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Studies in Nuclear Magnetic Resonance Spectroscopy. Long-range Shielding by Triple Bonds

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The magnetic shielding of nuclei due to distant chemical groups may be calculated from the knowledge of the magnetic anisotropy of the bonds in these groups. The reverse procedure, namely, the calculation of the magnetic anisotropy of bonds from NMR relative chemical shifts has been employed here to estimate the magnetic anisotropy of $-C\equiv C$, $-C\equiv N$, and $-N\equiv C$ triple bonds. The paramagnetic contribution to the shielding of the acetylenic proton was estimated from the calculated value of $\Delta\chi^{C\equiv C}$, and from the known geometry of the molecule. The value thus obtained is compared with that calculated by quantum mechanical methods.

One of the persistent problems encountered in interpreting chemical shifts in NMR spectroscopy is of adequately taking account of effects produced by the magnetic anisotropy of neighboring atoms or groups. Unless this is done, it is difficult to decide what portion of an observed shift is indeed chemical. In certain cases, *e. g.*, acetylene and hydrogen cyanide, the occurrence of serious discrepancies between experimental shift and expectations have served to call attention to the existence of important anisotropic contributions. Unfortunately, no reliable and generally applicable methods for independently estimating such contributions have yet appeared.

The magnetic shielding ζ of a proton in a molecule can be calculated theoretically using the second-order perturbation theory of Ramsey,[1] or the variational methods.[2,3] Application of the second-order perturbation theory to this problem is possible only if the excited-state wave functions in addition to the ground-state wave functions are available for the molecule in question. Hence, very few direct theoretical calculations of ζ have been made.

McConnell,[4] have derived a quantum mechanical expression for calculating the chemical shifts due to long-range bonds or groups. For an axially symmetric bond, the expression appears in the form:

$$\zeta = \Delta\chi(1-3\cos^2\theta_z)/3L_0R^3 \qquad (1)$$

Where, R, is the radius vector for the proton, θ_z, is the angle between R and the symmetry axis of the bond (usually the bond axis itself). The scalar $\Delta\chi=\chi_L-\chi_T$, where the scalars χ_L and χ_T are the average of the susceptibility components parallel and perpendicular to the symmetry axis.

The theory has been extended by Narasimhan and Rogers,[5] to the three dimensional case, where all the three principal magnetic susceptibilities are different. These authors have also derived expressions for the case of rotating methyl groups, in which the shielding is averaged over all possible orientations.

The theory of McConnell for long-range shielding appears capable of fairly general applicability, although it is not very well suited to quantitative calculations of aromatic proton shieldings, since it has been developed only to the extent that the shielding fields are approximated by dipolar fields. Quantitative application of the shielding equation due to the magnetic anisotropy of a long-range bond in a molecule suffer from two very important difficulties. The first difficulty is that the shielding of a proton is a function of the anisotropy in the magnetic susceptibility of the distant group, and only very few data for the magnetic anisotropies of bonds are known. The second difficulty is that R, appears in the equation as R^{-3}, so that with decreasing R, the shielding becomes larger and more important, and the dipolar approximation becomes less and less accurate.[4,6,7]

For distances less than 5 Å, we have followed Pople's suggestion[7] of describing the anisotropy of the acetylenic bond in terms of the atomic

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[1] N. F. Ramsey, *Phys. Rev.*, **86**, 243 (1952).

[2] B. R. McGarvey, *J. Chem. Phys.*, **27**, 64 (1957).

[3] R. Stephen, *Proc. Roy. Soc. (London)*, **A243**, 264 (1957).

[4] H. J. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

[5] P. T. Narasimhan and M. T. Rogers, *J. Phys. Chem.*, **63**, 1388 (1959); *J. Chem. Phys.*, **31**, 1302 (1959).

[6] J. R. Didry and J. Guy, *Compt. Rend.*, **253**, 422 (1961).

[7] J. A. Pople, *Discussions Faraday Soc.*, **34**, 7 (1962).

anisotropy of the acetylenic carbons, and the shielding expression becomes,

$$\xi = \Delta\chi[\tfrac{1}{3}R_1^3(1-3\cos^2\theta_1) + \tfrac{1}{3}R_2^3(1-3\cos^2\theta_2)] \quad (2)$$

Where, R_1, R_2, θ_1, and θ_2 are shown in Fig. 1.

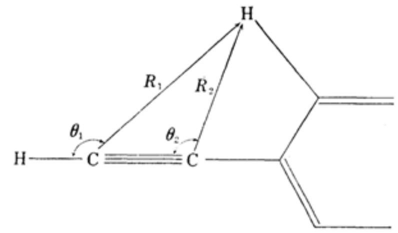


Fig. 1. Dipole approximation for the magnetic anisotropies of the acetylenic carbons in phenylacetylene.

