The Anisotropies of the Carbonyl Group

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Using the general approach outlined in previous Communications,[1,2] anisotropies have been derived for the carbonyl group. Magnetic anisotropy[2] and electric field effects have both been taken into account in our calculations. For the latter, the original treatment[3] has been modified to define the screening effect of a methyl group as that component of the electric field at the centre of the circle of rotation of the hydrogen atoms, resolved parallel to one of the carbon–hydrogen bonds and averaged over 360° of rotation. Thus in the case of the freely rotating methyl group

σ_E (p.p.m.) $= K[\cos\omega\,(3\cos\beta\cos\psi - \cos\phi)R^{-3}]$
in which $K = k\mu$ where k is a proportionality constant, μ is the dipole moment (in Debyes) of the carbonyl bond and ω (70°32′) is the angle defined by the C–C axis of the methyl group and a C–H bond: ϕ is the angle made by the carbonyl bond axis and a line drawn parallel to the carbon–carbon bond of the methyl group involved. Other symbols are defined in Figure 1.

Geometric measurements of distances (R in Å) and angles depend on the positions along the carbonyl bond, taken for the electric and magnetic dipoles: they are considered to act at the same point. This point has been varied along the C=O axis[4–6] as shown in the Table.

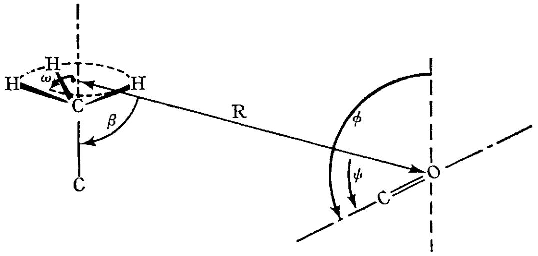

FIGURE 1

Equations were set up for fifteen mono-oxo-androstanes using the shifts of the C-18 and C-19 methyl groups relative to androstane. Least-squares analysis of the thirty equations gave the following results:

TABLE

Position of dipole (Å) distance from carbon atom	$\Delta\chi_1^{C=O}$*	$\Delta\chi_2^{C=O}$*	K
0·6	$-27{\cdot}4 \times 10^{-30}$	$-21{\cdot}0 \times 10^{-30}$	$-6{\cdot}2 \times 10^{-30}$
0·9	$-33{\cdot}5 \times 10^{-30}$	$-24{\cdot}7 \times 10^{-30}$	$-3{\cdot}0 \times 10^{-30}$
1·2	$-40{\cdot}2 \times 10^{-30}$	$-28{\cdot}8 \times 10^{-30}$	$+0{\cdot}8 \times 10^{-30}$

The range of susceptibilities ($\times 10^{30}$) in cm.^{3} molecule^{-1} corresponding to these anisotropies is as shown in Figure 2.

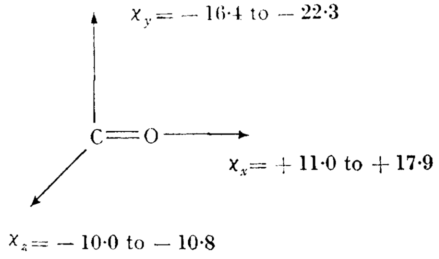

FIGURE 2

The order of magnitude of χ_y is in agreement with the value[4] $-16{\cdot}3 \times 10^{-30}$cm.^{3} molecule^{-1}. The paramagnetic nature of χ_x is in line with the work of Pople.[7] The tendency for K to approximate to zero as the dipoles are moved towards the oxygen atom is in accord with previous findings[4-6] and would suggest that if the electric and magnetic dipoles are placed on the oxygen atom of the carbonyl group, only magnetic anisotropy need be invoked in any calculations. Thus if the electric field effect be excluded from the calculations, anisotropy values are obtained as follows: $\Delta\chi_1^{C=O} = -39{\cdot}7 \times 10^{-30}$, $\Delta\chi_2^{C=O} = -27{\cdot}9 \times 10^{-30}$ cm.^{3} molecule^{-1}. If these values are used to calculate shifts for the C-18 and C-19 methyl group of the fifteen, isomeric oxoandrostanes, all but three of the thirty calculated values agree within (±) 4 c./sec. with the observed value. Agreement between observed and calculated shifts values for the C-17 and C-18 methyl group has also been obtained for a selection of oxo-diterpenes. An essentially similar result is obtained if the anisotropy values shown in the Table are used with the *inclusion* of the electric field effect.

With the position of the dipoles at the centre of the carbonyl bond the value of K in the electric field equation is $-6{\cdot}2 \times 10^{-30}$, whence $k = -2{\cdot}1$ to $-2{\cdot}7 \times 10^{-12}$, in excellent agreement with previous values.[3,8] (Contrast reference 6.)

Calculations were carried out on the Atlas computer of the University of London.

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* $\Delta\chi_1^{C=O}$ is defined as χ_y—χ_x, $\Delta\chi_2^{C=O}$ as χ_z—χ_x as in the previous Communication (Ref. 1).