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PURE QUADRUPOLE RESONANCE OF HALOGENS IN COMPOUNDS CONTAINING A NITROGEN-HALOGEN BOND

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Abstract—The pure quadrupole resonance frequencies of Cl, Br and I in various N-halo compounds were determined at liquid nitrogen temperature. The ionic character of nitrogen–halogen bonds was evaluated by use of the Townes–Dailey relation. In these compounds, Br and I are electrically positive whereas Cl is negative against N. The nitrogen-halogen bond moments as well as the succinimide group moment of N-halosuccinimides were calculated from the estimated ionic character.

THE nature of nitrogen–halogen (N–X) bonds in organic compounds has been a subject of considerable dispute: even the direction of the bond moment still presents a debatable problem. Lumbroso *et al.*[1] determined the dipole moments of N-chloro-, N-bromo-, and N-iodosuccinimides. From the analysis of observed data, they derived N–X bond moments as $\mu(N^+–Cl^-) = 1{\cdot}4$ D, $\mu(N^+–Br^-) = 0{\cdot}4$ D, and $\mu(N^-–I^+) = 1{\cdot}5$ D. As they pointed out, the values (and possibly the direction of N–Br bond moment also, as the present authors suspect) are subject to changes depending on the choice between the pyramidal and trigonal structures for the valency bonds of nitrogen. For N-chlorosuccinimide, Lumbroso[2] calculated the N–Cl bond moment as $\mu(N^+–Cl^-) = 1{\cdot}55$ D. He carried out theoretical calculations based on experimental data and concluded that the intrinsic polarity is surely small for N–Cl and N–Br bonds and its sense is represented by $N^+–X^-$,[3] notwithstanding that in some organic reactions, N-chloro- and N-bromosuccinimides behave as if they are composed of positive halogen ions and negative radicals.[4]

Segel *et al.*[5] determined the nuclear quadrupole resonance of halogens in some heterocyclic compounds, two of which yielded the resonance absorptions of chlorine directly bonded to nitrogen. The observed frequency in N-chlorosuccinimide differs from that in a chlorine molecule by only 0·3% as expected from the customary assignment of the same electronegativity to nitrogen and chlorine. However, they presume this agreement to be fortuitous, since the resonance in N-chloro-*p*-benzoquinone imine (or N-chloro-*p*-quinoneimide) is 18% below that in a chlorine molecule.

The present investigation on nuclear quadrupole resonance has been undertaken with the object of discussing the nature of N–X bonds in a variety of organic molecules and deriving an unequivocal conclusion on the direction of N–X bond moments.

EXPERIMENTAL

Apparatus. The frequencies of the pure quadrupole resonance were determined by means of self-quenching super-regenerative spectrometers already described.[6]

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[1] H. Lumbroso, L. Gasco and C. Malén, *Bull. Soc. Chim. Fr.* 823 (1951).
[2] H. Lumbroso, *Bull. Soc. Chim. Fr.* 887 (1959).
[3] H. Lumbroso, *Bull. Soc. Chim. Fr.* 373 (1961); 2519 (1963).
[4] L. F. Fieser and M. Fieser, *Organic Chemistry* (2nd Edition) p. 239. D. C. Heath, Boston (1950).
[5] S. L. Segel, R. G. Barnes and P. J. Bray, *J. Chem. Phys.* **25**, 1286 (1956).
[6] D. Nakamura, Y. Kurita, K. Ito and M. Kubo, *J. Amer. Chem. Soc.* **82**, 5783 (1960).

Materials. N-Chloropiperidine was prepared by a modified Lellmann–Geller method.[7] A mixture of piperidine (about 8 g), chlorinated lime (30 g), and water (150 ml) was warmed over an oil-bath, and a fraction distilling at about 92° was collected. Crude N-chloropiperidine (about 7 g) thus obtained was purified by distillation under red. press., the yield being about 4 g. The volumetric determination of halogens in this and succeeding compounds was carried out by iodometry.[8] (Found: Cl, 28·3. Calc. for $C_5H_{10}NCl$: Cl, 29·6%.) N-Bromoacetamide was extracted with $CHCl_3$ from the product of reaction between acetamide and Br_2 in KOHaq. On adding n-hexane to the $CHCl_3$ solution, white needle crystals separated, which were washed with n-hexane.[9] (Found: Br, 57·2. Calc. for C_2H_4ONBr: Br, 57·9%.) N-Bromo-2-pyrrolidinone was prepared by adding Br_2 to 2-pyrrolidinone dissolved in KOHaq. White crystals separated and were washed several times with ice water.[10] (Found: Br, 49·3. Calc. for C_4H_6ONBr: Br, 48·7%.) N-Bromo-ε-caprolactam (or 1-bromohexahydro-2H-azepin-2-one) was synthesized after the Taub-Hino procedure as white crystals.[11] (Found: Br, 39·3. Calc. for $C_6H_{10}ONBr$: Br, 41·6%.) A preparation of N-bromosuccinimide procured from Wako Pure Chemicals Company was used after recrystallization from hot water. (Found: Br, 45·2. Calc. for $C_4H_4O_2NBr$: Br, 44·9%.) N-bromophthalimide was prepared by the bromination of phthalimide in NaOHaq. White crystals obtained were washed with ice water and recrystallized from acetic acid.[12] (Found: Br, 35·1. Calc. for $C_8H_4O_2NBr$: Br, 35·4%.) N-Iodosuccinimide was prepared in accordance to a procedure described by Djerassi and Lenk.[13] White crystals obtained were recrystallized from dioxane. (Found: I, 53·4. Calc. for $C_4H_4O_2NI$: I, 56·4%.)