The present work represent an attempt to investigate the role of the neighbor-anisotropy effect and to calculate the electrostatic effects due to electric fields at a particular nucleus arising from polar groups in other parts of the molecule. From the relative chemical shifts and the known molecular geometries, we determine the anisotropy in the magnetic susceptibilities of the C≡C, C≡N, and N≡C triple bonds. In doing so, we have shown experimentally that long-range shielding does exist and that it is correctly explained to lower order of accuracy by the McConnell's expression. We have also shown that the electrostatic effects in the case of –C≡N, and –N≡C triple bonds are very important in determining the chemical shift of a particular proton.

Experimental

The NMR Spectrometer. The measurements were made on a Varian Associates high-resolution spectrometer, operating at a fixed frequency of 56.45 Mc/s. The measurements of the NMR spectra of the bicyclo-compounds were made at 60 Mc/s. The frequency separation between lines were measured using the usual audiomodulation side-band technique. The chemical shifts were measured for several concentrations in carbon tetrachloride solutions containing 1% TMS, used as an internal standard, extrapolated to infinite dilution, and are quoted as τ-values. All τ-values which were employed in the calculations are the average of four determinations and are accurate to ±0.01 ppm.

Results and Calculations

a. Diamagnetic Anisotropy. In order to simplify the problem of calculating magnetic anisotropy of a long-range bond, we have followed the general method adopted by Narasimhan and Rogers.[5] For a given proton the net shielding ζ, can be written as the sum of two quantities, namely, ζ_l and ζ_d, where ζ_l, denotes the shielding due to the immediately surrounding electron cloud (primary shielding), and it corresponds to Pople's local diamagnetic term. The second term, ζ_d, arises from distant electron distributions within the molecule itself (secondary shielding), and corresponds to Pople's neighbor-anisotropy effect. ζ_l can be calculated by using the wave functions of the bond attached to the proton of interest.[3] ζ_d can be evaluated from a knowledge of the magnetic anisotropy $\Delta\chi$ of the various charge distributions in the molecule.[3–5] Thus we may write:

$$\zeta = \zeta_l + \zeta_d$$

A difference in the net shielding, or the internal chemical shift $\Delta\zeta$, between two protons A and B in a molecule may originate from differences in ζ_l and/or ζ_d ($\Delta\zeta_l$ and $\Delta\zeta_d$ respectively). Thus we have;

Table 1. The chemical shifts of all protons in I—IX

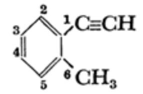
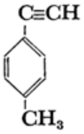
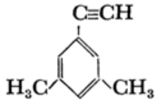
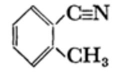
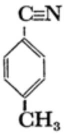
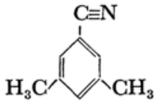
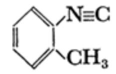
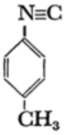
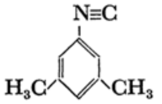
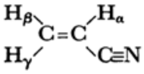
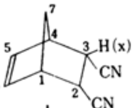
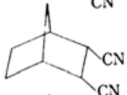
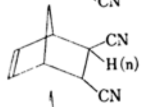
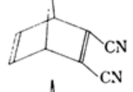
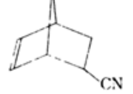
	Compound	CH_3	H-2	H-3	H-4	≡CH
I		7.58				6.90
II		7.69	2.8	2.9		7.13
III		7.73	3.25		3.07	6.65
IV		7.48				
V		7.59	2.53	2.77		
VI		7.6	2.8		2.8	
VII		7.62	2.8	2.8	2.8	
VIII		7.65	2.9	2.9		
IX		7.75	3.0		3.0	

TABLE 2. THE CHEMICAL SHIFT OF ALL PROTONS IN I—VII

	Compound	α-H	β-H(CH_3)	γ-H(or CH_3)	$\equiv$CH	$(\zeta_T^{\beta}-\zeta_T^{\gamma})\times 10^{-6}$
I		4.52	4.22_5	4.14		0.18*
II	$(CH_3)_2C{=}CH{-}C\equiv N$	4.89	7.63	8.06		0.43
III	$CH_2{=}CH{-}C\equiv CH$[8]				7.00	0.18
IV	$(CH_3)_2C{=}CH{-}C\equiv CH$	4.83	8.18 or 8.11	8.11 or 8.18	6.90	0.07
V	$\overset{\gamma}{C}H_3\cdot\overset{\beta}{C}H_2\cdot C\equiv CH$[9]		8.10	9.04	6.32	0.94
VI	$CH_3\cdot CH_2\cdot C\equiv N$[10]		7.00	8.04		1.04
VII	$CH_3\cdot CH_2\cdot N\equiv C$		7.19	8.77		1.58

* Complete analysis of the NMR spectrum of acrylonitrile and α-D-acrylonitrile are carried out by Goldstein and co-workers.[11] Several other workers have analysed the spectrum of acrylonitrile.[11–14] The results of Banwell and Sheppard[12] are different from that of Goldstein and co-workers,[11] and Bruegel,[13] in that the two protons at the β-position have been interchanged. There are some variations in the values of the chemical shifts of the three protons. The most reliable analysis is that of Castellano and Waugh.[14] In this work, the values of the chemical shifts obtained by the later authors are employed in the calculation of the magnetic anisotropy of the $-C\equiv N$ group.

