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 1^1 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

 $\Delta \chi_1^{C=0} = -12.75 \times 10^{-30}$, and $\Delta \chi_2^{C=C} = -14.27 \times 10^{-30} \text{ cm}^3 \text{ molecule}^{-1}$.

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 paper¹ 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 represented² 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. McConnell⁶ 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

- 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).

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).

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 1, m and n are the direction cosines of ON, and $\mathbf{R} = \mathbf{ON}$, then it follows that the shielding due to the dipole is given by the expression

$$\sigma = \frac{1}{3R^3} \left[\chi_{\rm X} (1 - 31^2) + \chi_{\rm Y} (1 - 3m^2) + \chi_{\rm Z} (1 - 3n^2) \right] \tag{1}$$

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 $\chi_{\rm X}(=\chi_{\rm Z})$ is the susceptibility transverse to the internuclear axis and $\chi_{\rm X}$ is the susceptibility along the bond axis. Using the relationship between the direction cosines of

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

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.

$$\sigma = \frac{1}{3R^3} [\chi_{\rm X}(1-3l^2) + \chi_{\rm Y}(1-3m^2) + \chi_{\rm Y}(1-3+3l^2+3m^2)]$$

= $\frac{\chi_{\rm X} - \chi_{\rm Y}}{3R^3} (1-3l^2)$
 $\sigma = \frac{\Delta\chi}{3R^3} (1-3\cos^2\theta)$

(2)

i.e.

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:

$$\sigma = \frac{1}{3R^3} [\chi_{\rm X}(1-3m^2) - \chi_{\rm X}(1-3m^2) - \chi_{\rm X}(1-3n^2) + \chi_{\rm Z}(1-3n^2)]$$

= $\frac{1}{3R^3} [\Delta \chi_1(1-3m^2) + \Delta \chi_2(1-3n^2)]$
Term I(i) Term I(ii)
= $\frac{1}{3R^3} [\Delta \chi_1(1-3\cos^2\theta) + \Delta \chi_2(1-3\sin^2\theta, \sin^2\gamma)]$ (3)

where $\Delta \chi_1 = \chi_{\rm Y} - \chi_{\rm X}$ is the anisotropy between the axis perpendicular to the nodal plane of the π orbitals and the σ bond direction and $\Delta \chi_2 = \chi_{\rm Z} - \chi_{\rm X}$ 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 paper¹) 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):



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 Csp₂—H bond is the same as that of a Csp₃—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 Tillieu⁷ 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 taken⁸ 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 ¹³C—H coupling constants have been shown⁹ to be different for cyclopentene and cyclohexene, and in view of the postulated relationship¹⁰ 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).

¹⁰ N. Muller and D. E. Pritchard, J. Chem. Phys. 31, 768, 1471 (1959).

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.

$$a\Delta\chi_1^{C=C} + b\Delta\chi_2^{C=C} = \text{observed shift in ppm} \times 10^{-6}$$

 $- c\Delta\chi^{CH} + (e+f)\Delta\chi^{CH} + d\Delta\chi^{C-C}$ (5)

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

$$\Delta \chi^{\rm C-C} = +21.33 \times 10^{-30} \qquad \Delta \chi^{\rm CH} = +12.57 \times 10^{-30} \tag{6}$$

$$\Delta \chi^{\rm C-C} = +13.98 \times 10^{-30} \qquad \Delta \chi^{\rm CH} = +11.00 \times 10^{-30} \tag{7}$$

obtained in the preceding paper¹ 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 $\Delta \chi_2^{C-C}$

$$\Delta \chi_1^{\rm C=C} = -11.82 \times 10^{-30}, \qquad \Delta \chi_2^{\rm C=C} = -15.84 \times 10^{-30} \, \rm cm^3 \, molecule^{-1}$$
(8)

$$\Delta \chi_1^{\rm C=C} = -12.75 \times 10^{-30}, \qquad \Delta \chi_2^{\rm C=C} = -14.27 \times 10^{-30} \, \rm cm^3 \, molecule^{-1} \qquad (9)$$

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

$$\frac{1}{3}(\chi_{\rm X} + \chi_{\rm Y} + \chi_{\rm Z}) = -3.2 \times 10^{-30} \tag{10}$$

