Shielding Effects in Substituted Cyclopropanes

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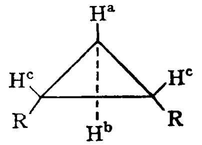
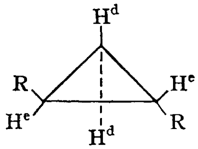
NUCLEAR MAGNETIC RESONANCE (n.m.r.) spectroscopy is a powerful tool for the detection of cyclopropene and cyclopropane portions in fatty acids and related natural products.[1] The spectra of a variety of long-chain *cis*- and *trans*-1,2-disubstituted cyclopropanes have been described.[2–8] Of particular interest are the spectra of long-chain *cis*-1,2-disubstituted cyclopropanes because this structural unit occurs in a number of diverse natural materials[3–6] or is obtained by *cis*-hydrogenation of the corresponding cyclopropenoid.[2,8] The *cis*-cyclopropane (I) is characterized[2–8] by a multiplet at τ 10·3, absent[5–7] in the *trans*-isomer (II) and the corresponding cyclopropene,[2] and an additional broad band at about τ 9·4. As summarized by Minnikin,[7] conflicting interpretations of these bands have been given. The unique band at τ 10·3 has been variously assigned to the methylene protons,[2] both methine protons,[4] one of the methine protons,[5] and the methylene proton (H^a) *trans* to the two substituents.[6,7] It is clear that all possible assignments save the most probable one have been suggested. We point out that the peak in question is due to the methylene proton (H^b) *cis* to the substituents. In addition, we summarize below a general treatment of the shielding effects of alkyl substituents which unifies the existing data in this field.

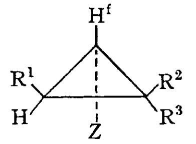
We have interpreted the chemical shifts of ring protons in alkyl-substituted cyclopropanes in terms of the long-range shielding effects associated with the diamagnetic anisotropy of carbon–carbon single bonds. Through the use of the McConnell equation[9] and appropriate structural parameters† we calculate that an alkyl group shields a *cis*-proton by 0·1—0·2 p.p.m. and deshields a *trans*-proton by about the same amount. Examination of the spectra of a large number of cyclopropanes reveals that the shielding effect of an alkyl group is generally greater (*ca.* 0·25 p.p.m.) than its deshielding effect (*ca.* 0·1 p.p.m.), on the appropriate protons.† Application of these data to the spectra of long-chain 1,2-disubstituted cyclopropanes is rewarding. In the *cis*-isomer (I), H^b, shielded by two alkyl groups should be shifted upfield by *ca.* 0·5 p.p.m. With cyclopropane as a reference structure (τ 9·78), H^b should appear as a multiplet at τ 10·3, broadened by spin–spin coupling to the remaining ring protons. Similarly, H^a is deshielded and should appear at τ 9·6; H^c, deshielded by the geminal alkyl group (average value: 0·5 p.p.m.)* and the *trans*-alkyl group, should appear at τ 9·2. Coupling of H^a and H^c involving these nuclei as well as H^b and neighbouring α-protons on the side-chains would give rise to a broad band (second-order splitting) centred at about τ 9·4. Analogously, the *trans*-cyclopropane (II) has predicted chemical shifts of τ 9·9 for H^d and τ 9·5 for H^e. Coupling would result in a complex band centred at about τ 9·7. These predicted chemical shifts are in good agreement with the observed values that have been reported thus far. In a most recent quantitative study,[7] Minnikin has examined the *cis*- and *trans*-isomers of methyl 9,10-methyleneoctadecanoate. The ring protons in the *cis*-isomer give rise to a three-proton band centred at τ 9·4 and a one-proton multiplet at τ 10·3; the *trans*-isomer has a four-proton band centred at τ 9·8 with fine structure between about τ 9·4 and 10·1.



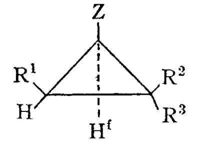
(I)



(II)



(III)



(IV)

We have utilized the shielding effects of alkyl substituents to make stereochemical assignments in more structurally complex cyclopropanes. A pair of stereoisomeric cyclopropanes (III and IV) results from the addition of carbenoid species CHZ to unsymmetric olefins of the type $RCH{=}CH_2$, *cis*-$R^1CH{=}CHR^2$, and $R^1R^2C{=}CHR^3$. In such cases

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† Full details will appear in a future publication.

structural assignments are most frequently made by comparison of vicinal ring proton coupling constants. The *cis*-coupling constants in cyclopropanes are generally larger than the *trans*-coupling constants. In accord with expectations we find, in all cases examined, the stereoisomer with the methine proton H^f at higher field is the one in which that proton is *cis* to the greater number of alkyl groups (III).[10] The magnitude of the difference in chemical shifts of H^f in (III) and (IV) is not constant but varies with the nature of substituent Z.*

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[9] *Cf.* A. G. Moritz and N. Sheppard, *Mol. Phys.*, 1962, **5**, 361. Our treatment parallels that used here in the analysis of axial and equatorial protons in cyclohexane.

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