TABLE 3. THE CHEMICAL SHIFT OF ALL PROTONS IN I—V

	Compound	Olefinic	Bridgehead	H_x(exo)	H_n(endo)	C_7–H_2
I		3.50	6.67	6.57		8.67, 8.37
II		(C-5,6) 8.21	7.33	6.82		8.44
III		3.52	6.60	7.48	6.83	8.31, 8.27
IV		3.02	5.93			7.63
V			7.03 6.86			

$$\begin{aligned}\Delta\zeta &= (\zeta^{A}-\zeta^{B}) = (\zeta_l^{A}-\zeta_l^{B}) + (\zeta_d^{A}-\zeta_d^{B})\\ &= \Delta\zeta_l + \Delta\zeta_d\end{aligned}$$

Since the magnitude of the shielding contribution from distant groups depend on their diamagnetic anisotropy and on molecular geometry, we have calculated the diamagnetic anisotropy of the $-C\equiv C-$, $-C\equiv N$, and $-N\equiv C$ groups, using the internal chemical shift between two protons located on the same carbon atom or on two different atoms with the same electron distribution around. Hence, $\Delta\zeta_l$, for such protons will be zero, and the difference in the chemical shift $\Delta\zeta_T$, will arise from the magnetic anisotropy of the distant groups alone.

To calculate ζ_d, for cases where θ and/or R changes with internal molecular motions, one must use appropriately averaged values. The component,

$$T_z = (1-3\cos^2\theta_z)/R^3 \qquad (3)$$

was calculated numerically in the following manner:

Let us consider the case of a nucleus H, which is free to move in a circular path around the axis of the bond AC*, this axis being taken to be in

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8) R. C. Hirst and D. M. Grant, *J. Am. Chem. Soc.*, **84**, 2009 (1962).

9) H. Heel and W. Zeil, *Z. Electrochem.*, **64**, 962 (1960).

10) J. R. Cavanaugh and B. P. Daily, *J. Chem. Phys.*, **34**, 1099 (1961).

11) G. S. Reddy, J. H. Goldstein and L. Mandel, *J. Am. Chem. Soc.*, **83**, 4729 (1961).

12) C. N. Banwell and N. Sheppard, *Mol. Phys.*, **3**, 351 (1960).

13) W. Bruegel, *Z. Electrochem.*, **64**, 1121 (1960).

14) S. Castellano and J. S. Waugh, *J. Chem. Phys.*, **34**, 295 (1961).

the Z–Y plane, with point dipole placed at "0" as shown in Fig. 2.

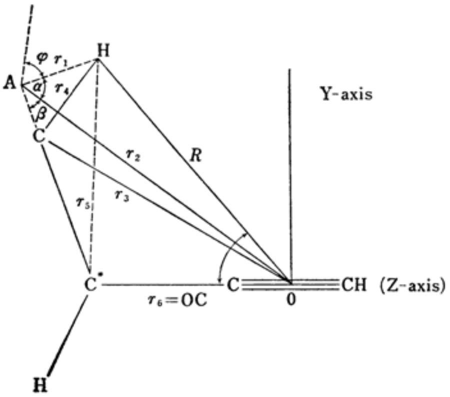

Fig. 2. Evaluation of T_z value.
The dipole is located at "0", and nucleus H free to rotate around the axis AC*.

Since r_1 and AC* are chosen to be at right angles to each other, we can express α in terms of β and φ (φ is the angle of rotation of r_1, in its plane). Thus it can be shown that,

$$\cos\alpha = \sin\beta\cdot\cos\varphi \tag{4}$$

and hence we can express R as,

$$R = (r_1^2+r_2^2-2r_1r_2\sin\beta\cdot\cos\varphi)^{1/2} \tag{5}$$

now we also have,

$$\cos\theta_z = (R^2+r_6^2-r_5^2)/2R\,r_6, \tag{6}$$

and hence we can write,

$$\begin{aligned} T_z &= (1-3\cos^2\theta_z)/R^3 \\ &= \{R^{-3}[1-3(R^2+r_6^2-r_5^2)^2/(2R\,r_6)^2]\}_{\text{av}}. \end{aligned} \tag{7}$$

