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THE CHEMICAL SHIFT—II

THE ANISOTROPIES OF THE CARBON–CARBON DOUBLE BOND

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Abstract—The calculation of chemical shifts by the methods used in Part I[1] has been extended to include the shielding effects of the carbon–carbon double bond. By the application of this treatment to a series of conformationally rigid steroids the values of the two anisotropies of the carbon-carbon double bond have been deduced as

$$\Delta\chi_1^{C=O} = -12{\cdot}75 \times 10^{-30}, \quad \text{and} \quad \Delta\chi_2^{C=O} = -14{\cdot}27 \times 10^{-30}\ \text{cm}^3\ \text{molecule}^{-1}.$$

It has been established that the shift for any distant nucleus in proceeding from an alkane to the corresponding alkene comprises the algebraic sum of the screening constants for the displaced C—C and C—H bonds and the introduced C=C and olefinic C—H bonds. On this basis, in only a minority of cases examined is the contribution of the double bond to the total shift clearly predominant.

The conventional picture of the shielding cone around the carbon-carbon double bond appears to require substantial modification. It would seem that deshielding is confined to a restricted region at the ends of the double bond: outside this region a nucleus is shielded whether it lies in the "plane" of the double bond or above it.

IN THE preceding paper[1] the McConnell equation was modified to include short range effects. It was also established that in the calculation of chemical shifts, the screening effect of bonds displaced by a substituent must be taken into consideration as well as that of all the bonds of the substituent. The present paper describes the extension of these concepts to the shielding effect of the double bond.

Thus, the shielding of a nucleus by a double bond has been represented[2] qualitatively by the familiar so-called shielding cones in which a nucleus situated above the double bond is shielded (i.e. moved to higher field values) whilst a nucleus in the plane of the bond is deshielded. Although diagrams of this kind have been used qualitatively to explain the shift of a distant proton, previous attempts (cf. e.g. Refs 3, 4 and 5) to derive a quantitative treatment have applied the McConnell equation (2) in a manner which is theoretically unsound. McConnell[6] clearly derived his equation for a group of electrons possessing *cylindrical* or *conical* symmetry. In such cases only two susceptibilities are necessary to describe the anisotropy in the group susceptibility. There

[1] Part I. J. W. ApSimon, W. G. Craig, P. V. Demarco, D. W. Mathieson, L. Saunders and W. B. Whalley, *Tetrahedron* **23**, 2339 (1967).
[2] L. M. Jackman, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry* p. 129. Pergamon Press, Oxford (1962).
[3] R. R. Fraser, *Canad. J. Chem.* **40**, 78 (1962).
[4] S. Yamaguchi, S. Okuda and N. Nakagawa, *Chem. Pharm. Bull.* **11**, 1465 (1963).
[5] K. Tori, Y. Hata, R. Muneyuki, Y. Takano, T. Tsuji and H. Tanida, *Canad. J. Chem.* **42**, 926 (1964).
[6] H. M. McConnell, *J. Chem. Phys.* **27**, 226 (1957).

is consequently only *one* anisotropy for a group with these symmetry elements and Eq. (2) thus follows. However, a double bond, e.g. C=C or C=O, does not possess either cylindrical or conical symmetry and hence *three* susceptibilities (i.e. *two* anisotropies) are necessary to describe the anisotropy in the magnetic susceptibility. Consequently, McConnell's equation cannot be applied directly in these circumstances.

In developing our argument it is useful to recapitulate certain aspects of McConnell's equation. If, in Fig. 1, N be a nucleus and O the position of a point dipole induced in a distant group by a randomly oriented magnetic field **H**, then the secondary field at N may be calculated and integrated over all orientations of **H**. If complete magnetic

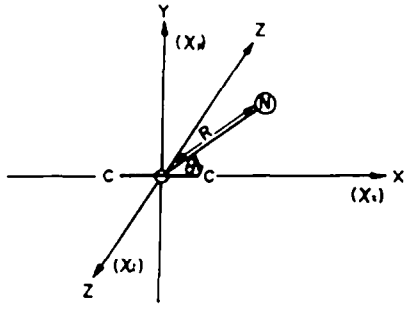

FIG. 1.

anisotropy be assumed at O, then the dipole at O may be resolved into three orthogonal components, each component having a susceptibility χ_X for the X direction, χ_Y for the Y direction and χ_Z for the Z direction. If l, m and n are the direction cosines of ON, and $\mathbf{R} = \mathrm{ON}$, then it follows that the shielding due to the dipole is given by the expression

$$\sigma = \frac{1}{3R^3}[\chi_X(1 - 3l^2) + \chi_Y(1 - 3m^2) + \chi_Z(1 - 3n^2)] \tag{1}$$

Should the bond in which the dipole at O originates possess conical or cylindrical symmetry (e.g. C—C, C—H), then the co-ordinate system can be chosen so that the X axis and the bond axis coincide. The susceptibility $\chi_Y(= \chi_Z)$ is the susceptibility transverse to the internuclear axis and χ_X is the susceptibility along the bond axis. Using the relationship between the direction cosines of

$$l^2 + m^2 + n^2 = 1$$

and making these substitutions in Eq. (1), we obtain Eq. (2), i.e. the McConnell equation which is applicable only to bonds where a symmetry axis is coincident with the bond axis.

$$\sigma = \frac{1}{3R^3}[\chi_X(1 - 3l^2) + \chi_Y(1 - 3m^2) + \chi_Y(1 - 3 + 3l^2 + 3m^2)]$$

$$= \frac{\chi_X - \chi_Y}{3R^3}(1 - 3l^2)$$

i.e. $$\sigma = \frac{\Delta\chi}{3R^3}(1 - 3\cos^2\theta) \tag{2}$$

In our treatment of the double bond, for which complete magnetic anisotropy must be assumed, we take the X axis (cf. Fig. 2) as coincident with the internuclear (bond) axis and the Y axis as the direction orthogonal to the nodal plane of the π orbitals: the Z axis is then orthogonal to these two axes (i.e. in the nodal plane of the π orbitals); χ_X is the magnetic susceptibility along the internuclear (σ bond) axis, χ_Y is the susceptibility along the pseudo-axis of symmetry of the π orbitals and χ_Z is the susceptibility orthogonal to X and Y in the nodal plane of the π orbitals. It is mathematically convenient to redefine the angles as follows: thus θ is the angle between **R** and the Y axis and γ the angle between the projection of **R** in the XZ plane and the X axis. Equation (1) then becomes:

$$\sigma = \frac{1}{3R^3}[\chi_Y(1 - 3m^2) - \chi_X(1 - 3m^2) - \chi_X(1 - 3n^2) + \chi_Z(1 - 3n^2)]$$

$$= \frac{1}{3R^3}[\Delta\chi_1(1 - 3m^2) + \Delta\chi_2(1 - 3n^2)]$$

Term I(i) Term I(ii)

$$= \frac{1}{3R^3}[\Delta\chi_1(1 - 3\cos^2\theta) + \Delta\chi_2(1 - 3\sin^2\theta.\sin^2\gamma)] \quad (3)$$

where $\Delta\chi_1 = \chi_Y - \chi_X$ is the anisotropy between the axis perpendicular to the nodal plane of the π orbitals and the σ bond direction and $\Delta\chi_2 = \chi_Z - \chi_X$ is the anisotropy between the axis through O in the nodal plane of the π orbitals and the σ bond direction.