These compounds decompose before they melt. Therefore, identification was made by IR spectroscopy.

RESULTS

The pure quadrupole resonance frequencies were measured at liquid nitrogen temperature. At room temperature, the signals were unobservable except for N-bromosuccinimide, which showed an intense resonance absorption at room temperature also. N-Chloropiperidine shows two resonance lines corresponding to chlorine isotopes, ^{35}Cl and ^{37}Cl. The isotope frequency ratio, $\nu(^{35}Cl)/\nu(^{37}Cl) = 1{\cdot}2687$, agrees with the known value. Two resonance lines were observed for ^{79}Br and ^{81}Br in each N-bromo compound, the observed isotope frequency ratio, $\nu(^{79}Br)/\nu(^{81}Br)$, being 1·1970 in agreement with data reported in the literature. Only a single resonance line was observed for N-iodosuccinimide, although two resonance lines, ν_1 and ν_2, were anticipated because the nuclear spin of ^{127}I is 5/2. The observed line was assigned to the ν_1 resonance of iodine, because nitrogen and chlorine have practically the same electronegativity and the ν_1 resonance absorption of iodine in iodine α-monochloride (cubic) is reported to appear at 457 Mc/sec.[14] Accordingly, the ν_2 resonance absorption is expected to appear at a high frequency beyond the region accessible to the spectrometers employed, whereas if the observed line is assigned to ν_2, ν_1 also should have been observed because it must fall in the observable frequency range. The observed resonance frequencies of ^{35}Cl, ^{81}Br and ^{127}I in N-halo compounds are listed in Table 1.

DISCUSSION

The pure quadrupole resonance frequency can be expressed as functions of the quadrupole coupling constant, eQq, and the asymmetry parameter, η, of the field

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[7] E. Lellmann and W. Geller, *Ber. Dtsch. Chem. Ges.* **21**, 1921 (1888).

[8] M. Z. Barakat and M. F. Abd El-Wahab, *Analyt. Chem.* **26**, 1974 (1954).

[9] R. S. Schreiber, *Organic Syntheses* Vol. 31; p. 17. J. Wiley, New York and Chapman and Hall, London (1951).

[10] J. Tafel and M. Stern, *Ber. Dtsch. Chem. Ges.* **33**, 2224 (1900).

[11] B. Taub and J. B. Hino, *J. Org. Chem.* **25**, 263 (1960).

[12] Y. Pasternak and J. C. Traynard, *Bull. Soc. Chim. Fr.* 23 (1960).

[13] C. Djerassi and C. T. Lenk, *J. Amer. Chem. Soc.* **75**, 3493 (1953).

[14] S. Kojima, K. Tsukada, S. Ogawa and A. Shimauchi, *J. Chem. Phys.* **23**, 1963 (1955).

TABLE 1. PURE QUADRUPOLE RESONANCE FREQUENCIES OF ^{35}Cl, ^{81}Br AND ^{127}I IN SOME N-HALO COMPOUNDS AT LIQUID NITROGEN TEMPERATURE

Compound	Frequency, Mc/sec
N-Chloropiperidine	43·889 ± 0·002
N-Bromoacetamide	344·1 ± 0·5
N-Bromo-2-pyrrolidinone	343·3 ± 0·3
N-Bromo-ε-caprolactam	341·9 ± 0·3
N-Bromosuccinimide	358·73 ± 0·02*
N-Bromophthalimide	370·8 ± 0·5
N-Iodosuccinimide	440·1 ± 0·5

* 353·22 ± 0·02 Mc/sec at 21°.

