^{127}I and ^{79}Br NQR spectra of halo-substituted phenols and phenylmercury phenoxides

G. K. Semin,* S. I. Gushchin, S. B. Karpov, E. V. Bryukhova, L. S. Golovchenko, and D. N. Kravtsov

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

The full ^{127}I NQR spectra of a series of iodo-substituted phenols and phenylmercury phenoxides have been studied. The quadrupole coupling constants and asymmetry parameters have been determined. The character of the OH...Hal hydrogen bond has been found to depend on the nature of substituents in the ring. Correlation dependences of the asymmetry parameters on the sum of the substituents resonance constants have been found for both coordinated as well as for non-coordinated iodine atoms.

Key words: ^{127}I, ^{79}Br NQR, hydrogen bond, halo-substituted phenols, phenylmercury phenoxides.

The NQR spectra of a wide variety of iodo- and bromo-substituted phenols have been studied previously.[1–4] However, for the ^{127}I NQR spectra the low frequency transition (1/2—3/2) was mostly studied. Full NQR spectra of 2,6-disubstituted *p*-iodophenols at 77 K were scarsely known. At the same time, such spectra enable us to obtain values of the quadrupole coupling constants (e^2Qq_{zz}) as well as those of the asymmetry parameter (η) of the electric field gradient (EFG) tensor. The intramolecular hydrogen bond in the molecules of 2,6-dihalophenols is known to be essentially dependent on the nature of the substituent in position 4[4]; the latter affects the nonequivalence of the halogen atoms in positions 2 and 6 and, hence, the magnitude of the NQR splitting in the spectrum. In this case, changes in the asymmetry parameter of the iodine atom in the series of substituted iodobenzenes are linearly related with changes in the $\sigma_R{}^o$-resonance constants of substituents in the benzene ring.[5] Assuming that the OH...Hal hydrogen bond is realized through the p_π-electron density of the halogen atom, we tried to correlate the asymmetry parameter with the sum of the resonance constants ($\Sigma\sigma_R{}^o$) of X- and Y-substituents in positions 4 and 6, *i.e.*, in *meta*-position with respect to the iodine atom in iodophenols of the 2-I-4-X-6-YC_6H_2OH type (**1—9**). The ^{127}I NQR frequencies for both transitions, values of the quadrupole coupling constants, and asymmetry parameters at 77 K are listed in Table 1. The $\eta(\Sigma\sigma_R{}^o)$ dependence is presented in Fig. 1, from which one can see that it falls into two dependences described by the following equations:

$$\eta = (12.87 + 22.97\ \Sigma\sigma_R{}^o) \pm 0.2\ \%;\quad n = 6;\ r = 0.997, \tag{1}$$

$$\eta = (1.33 - 12.80\ \Sigma\sigma_R{}^o) \pm 0.3\ \%;\quad n = 5;\ r = 0.979. \tag{2}$$

Dependence (2) is referred to the iodine atoms participating in the hydrogen bond since it contains a point which corresponds to 2,4-diiodophenol (point No. *6'* in Fig. 1). Dependence (1) corresponds to the iodine atoms which do not participate in the hydrogen bond formation. For these atoms η increases with decreasing the overall electron-donor conjugation effect of varied substituents in positions 4 and 6. The existence of dependences (1) and (2) for the studied compounds allows one to admit that the character of packing of their molecules in crystal and the contribution of the crystal effect into the NQR frequencies is not (or little) changed for the whole series. The same is also observed in case of 4-substituted iodobenzenes for which η linearly depends on $\sigma_R{}^o$ of the substituent.[5]

As is known, the iodine atom is characterized by the electron-donor effect of conjugation when interacting with the aromatic ring. In this connection the non-zero value of η for iodobenzene (6.9 %)[6] is due to the fact that the $5p_y$ orbital, perpendicular to the benzene ring, is less populated than $5p_x$ orbital lying in the ring plane because of a partial transfer of the electron density to the aromatic ring orbitals. Such an explanation is confirmed by increasing η in 4-substituted iodobenzenes with increasing the electron-acceptor effects of the substituent conjugation. An analogous effect could also be expected for 2-substituted iodobenzenes. However, in this case, spatial interactions and other short order effects can play an essential part. Because of this a linear dependence between η and $\sigma_R{}^o$ for 2-substituted iodobenzenes is not observed in contrast to that for