We have used this form of the equation in the present paper.

In calculating for any given nucleus the chemical shift produced by the introduction of a double bond into the molecule, it is important to reiterate (cf. the preceding paper[1]) that *the contribution from the* C—C *and the* C—H *bonds displaced, as well as from the* C=C *and* C—H *bonds inserted, must be taken into account.* Thus, the general form of the equation required in our calculations is (4):

Term I Term II

(i) (ii)

$$\Delta\sigma = \Delta\chi_1^{C-C}.f[R_1, \theta_1] + \Delta\chi_2^{C-C}.f[R_1, \theta_1, \gamma] + \Delta\chi^{CH}.nf[R_2, \theta_2]$$

Term III Term IV

$$- \{\Delta\chi^{C-C}.f[R_3, \theta_3] + \Delta\chi^{CH}.mf[R_4, \theta_4]\} \quad (4)$$

where Term I(i) and Term I(ii) are the shielding contributions from C=C [Eq. (3)], Term II is the contribution from the C—H bonds attached to the double bond (n may be 0, 1 or 2). Term III represents the shielding due to the C—C single bond displaced and Term IV that due to the C—H bonds on the original C—C (m may be 0 to 4). Terms II, III and IV are in the form of the McConnell equation (2).

These calculations have been applied to a series of steroids, and the changes in the chemical shift of the C-18 and C-19 Me groups caused by a double bond in various

positions computed. Since the protons observed are in every case at a distance greater than 3 Å from the double bond, no correction for the failure of the point dipole approximation is necessary. For simplicity we have assumed that:

(a) the anisotropy of a Csp_2—H bond is the same as that of a Csp_3—H bond,

(b) the anisotropy of a Csp_2—Csp_3 bond is the same as that of a Csp_3—Csp_3 bond: the calculations of Guy and Tillieu[7] would suggest that these two assumptions are reasonable,

(c) in taking account of the C—H bonds, equatorial C—H bonds in the alkane may be equated with the olefinic C—H bonds in the alkene provided that this be in the semi-chair conformation: the obvious exceptions to this treatment are those cases where an exocyclic methylene group is introduced. The small discrepancies in R and θ introduced by this approximation make a negligible difference to the shielding,

(d) the cyclohexane and cyclohexene systems are in the chair or semi-chair conformations,

(e) the distance R may be taken[8] as that from the geometrical centre of the double bond to the centre of the circle which would be described by a rotating Me hydrogen atom.

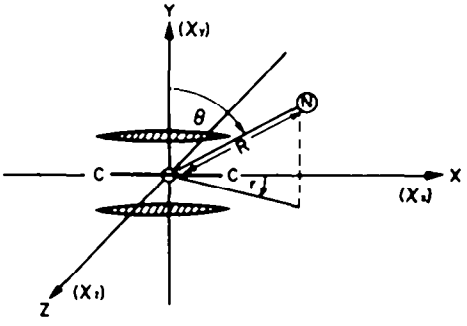

Fig. 2.

In deducing anisotropies for the C=C double bond, we have used only those steroids which are conformationally rigid: hence steroids with double bonds in positions 1, 2 and 3 have been omitted. Compounds with the double bond in ring D were not available to us. Since ^{13}C—H coupling constants have been shown[9] to be different for cyclopentene and cyclohexene, and in view of the postulated relationship[10] between such coupling constants and percentage *S* character of the C—H bonds, the values derived for the carbon-carbon double bond may not be directly applicable to five-membered rings. This point is at present under investigation. The proton resonances of the C-18 and C-19 methyl groups were determined at 60 Mc/s, in cyclohexane, carbon tetrachloride and deuterochloroform with TMS as internal standard. The complete list of compounds examined is shown in Table 1: changes in Me group resonances on adding double bonds appear in Table 2. Mean values of such changes are given in Table 3: the twelve examples listed all fulfil the condition of conformational rigidity. The examples included in the anisotropy calculations are listed in

[7] J. Guy and J. Tillieu, *J. Chem. Phys.* **24**, 1117 (1956).
[8] A. D. Cross and I. T. Harrison, *J. Am. Chem. Soc.* **85**, 3223 (1963).
[9] K. Tori, R. Muneyuki and H. Tanida, *Canad. J. Chem.* **41**, 3142 (1963).
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Tables 4, 5 and 6 together with the relevant measurements* and calculations. Data relevant to the 11-methylene derivatives were excluded from these calculations since models clearly indicate a distortion from the unstrained steroid skeleton produced by the interaction of the C-1 α proton and the C-11 substituent (see later). Equation (4) may be restated more conveniently as in (5): twenty-one equations were then written as in (5) where the factors *a* to *f* refer to geometric factors which are defined footnotes to Tables 4, 5 and 6.

$$a\Delta\chi_1^{C-C} + b\Delta\chi_2^{C-C} = \text{observed shift in ppm} \times 10^{-6} - c\Delta\chi^{CH} + (e+f)\Delta\chi^{CH} + d\Delta\chi^{C-C} \quad (5)$$

The two different sets of values (6) and (7)

$$\Delta\chi^{C-C} = +21{\cdot}33 \times 10^{-30} \qquad \Delta\chi^{CH} = +12{\cdot}57 \times 10^{-30} \quad (6)$$

$$\Delta\chi^{C-C} = +13{\cdot}98 \times 10^{-30} \qquad \Delta\chi^{CH} = +11{\cdot}00 \times 10^{-30} \quad (7)$$

obtained in the preceding paper[1] for $\Delta\chi^{C-C}$ and $\Delta\chi^{CH}$ were used separately in solving the twenty-one equations of type (5) by the method of least squares and the corresponding values (8) and (9) were obtained for $\Delta\chi_1^{C-C}$ and $\Delta\chi_2^{C-C}$

$$\Delta\chi_1^{C-C} = -11{\cdot}82 \times 10^{-30}, \qquad \Delta\chi_2^{C-C} = -15{\cdot}84 \times 10^{-30} \text{ cm}^3 \text{ molecule}^{-1} \quad (8)$$

$$\Delta\chi_1^{C-C} = -12{\cdot}75 \times 10^{-30}, \qquad \Delta\chi_2^{C-C} = -14{\cdot}27 \times 10^{-30} \text{ cm}^3 \text{ molecule}^{-1} \quad (9)$$

As is shown later in this paper the second set (7) and (9) is preferred. Susceptibilities corresponding to these anisotropies were then derived using a mean value of the susceptibility for the C···C bond.[11]

Thus:
$$\tfrac{1}{3}(\chi_X + \chi_Y + \chi_Z) = -3{\cdot}2 \times 10^{-30} \quad (10)$$

and solving with

$$\Delta\chi_1 = \chi_Y - \chi_X = -12{\cdot}75 \times 10^{-30} \quad (11)$$

$$\Delta\chi_2 = \chi_Z - \chi_X = -14{\cdot}27 \times 10^{-30} \quad (12)$$

we obtain

$$\chi_X = +3{\cdot}68 \times 10^{-30} \text{ cm}^3 \text{ molecule}^{-1}$$
$$= +2{\cdot}22 \times 10^{-6} \text{ cm}^3 \text{ mole}^{-1}$$
$$\chi_Y = -9{\cdot}07 \times 10^{-30} \text{ cm}^3 \text{ molecule}^{-1}$$
$$= -5{\cdot}47 \times 10^{-6} \text{ cm}^3 \text{ mole}^{-1}$$
$$\chi_Z = -10{\cdot}59 \times 10^{-30} \text{ cm}^3 \text{ molecule}^{-1}$$
$$= -6{\cdot}39 \times 10^{-6} \text{ cm}^3 \text{ mole}^{-1}$$

These susceptibilities may be compared (Fig. 3) with those derived[1] for the C—C and C—H bonds. In each case the susceptibility along the X axis (χ_X) (σ bond axis) is

* In this and subsequent papers, the measurements of the requisite angles and distances have been made on Dreiding models using an instrument, designed by one of us (J. W. ApS. and his Associates). Details will be published elsewhere.

