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Abstract

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Chemical Shifts of Nuclear Magnetic Resonance in the Light of the Latest Studies of Magnetic Properties

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As early as 1923 (^{1}), the prospect was emphasized of using the paramagnetic-resonance effect for measurements of interatomic and intra-atomic magnetic fields. After the discovery of nuclear paramagnetism it became clear that the chemical shifts of nuclear magnetic resonance are the most powerful means of studying local magnetic fields in diamagnetic substances. Of great interest is the question of the extent to which the features of magnetic properties are reflected in chemical shifts. An attempt to answer this question was undertaken (^{2}) on the basis of the method of analyzing the susceptibilities of diamagnetic substances (^{3}). Let us recall that this new method, which differs fundamentally from the universally known additive Pascal scheme, makes it possible to find approximately the true contributions of individual atoms (or bonds) to the total susceptibility, whereas Pascal' s scheme assigns to them purely conventional values. At that time (^{2}), however, we relied on a still very imperfect theory of chemical shifts. Now, thanks to the work of I. V. Aleksandrov (^{4}), McConnell (^{5}), and Pople (^{6}), the general theory of chemical shifts has been considerably improved. This has enabled us now to carry out our calculations anew with more perfect means and on a much larger body of experimental material.

According to the modern theory, the magnitude of the chemical shift averaged over directions is

$$\delta\sigma = \delta\sigma_a + \delta\sigma_v, \tag{1}$$

where σ_a is a constant characterizing the magnetic action on the resonating nucleus of the electron shells of its own atom, and σ_v is a constant characterizing the magnetic action of neighboring atoms on the indicated nucleus. Approximately one may assume that

$$\sigma_a \approx \frac{\overline{\chi_a}}{N} \overline{\left(\frac{1}{r^3}\right)}, \tag{2}$$

where $\overline{\chi_a} = \overline{\chi}_{ad} + \overline{\chi}_{ap}$ is the direction-averaged diamagnetic susceptibility of atoms of this kind, with χ_{ad} being the component of Langevin diamagnetism and χ_{ap} the component of Van Vleck paramagnetism. For an undistorted atom $\overline{\chi}_{ap} = 0$. For this case the values of σ_a as a function of the number of electrons z were calculated quite rigorously by Dickinson and tabulated (^{7}). The corresponding values of $\overline{\chi_a}$ can be estimated from magnetochemical data. A change in the chemical bond of an atom is accompanied by a change of χ_a by $\delta\chi_a$ and of σ_a by $\delta\sigma_a$.

Approximately one may suppose that

$$\delta\sigma_a = \frac{\delta\chi_a}{\chi_a}\sigma_a. \tag{3}$$

In the liquids and gases with which we are concerned here, σ_v must depend chiefly on the magnetic anisotropy of neighboring atoms (or bonds). In the case of their axial symmetry one may write, approximately, $^{(5)}$

$$\delta\sigma_v = \delta\sum_i \frac{\Delta\chi_i}{3NR_i^3}(1 - 3\cos^2\theta_i), \tag{4}$$

where $\Delta\chi_i = \chi_{\|i} - \chi_{\perp i}$ (with $\chi_\|$ the component of the susceptibility tensor of the neighboring atom (or bond) along its axis, $\chi_\perp$ the component of the susceptibility tensor perpendicular to the axis, R the distance from the nucleus under study to the center of the neighboring particle (or bond), and θ the angle between R and the axis.

Thus, in order to calculate σ_v, it is necessary to know either all the $\Delta\chi_i$, or all the corresponding components of the susceptibility tensor. So far these quantities have not been investigated experimentally. An attempt at their purely theoretical calculation has likewise not yet led to sufficiently reliable data. This circumstance is, as is well known, the principal obstacle to a quantitative theoretical interpretation of chemical shifts. Meanwhile, the experimental value of the quantities $\Delta\chi$ can be obtained from the relation derived by Hanson and Mrovka $^{(8)}$, which connects $\Delta\chi$ with $\bar{\chi}_d$ and $\bar{\chi}_p$. On the other hand, our new method of analyzing susceptibilities makes it possible to separate $\bar{\chi}$ into $\bar{\chi}_d$ and $\bar{\chi}_p$. For the case of axial symmetry, the Hanson–Mrovka relation has the form

$$\chi_{p\perp} = -\frac{(\chi_{d\|} - \chi_{d\perp})^2}{\chi_{d\perp}} = -\frac{(\Delta\chi_d)^2}{\chi_{d\perp}}, \qquad \chi_{p\|} = 0. \tag{5}$$

