Tetrahedron, 1964, Vol. 20, pp. 909 to 912. Pergamon Press Ltd. Printed in Northern Ireland

PURE QUADRUPOLE RESONANCE OF BROMINE IN BROMOTROPOLONES

R. IKEDA, D. NAKAMURA, S. ITÔ, H. SUGIYAMA and M. KUBO
Chemistry Department, Nagoya University, Chikusa, Nagoya
and Department of Chemistry, Tohoku University,
Sendai, Japan

(*Received* 24 *October* 1963; *in revised form* 3 *December* 1963)

Abstract—The pure quadrupole resonance frequencies of ^{81}Br were determined for various bromotropolones at liquid nitrogen temperature. Each of monobromotropolone isomers shows a single resonance line, indicating that all bromine atoms in the crystals are equivalent. 3,5-Dibromotropolone gives rise to two resonance signals in agreement with the presence of two kinds of non-equivalent bromine atoms in a molecule. 3,7-Dibromotropolone yields a closely spaced doublet presumably due to the crystal effect. Only one line attributable to bromine atoms at position 5 was observed for 3,5,7-tribromotropolone. The ionic character of C–Br bonds in these molecules can be explained by means of the inductive effect.

OWING to high accuracy obtainable in radiowave spectroscopy, the nuclear quadrupole resonance can afford to give valuable information on the nature of bonds involving an atom having a quadrupole moment. The quadrupole coupling constants in molecules are closely related to molecular electronic structure and give quantitative data about the ionic nature of chemical bonds. Although the estimated ionic character still leaves much to be desired as to various parameters involved, observed frequencies permit one to disclose subtle difference of qualitative importance in the nature of bonds of one and the same type in a molecule or in molecules of similar structure. The present investigation on the nuclear quadrupole resonance has been undertaken in order to clarify the bond nature of C–Br bonds in various bromotropolones and to discuss electronic interactions between substituents in these molecules.

EXPERIMENTAL

Apparatus. The quadrupole resonance signals of bromine were displayed on an oscilloscope of a self-quenching super-regenerative spectrometer already described.[1]

Materials. 3-Bromotropolone[2] (m.p. 107–108°), 4-bromotropolone[3] (m.p. 87–88·5°), 5-bromotropolone[2] (m.p. 190–191°), 3,5-dibromotropolone[4] (m.p. 152·5–153°), 3,7-dibromotropolone[4] (m.p. 159–160°) and 3,5,7-tribromotropolone[2] (m.p. 126–127°) were synthesized in Tohoku University according to methods already reported.

Experimental results. Frequency measurements were made at liquid nitrogen temp. The signals of monobromotropolones and 3,5,7-tribromotropolone were weak, the signal-to-noise ratio being 2 or less. They escaped detection at room temp. On the other hand, dibromotropolones showed intense absorptions, which could be observed even at room temp.

The observed signals, except for one mentioned below, are attributable to a bromine isotope ^{81}Br for the following reasons. In the first place, if ^{79}Br is responsible for them, the resonance absorptions by ^{81}Br are expected to appear in the lower frequency region, where available spectrometers had high sensitivity. Actually, the anticipated absorptions were not observed. Secondly, 3,5-dibromotropolone yielded three resonance frequencies at room temp. The ratio of the highest frequency to the lowest one was 1·197 in perfect agreement with the known isotope frequency ratio of ^{79}Br and ^{81}Br.

---

[1] D. Nakamura, Y. Kurita, K. Ito and M. Kubo, *J. Amer. Chem. Soc.* **82**, 5783 (1960).

[2] T. Nozoe, S. Seto, Y. Kitahara, M. Kunori and Y. Nakayama, *Proc. Japan Acad.* **26**, 38 (1950).

[3] T. Sato, *J. Chem. Soc. Japan, Pure Chem. Sect.* **80**, 1171 (1959).

[4] T. Nozoe, Y. Kitahara, K. Yamane and A. Yoshikoshi, *Proc. Japan Acad.* **27**, 18 (1951).