[11] P. Pascal, A. Pacault and J. Hoarau, *C. R. Acad. Sci., Paris* **233**, 1078 (1951).

positive and the most paramagnetic whilst the susceptibilities in the other Cartesian co-ordinates, Y and Z, are negative.

The anisotropies (6) and (8) and the alternative pair of values (7) and (9) were used to calculate the chemical shifts of the C-18 and C-19 Me groups in the examples in Table 3. Tables 7 and 8 show the results of these calculations and illustrate the individual contribution to the shift made by each term. Figures 4 and 5 show a plot of the calculated against the observed values. It will be seen that the second set of anisotropies, (7) and (9), is to be preferred and that the line of best fit in this case (Fig. 5) is

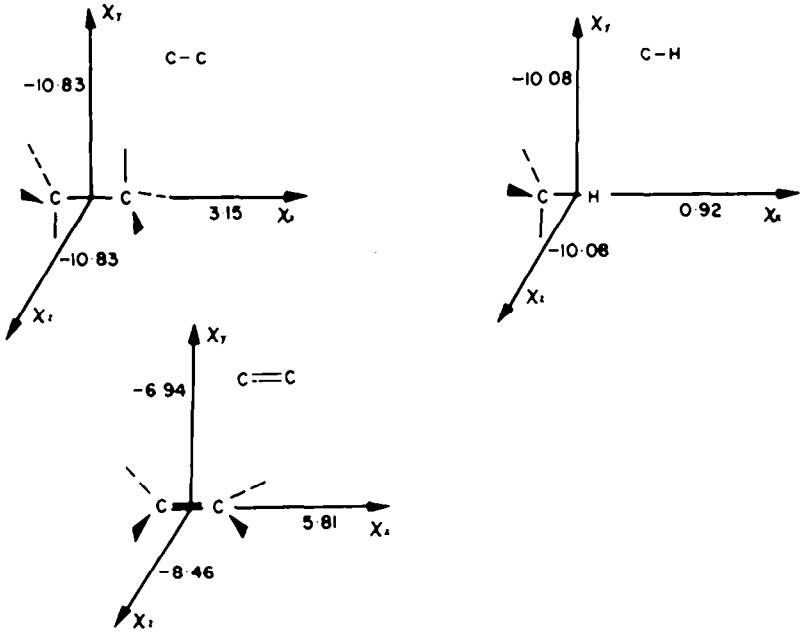

FIG. 3.

approximately that of the theoretical line. With two exceptions all calculated values of the methyl resonances fall within ±3 c/s of the observed values. Agreement is less satisfactory (Fig. 4) with the first set, (6) and (8), and the line of best fit does not strictly coincide with the theoretical line: in this case the calculated values for nine examples fall outside the range ±3 c/s. Previous calculations[3–5] have been based on a misapplication of McConnell's original work[6] and it was implied that agreement between the calculated and observed shifts was satisfactory. When such methods are applied to our examples, the lack of agreement clearly illustrates the errors of the assumptions involved: for example, when the appropriate calculations are made using Fraser's approach[3] the line of best fit (Fig. 6) bears no relationship to the theoretical line. This conclusion is independent of the value used for the anisotropy.

The chemical shift difference, $\Delta\sigma = (\sigma_{alkane} - \sigma_{alkene})$, consists of two distinct parts, namely the shielding of the C—C and C—H bonds which are displaced and whose contributions is *subtracted*, together with the shielding of the C=C bond whose contribution together with that of any olefinic C—H bonds is *added*. Table 9 shows the total contribution from these two sources. In only six cases out of twenty-one, namely C-19, Δ^6, $3CH_2$, $7CH_2$ and C-18, Δ^4, Δ^8, and $\Delta^{9,11}$, is the contribution from

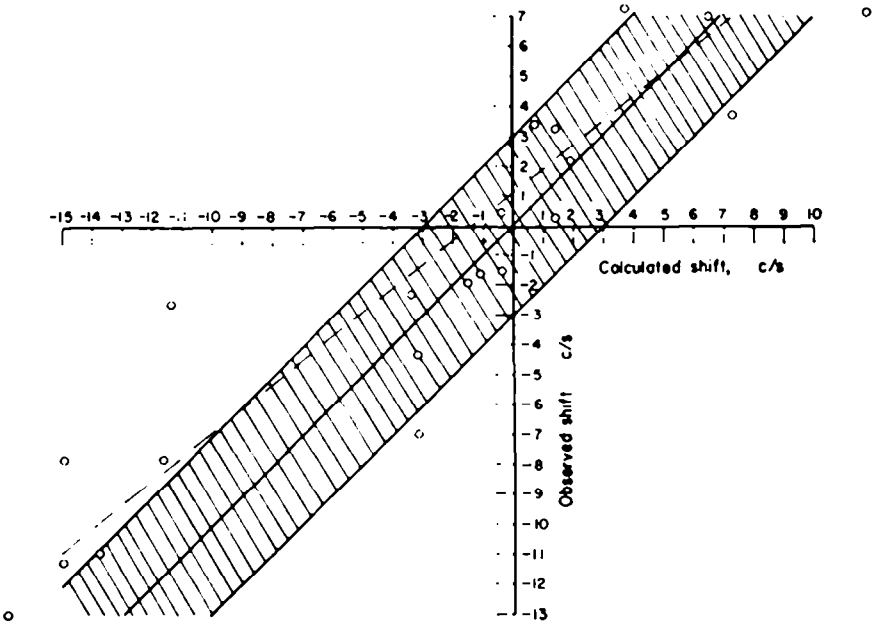

FIG. 4. Data taken from last two columns of Table 7. Dotted line indicates approximate line of 'best fit' of the individual points. The shaded area indicates the region $+3$ c/s of the observed shift.

