseudo-equatorial position. Trityl may thus be regarded as a conformation-holding group, with the structures drawn for (I) and (II) representing the actual conformations of these molecules. Furthermore, it seems extremely improbable that the *cis*-isomer (I), with a second pseudo-equatorial substituent, would be *less* puckered than the *trans* (II). However, if we apply the Karplus treatment to these two molecules using the coupling constants cited above, and with the assumptions (i) that the substituents do not impart appreciable unsymmetrical distortion to the cyclohexadiene ring, and (ii) that only the conformation shown contributes in each case, we obtain $\alpha(\text{trans}) \hat{=} 166^\circ$ and $\alpha(\text{cis}) \hat{=} 174^\circ$. One cannot attach too much significance to these absolute values because of the average energy approximation in the theory,(11) however the *relative* values of α are clearly at odds with the foregoing discussion: the Karplus treatment leads to a more puckered ring for the isomer (II) which chemical intuition suggests should be the less puckered.

If $\alpha(\text{trans})$ is 166° then a reasonable value for $\alpha(\text{cis})$ would seem to be in the range 160°-166°; the Karplus theory predicts that the coupling for the *cis*-isomer would then be in the range 14.9-13.4 Hz, or 36-22% larger than the measured value.

It seems more than coincidence that for unsubstituted cyclohexadiene, inserting the value of $\alpha = 159.3$ in equations (iii) and (i) leads to a calculated value of $J_{\underline{cis}}/J_{\underline{trans}}$ $= 1.45$, again ca. 22% larger than the experimental(2) value!

For the generalised system depicted in Fig. 2, in which carbon atoms 1-8 are in a common plane, the Karplus analysis predicts that all the homoallylic couplings J_{AB} - J_{AE} are equal. (One important assumption is that there is negligible interaction through the sigma framework). It would seem perfectly reasonable to expect that calculations utilising a more sophisticated molecular wave function might differentiate between these couplings - in particular, it might be possible to adduce theoretical support for the present experimental observation that J_{AC} appears to be greater than J_{AB}.

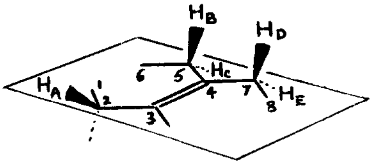


Fig. 2

Acknowledgements

We are deeply indebted to Mr. R. Hulme of St. Andrews University for his invaluable help with the X-ray structure determination on bromo(II). We are also grateful to Mr. C. Noel of Varian Associates Ltd., for re-determining $J_{1,4}$ (II) with the vinyl protons decoupled.

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of p-bromophenylazotriphenylmethane in benzene. It was spectrally similar to (II), but quite distinct from (I). A three-dimensional crystal structure determination was undertaken in conjunction with R. Hulme, details of which will be presented elsewhere.[9] In summary, it was found that the cyclohexadiene ring was puckered in the crystal, with $\alpha \simeq 165^\circ$, and that the trityl group occupied a pseudo-equatorial, and the <u>p</u>-bromophenyl a pseudo-axial position, as depicted for the parent hydrocarbon in structure (II). The conformation of the cyclohexadiene ring found in the crystal does not necessarily reflect its preferred conformation in solution because of the balance between conformational and lattice forces in the crystalline state (<u>cf.</u> reference 10).

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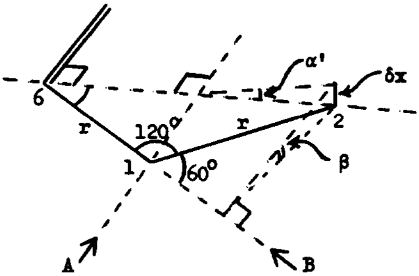

Fig. 3.

Equation (iii) may be derived by a consideration of figures 1 and 3. Figure 3 represents the planar conformation for which it is assumed that all ring angles approximate to 120°. A small puckering of the ring is then obtained by raising C-2 a distance δx above the original plane. This corresponds to a small rotation about the bond C-1 to C-6. The extent of this rotation, β, viewed from B (Fig.3) is given by

$$\tan\beta \simeq \frac{\delta x}{r \sin 60^\circ}$$

where r is the length of the C-1 to C-2 and C-1 to C-6 bonds.

Viewed from A, the puckering of the ring defined by α' is given by

$$\tan\alpha' \simeq \frac{\delta x}{r \sin 60^\circ}$$

$$\text{therefore} \quad \alpha' = \beta$$

$$\text{now} \quad \alpha' = 180^\circ - \alpha \quad \text{(see Fig. 1)}$$

$$\text{and, assuming } W_1 = W_2 = 120^\circ$$

$$\beta = |60^\circ - \theta| \quad \text{(see Fig. 1)}$$

$$\text{therefore} \quad \alpha = 180^\circ - |60^\circ - \theta|$$

This relationship, as derived, applies only when δx is small. However the errors introduced by increasing δx and at the same time reducing $\angle C_2\text{-}C_1\text{-}C_6$ tend to cancel.