Since φ varies from 0 to 2π, we can find the average value by integrating the left-hand side of Eq. (7), after substituting of Eq. (5) for R, and dividing finally by 2π. Thus after rearranging we obtain:

$$\begin{aligned} T_z = \tfrac{1}{2}\Pi\{J_{\text{B}}-\tfrac{3}{4}r_6^2[(r_6^2-r_5^2)J_{\text{C}} \\ + 2(r_6^2-r_5^2)J_{\text{B}}+J_{\text{A}}]\}_{\text{av}}. \end{aligned} \tag{8}$$

where,

$$J_{\text{A}} = \int_0^{2\pi}(a+b\cos\varphi)^{-1/2}\,\mathrm{d}\varphi$$

$$J_{\text{B}} = \int_0^{2\pi}(a+b\cos\varphi)^{-3/2}\,\mathrm{d}\varphi$$

$$J_{\text{C}} = \int_0^{2\pi}(a+b\cos\varphi)^{-5/2}\,\mathrm{d}\varphi$$

with, $a = r_1^2+r_2^2$, and
$b = -2r_1r_2\sin\beta$

The evaluation of the integrals in Eq. (8), is necessary for the calculation of T_z, for the methyl groups. These integrals are of the elleptical type and cannot be evaluated in a closed form. These were calculated numerically using the Gauss quadrature method.

b. Electrostatic Effects. In dealing with bonds which are more highly polar than the –C≡C– triple bond, account must be taken of direct electrostatic contributions to ζ_e. This problem arises in the case of the –C≡N and –N≡C triple bonds. A treatment of this problem has been given by Buckingham.[15] Buckingham has shown that molecules containing polar bonds produce an electric field at a particular nucleus, and this leads to chemical shifts proportional to the first powder of the field strength.

The electric field at any point due to a dipole can be evaluated in the usual manner.[16] In our calculations, an improved approximation for the electrostatic effect is made by replacing the point dipole by partial positive and negative charges placed at the two atoms forming the polar bond. These partial charges are derived from the dipole moment and the length of the bond.

According to Coulomb's law, the force exerted by the positive charge ($+e$) on the unit charge placed at the nucleus H in Fig. 3, is

$$E_1 = e/R_1^2$$

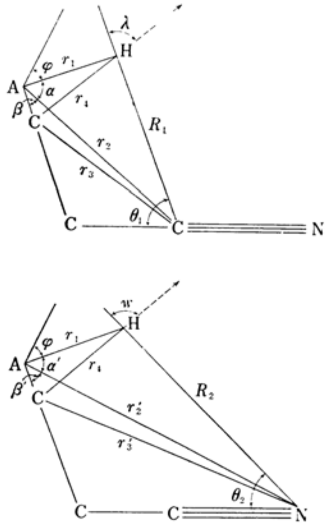

Fig. 3. Calculation of a electrical shielding for rotating methyl groups, based on the point charge approximation.

The component of this force along the C→H bond is given by,

$$E_1^{\text{C}\to\text{H}} = e/E_1^2\cdot\cos\lambda$$

Similarly,

$$E_2 = -e/R_2^2,\ \text{and}\ E_2^{\text{C}\to\text{H}} = -e/R_2^2\cdot\cos w$$

The electrical field at the nucleus H is completely defined by the total force exerted by the two charges ($+e$) and ($-e$), and is given by:

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[15] A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).

[16] V. C. A. Ferraro, "Electromagnetic Theory," The Athlone Press, London (1954), p. 70.

$$E_T = e/R_1^2 \cdot \cos\lambda - e/R_2^2 \cdot \cos w \quad (9)$$

From the geometry of the figure, we can show,

$$\cos\lambda = (R_1^2 + r_4^2 - r_3^2)/2R_1 r_4,$$

$$\text{and} \quad \cos w = (R_2^2 + r_4^2 - r_{3'}^2)/2R_2 r_4$$

Therefore,

$$\begin{aligned}\langle E\rangle = e/R_1^2[(R_1^2 + r_4^2 - r_3^2)/2R_1\, r_4] \\ - e/R_2^2[R_2^2 + r_4^2 - r_{3'}^2)/2R_2\, r_4] \quad (10)\end{aligned}$$

Since, $\mu = el$, therefore

$$\begin{aligned}\langle E\rangle = \mu/2lr_4[(R_1^{-1} + R_1^{-3}(r_4^2 - r_3^2) \\ - R_2^{-1} - R_2^{-3}(r_4^2 - r_{3'}^2)]_{\mathrm{av.}}\end{aligned}$$

Since φ varies from 0 to 2π, we can find the average value by integrating the left-hand side of this equation after substituting the values of R_1 and R_2 given by:

$$R_1 = (r_1^2 + r_2^2 - 2r_1 r_2 \sin\beta \cdot \cos\varphi)^{1/2}$$

$$R_2 = (r_1^2 + r_2^2 - 2r_1 r_{2'} \sin\beta' \cdot \cos\varphi)^{1/2}$$

Thus after rearranging, we obtain,

$$\begin{aligned}E = \mu/4l\pi r_4[J_{\mathrm{A}1} + J_{\mathrm{B}1}(r_4^2 - r_3^2) \\ - J_{\mathrm{A}2} - J_{\mathrm{B}2}(r_4^2 - r_{3'}^2)]_{\mathrm{av.}} \quad (11)\end{aligned}$$