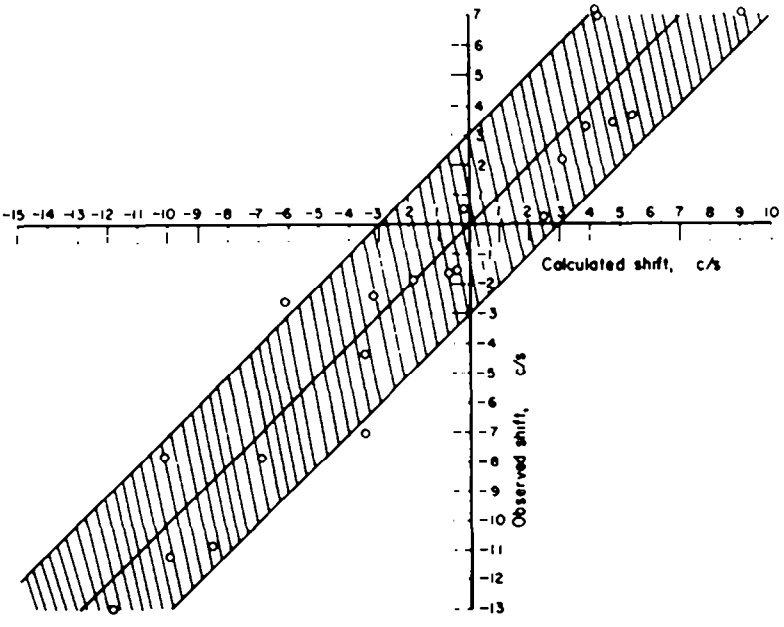

FIG. 5. Data taken from last two columns of Table 8. Theoretical line represents line of best fit. The shaded area indicates the region ± 3 c/s of the observed shift.

the double bond clearly predominant. For seven cases namely, C-19, Δ^5, Δ^8, $\Delta^{9,11}$, and $\Delta^{8,14}$ and C-18, Δ^7, Δ^{11}, $\Delta^{8,14}$, it is the removal of the C—C single bond with its axial hydrogens which provides the major contribution to the shift. In the remaining eight examples, C-19, Δ^4, Δ^7, Δ^{11}, $6CH_2$ and C-18, Δ^5, Δ^6, $6CH_2$ and $7CH_2$, the contributions of both components are approximately equal. These observations underline the importance of considering all the bonds involved when calculating chemical shift differences.

It follows therefore that the pictures of shielding cones currently presented in texts[2] must be rejected. For the olefinic bond it is widely implied that in terms of angular dependence, protons *above* the plane of the bond are shielded whilst protons *in* the

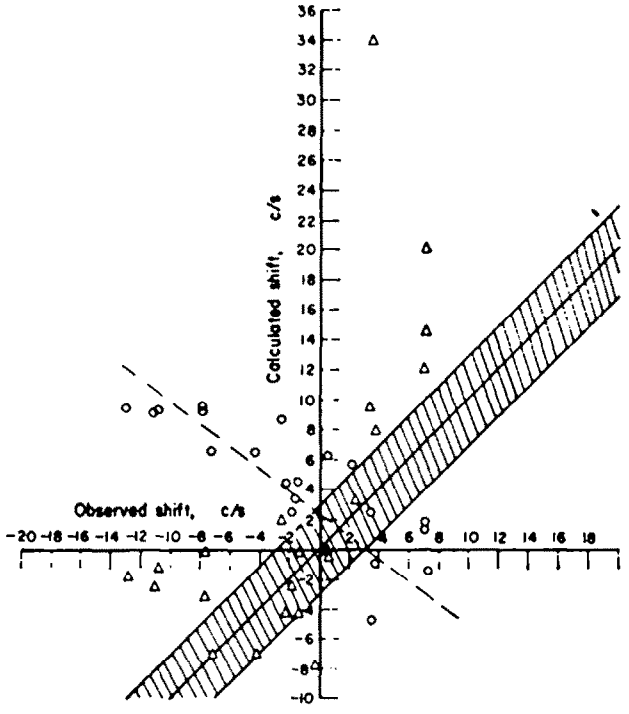

FIG. 6. ○ Plot of points made using method adopted by Frazer[3]. △ Plot of points using method of Nakagawa[4,5]. The shaded area indicates the region ±3 c/s of the observed shift.

plane of the bond are deshielded. Such a picture is apparently based on the simple $(1-3\cos^2\theta)$ relationship. As we have shown earlier in this paper *two* interdependent functions must be considered and using these functions [Eq. (3)] a picture of the shielding about the double bond has been obtained as in Fig. 7: the dimensions of the "cone" are 114° in the Y axis and 104° in the Z axis. Thus, *deshielding of a proton occurs only within a restricted region at the ends of the double bond. Outside this region a proton is shielded whether it lies in the "plane" of the double bond or above it.*

In the case of 11-methylene-androstane, calculations based upon the undistorted Dreiding model predict a chemical shift (androstane/11-methylene-androstane) for the C-19 methyl group of +4·1 c/s whereas the observed figure is −13·4 c/s. Taking the

TABLE 1. TABLE OF METHYL RESONANCE POSITIONS (IN C/S FROM TMS AT 60 Mc/s)

Compound	Solvent					
	Cyclohexane		CCl_4		$CDCl_3$	
	C-19	C-18	C-19	C-18	C-19	C-18
Cholestane[13]	49·8	42·0	46·4	38·7	46·5	39·0
Cholestan-3β-ol[13,14]	49·2	41·2	48·2	39·1	48·6	39·4
3β-Acetoxycholestane[13]	50·7	41·8	49·4	39·0	49·3	39·2
Cholestan-3-one[15,16]	61·2	43·4	61·4	41·4	60·6	41·0
Cholest-1-en-3β-ol[17]	59·0	41·8	60·3	41·5	54·6	40·0
Cholest-1-en-3-one[18]	59·7	43·7	60·3	41·7	60·6	42·4
3β-Acetoxycholest-1-ene[17,19]	55·4	42·1	55·0	40·0	55·6	40·5
Cholest-4-ene[20]	62·2	43·6	62·0	43·5	60·5	41·0
Cholest-4-en-3β-ol[21]	62·6	43·1	62·1	40·5	63·2	41·2
Cholest-4-en-3-one[22]	70·3	44·7	71·3	42·0	71·2	43·0
3β-Acetoxycholest-4-ene[23]	63·6	42·7	64·0	41·4	63·8	41·0
Cholest-5-en-3β-ol[15,23]	61·2	43·1	59·6	40·6	60·7	40·0
Cholest-5-en-3-one[23]	70·8	44·6	71·0	43·2	71·0	43·0
3β-Acetoxycholest-5-ene[15,14]	62·1	42·9	61·4	41·3	61·6	41·1
3-Methylenecholestane[24]	52·6	41·9	51·4	39·2	51·5	39·5
Cholest-6-en-3β-ol[25]	48·7	43·7	46·2	41·5	47·2	41·8
Cholest-6-en-3-one[26]	55·3	45·0	56·7	43·2	58·5	43·7
3β-Acetoxycholest-6-ene[25]	49·2	43·6	48·6	42·4	48·2	41·7
Cholest-7-ene-3β-ol[27]	49·5	34·1	47·3	31·6	48·1	32·4
Cholest-7-en-3-one[28]	61·4	36·6	60·6	33·7	61·0	33·9
3β-Acetoxycholest-7-ene[27]	49·8	34·6	49·2	32·0	49·1	32·4
Cholest-7-ene[29]	48·4	34·5	46·7	32·3	46·4	32·4
6-Methylenecholestan-3β-ol[30]	42·4	41·2	40·5	38·9	41·2	39·0
6-Methylenecholestan-3-one[31]	53·6	42·1	53·5	40·5	54·0	40·8
7-Methylenecholestan-3β-ol[32]	55·8	43·0	55·8	40·9	56·3	41·3
7-Methylenecholestan-3-one[33]	67·9	42·4	68·3	43·4	67·4	42·7
3β-Acetoxy-7-methylenecholestane[32]	55·5	43·6	57·3	40·7	57·3	41·2
Cholest-8-en-3β-ol[33]	57·2	36·6	54·5	35·3	57·0	36·8
Cholest-8-en-3-one[34]	68·1	37·8	68·4	38·0	68·7	38·6
3β-Acetoxycholest-8-ene[35]	58·7	39·1	58·1	36·4	58·2	36·8
Cholest-8(14)-en-3β-ol[36]	42·9	52·8	40·7	49·7	41·7	51·9
Cholest-8(14)-en-3-one	54·0	52·6	53·5	51·8	54·6	52·9
3β-Acetoxycholest-8(14)-ene[35]	43·6	50·5	42·5	49·9	42·7	51·8
Cholest-8(14)-ene[36]	41·7	50·6	39·5	49·6	39·8	51·7
5α,22α-Spirostan-3-one[37]			61·8	46·1	62·0	48·2
5α,22α-Spirost-9(11)-en-3-one[38]			69·1	42·3	70·2	45·4
5α,22α-Spirost-11-en-3-one[39]			57·8	48·3	58·7	51·1
11-Methylene-5α,22α-spirostan-3-one[38]			75·1	42·5	75·5	42·4