Lastly, the resonance frequencies of ^{81}Br in bromophenols[5] are reported to appear in 224–230 Mc, whereas those of ^{79}Br are as high as about 270 Mc.

The results are shown in Table 1.

Table 1. Pure quadrupole resonance frequencies of ^{81}Br in bromotropolones at liquid nitrogen temperature

Compound		Frequency, Mc/sec	S/N ratio	Ionic character, %
3-Bromotropolone		232·05	Very weak	21
4-Bromotropolone		226·96	2	23
5-Bromotropolone		226·15	2	23
3,5-Dibromotropolone		233·17	10	21
		240·86	10	18
	20°	230·85	8	
		238·30	8	
		276·39 (^{79}Br)	5	
3,7-Dibromotropolone		237·21	10	19
		237·86	10	19
	20°	234·37	8	
		235·77	8	
3,5,7-Tribromotropolone		241·40	Very weak	18

DISCUSSION

Each of monobromotropolones shows a single resonance line as can be expected from the chemical formulas of these compounds. The resonance frequency of 3-, 4- and 5-bromotropolones decreases in this order. However, those of 4- and 5-isomers are very close to each other. This can be explained by the inductive effect: oxygen atoms in bromotropolones decrease the partial ionic character of C–Br bonds especially at position 3 (or 7). Similar effect has been observed for bromophenols[5] and halogenated paraffin hydrocarbons.[6]

Molecular-orbital calculations[7] have shown that carbon atoms 3 and 5 in tropolone have nearly the same π-electron density, which is greater than that of carbon atom 4. The partial double bond character of C–Br bonds decreases the π-electron density at the bromine atom and hence decreases the pure quadrupole resonance frequency of the bromine nucleus. Accordingly, if the effect of partial double bond character of C–Br bonds were appreciable, one would have a high resonance frequency for 4-bromotropolone as compared with those of 3- and 5-bromotropolones in contradiction with experimental results. Therefore, the effect of double bond character of C–Br bonds on quadrupole resonance frequencies is presumed to be insignificant. In fact, the double bond character of carbon-halogen bonds attached to a benzene ring has been estimated from nuclear quadrupole resonance spectroscopy[8–13] to amount to only a few per cent.

---

[5] P. J. Bray, *J. Chem. Phys.* **22**, 1787 (1954); P. J. Bray and R. G. Barnes, *Ibid.* **22**, 2023 (1954).

[6] H. O. Hooper and P. J. Bray, *J. Chem. Phys.* **33**, 334 (1960); R. Livingston, *J. Phys. Chem.*, **57**, 496 (1953).

[7] Y. Kurita and M. Kubo, *Bull. Chem. Soc. Japan* **24**, 13 (1951).

[8] R. Bersohn, *J. Chem. Phys.* **22**, 2078 (1954).

[9] S. Kojima, K. Tsukada and Y. Hinaga, *J. Phys. Soc. Japan* **10**, 498 (1955).

[10] H. C. Meal, *J. Chem. Phys.* **24**, 1011 (1956).

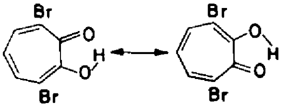
[11] G. W. Ludwig, *J. Chem. Phys.* **25**, 159 (1956).

[12] Y. Morino and M. Toyama, *J. Phys. Soc. Japan* **15**, 288 (1960).

[13] G. K. Semin, *J. Struct. Chem.* **3**, 275 (1962).

As is anticipated from the presence of nonequivalent bromine atoms in a molecule, 3,5-dibromotropolone gives rise to two resonance lines, the frequency difference (about 8 Mc) being much greater than can be expected from the crystal effect.[14] Considering the inductive effect, one of the two lines appearing on the high frequency side (240·86 Mc) is assigned to bromine at position 3 while the other (233·17 Mc) is attributable to that at position 5. The increase in frequency of these lines over the corresponding frequency of monobromotropolones (8·8 Mc for position 3 and 7·0 Mc for position 5) is reasonably considered as resulting from the inductive effect due to an additional bromine atom.

