On determination of the strength of local electric fields at the bromine atoms in the series of compounds $BrCH_2R$ by ^{79}Br NQR spectroscopy

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The values of changes in the strength of local electric fields at the bromine atoms for a series of compounds $BrCH_2R$ were determined from a hyperbolic equation relating the ^{79}Br NQR frequencies to their field constants. The totalities of electron-acceptor and electron-donor substituents R are described by equations of the same type differing in their parameters.

Key words: NQR frequency; field constant of NQR frequency; local electric field.

It is known that the outcome of processes occurring in the reaction center is predetermined by both the quantum state of interacting molecular systems and the configuration of electric fields around the reaction center. Therefore, the problem of separating these effects in general form and relating them to the molecular structure is of interest. Particular difficulties arise in the case of solids and in studies of heavy atoms whose polarizability is dependent on the magnitude of the local electric field.

It is possible to solve this problem using the spectral parameters of nuclear quadrupole resonance (NQR) for series of compounds of the same type (for instance, $BrCH_2R$). The experimentally measured NQR frequency (ν) is proportional to the electric field gradient (EFG) at the nucleus of resonance atom, *i.e.*, to the second derivative of the electrostatic potential with respect to a specified direction (z) (in our case, it coincides with the direction of the C—Br bond axis in $BrCH_2R$). The maximum EFG component usually denoted as eq_{zz} (where e is the electron charge) is determined by both the electron distribution (q_{zz}(elec.)) and electric fields, the sources of which are exterior to the atomic radius (q_{zz}(field)).[1,2]

$$q_{zz} = q_{zz}(\text{elec.}) + q_{zz}(\text{field}) \qquad (1)$$

Application of an external electric field along the specified direction (z) makes it possible to determine experimentally the derivative of the NQR frequency with respect to the strength of electric field, called the field constant of the NQR frequency. The strength of the external electric fields in these experiments ranges from 10^{-3} to 10^{-4} of the expected strength of local electric fields.[3]

Strictly speaking, the procedure of separating q_{zz} into components q_{zz}(elec.) and q_{zz}(field) belongs to the class of incorrect problems. However, to find an equation relating two physical quantities, one of which is the derivative of the other with respect to the desired argument, one can use a procedure known in theoretical physics, namely, comparison of the two series of their experimental values. Assuming that both NQR frequency and its field constant ($d\nu/dE_z$) are dependent on the strength of the local field E_z, the derived differential equation can be solved with respect to E_z.

This work was aimed at finding the equation relating the ^{79}Br NQR frequencies to their field constants, solving corresponding differential equation, determining the values of the strength of the local electric fields, and revealing differences in the behavior of electron-acceptor and electron-donor substituents in the series of compounds $BrCH_2R$.

A series of compounds $BrCH_2R$, where R is an electron-acceptor or electron-donor substituent with the carbon (or other second-row elements of the Periodic Table) key atom, was chosen for ^{79}Br NQR studies.

Experimental

The experimental values of the field constants of ^{79}Br NQR frequencies for compounds $BrCH_2R$ at 77 K were obtained using the pulse technique.[4–11] The ^{79}Br NQR frequencies of these compounds at 77 K were taken from the literature,[2,12] and some of them were refined. The experimental data are listed in Table 1 (numbers *1—18* correspond to compounds containing electron-donor substituents whereas points *19—27* correspond to compounds containing electron-acceptor substituents). The substituents in the reference compounds (numbers *28—30*) contain the key atoms of elements that are not second-row elements of the Periodic Table. The meaning of the columns corresponding to the ΔE_z values will be explained below.

[†] Deceased.