Thus:

and solving with

$$\Delta \chi_1 = \chi_{\rm Y} - \chi_{\rm X} = -12.75 \times 10^{-30} \tag{11}$$

$$\Delta \chi_2 = \chi_Z - \chi_X = -14.27 \times 10^{-30}$$
(12)

we obtain

$$\chi_{\rm X} = +3.68 \times 10^{-30} \,\text{cm}^3 \,\text{molecule}^{-1}$$

= +2.22 × 10⁻⁶ cm³ mole⁻¹
$$\chi_{\rm Y} = -9.07 \times 10^{-30} \,\text{cm}^3 \,\text{molecule}^{-1}$$

= -5.47 × 10⁻⁶ cm³ mole⁻¹
$$\chi_{\rm Z} = -10.59 \times 10^{-30} \,\text{cm}^3 \,\text{molecule}^{-1}$$

= -6.39 × 10⁻⁶ cm³ mole⁻¹

These susceptibilities may be compared (Fig. 3) with those derived¹ 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



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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 calculations³⁻⁵ have been based on a misapplication of McConnell's original work⁶ 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 approach³ 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 , 3CH₂, 7CH₂ 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 texts² 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. \odot Plot of points made using method adopted by Frazer³. \triangle Plot of points using method of Nakagawa^{4,5}. The shaded area indicates the region $\pm 3 \text{ c/s}$ 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 $+4\cdot1$ c/s whereas the observed figure is $-13\cdot4$ c/s. Taking the

	Solvent							
Compound	Cyclol	nexane	C	Cl ₄	CDCl ₃			
	C-19	C-18	C-19	C-18	C-19	C-18		
Cholestane ¹²	49.8	42·0	46.4	38.7	46.5	39.0		
Cholestan-3 β -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-3 β -ol ¹⁷	5 9·0	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-3 β -ol ^{13,22}	61.2	43·1	59.6	40.6	60.7	40 ∙0		
Cholest-5-en-3-one ²²	70 ∙8	44.6	71·0	43·2	71·0	43·0		
3β -Acetoxycholest-5-ene ^{13,14}	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-3 β -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-3 β -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-3 β -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-3 β -ol ³²	55-8	43·0	55.8	40.9	56-3	41.3		
7-Methylenecholestan-3-one ³²	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 ³³	58.7	3 9·1	58·1	36.4	58-2	36-8		
Cholest-8(14)-en-3 β -ol ³⁵	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		
$^{3}\beta$ -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		
5a,22a-Spirostan-3-one ⁸⁷			61.8	46.1	62.0	48·2		
5a,22a-Spirost-9(11)-en-3-one ³²			69·1	42.3	70-2	45.4		
5a,22a-Spirost-11-en-3-one ³²			57.8	48·3	58.7	51.1		
11-Methylene-5x,22x-spirostan-3-one ³⁸			75-1	42.5	75.5	42.4		

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

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²³ C. W. Shoppee, B. D. Agashe and G. H. R. Summers, J. Chem. Soc. 3107 (1957).

			Solve	nt			
Examples	Cyclohexane		CC	la	CD	CDC3	
	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, 3 β -acetate	-12.9	-0.9	-14.6	2.4	-14.5	-1.8	
5-ene, 3β -ol	-12.0	-1.9		-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 ₂	-2.8	+0.1	-5.0	-0.2	-5.0	-0.2	
6-ene, 3β -ol	+0.2	-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	+0.2	+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	+0.5	+7.0	+0.2	+6.8	
7-ene	+1.4	+7.5	-0.3	+6.4	+0.1	+6.6	
$6CH_2, 3\beta$ -ol	+6.8	0.0	+7.7	+0.3	+7.4	+0.4	
6CH ₂ , 3-one	+7.6	+1.3	+7.9	+0.9	+6.6	+0.5	
$7CH_2$, 3β -ol	-6.6	-1.8	-7.6	-1.8	-7.7	-1.9	
7CH ₂ , 3-one	-6.7	+1.0	-6.9	-2.0	-6.8	-1.7	
$7CH_2$, 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	<u>-8·4</u>	+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		+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 ₂ , 3-one			-13·3	+3.6	-13.6	+5.8	

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)

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FIG. 7.