Where, J_{A_1}, J_{A_2}, J_{B_1}, and J_{B_2} are the elleptical integrals referred to before.

c. Electronegativity Effects. Following the original investigation of Meyer, Saika, and Gutowsky,[17] it was found empirically by Daily and Shoolery,[18] that for a series of ethyl derivatives, a linear relation exists between the internal chemical shift of the ethyl group protons and the electronegativity of the substituent. Cavanaugh and Daily[10] have re-examined this relationship, in which they replaced the solvent (benzene) by carbon tetrachloride. These results were reviewed and measurements were made on dilute solutions of these compounds in carbon tetrachloride and extrapolated to infinite dilution. The internal chemical shifts of the ethyl derivatives as measured in carbon tetrachloride differ slightly from those measured in benzene. A revised Daily and Shoolery equation was set up using the new data.

$$\text{Electronegativity} = 0.0114\,\delta\ (\text{internal}) + 1.78$$

Where, δ is in c/s at 60 Mc/s.

Since the electronegativity of the substituent determines the electron distribution around the protons; this equation may be taken as an empirical expression for estimating $\Delta\zeta_l$, between the methyl and methylene protons in ethyl and isopropyl acetylenes, nitriles and isonitriles. The estimation of $\Delta\zeta_l$, in this manner compares favourably with the theoretical values calculated from electron density distribution.[19,20]

Discussion

We wish now to demonstrate experimentally the presence of long-range contributions to the shielding of a proton in a molecule. The molecules are assumed to be in the liquid state and summations in the shielding expression is over all long-range triple bonds, which are assumed to be axially symmetric with magnetic anisotropies $\Delta\chi^{\mathrm{X}\equiv\mathrm{Y}}$. Therefore,

$$\Delta\zeta_d^{\mathrm{A-B}} = \Delta\chi^{\mathrm{X}\equiv\mathrm{Y}} \sum(T_z^{\mathrm{A}} - T_z^{\mathrm{B}})/3L_0$$

Thus, from the calculated value of $\sum(T_z^{\mathrm{A}} - T_z^{\mathrm{B}})/3L_0$, and the experimentally observed value of $\Delta\zeta_d^{\mathrm{A-B}}$, we determine $\Delta\chi^{\mathrm{X}\equiv\mathrm{Y}}$, where, X≡Y, represents a triple bond. In Tables 4, 5, and 6, are listed the values of $\sum(T_z^{\mathrm{A}} - T_z^{\mathrm{B}})/3L_0$ for specific nuclei, also are listed in the tables the appropriate experimental NMR relative chemical shifts for these nuclei, in a series of molecules containing the three different triple bonds. The values from Tables 4, 5 and 6, are plotted with $\Delta\zeta_d^{\mathrm{A-B}}$ as abscissa and $\sum(T_z^{\mathrm{A}} - T_z^{\mathrm{B}})/3L_0$ as the ordinate. A marked linear dependence of these points is found, enabling us to conclude that such long-range bonds do contribute to the shielding. Drawing the line of best fit through these points, we obtain from its slope the values of:

$$\begin{aligned}\Delta\chi^{\mathrm{C\equiv C}} = \chi_{\mathrm{L}}^{\mathrm{C\equiv C}} - \chi_{\mathrm{T}}^{\mathrm{C\equiv C}} &= -35.27 \pm 0.23 \times 10^{-6}\mathrm{cm^3 \cdot mol^{-1}} \\ &= -5.859 \pm 0.039 \times 10^{-29}\mathrm{cm^3 \cdot molecule^{-1}}\end{aligned}$$

$$\begin{aligned}\Delta\chi^{\mathrm{C\equiv N}} = \chi_{\mathrm{L}}^{\mathrm{C\equiv N}} - \chi_{\mathrm{T}}^{\mathrm{C\equiv N}} &= -39.75 \pm 0.33 \times 10^{-6}\mathrm{cm^3 \cdot mol^{-1}} \\ &= -6.60 \pm 0.055 \times 10^{-29}\mathrm{cm^3 \cdot molecule^{-1}}\end{aligned}$$

$$\begin{aligned}\Delta\chi^{\mathrm{N\equiv C}} = \chi_{\mathrm{L}}^{\mathrm{C\equiv N}} - \chi_{\mathrm{T}}^{\mathrm{N\equiv C}} &= -39.05 \pm 0.19 \times 10^{-6}\mathrm{cm^3 \cdot mol^{-1}} \\ &= -6.48 \pm 0.032 \times 10^{-29}\mathrm{cm^3 \cdot molecule^{-1}}\end{aligned}$$

The fact that these points do not lie on a straight line, indicates that the assumptions we have made are not frequently valid. We feel, however, that our conclusions are justified and give every indication that other contributing effects are of high order.