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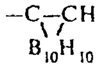
Table 1. ^{79}Br NQR spectra of $BrCH_2R$ derivatives at 77 K

Number	Compound	ν /MHz	α /Hz cm kV^{-1}	ΔE_z /MV cm^{-1}
1	$BrCH_2Me$	248.74	490	−13.037
2	$Br(CH_2)_2Me$	251.72	515	−7.084
3	$Br(CH_2)_3Me$	249.96	550	−9.552
4	$Br(CH_2)_5Me$	249.26	495	−11.973
5	$Br(CH_2)_2Br$	259.12	660	5.654
6	$Br(CH_2)_2Br$	261.68	683	9.457
7	$Br(CH_2)_3Br$	252.41	520	−5.748
8	$Br(CH_2)_3Br$	249.75	545	−9.727
9	$Br(CH_2)_4Br$	250.09	625	−9.191
10	$Br(CH_2)_5Br$	254.04	650	−2.155
11	$Br(CH_2)_6Br$	250.10	625	−8.980
12	$Br(CH_2)_{10}Br$	250.74	600	−7.942
13	$BrCH_2CH{=}CH_2$	254.43	530	−1.899
14	$BrCH_2Ph$	259.13	660	5.669
15	$BrCH_2AdBr$*	253.14	655	−3.536
16	$Br(CH_2)_2CONH_2$	255.90	530	0.876
17	$Br(CH_2)_2COOH$	260.08	600	7.828
18	$BrCH_2C_6H_4NO_2$-4′	264.70	690	14.930
19	$[Br(CH_2)_2NH_3]^+Br^-$	263.86	600	−12.487
20	$BrCH_2C{\equiv}CH$	274.69	605	6.445
21	$BrCH_2C(O)Ph$	276.09	535	9.469
22	$BrCH_2C(O)AdBr$*	275.06	495	8.340
23	$BrCH_2C(O)C_6H_4Br$-4′	278.00	505	13.162
24	$BrCH_2{-}C_2B_{10}H_{11}$**	279.85	481	16.915
25	$BrCH_2COOH$	287.01	415	32.940
26	$BrCH_2COOH$	284.76	435	27.635
27	$BrCH_2NO_2$	296.42	320	61.178
28	BrMe	264.50	493	—
29	$BrCH_2Br$	281.099	546	—
30	$BrCH_2Br$	280.899	546	—

* Ad is adamantyl. **  $\underset{B_{10}H_{10}}{-C{-}CH}$.

The NQR spectra of some compounds are multiplets due to crystallographic splittings. For this reason, the number of points in the figures (in accordance with the numbering in Table 1) exceeds the number of compounds since no averaging of NQR frequencies was performed and the numbers were ascribed to the spectral lines.

Results and Discussion

Dependence between ν and dν/dE_z. Assuming that both NQR frequencies and their field constants depend on the strength of the local electric field (E_z) and denoting $d\nu/dE_z = \alpha$, we expand both quantities into power series in terms of E_z, restricting ourselves to quadratic terms:

$$\nu(E_z) = \nu_0 + nE_z + mE_z^2..., \qquad (2)$$

$$\alpha(E_z) = \alpha_0 + AE_z + BE_z^2...$$

After eliminating E_z and performing simple transformations we get the relationship

$$a_1\nu^2 + a_2\nu\alpha + a_3\alpha^2 + a_4\nu + a_5\alpha + a_6 = 0. \qquad (3)$$

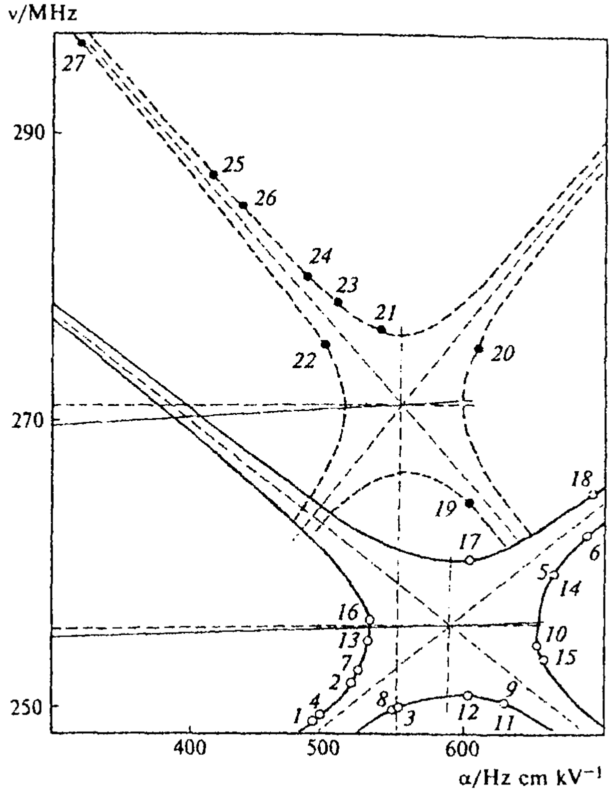


Fig. 1. Dependence $\nu(\alpha)$ (4) for the series of compounds $BrCH_2R$ with electron-donor (solid lines) (numbers *1—18* in Table 1) and electron-acceptor (dashed lines) (numbers *19—27* in Table 1) substituents.