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

	Solvent							
Double bond	Cyclohexane		CC	CCl4		CDCl ₃		an
position	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	+0.2	+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
9,11ª			-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	-2.5	+3.3	-2.9	+3.7	-2.6
exo 3	-2·8	+0.1	-5.0	-0.2	-5.0	-0.2	-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	+0.2
exo 11ª		<u> </u>	-13.3	+3.6	-13·5	+5.4	-13.4	+4.7
1,2 ^b	-7.3	0.5	-8.9	-1·7	-6.5	-1.0	7.5	-1.1

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

		or for	$\frac{c_{1}}{c_{1} \times \Delta \chi^{0H}}$			-0.006 0.006	-0-021			0-007 0-036	entre of the ear axis. e CH bond actors have
	netric fact	$C_1 \times \Delta \chi^{01}$			900•0	+0-057			+0.012 +0.030	metrical c J internucl ooint on th	
		$^{\rm H} \times {\rm Geol}$	$\mathbb{E}_{C_1 \times \Delta \chi^{01}}$							-0.008 -0.041	to the geo d the C=C ms and a p ssociated g
		$\nabla^{\nabla}_{\chi^{0}}$	$C_1 \times \Delta \chi^{0}$			-0007	+0-065			+0.013 +0.034	nt. ygen atoms Fig. 2) an drogen ato vith their a
		group	(c _j) Geometric factor (cm ⁻³ .10 ²²)			0-0507 0-0507	0-1878			0-0670 0-3230	o be significated by the signification of the second second second second θ_{2} v R ₂ and θ_{2} v
		methylene	$ heta_{z_j}$ (degrees)	Η̈́		50 50	46			43 11	(). (). (). (). (). (). (). (). (). ().
`	\ /	in Exo-	•R _{2j} (Å))		5.4 5.4	4.3			6.7 5.8	ant for 1 g paperi g paperi ed by th tals. of R_1 o tibed by is of the
H ^I C	ogen bonds	(c_1) Geometric factor $cm^{-3}.10^{22}$)			0-0507 0-0507	+0.5153	·		+0.1065 +0.2740	8 is too dist 1, precedin 1, precedin 2, precedin ricle describu- f the π orbit e projection e circle desc to and the ax roups.	
	TABLE 4.	arbon-hydr	$\theta_{2^{i}}$ (degrees) (H		50 50	77			75 84	or C19: C1 Method No. Method No. Method No. intre of the ci symmetry of by the plan centre of th scribed by R
			$\mathbb{R}_{2^{\mathrm{f}}}(\mathrm{\AA})$)		5.5 44	3.8			6-3 4-9	1 only for cule ⁻¹ (1 cule ⁻¹ (1 cule ⁻¹ (1 cule ⁻¹ (1 axis of a axis of a scribed reen the angle de
			c factors $\begin{pmatrix} b \\ C = C \\ C = C \\ \cdot 10^{22} \end{pmatrix}$	+0.4058 +0.2692	-0.7624 -0.7624 +0.2065	+0.4050 +0.4878 +0.4193 +0.4193	+0.4306	+0.1278 -0.4629 -0.0015	+0.6991 -0.2927 -0.0179	+0.0189 +0.1033 -0.2985	considered considered of cm ³ mole of cm ³ mole stance from X_1 and the ne angle de tance betw θ_2 is the i) of the ex
	bonds	Geometri $\begin{pmatrix} a \\ C = C \\ (cm^{-3}) \end{pmatrix}$	+0.2319 +0.1461	-0.722 -0.0734 +0.1120 +0.2319	-0.3433 -0.8591 +0.3813 +0.3813	-0-5510	+0.1463 +0.2293 +0.2277 +0.2577	-1.9455 -0.7210 -0.0408	+0.1120 -0.0339 +0.2387	H_{3} group is $\cdot 57 \times 10^{-3}$ $\cdot 57 \times 10^{-3}$ R_{1} is the dii here γ is the here γ is the f the C=C (H ₁ and H ₁	
		double	$\theta_1^{}$ grees)	35	884 88 88 9 8 8	0 4 0 0 1 4 0 0	36	38 81 38 82 38 12	87	51	he 3C] I = 12 I = 12 M = 12
		urbon) (de	28 28 00	88798	9 6 8 8 8	41	8888 888 100 100 100 100 100 100 100 100	2945	22.25	ct of t s $\Delta \chi^{01}$ R_1^{-3} R_2^{-3} R_2^{-3} R_2^{-3} the an
		bon-ca	$R_1(Å$,	0 4 9 4 9 4 9 9	3.5		9999 999	6.0.4 1.0.1	ng effe sed wa sed wa sed wa sed wa sed wa θ_1 is θ_1 is θ_1 is θ_1 is $\cos^2 \theta_2$, $\cos^2 \theta_1$ is t from t
		Car	Double bond position	C-19 5,5	8,9 8,9 9,11	0,14 11,12 3CH ₂ ^a 7CH ₂	6CH ₂ C-18	5,5 5,6 8,7 8,7 8,7 8,7 8,7 8,7 8,7 8,7 8,7 8,7	8,9 9,11 1,12	8,14 8,14 6CH _a 7CH _a	deshieldi sotropy u sotropy u $\frac{1}{3}(1-3)(1-3)(1-3)(1-3)(1-3)(1-3)(1-3)(1-3)$
			Example No.	- 9 9	04001	8 9 01	11	122	110	51 2 2 1 2 1 3	a The b Anii c Anii c Anii d ou d ou c = = c = 1 c b