The value of $\Delta\chi$ for –C≡N and –N≡C bonds depend strongly on various parameters, such as the location of the –C≡N and –N≡C dipoles. For mathematical simplification, we have idealised the dipoles by point dipoles, and such idealization is valid only when we consider the field due to these dipoles at very large distances. For actual calculations, it is customary to locate this dipole somewhere along the bond by making certain assumptions; one such assumption is to locate the dipole at the electrical centre of gravity of the electron distribution constituting the bond.

The negative sign of $\Delta\chi$ indicates that the diamagnetic susceptibility perpendicular to the axis of symmetry $|\chi_{\mathrm{T}}^{\mathrm{D}}|$, must be considerably smaller in magnitude than $|\chi_{\mathrm{L}}^{\mathrm{D}}|$. This is so because in an axially symmetric system, $\chi_{\mathrm{L}}^{\mathrm{P}} = 0$, and only $\chi_{\mathrm{T}}^{\mathrm{P}}$

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[17] L. H. Meyer, A. Saika and H. S. Gutowsky, *J. Am. Cmem. Soc.*, **75**, 4567 (1953).

[18] B. P. Daily and J. N. Shoolery, *ibid.*, **77**, 3977 (1956).

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TABLE 4. OBSERVED CHEMICAL SHIFT DIFFERENCES BETWEEN THE TWO PROTONS A AND B, AND THE VALUES OF $\Delta T_z^{A-B}/3L_0$, FOR THESE PROTONS, TOGETHER WITH THE VALUES OF THE MAGNETIC ANISOTROPY OF THE $-C\equiv C-$ BOND ($cm^3\cdot mol^{-1}$)

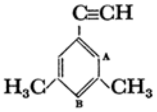
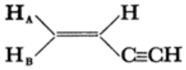
Compound	$10^6\Delta\zeta_d$	$10^6\Delta\zeta_l$	$10^6\Delta\zeta_T$	$\Delta T_z^{A-B}/3L_0$	$10^6\Delta\chi^{C\equiv C}$
$\overset{B}{C}H_3\cdot\overset{A}{C}H_2\cdot C\equiv CH$	− 1.268	+ 2.208	+ 0.94	+ 0.0359	− 35.26
	+ 0.179	assumed ‘0’	+ 0.179	− 0.0056	− 31.90
$(CH_3)_2\cdot CH\cdot C\equiv CH$	− 1.267	+ 2.707	+ 1.44	+ 0.0359	− 35.26
	− 0.18	0	− 0.18	+ 0.0051	− 35.40

TABLE 5. OBSERVED CHEMICAL SHIFT DIFFERENCE BETWEEN THE PROTONS A AND B AND THE VALUES OF $\Delta T_z^{A-B}/3L_0$ FOR THESE PROTONS, TOGETHER WITH THE VALUES OF THE MAGNETIC ANISOTROPY OF THE $-C\equiv N$ BOND ($cm^3\cdot mol^{-1}$)

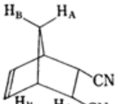
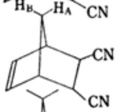
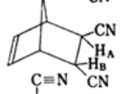
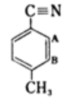
Compound	$\Delta\zeta_T$	$\Delta\zeta_e$	$\Delta\zeta_d$	$\Delta\zeta$	$\Delta T_z^{A-B}/3L_0$	$\Delta\chi^{-C\equiv N}$
$CH_3\cdot CH_2\cdot C\equiv N$	+ 1.033	+ 0.465	− 1.1376	+ 1.944	+ 0.0347	− 39.62
$(CH_3)_2CH\cdot C\equiv N$	+ 1.333	+ 0.465	− 1.376	+ 2.244	+ 0.0347	− 39.62
$CH_2{=}CH\cdot C\equiv N$	− 0.177	− 0.10	− 0.077		+ 0.0037	− 20.80
$CH_2{=}CH\cdot C\equiv N$	− 0.177	− 0.61	− 0.077		+ 0.0037	− 31.60
$(CH_3)_2C{=}CH\cdot C\equiv N$	− 0.433	− 0.057	+ 0.376		+ 0.0012	− 31.60
	+ 0.315	+ 0.030	+ 0.285		− 0.0074	− 38.77
	0.00	+ 0.318	− 0.318		+ 0.0085	− 37.65
	− 0.17	− 0.129	− 0.040		+ 0.001	− 40.40
	− 0.209	− 0.282	+ 0.071		− 0.0021	− 34.18

