^{79,81}Br NQR Spectra of Alkyl(4-Bromophenyl)Sulphides

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The ^{79,81}Br NQR spectra of compounds of the series 4-BrC_6H_4SR with $R = (CH_2)_nH$ ($n = 1$, 2, 4–9), $(CH_2)_nCH(CH_3)_2$ ($n = 0$–2) and $CH_m(CH_3)_{3-m}$ were obtained at 77 K. The halogen atom electron densities in these compounds and chlorine-containing analogs are compared. The ratio of the amplitudes of the NQR frequency oscillations in chlorine- and bromine-containing compounds with $R = (CH_2)_nH$ corresponds to the ratio of the polarizabilities of ^{35}Cl and ^{79}Br. The variation of the alkyl groups R influences the electron distribution of the halogen atom.

Key words: NQR spectra, Frequency, Alkyl(4-bromophenyl)sulphides, Oscillation effect.

Introduction

The NQR frequencies of halogen atoms in molecules of the series $Y(CH_2)_nX$ (where Y is a halogen atom or a group containing it) usually oscillate when the n increases successively (see, e.g., [1–5]). The most convincing explanation of this oscillation is the polarization of a chemical bond by the charge of a geminal atom and the transmission of this effect along a chain of atoms [2]. This way the peculiarities of electron effects in alkyl groups $CH_m(CH_3)_{3-m}$ of various compounds were explained (see, e.g., [2, 4, 6]). The effects were mostly studied by NQR in chlorine-containing compounds, but also in some bromine- and iodine-containing ones (see, e.g., [1, 7]). In the latter compounds the effects should be greater because the polarizability of Br and I is higher than that of Cl [2, 7].

We have measured at 77 K the ^{79,81}Br NQR spectra of some alkyl(4-bromophenyl)sulphides of the series 4-$BrC_6H_4S(CH_2)_nH$ ($n = 1$, 2, 4–9) (Table 1), 4-$BrC_6H_4S(CH_2)_nCH(CH_3)_2$ ($n = 0$–2) and 4-$BrC_6H_4SCH_m(CH_3)_{3-m}$ ($m = 0$–3) (Table 2). All these compounds were synthesised by the reaction of 4-bromophenol with the corresponding alkylhalogenide [8]. The ^{79,81}Br NQR spectra are singlet with the exception of 4-$BrC_6H_4S(CH_2)_2H$ which shows a doublet. The line in the spectrum of 4-$BrC_6H_4S(CH_2)_9H$ is somewhat broadened. Evidently it represents an undecided doublet. The NQR spectrum of 4-$BrC_6H_4S(CH_2)_3H$ was not observed.

The ^{35}Cl NQR spectra of the series 4-$ClC_6H_4S(CH_2)_nH$ were studied in [3]. When n increases from $n = 1$ to $n = 6$, the ^{35}Cl NQR frequency increases linearly, and on further increase of n the NQR frequency oscillates near ν^{77} 35 MHz (Figure 1). The ^{79,81}Br NQR frequencies of the compounds 4-$BrC_6H_4S(CH_2)_nH$, on the contrary, decrease on going from $n = 1$ to $n = 2$ in conformity with the slightly greater electronegativity of the ethyl group as compared with the methyl group (Table 1, Figure 1). The same change with $n = 1$ and 2 is observed for compounds of the series 4-$BrC_6H_4O(CH_2)_nH$ ($\nu(^{79}Br) = 271.371$ and 266.818 MHz [9]) and the series 4-$ClC_6H_4O(CH_2)_nH$ ($\nu(^{35}Cl) = 34.753$ and 34.381 MHz [9]). The ^{79,81}Br NQR frequencies of the compounds 4-$BrC_6H_4S(CH_2)_nH$ increase practically linearly when n increases from $n = 4$ to $n = 7$, and on further increase of n they oscillate (Table 1, Fig. 1) just as that for the chloro-containing analogs [3] (Figure 1). Analogously to the latter compounds, the NQR frequencies for compounds of the series 4-$BrC_6H_4S(CH_2)_nH$ are higher at odd n values than those at even ones. Thus, the character of the change of the ^{79,81}Br NQR frequencies and, consequently, of the halogen atom electron density in alkyl(4-bromo-