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Example ^a R₃(Å)		θ_3 (degrees)	Geometric factor (d) $(cm^{-3} \cdot 10^{22})$	$\Delta \chi^{0-0} \times 0$ factor (<i>d</i>) for (in ppm.)	$\Delta \chi^{0-0} \times \text{Geometric}$ factor (d) for term (III) (in ppm.) [Eq. (4)]		
				Ь	с		
1	2.9	77	+1.1593	+0.247	+0.162		
2	2.9	77	+1.1593	+0.741	+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	+0.542	+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	_	·		<u> </u>			
12	6.1	41	-0·1041	-0.022	-0.012		
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							

TABLE 5. CARBON-CARBON SINGLE BOND

^a See table 4 for key to examples.

^b Anisotropy used was $\Delta \chi^{0-0} = +21.33 \times 10^{-30}$ (Method No. 1 preceding paper¹). ^c Anisotropy used was $\Delta \chi^{0-0} = +13.98 \times 10^{-30}$ (Method No. 2, preceding paper¹).

 $d = \frac{1}{3}(1 - 3\cos^2\theta_3)R_3^{-3}$ where R₃ 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_a is the angle described by R₃ 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 H

bond and the double bond at C-11 is approximately 10°, with the C= \acute{C} 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

ALKANE
THE
Z
BONDS
CARBON-HYDROGEN
AXIAL

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Ή

TABLE 6.

+0.055Observed -0.130+0.062-0.072-0.032-0-027 --0.038 -0.025+0.037-0.182-0-217 -0.187+0.005-0.130-0.122 +0.117+0.118+0.057-0-043 -0-008 mqq +0.117shift $f imes \Delta \chi^{
m OH_0}$ -0.014-0-028 -0.004 +0.048-0.035 -0.003-0.028 -0.020 -0.057 -0.109-0.028 +0.037-0.121-0.048 -0.121 +0.071-0-071 +0.071+0.071-0.121 $e \times \Delta \chi^{\mathrm{CH}e}$ Term IV (in ppm.) [Eq. (4)] $\Delta \chi^{\rm OH} \times {\rm Geometric factor for}$ -0.135 -0.035 -0.035 -0.093 +0.013+0.026+0.026-0.020-0.057 -0·048 +0.048+0.071-0.121 +0.071+0.071-0.121+0.071+0.071+0.048 -0.020 +0.026 $e \times \Delta \chi^{\text{OHb}} f \times \Delta \chi^{\text{OHb}}$ -0.040 -0.138-0.016 -0.004-0.032-0.005-0.005 +0.055-0.138-0.1241-0-043 -0.138+0.081+0.081+0.081-0.032+0.081+0.055 -0.065 -0·032 -0.023-0.138 +0.014-0-023 -0.138+0.081-0.040 -0.106+0.030+0.030+0.055+0.055+0.030-0.023+0.081-0.040+0.081+0.081-0.040 +0.055-0.065 +0.081 $(cm^{-3} \cdot 10^{22})$ Geometric factor (f)-1.1017-1.1017-0.1256-0.0296 -0-2535 -0-2535 -0.0370-0.0370-0.1822+0-4356 -0.5208 +0.4356-1.1017+0.6431-0.3177+0.6431+0.6431-0.9871 -0.2561+0.3406 +0.6431(degrees) θ_{4j} 82 $\mathbb{R}_{4j}(\mathbf{\hat{A}})$ 6 6 8 9 9 6 9 9 9 3.6 5.8 4.4 5. 80 10 10 3.6 5. 8. 4.6 6.0 4.8 8 2:5 3.64.2 <u>S</u>.1 4-4 ÷. $(\text{cm}^{-3} \cdot 10^{22})$ Geometric factor (e) -0-8450 +0.1143+0.2408+0.2408-0.1822-0.4356 -0.5208+0.4356+0.4356+0·2408 -0.1822-1.1017-0-3177 -0.3177+0.6431+0.6431-0-3177 +0.6431-1.1017+0.6431+0.6431(degrees) θ_{41} $\mathbb{R}_{4i}(\mathbf{\mathring{A}})$ 9.9 4.5 4.5 5.5 50 00 00 3.6 5.00 4:4 5 5 9 9 5 5 5 9 5 5 5 9 5 4.4 4:4 6.5 4.8 4·8 2:5 2:5 4·8 4.8 Example^a 2101281128128 4 ŝ 9 ~ 8 9 0 11 12 13