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TABLE 2. CHANGES IN CHEMICAL SHIFTS ON ADDING DOUBLE BONDS
(in c/s at 60 Mc/s: a +ve sign indicates an upfield shift on introducing the double bond)

Examples	Solvent					
	Cyclohexane		CCl_4		$CDCl_3$	
	C-19	C-18	C-19	C-18	C-19	C-18
1-ene, 3β-ol	−9·8	−0·6	−12·1	−2·4	−6·0	−0·6
1-ene, 3-one	−1·5	0·3	+1·1	0·3	0·0	−1·4
1-ene, 3β-acetate	−4·7	−0·3	5·6	−1·0	−6·3	−1·3
4-ene	−12·4	1·6	15·6	−4·8	−14·0	−2·0
4-ene, 3β-ol	13·4	1·9	−13·9	−1·4	14·6	−1·8
4-ene, 3-one	−9·1	−1·3	−9·9	−0·6	−10·6	−2·0
4-ene, 3β-acetate	−12·9	0·9	−14·6	−2·4	−14·5	−1·8
5-ene, 3β-ol	12·0	−1·9	−11·4	1·5	−12·1	−0·6
5-ene, 3-one	−9·6	−1·2	−9·6	−1·8	−10·4	−2·0
5-ene, 3β-acetate	11·4	−1·1	−12·0	−2·3	−12·3	−1·9
$3CH_3$	−2·8	+0·1	−5·0	−0·5	−5·0	−0·5
6-ene, 3β-ol	+0·5	2·5	−2·0	−2·4	+1·4	−2·4
6-ene, 3-one	+5·9	−1·6	+4·7	−1·8	−2·1	−2·7
6-ene, 3β-acetate	+1·5	−1·8	+0·8	−3·4	+1·1	2·5
7-ene, 3β-ol	0·3	+7·1	+0·9	+7·5	−0·5	+7·0
7-ene, 3-one	−0·2	+6·8	+0·8	+7·7	0·4	+7·1
7-ene, 3β-acetate	−0·9	+7·2	+0·2	+7·0	−0·2	+6·8
7-ene	+1·4	+7·5	−0·3	+6·4	−0·1	+6·6
$6CH_3$, 3β-ol	+6·8	0·0	+7·7	+0·3	+7·4	+0·4
$6CH_3$, 3-one	+7·6	+1·3	+7·9	+0·9	+6·6	+0·2
$7CH_3$, 3β-ol	−6·6	1·8	−7·6	−1·8	−7·7	−1·9
$7CH_3$, 3-one	−6·7	+1·0	−6·9	2·0	−6·8	−1·7
$7CH_3$, 3β-acetate	−4·8	1·8	−7·9	−1·7	−8·0	−2·0
8-ene, 3β-ol	8·0	+4·6	6·3	+3·8	−8·4	+2·6
8-ene, 3-one	−6·9	+5·6	−7·0	3·4	−8·1	−2·4
8-ene, 3β-acetate	−8·0	+2·7	−8·7	+2·6	−8·9	+2·4
8(14)-ene, 3β-ol	−6·3	−11·6	+7·5	−10·6	+6·9	−12·5
8(14)-ene, 3-one	+7·2	−9·2	+7·9	−10·4	+6·0	−11·9
8(14)-ene, 3β-acetate	+7·1	−8·7	+6·9	10·9	+6·6	−12·6
8(14)-ene	+8·1	−8·6	+6·9	10·9	+6·7	−12·7
9(11)-ene, 3-one			7·3	+3·8	−8·2	+2·8
11-ene, 3-one			+4·0	−2·2	+3·3	−2·9
$11CH_3$, 3-one			−13·3	3·6	−13·6	+5·8

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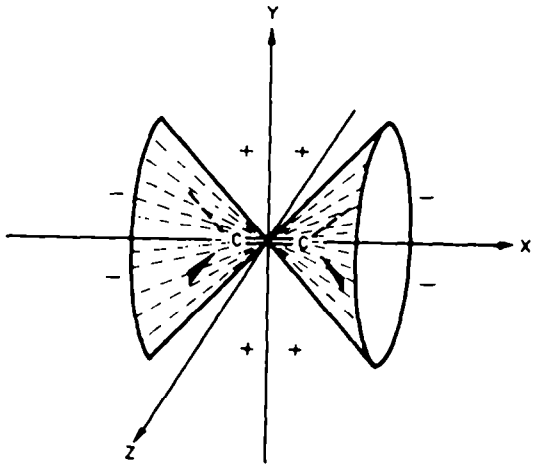


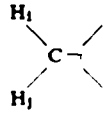
FIG. 7.

TABLE 3. MEAN CHANGES IN THE CHEMICAL SHIFT ON INTRODUCING DOUBLE BONDS
(in c/s at 60 Mc/s: a +ve sign indicates an upfield shift)

Double bond position	Solvent							
	Cyclohexane		CCl_4		$CDCl_3$		Mean	
	C-19	C-18	C-19	C-18	C-19	C-18	C-19	C-18
4,5	−12·0	−1·4	−13·5	−2·3	−13·4	−1·9	−13·0	−1·9
5,6	−11·0	1·4	−11·0	−1·9	−11·6	−1·5	−11·2	−1·6
6,7	+2·6	−2·0	+2·5	−2·5	+1·5	−2·5	+2·2	−2·3
7,8	+0·5	+7·2	+0·4	+7·2	+0·1	+6·9	+0·3	+7·1
8,9	−7·6	+4·3	−7·3	+3·3	−8·5	+2·5	−7·8	+3·4
9,11[a]	—	—	−7·3	+3·8	−8·2	+2·8	−7·8	+3·3
8,14	+7·2	9·6	+7·3	−10·7	+6·6	−12·4	+7·0	−10·9
11,12[a]	—	—	+4·0	−2·2	+3·3	−2·9	+3·7	−2·6
exo 3	−2·8	+0·1	−5·0	−0·5	−5·0	−0·5	−4·3	−0·3
exo 7	−6·0	−0·9	−7·5	−1·8	−7·5	−1·9	−7·0	−1·5
exo 6	+7·2	+0·7	−7·8	+0·6	+7·0	+0·3	+7·3	+0·5
exo 11[a]	—	—	−13·3	+3·6	−13·5	+5·4	−13·4	+4·7
1,2[b]	−7·3	−0·5	−8·9	−1·7	−6·2	−1·0	−7·5	−1·1

[a] Compounds only sparingly soluble in cyclohexane.
[b] These values are the average from the 3β-ol and 3β-acetate.