gradient. These two constants cannot be determined uniquely from a single observed frequency. However, if it is assumed that $\eta = 0$, the quadrupole coupling constant is equal to twice the resonance frequency for a 3/2 nuclear spin and to 20/3 times the ν_1 resonance frequency for a 5/2 spin.[15] With this assumption, we have calculated the quadrupole coupling constants as shown in Table 2. The adequacy of this assumption for N-bromosuccinimide is supported, although indirectly, by the following reasoning. The conceivable main factor leading to the asymmetry of the field gradient in molecules of this type is the π-bond character of the nitrogen–halogen bond, because the axially symmetric charge distribution of σ-electrons does not contribute to the asymmetry parameter. Now, the crystal of N-bromosuccinimide is isostructural with that of N-chlorosuccinimide,[16] in which molecules are planar[17] and the N–Cl bond distance (1·69 Å) is practically equal to the sum of the covalent radii (0·70 + 0·99 = 1·69 Å). This suggests that the π-bond character of N–X bonds is inappreciable.

TABLE 2. QUADRUPOLE COUPLING CONSTANTS (FOR ^{35}Cl, ^{81}Br AND ^{127}I) AND THE APPROXIMATE IONIC CHARACTER OF N–X BONDS IN SOME N-HALO COMPOUNDS

Compound	eQq Mc/sec	i
N-Chloropiperidine	87·78	(−) 0·20*
N-Chlorosuccinimide	108·20	(−) 0·01
N-Bromoacetamide	688·2	0·06
N-Bromo-2-pyrrolidinone	686·6	0·05
N-Bromo-ε-caprolactam	683·8	0·05
N-Bromosuccinimide	717·46	0·09
N-Bromophthalimide	741·6	0·12
BrCl (^{81}Br)	732·5	0·11
N-Iodosuccinimide	2934	0·23
ICl (^{127}I)	2944	0·23

* The minus sign indicates that the halogen bears a negative charge.

The quadrupole coupling constant calculated for N-chloropiperidine is smaller than that of a chlorine atom. This indicates that the chlorine atom in an

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[15] T. P. Das and E. L. Hahn, *Solid State Physics* Suppl. 1. Academic Press, New York (1958).

[16] R. N. Brown, *Acta Cryst.* **9**, 193 (1956).

[17] R. N. Brown, *Acta Cryst.* **14**, 711 (1961).

N-chloropiperidine molecule has a negative fractional charge. The molecular quadrupole coupling constant, eQq, is given by

$$eQq = (1 - i)(eQq)_{\mathrm{atom}}$$

where i stands for the bond ionicity and $(eQq)_{\mathrm{atom}}$ denotes the atomic quadrupole coupling constant of halogens (109·74 Mc/sec for ^{35}Cl as determined by atomic beam experiment). Here, the s-character of the bonding orbital of chlorine is ignored, because the electronegativity of chlorine is practically the same as that of nitrogen.[18] On the other hand, the calculated quadrupole coupling constants of bromine and iodine in N-halo compounds studied are larger than those of the corresponding halogen atoms (643·03 and 2292·7 Mc/sec for ^{81}Br and ^{127}I, respectively). Evidently this indicates that the halogen atoms in these compounds have a positive fractional charge. According to Dailey and Townes,[18] the quadrupole coupling constant, eQq, for a partially positive ionic bond can be related to the bond ionicity, i, by the following relation.

$$eQq = [(-1 + s - d)(1 - i) - 2(1 + \varepsilon)i](eQq)_{\mathrm{atom}}$$

where s and d denote the extents of admixture of s- and d-character in the bonding orbital of halogens, respectively. The second term in square brackets takes into account that the interaction between a valency p electron and the nucleus is somewhat larger when the atom is positively ionic than for the case of a neutral atom, the empirical constant, ε, being estimated by Dailey and Townes as 0·13 and 0·12 for bromine and iodine, respectively. Neglecting s and d for the present case, one has

$$eQq = (1 - i + 2\varepsilon i)(eQq)_{\mathrm{atom}}$$

since the sign of quadrupole coupling constants is immaterial in pure quadrupole resonance spectroscopy. By use of these two relations, the ionic character of the N–X bonds were evaluated as shown in Table 2, in which data for N-chlorosuccinimide,[5] bromine monochloride,[19] and iodine α-monochloride[14] are included for comparison. It must be borne in mind in view of various assumptions made in the derivation that the values of ionicity are approximate and probably overestimated because of the neglect of s- and d-character.