^a See Table 4 for key to examples.

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

from the carbon atom along the axial C-H bond and θ_4 is the angle described by R_4 and the C-H internuclear axis. The geometric factor e refers to e and $f = \frac{1}{2}(1 - 3\cos^2\theta_4)R_4^{-3}$ where R_4 is the distance from the centre of the circle described by the rotating methyl hydrogen atoms to a point 0.77 Å the proton H_i and the geometric factor f to the proton H_j .

^b Anisotropy used was $\Delta\chi^{OH} = 12.57 \times 10^{-40}$ cm³ molecule⁻¹ (Method No. 1, preceding paper¹). ^e Anisotropy used was $\Delta\chi^{OH} = 11.00 \times 10^{-80}$ cm³ molecule⁻¹ (Method No. 2, preceding paper¹).

			Hydrogen atoms on C=C double bond (exo-	Term III CC	Term IV hydrogen	Calcul- ated shif in c/c	Observed t shift in c/c
 Examples⁰	C=C Do Term I(i)	uble bond Term I(ii)	methylene groups)	single bonds	atoms in the alkane	at 60 Mc/s	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		11-2
3	+1.6	+6.6		+3.8	+4.9 -2.4	+1.9	$+2\cdot 2$
4	+0.2	+7.2		+3.8	-2.4 + 4.9	+1.4	+0.3
5	0.8	+0.2		+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	+0.5		+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	+0.5	-1·0	-0.8 -0.5		+1.8 - 1.9	-0.4	+0.2
21	-1.7	+2.8	+2.1 -2.4		-1.4 + 2.6	0·4	-1.5

TABLE 7. CHEMICAL SHIFT CONTRIBUTIONS IN C/S AT 60 MC/S FROM EACH TERM OF EQUATION (4)

^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 semichair conformation. Under these circumstances the calculated chemical shift (-7.2 c/s) for C-19 in cholest-1-en-3 β -ol and the corresponding acetate agree satisfactorily with the observed values for these substances.

Examples⁴	C—C double bond Term I(i) 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	Calcul- ated 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	$+4\cdot 1$	+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	0.5	+ 0 ·5
21	-1.8 + 2.6	+1.8 -2.1		-1.2 + 2.2	-0.2	-1.5

TABLE 8. CHEMICAL SHIFT CONTRIBUTIONS IN C/S AT 60 MC/S FROM EACH TERM OF EQUATION (4)

^a 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-3 β -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 [α]²⁰_D +41° (c, 1.02 in Chf). (Found: C, 84.2; H, 11.7. C₂₇H₄₄O requires: C, 84.3; H, 11.5%.)

Calculations were carried out on the Atlas computer of the University of London using CHLF₂ autocode language.

			Chemical shift contributions (c/s)			
Ex	amples	Double bond position	For bonds added ^a	For bonds removed ^a		
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	+0.2	-1.0		

^a 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 -2.3×10^{-6} . Using this new constant we have rederived the anisotropies and susceptibilities (in cm.³ molecule⁻¹ × 10⁻³⁰) for the C—H, C—C, and C—C bonds as follows:

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.

TABLE 9