TABLE 4.



Example No.	Double bond position	Carbon-carbon double bonds: R_1(Å)	θ_1 (degrees)		Geometric factors (a) C ··C (cm^{-3}.10^{33})	(b) C —C	Carbon-hydrogen bonds in Exo-methylene group: R_{s1}(Å)	θ_{s1} (degrees)	(c_1) Geometric factor (cm^{-3}.10^{33})	R_{s1}(Å)	θ_{s1} (degrees)	(c_1) Geometric factor (cm^{-3}.10^{33})	$\Delta\chi^{CH}$ × Geometric factor for Term II (in ppm.) [Equation (4)]: b $C_1\times\Delta\chi^{CH}$	b $C_1\times\Delta\chi^{CH}$	c $C_1\times\Delta\chi^{CH}$	c $C_1\times\Delta\chi^{CH}$
	C-19								H$_1$			H$_1$				
1	4,5	3·3	60	30	+ 0·2319	+ 0·4058										
2	5,6	3·3	58	35	+ 0·1461	+ 0·2692										
3	6,7	3·3	50	86	— 0·2222	- 0·6974										
4	7,8	3·4	53	85	— 0·0734	- 0·7624										
5	8,9	3·2	57	45	+ 0·1120	- 0·0560										
6	9,11	3·3	60	36	+ 0·2319	+ 0·2065										
7	8,14	3·6	40	36	- 0·5433	+ 0·4085										
8	11,12	3·4	35	41	- 0·8591	+ 0·4878										
9	3CH$_3$[a]	4·3	80	0	+ 0·3813	+ 0·4193	5·4	50	— 0·0507	5·4	50	- 0·0507	+ 0·007	— 0·007	— 0·006	- 0·006
10	7CH$_3$	4·3	80	0	+ 0·3813	+ 0·4193	5·4	50	— 0·0507	5·4	50	— 0·0507	— 0·007	— 0·007	- 0·006	— 0·006
11	6CH$_3$	3·5	41	36	0·5510	+ 0·4306	3·8	77	+ 0·5153	4·3	46	— 0·1878	+ 0·065	— 0·024	+ 0·057	— 0·021
	C-18															
12	4,5	6·1	88	12	+ 0·1463	+ 0·1278										
13	5,6	5·2	84	86	+ 0·2293	— 0·4629										
14	6,7	4·9	80	36	+ 0·2577	- 0·0015										
15	7,8	3·3	31	29	— 1·1170	+ 0·7541										
16	8,9	2·9	26	67	— 1·9455	+ 0·6991										
17	9,11	3·2	41	87	— 0·7210	- 0·2927										
18	11,12	3·1	54	46	- 0·0408	- 0·0179										
19	8,14	3·2	57	43	+ 0·1120	+ 0·0189										
20	6CH$_3$	5·7	51	29	- 0·0339	+ 0·1033	6·3	75	+ 0·1065	6·7	43	— 0·0670	+ 0·013	- 0·008	+ 0·012	- 0·007
21	7CH$_3$	4·7	73	57	+ 0·2387	— 0·2985	4·9	84	+ 0·2740	5·8	11	— 0·3230	+ 0·034	— 0·041	+ 0·030	— 0·036

[a] The deshielding effect of the 3CH$_3$ group is considered only for C19: C18 is too distant for the effect to be significant.
[b] Anisotropy used was $\Delta\chi^{CH} = 12{\cdot}57 \times 10^{-30}$ cm^3 molecule^{-1} (Method No. 1, preceding paper[1]).
[c] Anisotropy used was $\Delta\chi^{CH} = 11{\cdot}00 \times 10^{-30}$ cm^3 molecule^{-1} (Method No. 2, preceding paper[1]).

$a = \frac{1}{2}(1 - 3\cos^2\theta_1)R_1^{-3}$ where R_1 is the distance from the centre of the circle described by the rotating methyl hydrogen atoms to the geometrical centre of the double bond: θ_1 is the angle described by R_1 and the axis of symmetry of the π orbitals.

$b = \frac{1}{2}(1 - 3\sin^2\theta_1\sin^2\gamma)R_1^{-3}$ where γ is the angle described by the plane projection of R_1 on to the XZ plane (see Fig. 2) and the C··C internuclear axis.

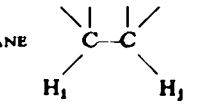
$c = \frac{1}{2}(1 - 3\cos^2\theta_2)R_2^{-3}$ where R_2 is the distance between the centre of the circle described by the rotating methyl hydrogen atoms and a point on the CH bond 0·77 Å distant from the C atom of the C—C. θ_2 is the angle described by R_2 and the axis of the CH bond. R_2 and θ_2 with their associated geometric factors have to be obtained for both protons (H_1 and H_1) of the exocyclic methylene groups.

TABLE 5. CARBON-CARBON SINGLE BOND

Example[a]	R_s(Å)	θ_s (degrees)	Geometric factor (d) ($cm^{-3} \cdot 10^{24}$)	$\Delta\chi^{O-O} \times$ Geometric factor (d) for term (III) (in ppm.) [Eq. (4)]	
				b	*c*
1	2·9	77	+1·1593	+0·247	+0·162
2	2·9	77	+1·1593	+0·247	+0·162
3	3·5	63	+0·2967	+0·063	+0·041
4	3·5	63	+0·2967	+0·063	+0·041
5	2·9	77	+1·1593	+0·247	+0·162
6	2·9	77	+1·1593	+0·247	+0·162
7	3·9	25	−0·8228	−0·175	−0·115
8	3·9	25	−0·8228	−0·175	−0·115
9	—	—	—	—	—
10	—	—	—	—	—
11	—	—	—	—	—
12	6·1	41	−0·1041	−0·022	−0·015
13	5·3	76	+0·1846	+0·039	+0·026
14	4·7	61	+0·0947	+0·020	+0·013
15	3·7	22	−1·0391	−0·222	−0·145
16	3·2	67	+0·5513	+0·118	+0·077
17	3·2	67	+0·5513	+0·118	+0·077
18	2·9	84	+1·3219	+0·282	+0·185
19	2·9	84	+1·3219	+0·282	+0·185
20	—	—	—	—	—
21	—	—	—	—	—

[a] See table 4 for key to examples.
[b] Anisotropy used was $\Delta\chi^{O-O} = +21{\cdot}33 \times 10^{-30}$ (Method No. 1 preceding paper[1]).
[c] Anisotropy used was $\Delta\chi^{O-O} = +13{\cdot}98 \times 10^{-30}$ (Method No. 2, preceding paper[1]).
$d = \frac{1}{3}(1 - 3\cos^2\theta_s)R_s^{-3}$ where R_s is the distance from the centre of the circle described by the rotating methyl hydrogen atoms to the centre of the C—C bond in the alkane and θ_s is the angle described by R_s and the C—C internuclear axis.