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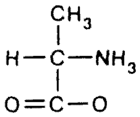
Table 1. ^{127}I NQR spectra at 77 K in the 2-I-4-X-6-YC_6H_2OH series

Compound	Y	X	Assignment	NQR frequency/MHz 1/2—3/2	S/N*	3/2—5/2	S/N	e^2Qq_{zz}** MHz	η(%)	Notes ν/MHz
1	I	NO_2	2	308.56	40	605.47	40	2024.34	12.2	
			6	297.70	20	595.26	20	1984.28	1.3	
2	I	F	2	295.35	3	590.49	10	1968.41	1.6	
				290.85	3	581.53	15	1938.52	1.5	
			6	290.10	3	574.81	20	1918.87	8.5	
				288.35	3	574.57	25	1916.35	5.3	
3	I	 $H{-}\overset{\displaystyle CH_3}{\underset{\displaystyle O{=}C{-}O}{C}}{-}NH_3$	2	289.94	6	577.48	5	1924.39	5.7	
			6	297.11	6	591.10	5	1971.96	6.4	
4	Br	CH_3	2	293.70	5	583.84	10	1947.98	6.9	^{79}Br 274.24
5	I	CH_3	2	294.15	20	583.77	20	1948.12	7.8	
			6	278.58	20	555.59	20	1852.75	4.7	
6	H	I	6	285.72	20	570.95	50	1903.42	2.6	
			4	288.27	20	564.88	25	1888.98	12.7	
7	Cl	I	2	286.89	4	571.26	6	1905.54	5.8	^{35}Cl 35.448
			4	299.34	7	595.20	10	1985.84	6.7	
8	Cl	Cl	2	301.11	2	601.01	16	2004.02	3.9	^{35}Cl 36.047
			(6)	305.82	1.5	—				36.047
										35.354
9	I	NH_2		284.88	10	—				
				282.87	12	—				

* Signal-to-noise ratio (the intensity measure).

** Q is the nuclear quadrupole moment; q_{zz} is the electric field gradient along the maximum gradient axis.

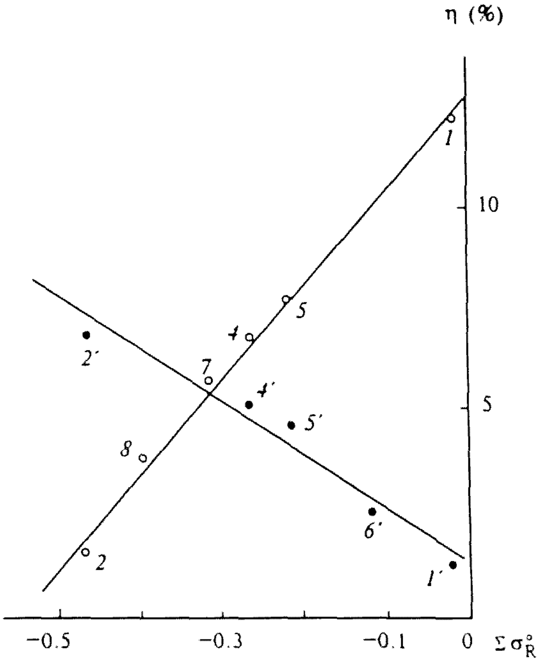


Fig. 1. Dependence of the asymmetry parameter (η) on the sum of the substituents resonance constants ($\Sigma\sigma_R^o$) in the 2-I-4-X-6-YC_6H_2OH series. The point numbers on the plot correspond to the numbers of the compounds in Table 1.

4-substituted ones. At the same time, one has to consider that a competing electron-donor conjugation of the iodine atom and of the OH-group with the aromatic ring must exist; it should decrease the extent of conjugation of the iodine atom with the aromatic ring and its asymmetry parameter. Because of this the competing electron-donor conjugation of the OH-group and of the 4- and 6-substituents with the aromatic ring must strengthen its competing conjugation with the iodine atom in *o*-position and hinder the conjugation of the latter with the aromatic ring. The introduction of substituents possessing the electron-donor effect of conjugation in positions 4 and 6 must weaken the competing conjugation of OH-group with the iodine atom and make easier its electron-donor conjugation with the aromatic ring, which results in increasing η. The preceding concepts are in agreement with the data obtained; according to those data the substituents with the electron-donor conjugation effect in positions 4 and 6 decrease η of the iodine atom not participating in the hydrogen bond formation, while the electron-acceptor substituents increase it.