TABLE 6. OBSERVED CHEMMICAL SHIFT DIFFERENCE BETWEEN THE PROTONS A AND B AND THE VALUES OF $\Delta T_z^{A-B}/3L_0$ FOR THESE PROTONS, TOGETHER WITH THE VALUES OF THE MAGNETIC ANISOTROPY OF THE $-N\equiv C$ BOND ($cm^3\cdot mol^{-1}$)

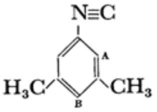
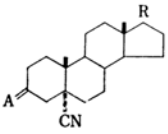
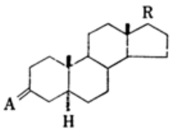
Compound	$\Delta\zeta_T$	$\Delta\zeta_e$	$\Delta\zeta_d$	$\Delta\zeta_l$	$\Delta T_z^{A-B}/3L_0$	$\Delta\chi^{-N\equiv C}$
$CH_3\cdot CH_2\cdot N\equiv C$	+ 1.585	+ 0.437	− 1.352	+ 2.50	+ 0.0347	− 38.92
$(CH_3)_2\cdot CH\cdot N\equiv C$	+ 2.420	+ 0.437	− 1.352	$+ 3.33_5$	+ 0.0347	− 38.92
	+ 0.045	− 0.209	+ 0.165		− 0.0041	− 40.45
	+ 0.044	− 0.234	+ 0.19		− 0.0047	− 40.75

TABLE 7. CALCULATED AND OBSERVED RESONANCE FREQUENCIES FOR C-19 METHYL PROTONS OF SOME 5-CYANO-STEROIDS IN COMPARISON WITH 5-H-STEROIDS[29]

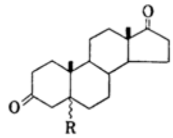
Cyano-steroid	ζ_d^{CN} (ppm)	ζ_e^{CN} (ppm)	ζ_{Total}^{CN} (ppm)	ζ_{Total}^{CN} (c/sec) at 60 Mc/s	Parent steroid	Observed 19-H (c/sec) from TMS	Calcd 19-H (c/sec)	Obsd 19-H (5α-CN)	$\zeta_{calc}-\zeta_{obs}$ (c/sec)
5α-CN					5α-H				
Ia	+0.322	−0.125	+0.197	+11.8	IIa	49.6	37.8	60.2	−22.4
Ib	+0.322	−0.125	+0.197	+11.8	IIb	61.0	49.2	69.0	−19.8
Ic	+0.322	−0.125	+0.197	+11.8	IIc	61.5	49.7	68.5	−18.8
Id	+0.322	−0.125	+0.197	+11.8	IId	48.1	36.3	57.3	−21.0
Ie	+0.322	−0.125	+0.197	+11.8	IIe	48.8	37.0	59.6	−22.6
IIIa	+0.322	−0.125	+0.197	+11.8	IIIb	63.2	51.4	70.7	−19.3
5β-CN					5β-H				
IIIc	+0.072	−0.297	−0.225	−13.5	IIId	62.9	76.4	77.8	−1.4
IVa	+0.101	−0.297	−0.196	−11.75	Va	62.3	74.05	75.8	−1.75
IVb	+0.129	−0.297	−0.225	−10.8	Vb	57.2	70.7	70.8	−0.10



(I)



(II)



(III)

a, R=OAc, A=3β-OAc, 3α-H; b, R=OAc, A= =O;
c, R=Ac, A= =O; d, R=OAc, A=3α-OAc, 3β-H;
e, R=OAc, A= O-CH$_2$- | O-CH$_2$-
IVa, A= =O, R=OAc, IVb, A=3α-OAc, 3β-H

a, R=α-CN, b, R=α-H
c, R=β-CN, d, R=β-H

$(>)\neq 0$, therefore, $\Delta\chi^{X\equiv Y}=\chi_L-\chi_T=\chi_L^D-\chi_T^D-\chi_T^P<0$, therefore $|\chi_L^D|$, must be large and negative.

The measurement of $\Delta\chi$ for a triple bond by this method accomplishes what would be very difficult to do by any other method. The ideal experiment for measuring susceptibility of a triple bond in both the transverse and longitudinal directions would be to freeze acetylene, as an example, in a crystal in which all the acetylenic bonds are parallel and then performing the magnetic susceptibility measurements. By using the experimental value of $\Delta\chi$ and the quantum mechanical expression of $\Delta\chi$, the validity of different possible wave functions for the triple bond can be determined.

The present semi-quantitative treatment indicates that, in the case of ethylacetylene, ethyl cyanide, and ethyl isocyanide, the major contribution to the observed chemical shift comes from $\Delta\zeta_l$, and that the observed chemical shift cannot be satisfactorilly explained on the basis of bond magnetic anisotropy alone. It seems probable from the present work, that both bond magnetic anisotropies and electronegativity differences contribute to the chemical shift between the methyl and methylene protons in these three molecules and that both effects are of the same order of magnitude. The local shielding differences perhaps being somewhat the more important.