Consequently, one may write approximately

$$\bar{\chi}_p = -\frac{2}{3}\frac{(\Delta\chi_d)^2}{\bar{\chi}_d}. \tag{6}$$

Further, bearing in mind that $\Delta\chi_p = \chi_{p\parallel} - \chi_{p\perp} = -{}^3/_2\bar{\chi}_p$, we obtain

$$\Delta\chi = \Delta\chi_d + \Delta\chi_p = \sqrt{-{}^3/_2(\bar{\chi}_d \times \bar{\chi}_p)} - {}^3/_2\bar{\chi}_p. \tag{7}$$

It should be noted that for given $\bar{\chi}_d$ and $\bar{\chi}_p$ formula (7) always corresponds to two possible values of $\Delta\chi$. The choice between them, however, in most cases presents no special difficulty.

The distribution of $\bar{\chi}_d$, required for calculating chemical shifts, among the individual atoms (or bonds) in a chemical compound, according to Kirkwood' s approximate theory (9), is proportional to $\sqrt{\alpha z}$, where α is the polarizability of the corresponding atom in the compound and z is the number of electrons it possesses. The distribution of χ_p among small groups of atoms is found, as shown in (3), by comparison with experimental data. On the basis of a number of considerations it may be assumed that within these groups χ_p is distributed among the atoms approximately in proportion to their polarizabilities α. In this way we find the corresponding χ_a, χ_{p_i}, and χ_{d_i} entering into formulas (3), (4), and (7), and can approximately calculate the chemical shifts. The values calculated by us are compared with experimental data in Table 1.

The satisfactory agreement of the calculated and experimental data in Table 1 indicates that the local magnetic fields determined by the nuclear-resonance method can be approximately estimated in an independent and comparatively simple way on the basis of measurements of magnetic

susceptibilities. Our method of interpreting diamagnetic susceptibilities has received new confirmation.

On the whole, these results convincingly show that nuclear magnetic resonance studies and studies of magnetic susceptibilities

Table 4

	$\delta\sigma \cdot 10^6$ calc.	$\delta\sigma \cdot 10^6$ exp.	Reference substance
$^*CH_2$	~ -0.58	$-0.3 \sim -0.4$ (10)	$^*CH_3$
$C_2{}^*H_6$	-0.5	-0.75 (10)	$^*CH_4$
	~ -0.82		
$C_2{}^*H_4$	~ -5.58	-5.18 (10)	$^*CH_4$
$C_2{}^*H_2$	~ -1	-1.35 (10)	$^*CH_4$
$^*H_2S$	~ 0	-0.08 (10)	$^*CH_4$
$^*CH_3Cl$	~ -0.93	-1.2 (10)	$^*CH_4$
$CH_3{}^*CO$	~ -180	-176 (11)	$CH_3{}^*CO$
$CH_3{}^*COOH$	~ -143	-158 (11)	$^*CH_3COOH$
$^*C = C$	~ -108	$-100 \sim -120$ (11)	$^*CH_3$
$^*C = C$	~ -48	-44 (12)	$^*CH_3$

	$\delta\sigma \cdot 10^6$ calc.	$\delta\sigma \cdot 10^6$ exp.	Reference substance
*CsCl (solution)	~ -265	-170 ± 30 (13)	*CsCl, crystalline powder
*CsJ (solution)	~ -360	-250 ± 40 (13)	*CsJ, same
Cs*J (solution)	~ -550	-500 ± 30 (13)	Cs*J, same

* The nucleus whose resonance is being investigated is marked with an asterisk.

must successfully complement one another in the practice of studying chemical structure.

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