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Abstract

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MANIFESTATION OF INDUCTIVE TRANSMISSION OF INFLUENCE ALONG A CARBON CHAIN IN NUCLEAR QUADRUPOLE RESONANCE SPECTRA

(ON AN EMPIRICAL SCHEME FOR CALCULATING N.Q.R. FREQUENCIES OF Br^{79} AND Cl^{35} IN ALIPHATIC MOLECULES)

(Presented by Academician M. I. Kabachnik, June 9, 1964)

When the N.Q.R. frequencies* of Br^{79} or Cl^{35} (ν) are varied in a series of compounds of the type $Hal(CH_2)_nHal$ (see Fig. 1), the relative shift decreases sharply with increasing number of methylene groups separating the halogens ([1], [2]), and beginning with $n = 4$ only oscillations of the dependence $\nu(n)$ for even and odd n are observed about a certain mean value $\nu_{0\mathrm{I}} = \mathrm{const}$ (for Cl^{35}, $\nu_{0\mathrm{I}} = 33.0$ MHz, and for Br^{79}, $\nu_{0\mathrm{I}} = 250.0$ MHz). Thus, an almost complete damping of the inductive influence of the halogens on one another is observed at sufficiently large n.

An analogous dependence is also observed for monohalogen derivatives of the type $CH_3(CH_2)_{n-1}Hal$. In this case the N.Q.R. frequencies of halogens located at primary carbon atoms also attain the mean value $\nu_{0\mathrm{I}}$ as n increases.

The N.Q.R. frequencies of halogens attached to secondary, tertiary, etc. carbon atoms tend to the value $\nu_{0\mathrm{II}} = \mathrm{const}$ ($\nu_{0\mathrm{II}} = 32.0$ MHz for Cl^{35} and $\nu_{0\mathrm{II}} = 243.3$ MHz for Br^{79}). It proved possible to find the form of the functional dependence relating the change in the differences between the N.Q.R. frequencies of the halogen and $\nu_{0\mathrm{I}}$ to n. The dependence of the frequency shift ($\Delta_n\nu = \nu_n - \nu_{0\mathrm{I}}$) of a halogen separated from another by n methylene groups can be approximately expressed through the primary shift ($\Delta_1\nu$) according to the law of a geometric progression

Fig. 1. Dependence of the N.Q.R. frequencies of Cl^{35} (ν) in $Cl(CH_2)_nCl$ on the number of methylene groups separating the halogens (n). 1 –calculated curve at $\Delta_1\nu = 2.4$ MHz and $\xi = 0.47$; 2 –experimental dependence $\nu(n)$

Figure 1: Dependence of the N.Q.R. frequencies of Cl^{35} (ν) in $Cl(CH_2)$ Cl on the number of methylene groups separating the halogens (n). 1 –calculated curve at $\Delta_1\nu = 2.4$ MHz and $\xi = 0.47$; 2 –experimental dependence $\nu(n)$.

Figure 1: Figure 1: Dependence of the N.Q.R. frequencies of Cl^{35} (ν) in $Cl(CH_2)$ Cl on the number of methylene groups separating the halogens (n). 1 –calculated curve at $\Delta_1\nu = 2.4$ MHz and $\xi = 0.47$; 2 –experimental dependence $\nu(n)$.

$$\Delta_n\nu = \xi^{n-1}\Delta_1\nu. \tag{1}$$

* All frequency values, both calculated and experimental, are given at the temperature of liquid nitrogen (77°K).

Here ξ is the attenuation coefficient for transmission of influence along a chain of carbon atoms ($\xi < 1$). The expression for the frequency of a halide at a primary carbon atom can be written in the following form:

$$\nu_{n\mathrm{I}} = \nu_{0\mathrm{I}} + \xi^{n-1}\Delta_1\nu. \tag{2}$$

Figure 1 presents the calculated curve $\nu_{n\mathrm{I}} = f(n)$ for $\Delta_1\nu = 2.4$ MHz and $\xi = 0.47$.

