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Long range chemical shifts in aceto-acetic ester and acetylaceton

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Because of the small electron density near the protons in molecules one must consider the possibility, that large numbers of electrons in groups relatively far from the proton will produce significant shielding effects. McConnell [1] showed, that these long range shielding effects may be estimated in terms of the diamagnetic anisotropies of these distant electron groups. He gives the following formula for the part of the shielding tensor due to this group

$$\delta_d = \frac{1}{L_0}\left[\frac{\chi}{R^3} - \frac{3\chi \cdot \mathfrak{R}\mathfrak{R}}{R^5}\right].$$

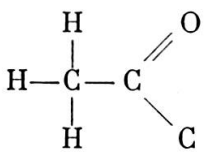
This gives for axial symmetry of the group

$$\delta_d = \frac{\Delta\chi}{3 L_0 R^3}\,(1 - 3\cos^2\theta_z).$$

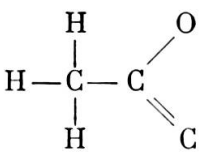
θ_z is the angle between $\mathfrak{R}$, the vector from the induced dipole to the regarded proton, and the symmetry axis of the distant group.

Guy and Tillieu [3] and Baudet, Tillieu and Guy [4] gave the theoretical values for the molar diamagnetic susceptibilities of some bonds. Narasimhan and Rogers [2] have calculated the diamagnetic anisotropy of the C = O bond with the aid of the chemical shifts in formamide and dimethylformamide.

It is possible with the above formulas to calculate the relative chemical shifts of the CH_3 lines in substances with keto enol tautomerism. The two groups have the forms



keto,



enol.

The screening constant of the CH_3 protons must be averaged over the possible spatial arrangements. The location of the induced magnetic dipole has been taken at the middle of the bonds for C = C and C — C and at the oxygen atom for C = O and C — O [2].

TABLE 1.

Diamagnetic susceptibilities . 10^6	
$\Delta\chi$ (C — C) = 1,16 [3]	$\Delta\chi$ (C — O) = 0,97 [4]
χ_{xx} (C = O) = — 6.77 [2]	χ_{xx} (C = C) = — 6.90 [3]
χ_{yy} (C = 06 = 2.64 [2]	χ_{yy} (C = C) = — 5.03 [3]
χ_{zz} (C = O) = 1.09 [2]	χ_{zz} (C = C) = — 4.13 [3]

In table 1 are given the values of the diamagnetic susceptibilities. The evaluation gives

$$\delta_d\ (CH_3 \text{ keto}) = -\ 0.17.10^{-6}, \quad \delta\alpha\ (CH_3 \text{ enol}) = -\ 0.06.10^{-6},$$

$$\Delta\delta = 0.11.10^{-6} = 2.75 \text{ c/s at } 25 \text{ Mc/s}.$$

The experimental values are

Aceto-acetic ester: $\Delta\delta$ = 6.8 c/s
$\Delta\delta$ = 6.0 c/s at ∞ dilution in isotropic solv.
Acetylaceton: $\Delta\delta$ = 4.3 c/s
$\Delta\delta$ = 3.5 c/s at ∞ dilution in isotropic solv.

In view of the crude susceptibility values and the approximative method the results seems to be good.

I am greatly indebted to Dr Weissenfels for preparation of the substances.

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2. Narasimhan, P. T., M. T. Rogers, *J. Phys. Chem.*, *63*, 1388, 1959.
3. Guy, J., J. Tillieu, *J. Chem. Phys.*, *24*, 1117, 1956.
4. Baudet, J., J. Tillieu, J. Guy, *C. R.*, *244*, 2920, 1957.