C-9–C-11 bond as an axis, the dihedral angle described by the C-9–C-10 C—C single bond and the double bond at C-11 is approximately 10°, with the  lying towards the α face of the androstane skeleton. By making the C-9–C-10 bond and the olefinic bond co-planar (dihedral angle, zero) the calculated shift moves to negative values (to approximately −19 c/s) a figure more in agreement with the observed shift. Such a distortion moreover moves the methylene proton from a point ~1 Å distant from the C-1 equatorial hydrogen (~2 Å distant from the circumference of the circle

TABLE 6. AXIAL CARBON-HYDROGEN BONDS IN THE ALKANE 

Example[a]	R_{ei} (Å)	θ_{ei} (degrees)	Geometric factor (e) ($cm^{-3} \cdot 10^{24}$)	R_{ej} (Å)	θ_{ej} (degrees)	Geometric factor (f) ($cm^{-3} \cdot 10^{24}$)	$\Delta\chi^{CH}$ × Geometric factor for Term IV (in ppm.) [Eq. (4)] $e \times \Delta\chi^{CH_3}$	$f \times \Delta\chi^{CH_3}$	$e \times \Delta\chi^{CH_2}$	$f \times \Delta\chi^{CH_2}$	Observed shift ppm
1	2·8	64	+0·6431	3·6	23	−1·1017	+0·081	−0·138	+0·071	−0·121	−0·217
2	3·6	23	−1·1017	2·8	64	+0·6431	−0·138	+0·081	−0·121	+0·071	−0·187
3	2·8	64	+0·6431	4·4	39	−0·3177	+0·081	−0·040	+0·071	−0·035	+0·037
4	4·4	39	−0·3177	2·8	64	+0·6431	−0·040	+0·081	−0·135	+0·071	+0·005
5	2·8	64	+0·6431	3·6	23	−1·1017	+0·081	−0·138	+0·071	−0·121	−0·130
6	3·6	23	−1·1017	2·8	64	+0·6431	−0·138	+0·081	−0·121	+0·071	−0·130
7	2·8	64	+0·6431	5·1	45	−0·1256	+0·081	−0·016	+0·071	−0·014	+0·117
8	2·8	64	+0·6431	4·6	53	−0·0296	+0·081	−0·004	+0·071	−0·003	+0·062
9	4·4	39	−0·3177	4·3	43	−0·2535	−0·040	−0·032	−0·035	−0·028	−0·072
10	4·4	39	−0·3177	4·3	43	−0·2535	−0·040	−0·032	−0·035	−0·028	−0·122
11	3·9	24	−0·8450	2·8	64	+0·6431	−0·106	+0·081	−0·093	+0·071	+0·117
12	6·5	82	+0·1143	6·0	50	−0·0370	+0·014	−0·005	+0·013	−0·004	−0·032
13	4·8	75	+0·2408	6·0	50	−0·0370	+0·030	−0·005	+0·026	−0·004	−0·027
14	4·8	75	+0·2408	4·8	43	−0·1822	+0·030	−0·023	+0·026	−0·020	−0·038
15	4·8	43	−0·1822	2·5	59	+0·4356	−0·023	+0·055	−0·020	+0·048	+0·118
16	2·5	59	+0·4356	4·2	32	−0·5208	+0·055	−0·065	+0·048	−0·057	+0·057
17	4·2	32	−0·5208	2·5	59	+0·4356	−0·065	+0·055	−0·057	+0·048	+0·055
18	2·5	59	+0·4356	3·6	23	−1·1017	+0·055	−0·138	+0·048	−0·121	−0·043
19	2·5	59	+0·4356	3·6	27	−0·9871	+0·055	−0·124	+0·048	−0·109	−0·182
20	4·8	75	+0·2408	6·1	17	−0·2561	+0·030	−0·032	+0·026	−0·028	+0·008
21	4·8	43	−0·1822	4·4	78	+0·3406	−0·023	+0·043	−0·020	+0·037	−0·025

[a] See Table 4 for key to examples.

For cases 9, 10, 11, 20 and 21 protons H_i and H_j are on the *same* carbon atom.

e and $f = \frac{1}{4}(1 - 3\cos^2\theta_i)R_i^{-3}$ where R_i is the distance from the centre of the circle described by the rotating methyl hydrogen atoms to a point 0·77 Å from the carbon atom along the axial C—H bond and θ_i is the angle described by R_i and the C—H internuclear axis. The geometric factor e refers to the proton H_i and the geometric factor f to the proton H_j.

[b] Anisotropy used was $\Delta\chi^{CH} = 12{\cdot}57 \times 10^{-30}$ cm^3 $molecule^{-1}$ (Method No. 1, preceding paper[1]).

[c] Anisotropy used was $\Delta\chi^{CH} = 11{\cdot}00 \times 10^{-30}$ cm^3 $molecule^{-1}$ (Method No. 2, preceding paper[1]).

TABLE 7. CHEMICAL SHIFT CONTRIBUTIONS IN c/s AT 60 Mc/s FROM EACH TERM OF EQUATION (4)

Examples[a]	C=C Double bond Term I(i)	C=C Double bond Term I(ii)	Term II Hydrogen atoms on C=C double bond (exo-methylene groups)		Term III C—C single bonds	Term IV hydrogen atoms in the alkane		Calculated shift in c/c at 60 Mc/s	Observed shift in c/c at 60 Mc/s
1	−1·6	−3·9			+14·8	+4·9	−8·3	−16·9	−13·0
2	−1·0	−2·6			−14·8	−8·3	+4·9	−15·0	−11·2
3	+1·6	+6·6			+3·8	+4·9	−2·4	−1·9	+2·2
4	+0·5	+7·2			+3·8	−2·4	+4·9	+1·4	+0·3
5	−0·8	+0·5			−14·8	+4·9	−8·3	−11·7	−7·8
6	−1·6	−2·0			+14·8	−8·3	+4·9	−15·0	−7·8
7	+3·9	−3·9			−10·5	+4·9	−0·9	+6·5	+7·0
8	+6·1	−4·6			−10·5	+4·9	−0·2	−7·3	+3·7
9	−2·7	−4·0	−0·4	−0·4		−2·4	−1·9	−3·2	−4·3
10	−2·7	−4·0	−0·4	−0·4		−2·4	−1·9	−3·2	−7·0
11	+3·9	−4·1	+3·9	−1·4		−6·4	+4·9	−3·8	+7·3
12	−1·0	−1·2			−1·3	+0·9	−0·3	−1·5	−1·9
13	−1·6	+4·4			+2·4	+1·8	−0·3	−1·1	−1·6
14	−1·8	0·0			−1·2	+1·8	−1·4	−3·4	−2·3
15	+7·9	−7·2			−13·3	−1·4	+3·3	+12·1	−7·1
16	+13·8	−6·6			+7·1	+3·3	−3·9	+0·7	+3·4
17	+5·1	+2·8			+7·1	−3·9	+3·3	+1·4	+3·3
18	+0·3	+0·2			+16·9	+3·3	−8·3	−11·4	−2·6
19	−0·8	−0·2			+16·9	+3·3	−7·4	−13·8	−10·9
20	+0·2	−1·0	−0·8	−0·5		+1·8	−1·9	−0·4	+0·5
21	−1·7	+2·8	+2·1	−2·4		−1·4	+2·6	−0·4	−1·5

[a] See Table 4 for key to examples.
(A) Anisotropies (6) and (8) used in these calculations.
(B) Terms I to IV are those marked in equation (4).
(C) A + sign indicates a shift to higher field values; a − sign to lower field values.

described by the C-19 Me hydrogen atoms) to a position equidistant between the two groups.