in which coefficients a_i are functionally related to the coefficients of expansions (2). Equation (3) is the equation of a second-order curve in its general form.

A comparison of the experimental values of ν and α (see Table 1) makes it possible to correct the type of dependence (3):

$$\Delta_\nu^{-2}[(\nu - \nu_0) - k(\alpha - \alpha_0)]^2 - \Delta_\alpha^{-2}(\alpha - \alpha_0)^2 = \delta. \qquad (4)$$

Equation (4) is the equation of a hyperbola shifted with respect to the origin and rotated with respect to the coordinate axes. Here k is the slope of the hyperbola axes with respect to the coordinate axes (ν and α), ν_0 and α_0 are the coordinates of the center of the hyperbola, Δ_ν and Δ_α are the semi-axes of the hyperbola, and $\delta = \pm 1$. The equation for the asymptotes of hyperbola (4) is

$$\nu_a = \nu_0 + (k + \delta\Delta_\nu/\Delta_\alpha)(\alpha - \alpha_0). \qquad (5)$$

The plots in Fig. 1 show that the dependence $\nu(\alpha)$ is adequately described by Eq. (4). The totalities of points corresponding to compounds with electron-donor and electron-acceptor substituents belong to different sets described by Eq. (4) with different parameters (Table 2).

The statistical characteristics of the derived equations $\nu(\alpha)$ listed in Table 2 indicate that they are highly

Table 2. Parameters of Eq. (4) for the series of compounds $BrCH_2R$ with electron-donor (numbers *1—18* in Table 1) and electron-acceptor (numbers *19—27* in Table 1) substituents

Parameter	*1—18*	*19—27*
ν_0/MHz	255.444	270.869
Δ_ν/MHz	4.541	4.826
α_0/Hz cm kV^{-1}	588.230	550.908
Δ_α/Hz cm kV^{-1}	58.148	41.097
$k \cdot 10^6$/kV cm^{-1}	$1.5715 \cdot 10^{-3}$	$5.0 \cdot 10^{-3}$
$\pm\delta\nu$/MHz	0.18	0.14
$\pm\delta\alpha$/Hz cm kV^{-1}	1.6	1.4
n	18	9
r*	0.999	0.998

* Correlation coefficient (r) between the observed and calculated values of the ^{79}Br NQR frequencies in the series of compounds $BrCH_2R$.

accurate and that expansion (2) is sufficient. The reference compounds (numbers *28—30*) are not described by the above equations since their substituents contain the key atoms of the elements that are not second-row elements of the Periodic Table.

Determination of ΔE_z from Eq. (4). Differential equation (4) can be solved exactly with respect to E_z using a substitution

$$\Delta_\nu^{-1}[(\nu - \nu_0) - k(\alpha - \alpha_0)] + \Delta_\alpha^{-1}(\alpha - \alpha_0) = t, \qquad (6)$$

$$\Delta_\nu^{-1}[(\nu - \nu_0) - k(\alpha - \alpha_0)] - \Delta_\alpha^{-1}(\alpha - \alpha_0) = \delta t^{-1}.$$