3,7-Dibromotropolone shows a doublet, the separation of which is much smaller than the frequency difference between the two lines of 3,5-dibromotropolone. Since 3-bromotropolone and 7-bromotropolone have not been obtained as different chemical species, the lifetime of tautomerization must be much shorter than the observation time, leading to the chemical equivalence of bromine atoms in a molecule. In crystals, however, it is conceivable that the two bromine atoms are not on opposite sides of a crystal plane of symmetry owing to the existence of surrounding molecules unsymmetrically located across the plane. Presumably, the resulting asymmetric crystal field affects the molecule in such a way that the exchange of the hydroxyl hydrogen between two oxygens is hindered to some extent. The frequency of the doublet is intermediate between the two frequencies observed for 3,5-dibromotropolone. This is quite understandable, if one considers the inductive effect for various positions of substituents in these bromotropolones.



3,5,7-Tribromotropolone having two kinds of nonequivalent bromine atoms in a molecule is expected to show at least two resonance lines in the crystalline state. Actually, however, only a very weak signal was detected. This line is attributable to bromine at position 5 for the following reason. As mentioned above, the resonance frequency of ^{81}Br at position 5 in 3,5-dibromotropolone is 233·17 Mc. On substituting hydrogen at position 7 with bromine to form 3,5,7-tribromotropolone, the frequency will increase owing to the inductive effect by an amount approximately equal to the difference between the frequency of bromine at position 5 of 3,5-dibromotropolone and that of 5-bromotropolone.

$$\begin{aligned}&\nu_{(5)}(\text{3,5,7-tribromotropolone})\\&\quad=\nu_{(5)}(\text{3,5-dibromotropolone})\\&\qquad+\nu_{(5)}(\text{3,5-dibromotropolone})\\&\qquad-\nu_{(5)}(\text{5-bromotropolone})\end{aligned}$$

Similarly, one has

$$\begin{aligned}&\nu_{(3)}(\text{3,5,7-tribromotropolone})\\&\quad=\nu_{(3)}(\text{3,5-dibromotropolone})\\&\qquad+\nu_{(3)}(\text{3,7-dibromotropolone})\\&\qquad-\nu_{(3)}(\text{3-bromotropolone})\end{aligned}$$

---

[14] H. C. Allen, Jr., *J. Phys. Chem.* **57**, 501 (1953); G. W. Ludwig, *J. Chem. Phys.*, **25**, 159 (1956).

The frequency 241·40 Mc observed for 3,5,7-tribromotropolone is closer to $\nu_{(5)} = 240{\cdot}2$ Mc than to $\nu_{(3)} = 246{\cdot}3$ Mc. Presumably, the signals of bromine at positions 3 and 7 escaped detection owing to broadening due to crystal effect.

From observed quadrupole resonance frequency ν, the quadrupole coupling constant eQq was calculated[15] assuming that the asymmetry parameter η is zero because it is presumed to be small.

$$\nu = \tfrac{1}{2}(eQq)(1 + \eta^2/3)^{1/2}$$

The ionic character i of C–Br bonds was evaluated by means of a formula proposed by Dailey and Townes.[16]

$$eQq = (1 - s + d)(1 - i)(eQq)_{\text{atom}}$$

where s and d stand for the extents of admixture of s-character and d_σ-character in a C–Br bond, respectively. The atomic quadrupole constant $(eQq)_{\text{atom}}$ ($= 643{\cdot}03_2$ Mc/sec for ^{81}Br)[17] is obtainable from atomic data. The values for $s - d$ were assumed to be 8·6% in accordance to Dailey's evaluation for a number of bromoparaffins.[18] The results are shown in the last column of Table 1. Although the data of ionic character have been derived under rather drastic assumptions, they are of reasonable order of magnitude and are presumed to be qualitatively correct.

---

[15] H. Krüger, *Z. Physik* **130**, 371 (1951).

[16] B. P. Dailey and C. H. Townes, *J. Chem. Phys.* **23**, 118 (1955).

[17] J. G. King and V. Jaccarino, *Phys. Rev.* **94**, 1610 (1954).

[18] B. P. Dailey, *J. Chem. Phys.* **33**, 1641 (1960).