Calculations show that a distortion of the dihedral angle in the opposite sense to the above i.e. produced by bending the 11-methylene group further towards the α face of the molecule, also moves the calculated shift to negative values. This, however, has the effect of decreasing the methylene proton–C-1 equatorial hydrogen distance to about 0·5 Å and is thus unlikely.

Calculations for Δ^1-enes have been carried out assuming that ring A has the semi-chair conformation. Under these circumstances the calculated chemical shift (−7·2 c/s) for C-19 in cholest-1-en-3β-ol and the corresponding acetate agree satisfactorily with the observed values for these substances.

TABLE 8. CHEMICAL SHIFT CONTRIBUTIONS IN c/s AT 60 Mc/s FROM EACH TERM OF EQUATION (4)

Examples*	C=C double bond Term I(i)	C=C double bond Term I(ii)	Term II Hydrogen atoms on C=C double bond (exo-methylene groups)		Term III C≡C single bonds	Term IV hydrogen atoms in the alkane		Calculated shift in c/s at 60 Mc/s	Observed shift in c/s at 60 Mc/s
1	−1·8	−3·5			+9·7	+4·2	−7·3	−11·9	−13·0
2	−1·1	−2·3			+9·7	−7·3	+4·2	−10·0	−11·2
3	+1·7	+6·0			+2·5	+4·2	−2·1	+3·1	+2·2
4	+0·6	+6·5			+2·5	−2·1	+4·2	+2·5	+0·3
5	−0·9	+0·5			+9·7	−4·2	−7·3	−7·0	−7·8
6	−1·8	−1·8			+9·7	−7·3	+4·2	−10·2	−7·8
7	−4·2	−3·5			−6·9	−4·2	−0·8	+4·2	+7·0
8	+6·6	−4·2			−6·9	+4·2	−0·2	+5·3	+3·7
9	−2·9	−3·6	−0·4	−0·4		−2·1	−1·7	−3·5	−4·3
10	−2·9	−3·6	−0·4	−0·4		−2·1	−1·7	−3·5	−7·0
11	+4·2	−3·7	+3·4	−1·2		−5·6	+4·2	+4·1	+7·3
12	−1·1	−1·1			−0·9	+0·8	−0·2	−1·9	−1·9
13	−1·8	+4·0			+1·5	+1·6	−0·2	−0·7	−1·6
14	−2·0	0·0			+0·8	+1·6	−1·2	−3·2	−2·3
15	+8·5	−6·5			−8·7	−1·2	+2·9	+9·0	+7·1
16	+14·9	−6·0			+4·6	+2·9	−3·4	+4·8	+3·4
17	+5·5	−2·5			+4·6	−3·4	+2·9	+3·9	+3·3
18	+0·3	+0·2			+11·1	−2·9	−7·3	−6·2	−2·6
19	−0·9	−0·2			+11·1	+2·9	−6·5	−8·6	−10·9
20	+0·3	−0·9	+0·7	−0·4		+1·6	−1·7	−0·2	+0·5
21	−1·8	+2·6	+1·8	−2·1		−1·2	+2·2	0·5	−1·5

* See Table 4 for key to examples.

(A) Anisotropies (7) and (9) used in these calculations.

(B) Terms I to IV are those marked in equation (4).

(C) a +ve sign indicates a shift to higher field values; a −ve sign indicates a shift to lower field values.

EXPERIMENTAL

The NMR spectra were measured in cyclohexane, carbon tetrachloride and $CDCl_3$ solns in 10% w/v concentration and at room temp (ca., 20°). Measurements for each compound were made at 100 c/s sweep width on a Varian A-60 and the values in Table 1 represent the mean of 4 determinations. The spectrometer was calibrated using benzene (436 c/s) and TMS.

The physical constants (m.p. and $[\alpha]_D$) for previously recorded steroids agreed with the literature values. In every case the low field NMR profile and the infrared spectrum were in agreement with the accepted structures.

Chemical shifts were assigned on the basis of the additivity of substituent effects.

Cholest-8(14)-en-3-one. A soln of cholest-8(14)-en-3β-ol (460 mg) in acetone (25 ml) was treated at 0° with excess Jones' reagent. The resultant *cholest-8(14)-en-3-one* (330 mg) formed prisms, m.p. 95–96° from MeOH $[\alpha]_D^{20}$ +41° (*c*, 1·02 in Chf). (Found: C, 84·2; H, 11·7. $C_{27}H_{44}O$ requires: C, 84·3; H, 11·5%.)

Calculations were carried out on the Atlas computer of the University of London using CHLF, autocode language.

TABLE 9

Examples		Double bond position	Chemical shift contributions (c/s) For bonds added*	For bonds removed*
C-19	1	4,5	−5·3	−6·6
	2	5,6	−3·4	−6·6
	3	6,7	+7·7	−4·6
	4	7,8	+7·1	−4·6
	5	8,9	−0·4	−6·6
	6	9,11	−3·6	−6·6
	7	8,14	+0·7	+3·5
	8	11,12	+2·4	−2·9
	9	$3CH_2$	−6·5	+3·8
	10	$7CH_2$	−6·5	+3·8
	11	$6CH_2$	+2·7	+1·4
C-18	12	4,5	−2·2	+0·3
	13	5,6	+2·2	−2·9
	14	6,7	−2·0	−1·2
	15	7,8	+2·0	+7·0
	16	8,9	+8·9	−4·1
	17	9,11	+8·0	−4·1
	18	11,12	+0·5	−6·7
	19	8,14	−1·1	−7·5
	20	$6CH_2$	−0·3	+0·1
	21	$7CH_2$	+0·5	−1·0

* In cases 9, 10, 11, 20 and 21 bonds removed refer to axial and equatorial CH bonds: bonds added refer to the C=C and CH bonds contained in the exo-methylene group. In all other examples bonds removed refer to C—C single bonds with the attached axial C—H bonds: bonds added are the C—C linkages.

Anisotropies (7) and (9) used in these calculations.

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Note added in proof—Professor A. D. Buckingham kindly informs us that the most recent and reliable value for the constant in Eq. (13) of Part I (preceding paper), is $-2{\cdot}3 \times 10^{-6}$. Using this new constant we have rederived the anisotropies and susceptibilities (in $cm.^3$ $molecule^{-1} \times 10^{-30}$) for the C—H, C—C, and C=C bonds as follows:

$$\Delta\chi^{C-C} = +11{\cdot}26 \qquad \Delta\chi^{C-H} = +7{\cdot}54$$
$$\chi_L^{C-C} = +1{\cdot}37 \qquad \chi_L^{C-H} = -1{\cdot}37$$
$$\chi_T^{C-C} = -9{\cdot}87 \qquad \chi_T^{C-H} = -8{\cdot}90$$
$$\Delta\chi_1^{C-C} = -12{\cdot}00 \qquad \Delta\chi_2^{C-C} = -12{\cdot}06$$
$$\chi_X^{C=C} = +2{\cdot}69$$
$$\chi_Y^{C=C} = -9{\cdot}31$$
$$\chi_Z^{C=C} = -9{\cdot}37$$

Recalculation of chemical shifts using these revised constants yields values which fall within the same limits of error and differ only marginally from those reported in this series of papers.