After certain trivial transformations, Eq. (4) can be solved using tabulated integrals:

$$E_z = \left(k + \frac{\Delta_\nu}{\Delta_\alpha}\right)\int\frac{t\,\mathrm{d}t}{t^2 + 2a_0t - \delta} + \delta\left(k - \frac{\Delta_\nu}{\Delta_\alpha}\right)\int\frac{\mathrm{d}t}{t(t^2 + 2a_0t - \delta)} + E_{z_0}(\delta) =$$

$$= \frac{\Delta_\nu}{\Delta_\alpha}\left[\left(1 - k\frac{\Delta_\alpha}{\Delta_\nu}\right)\ln|t| + k\frac{\Delta_\alpha}{\Delta_\nu}\ln\left|t^2 + 2a_0t - \delta\right| - \frac{a_0}{\sqrt{a_0^2 + \delta}}\ln\left|\frac{t + a_0 - \sqrt{a_0^2 + \delta}}{t + a_0 + \sqrt{a_0^2 + \delta}}\right|\right] + E_{z_0}(\delta), \qquad (7)$$

$$t = \frac{\nu - \nu_0 \pm \sqrt{(\nu - \nu_0)^2 - (\Delta_\nu^2 - k^2\Delta_\alpha^2)\delta}}{\Delta_\nu + k\Delta_\alpha},$$

where $a_0 = \alpha_0/\Delta_\alpha$.

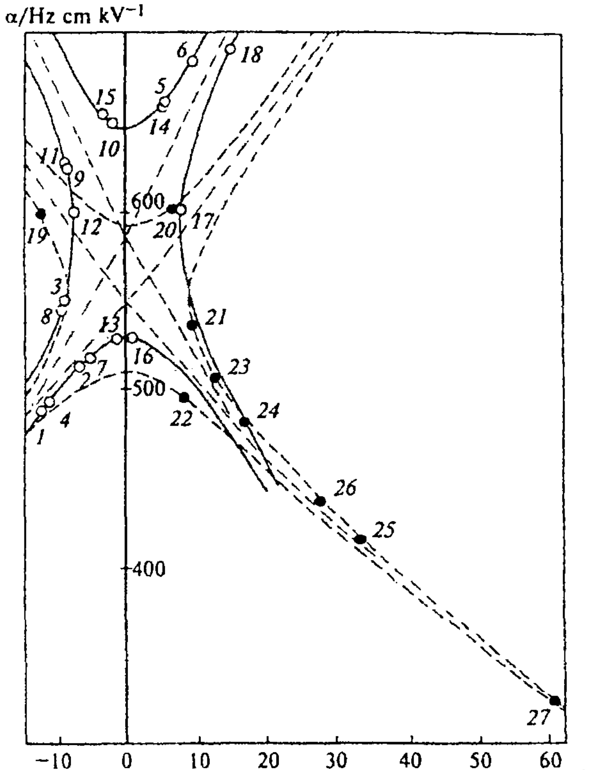


Fig. 2. The $\alpha(\Delta E_z)$ plot for the series of compounds $BrCH_2R$ with electron-donor (solid lines) (numbers *1—18* in Table 1) and electron-acceptor (dashed lines) (numbers *19—27* in Table 1) substituents.

It follows from the meaning of expression (7) that $E_{z0}(\delta)$ corresponds to $t = \pm 1$.

The average values of $\bar{E}_{z0}(\delta)$ and the values of $\Delta E_z = E_z - \bar{E}_{z0}(\delta)$ are listed in Table 3 and Table 1, respectively.

The E_{za} value corresponding to asymptotes of Eq. (4) can be determined by integrating Eq. (5)

$$E_{za} = \left(k + \delta\frac{\Delta_\nu}{\Delta_\alpha}\right)\ln\left|\left(\frac{\nu}{\nu_0} - 1\right) + \frac{\alpha_0}{\nu_0}\left(k + \delta\frac{\Delta_\nu}{\Delta_\alpha}\right)\right| + E_{z0a}(\delta). \qquad (8)$$

The $E_{z0a}(\delta)$ values for the asymptotes, *i.e.*, for $\nu = \nu_0$, are listed in Table 3.

