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The Iodine-127 Nuclear Quadrupole Resonance of Several Iodine Complexes with Sulfur-containing Organic Molecules

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The ^{127}I NQR spectra of 1,4-dithiane-2I$_2$, thiane-I$_2$, 1,4-thioxane-I$_2$, and 1,3,5-trithiane-I$_2$ are reported. Two distinct iodine atoms are observed in the former three complexes, whereas only one iodine atom is present in the last-named complex. The charge densities on the donors and the iodine atoms are obtained according to the Townes-Dailey approximation. The order of donor strength toward the iodine molecule is: thiane$>$1,4-thioxane$>$1,4-dithiane$\gg$1,3,5-trithiane. The thioethers can compete with amines in terms of the donor strength to iodine molecules. The no-bond ionic structure of the ground state is less important in the thioether-iodine complexes than in amine-iodine complexes. The positive temperature coefficients found previously in a few similar complexes of amines are observed for the terminal iodine atoms of 1,4-dithiane-2I$_2$, thiane-I$_2$, and 1,4-thioxane-I$_2$. This phenomenon is ascribed to the increasing shift of the dative structure to the no-bond covalent structure with the rise in the temperature.

Many *n*-*σ*-type charge-transfer (CT) complexes, such as amine–halogen and amine–interhalogen, have been successfully investigated by means of the halogen[1—4] and the nitrogen[4,5] nuclear quadrupole resonance (NQR). This method makes it possible to estimate the charge distribution on the atom related directly to the CT interaction from the quadrupole coupling constant ($e^2q_{zz}Q/h$). It has been indicated that, for strong *n*-*σ* complexes, 0.2—0.3 electrons transfer from the amine to the halogen molecule; further, the bridging halogen atom bonded to a nitrogen atom is charged positively, while the terminal halogen atom, on which the transferred charges mostly exist, is charged negatively.

Sulfur-containing organic molecules (thioethers) also can act as electron donors to iodine molecules. X-Ray-crystal-structure investigations were carried out for 1,4-dithiane-2I$_2$[6] and dibenzyl sulfide–I$_2$.[7] In each structure, a strong *n*-*σ* CT bond is found between the donor S atom and the iodine molecule; *i.e.*, one atom of each iodine molecule is bonded to the sulfur atom, while the remaining one is free from the intermolecular bonding, and the S$\cdots$I$_A$–I$_B$ arrangement is almost linear. The S$\cdots$I bond is shorter than the sum of the respective van der Waals radii, while the I$_A$–I$_B$ bond is longer than the I–I bond in solid I$_2$.

It is of interest to compare the CT interaction in intermolecular S$\cdots$I bonds with that in N$\cdots$I bonds on the basis of the charge distribution. We tried to observe the ^{127}I NQR for several thioether–iodine complexes: 1,4-dithiane–iodine (1:2) (DT–2I$_2$), thiane–iodine (1:1) (TH–I$_2$), and 1,4-thioxane–iodine (1:1) (TO–I$_2$), and 1,3,5-trithiane–iodine (1:1) (TT–I$_2$).

The most interesting feature of the halogen NQR in the amine–halogen complexes is the positive temperature coefficient found for terminal halogen atoms;[1,2,4] it has been suggested that this is due to a vibronic coupling effect.[2] The temperature dependence of the ^{127}I (1/2—3/2) transition frequency is precisely measured to investigate whether or not the same phenomenon is observed in the present compounds.

Experimental

Preparation of the Samples. All the chemicals were obtained commercially and were used without further purification. The TH–I$_2$ complex was prepared by mixing approximately stoichiometric amounts of the components in chloroform. The dark brown crystalline product was precipitated by then concentrating and cooling the solution. The product was filtered, washed, and dried in air. The product decomposed slowly in air. The iodine content was analyzed by means of iodimetry. (Found: I, 70.5%. Calcd for $C_5H_{10}S$–I$_2$: I, 71.5%). The orange-red TO–I$_2$ was prepared in hexane in the same manner. The stoichiometry was determined by means of elemental analysis. (Found: C, 13.2; H, 2.4; I, 67.5%. Calcd for C_4H_8OS–I$_2$: C, 13.4; H, 2.3; I, 70.9%). The purple crystalline complex of DT–2I$_2$ was obtained by adding a saturated iodine solution of carbon tetrachloride to a dithiane solution of the same solvent. (Found: C, 7.7; H, 1.4; I, 80.8%. Calcd for $C_4H_8S_2$–2I$_2$: C, 7.7; H, 1.3; I, 80.8%). The red crystalline complex of TT–I$_2$ was prepared in chloroform by a procedure similar to that used for the TH–I$_2$ complex. The complex easily decomposed to its components within 10—15 min in air at room temperature. (Found: I, 64.0%. Calcd for $C_3H_6S_3$–I$_2$: I, 64.7%).