Analysis of the NQR spectra of polyhalogenated chain aliphatic molecules leads to the conclusion that the conditions for transmission of influence on a given halide from the others do not depend on the number of substituents; i.e., $\nu_{0\mathrm{I}}, \nu_{0\mathrm{II}}, \Delta_1\nu$, and ξ remain unchanged, and formula (2) can be represented as the following sum:

$$\nu_{\mathrm{I}} = \nu_{0\mathrm{I}} + \sum_n \Delta_1\nu\xi^{n-1} = \nu_{0\mathrm{I}} + \Delta_1\nu \sum \xi^{n-1}. \tag{3}$$

The values of the parameters $\Delta_1\nu$ and ξ prove to be universal and can be used, under the same assumptions, also to calculate the NQR frequencies of halides located at secondary, tertiary, etc., carbon atoms, i.e.,

$$\nu_{\mathrm{II}} = \nu_{0\mathrm{II}} + \Delta_1\nu \sum \xi^{n-1}. \tag{4}$$

A very characteristic example for calculations by formula (3) is $ClCH_2CH_2CCl_3$.

The expression for the chlorine frequency in the CH_2Cl group can be written in the form

$$\nu_{\mathrm{I}}^{CH_2Cl} = \nu_{0\mathrm{I}}^{Cl} + 3\Delta_1\nu_{Cl}\xi_{Cl}^2,$$

and for the chlorine atoms in the CCl_3 group

$$\nu_{\mathrm{I}}^{\mathrm{CCl_3}} = \nu_{0\mathrm{I}}^{\mathrm{Cl}} + \Delta_1\nu_{\mathrm{Cl}}(2 + \xi_{\mathrm{Cl}}^2),$$

whence the corresponding frequencies are 34.59 and 38.33 MHz. The experimentally determined frequencies are

$$\mathrm{Cl}^{35}\nu_{\mathrm{I}}^{\mathrm{CH_2Cl}} = 34.629$$

and

$$\nu^{\mathrm{CCl_3}} = 38.426 \text{ MHz}.$$

The NQR spectrum of the trichloromethyl group is a triplet at 38.826, 38.304, and 38.150 MHz, arising because each of the three chlorine atoms occupies a nonequivalent position in the elementary cell of the crystal (crystalline splitting). The agreement of the calculated and experimental frequencies (averaged over crystalline splittings) to an accuracy of 0.1–0.3% should be regarded as very good, since the maximum crystalline splittings (in molecular crystals) do not exceed 1.5–2% of the measured frequency. An example of the application of formulas (3) and (4) is the calculation of the Br^{79} spectrum in $BrCH_2CHBrCH_2Br$ (for $\Delta_1\nu$ and ξ for Br^{79}, see Table 1): for bromine at a primary carbon atom,

$$\nu_{\mathrm{I}}^{\mathrm{CH_2Br}} = \nu_{0\mathrm{I}}^{\mathrm{Br}} + \Delta_1\nu_{\mathrm{Br}}(\xi_{\mathrm{Br}} + \xi_{\mathrm{Br}}^2),$$

and at a secondary one,

$$\nu_{\mathrm{II}}^{\mathrm{CHBr}} = \nu_{0\mathrm{II}}^{\mathrm{Br}} + 2\Delta_1\nu_{\mathrm{Br}}\xi_{\mathrm{Br}}.$$

The calculated values $\nu_{\mathrm{I}}^{\mathrm{CH_2Br}} = 266.5$ and $\nu_{\mathrm{II}}^{\mathrm{CHBr}} = 265.3$ MHz are in sufficiently good agreement with experiment: $\nu_{\mathrm{I}}^{\mathrm{CH_2Br}} = 269.148$, and $\nu_{\mathrm{II}}^{\mathrm{CHBr}} = 265.250$ MHz. Experimentally, for 1,2,3-tribromopropane, two frequencies, 268.634 and 269.653 MHz (crystalline splitting), were obtained for the chemically equivalent bromine atoms at primary carbon atoms.