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Table 1. ^{79,81}Br NQR frequencies at 77 K (ν^{77}) of compounds of the series 4-$BrC_6H_4S(CH_2)_nH$ and signal/noise (S/N) ratio in their NQR spectra.

n	$\nu^{77}(^{79}Br)$, MHz	S/N	$\nu^{77}(^{81}Br)$, MHz	S/N
1	269.670	60	225.280	60
2	268.081	5	223.930	15
	268.700	5	224.550	15
4	273.450	20	228.450	20
5	273.280	7	229.110	8
6	274.810	60	229.590	9
7	275.020	40	229.740	35
8	270.120	120	225.680	80
9	275.480	20	230.150	30

Table 2. ^{79,81}Br NQR frequencies at 77 K (ν^{77}) of compounds of the series 4-BrC_6H_4SR and signal/noise (S/N) ratio in their NQR spectra.

R	$\nu^{77}(^{79}Br)$ MHz	S/N	$\nu^{77}(^{81}Br)$ MHz	S/N
$C(CH_3)_3$	268.530	100	224.300	90
$CH(CH_3)_2$	271.590	40	226.890	90
$CH_2CH(CH_3)_2$	268.990	2	224.710	2
$(CH_2)_2CH(CH_3)_2$	271.170	15	226.530	40

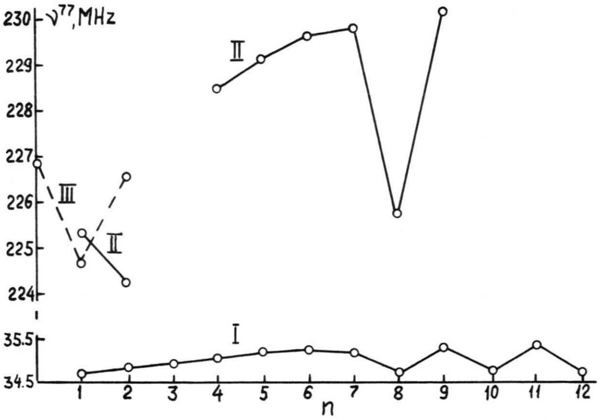

Fig. 1. Dependence on n of the ^{35}Cl NQR frequencies of the series 4-$ClC_6H_4S(CH_2)_nH$ (I), and of the ^{81}Br NQR frequencies of the series 4-$BrC_6H_4S(CH_2)_nH$ (II) and 4-$BrC_6H_4S(CH_2)_nCH(CH_3)_2$ (III).

phenyl)sulphides, when n increases, is the same as that for the chlorine-containing analogs. The only exception are compounds with $n=2$. Probably on further increase of n ($n>9$) the ^{79,81}Br NQR frequencies of the compounds 4-$BrC_6H_4S(CH_2)_nH$ will oscillate as do the chloro-containing analogs (Figure 1). The amplitude of oscillation of the ^{79,81}Br NQR frequencies for 4-$BrC_6H_4S(CH_2)_nH$ is much higher than that of the ^{35}Cl NQR frequencies for chloro-containing analogs. For the latters it is 0.5 MHz [3] (Figure 1). Unfortunately, the experimental data for the compounds 4-$BrC_6H_4S(CH_2)_nH$ are insufficient. However, analogously to the chloro-containing compounds, one may suppose that the further amplitude of the NQR frequency oscillations for the bromine-containing ones will be approximately the same as for $n=7-9$ (5.1 MHz). In this case the ratio of the oscillation amplitudes for bromine- and chlorine-containing analogs (10.2) is the same as the ratio of the Stark-shift values $d\nu/dE_z$ of these halogen atoms (12.5) which are bonded with an aromatic ring ($d\nu/dE_z = 480$ and 38.5 Hz $(Kv/cm)^{-1}$ for ^{79}Br and ^{35}Cl accordingly [10, 11]). Taking into account that the $d\nu/dE_z$ value characterizes the polarizability of the corresponding atom, the near ratio of amplitudes of the NQR frequency oscillations for 4-bromo- and 4-chlorophenyl(alkyl)sulphides and the $d\nu/dE_z$ shifts for Br and Cl atoms may serve as a confirmation of the correctness of explanation of the oscillation effect given above. Since the bromo- and chloro-containing analogs of the series 4-$YC_6H_4S(CH_2)_nH$ only differ in halogen atoms Y, the ratio of the amplitudes of their NQR frequency oscillations is mostly determined by the ratio of the polarizabilities of these halogen atoms. The polarization of a chemical bond in which the halogen atom takes part, is proportional to this polarizability [12].