A review of the literature on the values of the magnetic anisotropy of the acetylenic group, calculated either from theoretical quantum mechanical treatments or from experimental data have been made by Bothner-By and Pople.[20] The theoretical values range[20,21] from -1.61 to 1.94×10^{-6} cm$^3\cdot$mol^{-1}. The experimental ones from[22] -16.5 to[23-25] -34.0×10^{-6} cm$^3\cdot$mol^{-1}. In view of the widely scattered range of values reported in the literature, our datum must be considered in good agreement with the values given by Heel and Zwil,[9,24] and that obtained by Englert and Saupe[26] in a study of some acetylenic compounds oriented

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21) A. A. Bothner-By and J. A. Pople, *Ann. Rev. Phys. Chem.*, **16**, 43 (1965).

22) J. Tillieu and J. Guy, *Compt. Rend.*, **239**, 1203 (1954); *ibid.*, **241**, 382 (1955); *ibid.*, **242**, 1279, 1436 (1956); *J. Chem. Phys.*, **24**, 1117 (1956); *Ann. Phys.*, **2**, 471, 631 (1957).

23) G. S. Reddy and J. H. Goldstein, *J. Chem. Phys.*, **39**, 3509 (1963).

24) H. Heel and H. Buchert, *Z. Physk. Chem. (Frankfurt)*, **38**, 47 (1963).

25) S. Castellano and J. Lorenc, *J. Phys. Chem.*, **69**, 3554 (1965).

26) G. Englert and A. Saupe, *Mol. Crystals*, **1**, 503 (1966).

in a nematic phase.

In another attempt, Goldstein and Reddy,[27) have devised an empirical method of the estimation of diamagnetic anisotropy effects in NMR spectroscopy based upon correlations between proton chemical shift and C^{13}–H coupling constants. The anisotropy shift for the acetylenic hydrogen as obtained by this method is $+4.12$ ppm. This anisotropy effect for acetylene is considerably smaller than Pople's theoretical estimate of about $+10$ ppm. Although this result is qualitatively in the expected order with respect to ethylene and methane, the difference is considerably less than might have been anticipated.

The value of $\Delta\zeta_d^{\equiv CH}$ cantribution to the shielding of the proton in acetylene and methylacetylene could be estimated from the calculated value of $\Delta\chi^{C\equiv C}$ and the known geometry of these molecules.28) The corresponding paramagnetic contribution to ζ is $+9.03$ ppm. It is interesting to compare this value with that obtained by Pople29) in a quantum mechanical study of the proton chemical shift in acetylene. Pople found that the paramagnetic contribution to the shielding of the acetylenic proton is $+10$ ppm. Pople has emphasised that this value is only an order of magnitude for the effect, and is clearly large enough to account for the anomalous position of the acetylenic proton. Again, we may notice, that, both bond magnetic anisotropy and electronegativity effects of the –C≡CH group contribute to the chemical shift of the acetylenic proton.

Studies on steroids, which are available in great number, appear most promising the geometry of the steroid nucleus is well established and the effects of substituents have been shown to be nearly additive. Zürcher30) has obtained and analysed data on a large number of steroids. He gives additive contributions for substituents and discusses the contribution of groups from equivalent positions.

Corss and Harrison31) have studied a series of steroids with and without nitrile substituents in the 5α- or 5β-positions. In each case they observed a deshielding of the C-19 methyl protons, on substitution with –C≡N, although the dipolar formula predicts a shielding, whether the substituent is introduced α or β. The value of $\Delta\chi^{C\equiv N}$ employed in their calculations is that of Goldstein and collaborators.11) These authors have neglected the electrostatic effect of the –C≡N group. Our calculations on these steroids, using Eqs. (2) and (11) for estimating anisotropic and electrostatic effects, shows that the C-19 methyl protons in 5α-cyano-steroids should be shifted upfields by 11.8 c/s, relative to the 5α-H-steroid, contrary to the observed shift. The explanation given by Cross and Harrison that ring A in the 5α-cyano-steroids is distorted from the chair form due to dipole-dipole interaction between substituents at the 3- and 5-positions may explain part of the observed downfield shift.

When considering 5β-cyano-steroids, our results show that the electrostatic effect of the –C≡N group is very important in determining the C-19 methyl protons shift, and explain the deshielding of these protons, relative to the parent steroid. Table 7 shows the calculated and observed shifts of these protons. The agreement between calculated and observed shifts in the 5β-cyano-steroids, where the stereochemistry of ring A is normal and repulsion between the C=O and C≡N groups is minimum, gives an indication that our value for the diamagnetic anisotropy of the –C≡N group is correct. To obtain better agreement between observed and calculated shifts in these molecules, one may take into account the electronegativity effects of the –C≡N group, as both magnetic anisotropy and electronegativity effects contribute to the proton chemical shift.

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28) "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publication, No. 11, The Chemical Society, London (1958).

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