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Abstract

Full Text

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Magnetochemistry of Organic Compounds and "Chemical" Shifts of Nuclear Magnetic Resonance

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It is known that the "chemical" shifts of nuclear resonance are caused by intramolecular magnetic fields acting on the given nucleus and depending on the chemical bond of the given atom in the molecule. The calculation of these fields is closely connected with the distribution of magnetic moments induced by the external field in molecules (^{1}). Attempts at a theoretical calculation of these moments and of the chemical shifts caused by them (^{2}) encounter, in most cases, the same enormous difficulties as attempts at the theoretical calculation of susceptibilities.

Recently we have succeeded in reconstructing the magnetochemical scheme of organic compounds. This has enabled us to estimate the diamagnetic and paramagnetic components of the magnetism of various aliphatic and alicyclic compounds and to find the shares of the susceptibilities attributable to individual atoms and groups of atoms (^{3}). It seems natural to try to apply these results of magnetochemistry to the discussion and calculation of chemical shifts of nuclear magnetic resonance.

Let us first consider those cases in which protons are included in groups of atoms connected only by single bonds, such as, for example: CH_3—C <, NH_2, CH_3—N <, CH_2— in alicyclic compounds. Since it is customary to refer the observed shifts to the shift in H_2O, it is also necessary to consider the OH group. It is assumed that resonance is observed at some fixed frequency. Let us suppose that, under these conditions, for resonance of a proton in an isolated hydrogen atom an external field H_0 is required.

As magnetochemical data show (^{3}), the atoms C, N, and O in the indicated groupings exhibit diamagnetism (per 1 mole): $\chi_{dC} \simeq 8 \cdot 10^{-6}$, $\chi_{dN} \simeq 7 \cdot 10^{-6}$, $\chi_{dO} \simeq -9 \cdot 10^{-6}$. The paramagnetism of these atoms in the indicated groups is practically equal to zero.

Under the action of the external field, induced moments arise in these atoms, directed antiparallel to the external field. These induced moments create, at the place where the proton is located, fields directed parallel to the external field, i.e., strengthening it. Thus, for resonance of a proton in H_2O a field $H_r = H_0 - k_{\mathrm{OH}} H_r$ is required, while for resonance of a proton in any one of the indicated groups fields $H_{gr} = H_0 - k_{gr}H_{gr}$ are required, where k_{OH} is a constant characteristic of OH, and k_{gr} is a constant inherent in the corresponding group.

The shift referred to water is, as is known, the quantity

$$\delta_{gr} = \frac{H_r - H_{gr}}{H_r} = \frac{-k_{\mathrm{OH}}H_r + k_{gr}H_{gr}}{H_r}.$$

Since H_{gr} differs from H_r by negligible fractions of a percent, one may take $H_{gr}/H_r \simeq 1$, and $\delta_{gr} = -k_{\mathrm{OH}} + k_{gr}$. The constants k_{OH} and k_{gr} represent the values of the fields created at the location of the proton

its diamagnetic neighbors in an external field equal to 1. Thus,

$$k_{\mathrm{OH}} = \frac{\chi_{dO}}{d^3_{\mathrm{OH}}N}; \qquad k_{gr} = \frac{1}{N}\sum \frac{\chi_{dA}}{d^3_{\mathrm{AH}}},$$

where d_{OH} is the distance between the proton and the O nucleus in OH; N is Avogadro' s number; χ_{dA} is the susceptibility of one of the surrounding atoms; d_{AH} is the distance from the nucleus A of a given atom to the proton under study. Taking into account that $d_{\mathrm{OH}} = 0.96 \cdot 10^{-8}$ cm, $d_{\mathrm{CH}} = 1.09 \cdot 10^{-8}$ cm, $d_{\mathrm{NH}} = 1.01 \cdot 10^{-8}$ cm, and $d_{\mathrm{C-C}} = 1.54 \cdot 10^{-8}$ cm, we obtain the results given in Table 1; here $k_{\mathrm{OH}} = 1.54 \cdot 10^{-5}$. The good agreement between the calculated and experimental values of the shifts confirms the validity of the considerations underlying the calculation.

Table 1

	CH_3—C <	NH_2	CH_3—N <	CH_3 in alicyclic compounds
$10^5\delta_{\mathrm{calc}}$	−0.42	−0.41	−0.32	−0.31
$10^5\delta^{(4)}_{\mathrm{expt}}$	−0.40	−0.36	−0.25	−0.36

For groups of atoms containing a double or triple bond, for example $= CH_2$ or $\equiv$ CH, it follows from magnetochemical considerations that the paramagnetic component of the susceptibility increases appreciably. If this paramagnetism were due only directly to carbon atoms bonded to one another by a double or triple bond, then the above-noted action of diamagnetic carbon atoms on the protons would be weakened by the presence of the double or triple bond. In that case the fields required for resonance of protons in $= CH_2$ and in $\equiv$ CH would be larger than in $-CH_3$. Experiment (4) shows, on the contrary, that $\delta_{=\mathrm{CH}_2} = +0.05 \cdot 10^{-5}$–$0.02 \cdot 10^{-5}$, i.e., is close to zero, while $\delta_{\equiv\mathrm{CH}} = -0.25 \cdot 10^{-5}$, i.e., considerably smaller than δ_{CH_3}. On the other hand, experiments carried out on the resonance of ^{13}C nuclei (5) show that the paramagnetism of a double bond also decreases the magnitude of the field required for resonance of carbon nuclei. Thus the paramagnetism of a double or triple bond, by strengthening the external field, acts in the same direction both on carbon nuclei and on the protons nearest to them. This apparently means that the indicated paramagnetism is produced by electrons "enveloping" both the C atoms and the H atoms directly bonded to them.

The considerations and calculations presented make it possible to establish a connection between studies of nuclear resonance and magnetostatic susceptibility (magnetochemistry). It may be hoped that the combination of these two areas of research will prove very useful for the study of molecular structure.

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Note: Figure translations are in progress. See original paper for figures.