Dependence (2) is referred to the iodine atom taking part in the hydrogen bond formation. In this case the η value increases with increasing the electron-donor conjugation effect. Consideration of data for 4-substituted

Table 2. ^{79}Br and ^{35}Cl NQR spectra at 77 K

Compound	^{79}Br		^{35}Cl	
	ν/MHz	S/N	ν/MHz	S/N
2,6-Br_2-4-ClC_6H_2OH (**10**)	288.86		36.048	
	290.87			
2,6-Br_2-4-$NH_2C_6H_2OH$ (**11**)	281.25	15		
	277.82	15		
2-Cl-4,6-$Br_2C_6H_2OH$ (**12**)	288.80	2	36.613	
	282.45	1.5	35.810	
	280.82	4	35.683	
			35.547	
2,4-Cl_2-6-BrC_6H_2OH (**13**)	289.76		36.671	
	282.64		35.975	
	281.54		35.870	
			35.735	
			35.600	
2-Br-4-CH_3-6-ClC_6H_2OH (**14**)	283.38	4	36.058	4
	279.80	2	35.530	1.5
	278.50	3	35.397	4

2,6-diiodophenols shows that the iodine atoms participating in formation of the intramolecular hydrogen bond are characterized by a smaller η value. As is known the formation of a hydrogen bond is followed by a partial transfer of the electron density of the donor unshared electron pair to the σ*-orbital of the H—X bond.[7] In accordance with that, a decrease in η upon formation of the hydrogen bond with participation of the iodine atom is due to a decrease in the $5p_x$-orbital population resulting in a decreasing difference between $5p_y$- and $5p_x$-orbital populations. The substituents in positions 4 and 6 having the electron-donor conjugation mechanism must impede the conjugation of the OH-group with the aromatic ring, increase its electron density, weaken its proton-donor power, decrease the partial transfer of the electron density of the iodine unshared electron pair from the $5p_x$ orbital and, hence, to impede decreasing η. The substituents with the electron-acceptor conjugation effect must exert the opposite influence. The preceding concepts are in agreement with dependence (2). Generally, the competing conjugation effects must also affect the hydrogen-bonded iodine atom. However, the antibate character of dependences (1) and (2) is an evidence for the predominant influence of the hydrogen bond stability (but not of the competing conjugation) on the asymmetry parameter of the iodine atom participating in formation of the intramolecular hydrogen bond.

Of a special interest are compounds where not only iodine atoms but also chlorine and bromine atoms can occupy positions 2 and 6. Thus, a competition between the O-H...Br and O-H...I hydrogen bonds in 2-I-4-CH_3-6-BrC_6H_2OH (points No. *4* and *4'* in Fig. 1) might take place: therefore crystals of this compound contain the iodine atoms both participating or not participating in the hydrogen bond. This results in two non-equivalent states of the iodine atoms with differing populations, which manifests itself as a difference in the doublet lines intensities. Since the ^{79}Br NQR signal is essentially weaker, only the line corresponding to the coordinated bromine atom is observed in compound **4**, while one fails to observe the line of the non-coordinated atom. An analogous picture is observed for compounds **7** and **8** (see Table 1), where competition between the chlorine and iodine atoms for the hydrogen bond formation also takes place; however, in this case, the equilibrium is essentially shifted to the O-H...Cl bond formation, *i.e.*, ^{127}I NQR frequencies observed in compounds **7** and **8** are assigned to the non-coordinated iodine atom.

In continuation of previously conducted studies, the ^{79}Br and ^{35}Cl NQR spectra of a series of bromine and chlorine analogs (compounds **10—14** in Table 2) were studied and refined. Thus, the chlorine (^{35}Cl) and bromine (^{79}Br) NQR spectra of 2,6-Br_2-4-ClC_6H_2OH (**10**) were obtained. Previously known at room temperature, the 2,6-Br_2-4-NH_2-C_6H_2OH (**11**) NQR spectrum[8] was studied at liquid nitrogen temperature. A refinement of 2-Cl-4,6-$Br_2C_6H_2OH$ (**12**) and 2,4-Cl_2-6-BrC_6H_2OH (**13**) spectra was carried out. Weak, broad ^{35}Cl and ^{79}Br lines were detected in addition to those previously known.[4] Complication of spectra and broadening of