The dependences $\alpha(\Delta E_z)$ and $\nu(\Delta E_z)$ are presented in Figs. 2 and 3, respectively. It follows from these plots and from Fig. 1 that the totalities of electron-acceptor and electron-donor substituents are described by dependences

Table 3. Values of the auxiliary parameters for calculation of ΔE_z from Eq. (7)

Series	a_0	Δ_ν/Δ_α	k	$\bar{E}_{z0}(\delta)$/MV cm^{-1}		$E_{z0a}(\delta)$/MV cm^{-1}	
		MV cm^{-1}		$\delta = +1$	$\delta = -1$	$\delta = +1$	$\delta = -1$
1—18 (donors)	10.1161	78.0938	1.5715	238.6255	245.2495	−135.0969	132.8472
19—27 (acceptors)	13.4051	117.4295	5.000	400.5880	419.9749	−170.2122	165.8893

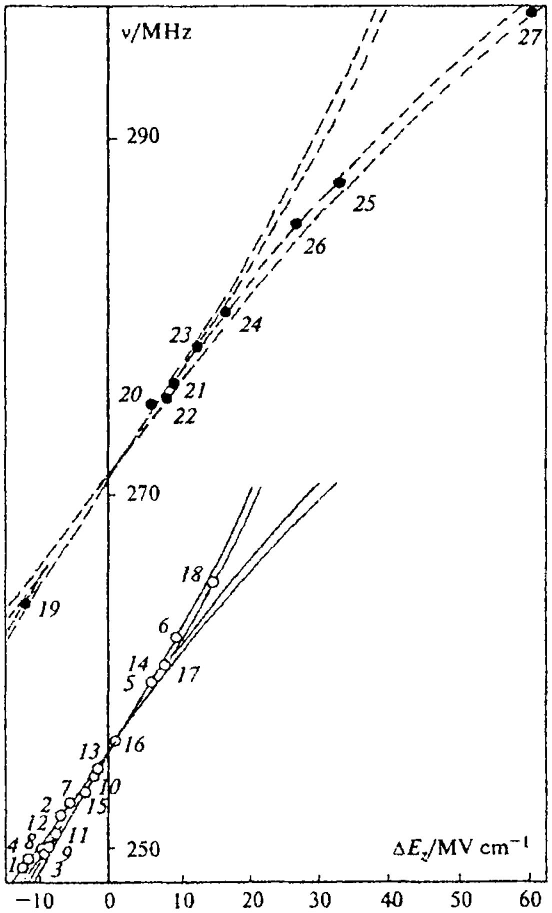


Fig. 3. The $\nu(\Delta E_z)$ plot for the series of compounds $BrCH_2R$ with electron-donor (solid lines) (numbers *1—18* in Table 1) and electron-acceptor (dashed lines) (numbers *19—27* in Table 1) substituents.

of the same type with different sets of parameters and the origins shifted with respect to each other. This fact is of fundamental importance, since it shows that differences between the electron-donor and electron-acceptor substituents cannot be reduced only to the difference in the signs of the field contributions they induce. The observed difference has a more profound discrete character and can likely be explained by quantum discrete differences in the states of the molecular skeleton or the bromine atom participating in corresponding C—Br bonds. Since merely alternation of the signs of the strength of local electric fields (ΔE_z) in the series of substituents under consideration can be determined experimentally, the strength of the fields induced by the most electron-acceptor substituents along the axis of the C—Br bond was taken as the positive direction of the field, which completely defines the distribution of the signs of changes in the strength of electric fields for both series of substituents (see Table 1 and Figs. 2, 3). Relative changes in the local electric fields for donor and acceptor substituents are equal to 11.6% and 18%, respectively. Relative changes in the frequencies are minimum (6—12%), whereas changes in the field constants are maximum (34—52%).

Noteworthy is that the crystallographic nonequivalence of chemically equivalent bromine atoms (see numbers *5, 6*; *7, 8*; and *25, 26* in Table 1) results in a shift of corresponding points on the plots in Figs. 1, 2, and 3; however, these shifts never make the points deviate from the trajectories described by Eqs. (4) and (7); this means that the shifts are of purely field nature and do not change the quantum state of the molecular system. We believe that the observed phenomenon serves as a reasonable model illustration of the manifestation of the nature of the so-called nonspecific solvation.

At $k = 0$, Eqs. (4) and (7) become tantamount to those reported previously.[13]

Thus, a general procedure for the determination of the strength of local electric fields at the resonance atom has been found, which opens the way to a more detailed consideration of the factors affecting the reactivity of compounds of the $BrCH_2R$ type.

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