Calculations of the same type were carried out for comparison with experimental data for polybromo- and chloroethanes, a series of tetrachloroalkanes, and a number of other compounds. This made it possible to estimate the accuracy of the calculations (0.1–2.0%) and to predict NQR frequencies for a large number of compounds. It should be noted that, as a rule, the discrepancies of the calcula-

the calculated frequencies and the experimental ones is systematic in nature: with a large number of substituents the calculated values somewhat exceed the experimental ones, whereas with a small number of substituents the calculated values are somewhat lower than the experimental ones.

Apparently, this is explained by the effects of intramolecular spatial interactions and by the peculiarities of the thermal vibrations of molecules in the crystal.

With further accumulation of experimental material it became clear that analogous regularities occur in the transmission of influence to a halide along the carbon chain also from other nonhalogen substituents (for example, NO_2, COOH, etc.).

The conditions for transmission of influence along a chain of carbon atoms from other substituents can be expressed analytically similarly to (3) and (4), but with different $\Delta_1 \nu_i$ and ξ_i (see Table 1)

$$\nu_{\mathrm{I}} = \nu_{0\mathrm{I}} + \sum_{n_i} \Delta_1 \nu_i \xi^{n_i - 1}, \tag{5}$$

$$\nu_{\mathrm{II}} = \nu_{0\mathrm{II}} + \sum_{n_i} \Delta_1 \nu_i \xi^{n_i - 1}. \tag{6}$$

Table 1

X	Cl^{35} ($\nu_{0\mathrm{I}} = 33.0$ MHz, $\nu_{0\mathrm{II}} = 32.0$ MHz)	Cl^{35} ($\nu_{0\mathrm{I}} = 33.0$ MHz, $\nu_{0\mathrm{II}} = 32.0$ MHz)
X	$\Delta_1 \nu$, MHz	ξ
Cl	2.40	0.47
COOH	2.80	–
NO_2	3.50	0.34
CH_3	−0.30	–

X	Br^{79} ($\nu_{0\mathrm{I}} = 250.0$ MHz, $\nu_{0\mathrm{II}} = 243.3$ MHz)	Br^{79} ($\nu_{0\mathrm{I}} = 250.0$ MHz, $\nu_{0\mathrm{II}} = 243.3$ MHz)
X	$\Delta_1 \nu$, MHz	ξ
Br	22.0	0.50
COOH	34.1	0.30
NO_2	36.5	0.31
CH_3	−1.3	–

For example, for $BrC(NO_2)_2CH_2(NO_2)_2CBr$ the expression is written in the form: $\nu_{\mathrm{I}}^{\mathrm{Br}} = \nu_{0\mathrm{I}}^{\mathrm{Br}} +$

$$+\, 2\Delta_1 \nu_{\mathrm{NO2}}^{\mathrm{Br}} \left(1 - \xi_{\mathrm{BrNO2}}^2\right) + \Delta_1 \nu_{\mathrm{Br}}^{\mathrm{Br}}\, \xi_{\mathrm{BrBr}}^2 .$$

The calculated frequency is $\nu_{\mathrm{I}} = 335.52$ MHz, and the experimental one is 335.552 MHz.

Comparisons of the calculated and experimental NQR frequencies* of Br^{79} and Cl^{35} were carried out for a large number of derivatives of methane, ethane, propane, and butane that, in addition to a halide, had other substituents (the discrepancies between the experimental and calculated data were 0.1-2%). The use of the approximate calculation scheme proposed above makes it possible to predict the NQR frequencies of Br^{79} and Cl^{35} in various halogen-substituted chain compounds of the aliphatic series (including the NQR frequencies of halides in hypothetical, hardly accessible compounds).

Comparison of the calculated and experimental data permits an unambiguous assignment of the frequencies and, consequently, the solution of structural problems connected with determining the positions of substituents.

Correlation of the chemical shifts of NQR frequencies with certain chemical constants (pK_a, σ, σ^*, etc.) makes it possible to predict the values of the latter and, consequently, the chemical properties of molecules determined by their ground state.

I consider it my duty to express my gratitude to A. I. Kitaigorodskii for his attention to the work.

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* Analogous regularities can also be established for iodine-containing chain compounds of the aliphatic series; however, at present there is insufficient experimental material for this.

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