Table 3. ^{127}I NQR spectra at 77 K in the 2-I-4-X-6-$YC_6H_2OHgC_6H_5$ series

Compound	Y	X	NQR frequency/MHz				e^2Qq_{zz}	η(%)	Notes
			1/2—3/2	S/N	3/2—5/2	S/N	MHz		ν/MHz
15	Br	I	281.40	3	559.1	3	1865.6	7.1	^{79}Br 274.29
			286.92	2	572.7	3	1909.6	3.9	
16	Cl	I	277.32	6	549.99	10	1835.7	8.1	^{35}Cl 35.20
			280.59	6	560.05	8	1867.4	3.9	
17	Cl	Cl	278.19	10	553.15	15	1845.5	6.7	^{35}Cl 35.22
18	Br	CH_3	273.96	2	541.94	2	1809.6	9.2	^{79}Br 271.44
			275.19	2	546.86	3	1824.7	7.1	270.09
19	I	CH_3	271.86	8	538.53	6	1797.8	8.6	
			275.91	10	542.07	30	1812.0	11.8	

lines might be due to statistically disordered positions of molecules in the crystals.[1]

We studied another coordination type, exemplified by 2,6-dihalo-substituted phenylmercury phenolates (compounds **15—19** in Table 3). An overall decrease in the NQR frequencies, splittings values and spreads in the asymmetry parameters compared with those of hydrogen analogs was found. Unfortunately, the small amount of spectral data does not allow one to make a quantitative comparison between the results obtained. One can only have qualitative characteristics. Thus, in accordance with the number of signals in the ^{127}I NQR spectra, compounds **15—17** have only one conformation in crystal. According to the data obtained previously,[9] the strength of the intramolecular coordination bond in the phenylmercury derivatives of 2,6-dihalo-4-fluorophenols is increased in the sequence Cl < Br < I. In this connection one should draw a conclusion that compounds **15—17** have such conformation in crystal when the phenylmercury group forms a coordination bond with the iodine atom. The intramolecular coordination of that type is a cause of an essential signals splitting in the ^{127}I NQR spectrum of compound **19**. At the same time, the splitting of the signals in the spectrum of compound **18** can be caused by two existing conformations; either the intramolecular coordination of the phenylmercury group with the iodine or bromine atom can be realized, or the splitting is due to the existence of two types of crystallographically nonequivalent molecules in crystal. In connection with results obtained for compounds **15**, the last variant seems to be more probable.

Thus, the character of the hydrogen bond OH...Hal was found to be dependent on the nature of substituents in the ring as was exemplified by substituted iodophenols of the 2-I-4-X-6-YC_6H_2OH type. In addition, there exist correlation dependences $\eta(\Sigma\sigma_R^{\circ})$ of the asymmetry parameter on the sum of the substituents resonance constants, both for the coordinated, as well as for non-coordinated iodine atom.

Experimental

The NQR spectra of compounds under study were recorded on pulse NQR spectrometers at liquid nitrogen temperature. The halophenols studied in the present work were obtained following the procedures described in the literature and were identified from their melting temperatures, which were in good agreement with literature data. The phenylmercury derivatives of substituted halophenols not described previously[4,10] were prepared by the action of phenylmercury hydroxide on corresponding phenols in methanol solution[11] and were recrystallized from suitable solvents. Melting temperatures, yields, and analytical data for compounds not described previously are given below.

Phenylmercury 2-bromo-4,6-diiodophenoxide (2-Br-4,6-I_2-C_6H_2OHgPh (15)), yield 87%, m.p. 178—180 °C ($C_6H_5CH_3$). Found (%): C, 20.58; P, 1.00; Hg, 28.32. $C_{12}H_7BrHgI_2O$. Calculated (%): C, 20.54; H, 1.00; Hg, 28.59.

Phenylmercury 2-bromo-6-iodo-4-methylphenoxide (2-Br-6-I-4-Me-C_6H_2OHgPh (18)), yield 82%, m.p. 132—134 °C (C_6H_6). Found (%): C, 25.81; H, 1.69; Hg, 34.35. $C_{13}H_{10}BrHgIO$. Calculated (%): C, 26.48; H, 1.69; Hg, 33.95.

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