Although the N–Cl bond in an N-chlorosuccinimide molecule is essentially covalent, the chlorine atom in N-chloropiperidine is negatively charged with as much as $-0{\cdot}20e$ (e denotes the absolute value of the electronic charge). The bromine atoms of N-bromosuccinimide and N-bromophthalimide are positively ionic to a greater extent than those of three other N-bromo compounds. These two facts can be explained as a result of inductive effect and resonance effect due to carbonyl groups attached to the nitrogen atom. Each molecule of N-chlorosuccinimide, N-bromosuccinimide and N-bromophthalimide has two carbonyl groups in the vicinity of the nitrogen atom, whereas N-chloropiperidine has no such electronegative group adjacent to the nitrogen atom. On the other hand, in N-bromoacetamide, N-bromo-2-pyrrolidinone and N-bromo-ε-caprolactam, only one carbonyl group is attached to the nitrogen atom. Strong inductive effect due to two carbonyl groups in

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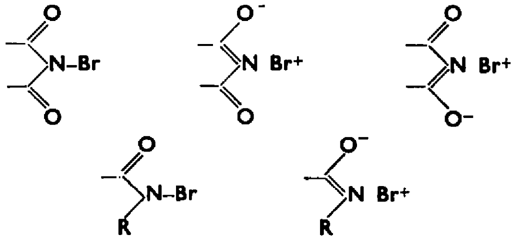
[18] B. P. Dailey and C. H. Townes, *J. Chem. Phys.* **23**, 118 (1955).

[19] D. F. Smith, M. Sidwell and D. V. P. Williams, *Phys. Rev.* **79**, 1007 (1950).

N-chlorosuccinimide decreases the (negative) ionic character of the N–Cl bond. In N-bromosuccinimide and N-bromophthalimide molecules, the inductive effect of the two carbonyl groups gives rise to an increase in the (positive) ionic character of the N–Br bond as compared with other N-bromo compounds. In addition, since the electronegativity of nitrogen is higher than that of bromine, the resonance of the following type would be possible for N-bromosuccinimide and N-bromophthalimide.



However, for other N-bromo compounds, only two resonance structures are conceivable. Accordingly, resonance effect also contributes to an increase in the (positive) ionic character of N–Br bonds in N-bromosuccinimide and N-bromophthalimide as compared with other N-bromo compounds investigated.

In N-halosuccinimides, the positive ionic character of N–X bonds increases progressively with increasing electronegativity difference between atoms involved in the bond. This suggests that the dipole moment of these compounds changes with the electronegativity value of halogens in the order of N-chloro-, N-bromo-, and N-iodosuccinimides. In fact, Lumbroso[1,3] have reported that the dipole moment of N-halosuccinimides decreases in this order. Now we can estimate the magnitude and direction of the N–X bond moments from the ionic character of the N–X bonds. The N–X bond moment is calculated as

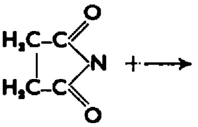
$$\mu(\text{N–X}) = ieR$$

where R is the N–X bond distance. The N–Cl bond distance in an N-chlorosuccinimide molecule has already been determined accurately by X-ray crystal analysis. However, the N–Br and N–I bond distances in the corresponding N-halosuccinimides have not been reported as yet. Therefore, we estimated the bond distances from Pauling's relation,[20]

$$R = r_{\text{N}} + r_{\text{X}} - 0{\cdot}08\,|\chi_{\text{N}} - \chi_{\text{X}}|$$

where r is the covalent bond radius and χ is the electronegativity value. The calculated values of N–X bond moments are listed in Table 3 together with the molecular dipole moments determined by Lumbroso.[1]

The molecular dipole moment of an N-halosuccinimide can be represented as the vector sum of the N–X bond moment and the succinimide group moment. From the



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[20] L. Pauling, *The Nature of the Chemical Bond* (3rd Edition) p. 229. Cornell University Press, Ithaca, N.Y. (1960).

molecular symmetry of N-halosuccinimides as confirmed by X-ray study on N-chlorosuccinimide, one can conclude that the directions of the N–X bond moment and the succinimide group moment are parallel to each other in an N-chlorosuccinimide molecule, while they are antiparallel in N-bromo- and N-iodosuccinimide molecules. The values calculated for the succinimide group moment are shown in Table 3. They are of reasonable magnitude and the agreement between them is fair in view of approximations made in the discussion.

TABLE 3. MOLECULAR DIPOLE MOMENTS, N–X BOND MOMENTS AND THE SUCCINIMIDE GROUP MOMENT OF N-HALOSUCCINIMIDES

Compound	Molecular moment, D	N–X bond moment, D	Succinimide group moment, D
N-Chlorosuccinimide	2·86	0·11	2·75
N-Bromosuccinimide	2·10	−0·80	2·90
N-Iodosuccinimide	0·97	−2·15	3·12