The ^{79,81}Br NQR frequency of compounds of the series 4-$BrC_6H_4S(CH_2)_nCH(CH_3)_2$ oscillates when the n value increases from $n=0$ to $n=2$. The amplitude of this oscillation is approximately half than for compounds of the series 4-$BrC_6H_4S(CH_2)_nH$. In contrast to the latters the NQR frequencies for compounds 4-$BrC_6H_4S(CH_2)_nCH(CH_3)_2$ with even n are higher than those with odd ones (Figure 1).

The dependence of the ^{35}Cl NQR frequencies of the compounds 4-ClC_6H_4SR on the induction constants of the substituents $R = CH_m(CH_3)_{3-m}$ is similar [3] to that for compounds of the series RCOCl and 4-$RC_6H_4CH_2Cl$ [2, 3, 6]: on going from $m=0$ to $m=2$ the NQR frequency correlates with the inductivity of the substituents R (it increases with it). The NQR frequencies of these compounds with $m=3$ deviate from this correlation towards lower frequencies. This change of the ^{35}Cl NQR frequencies of these compounds corresponds to the polarization of a bond under the action of a geminal atoms partial charge directly through the field, and this influence is transmitted along the chain [2]. On going from $m = 0$ to $m = 1$ the ^{79,81}Br NQR frequency of the compounds 4-$BrC_6H_4SCH_m(CH_3)_{3-m}$ also increases (Table 2). However, on further increasing m (up to $m = 2$) it decreases substantially (Tables 1 and 2) in contrast to the corresponding compounds of the series 4-ClC_6H_4SR, RCOCl and 4-$RC_6H_4CH_2Cl$. The NQR frequency of the compound with $m = 3$ is lower than that of compound with $m = 1$ (Tables 1 and 2). Thus, the character of dependence of the ^{79,81}Br NQR frequencies of compounds 4-$BrC_6H_4SCH_m(CH_3)_{3-m}$ would be the same as for the compounds RCOCl, 4-$RC_6H_4CH_2Cl$ and 4-ClC_6H_4R (with the same R), if the NQR frequency of 4-$BrC_6H_4SCH_2CH_3$ would not be anomalously low. The deviation of the NQR frequency of compounds of the series 4-$BrC_6H_4SCH_m(CH_3)_{3-m}$ with $m = 2$ from an appropriate change of the NQR frequencies of other compounds of this series is, evidently, caused by the peculiarities of this molecule conformation.

When the n or m values in molecules 4-$BrC_6H_4S(CH_2)_nH$, 4-$BrC_6H_4S(CH_2)_nCH(CH_3)_2$ or 4-$BrC_6H_4SCH_m(CH_3)_{3-m}$ is varied, the changes in molecule structure occur comparatively far from the indicator atom. Nevertheless, the electron density of this atom changes, in the main, naturally. Consequently, the varying of the far disposed alkyl substituents in these molecules influences the indicator atom electron distribution.

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