NQR Measurement. The NQR spectra were observed on an oscilloscope using an externally quenched super-regenerative Lecher-line oscillator similar to that described by Schawlow,[8] but incorporating minor changes. Temperature variation was attained by immersing the sample tube in a copper container, placed in a Dewar vessel filled with petroleum ether, and by then cooling the petroleum ether with dry ice or liq. N$_2$. The accuracy of the measurements was estimated to be within ±0.01 MHz in frequency and ±1 K in temperature.

Results and Discussion

Table 1 lists the resonance frequencies observed at 77 and 298 K, with the signal-to-noise ratios shown in parentheses. These are assigned to the ^{127}I (1/2—3/2)

TABLE 1. ^{127}I NQR FREQUENCIES IN IODINE-SULFUR-CONTAINING ORGANIC MOLECULE COMPLEXES[a)]

Compound	Frequency/MHz 77K	Frequency/MHz 298K	$(\mathrm{d}\nu/\mathrm{d}T)_{T=273\,\mathrm{K}}$ KHz/K	Assignment
1,4-Dithiane-2I$_2$	377.81(6)	374.83(3)	−16.5	I$_A$(1/2—3/2)
	233.37(2.5)	238.02(2)	+25.4	I$_B$(1/2—3/2)
Thiane-I$_2$	377.82(10)	373.69(1.5)	−23.4	I$_A$(1/2—3/2)
	197.22(10)[b)]	200.99(2)[b)]	+24.2	I$_B$(1/2—3/2)
	394.43(4)[b)]	401.98(1.5)[b)]	—	I$_B$(3/2—5/2)
1,4-Thioxane-I$_2$	374.78(2.5)	370.46(1.5)	−23.4	I$_A$(1/2—3/2)
	220.58(5)	226.01(1.5)	+30.0	I$_B$(1/2—3/2)
1,3,5-Trithiane-I$_2$	322.14(10)	320.39(1.5)	−9.8	I(1/2—3/2)

a) The numbers in parentheses are the signal-to-noise ratios as measured on an oscilloscope. b) $e^2q_{zz}Q/h$ and η are 1314.8 MHz and 0.004 at 77 K, and 1339.9 MHz and 0.000 at 298 K.

TABLE 2. CHARGE DISTRIBUTIONS IN SEVERAL CT COMPLEXES OF IODINE WITH SULFUR-CONTAINING ORGANIC MOLECULES

Complex	Charge on I$_A$	Charge on I$_B$	Charge on S
1,4-Dithiane-2I$_2$	+0.10	−0.32	+0.22
Thiane-I$_2$	+0.10	−0.43	+0.33
1,4-Thioxane-I$_2$	+0.09	−0.36	+0.27
1,3,5-Trithiane-I$_2$	−0.06		+0.06

transitions except for the resonance line with the highest frequency in TH–I$_2$, corresponding to the ^{127}I (3/2—5/2) transition. The existence of two resonance lines in DT-2I$_2$, separated in frequency by about 140 MHz, is consistent with its crystal structure, which has the S···I$_A$–I$_B$ arrangement.[6)] Since it is well established that the terminal iodine atom I$_B$ is negatively charged compared to the bridging iodine atom I$_A$, the lower frequency line can be assigned to the I$_B$ atom, and the higher line, to the I$_A$ atom. The similarity of the NQR spectrum in TH–I$_2$ or TO–I$_2$ to that in DT-2I$_2$ suggests that the S···I$_A$–I$_B$ arrangement also exists in both complexes. The O atom as well as the S atom in the TO molecule can act as the donor atom, though no solid complexes with the O···I$_A$–I$_B$ arrangement have yet been observed. However, the proximity of the ^{127}I NQR frequencies of TO–I$_2$ to those of DT–I$_2$ and TH–I$_2$ may show that not the O atom, but the S atom, acts as the donor atom toward the iodine molecule in TO–I$_2$.

On the other hand, only a single line is observed in TT–I$_2$; this suggests that all I atoms are equivalent in their crystals. This fact and the molar ratio of its component molecules (1:1) predict the existence of endless chains consisting of alternating TT and iodine molecules in the solid state of TT–I$_2$. Probably, the CT interaction is of a weak n-σ type. The resonance frequency in TT–I$_2$ is close to the 332 MHz[3)] of the ^{127}I (1/2—3/2) transition observed for the phenazine–I$_2$ complex, which contains a N···I–I···N bridge in its structure.[9)]

It has previously been pointed out that a three-center four-electron bonding scheme[1,10—13)] gives a good approximation for describing the bonding in trihalide anions, amine–halogen complexes, and bis(amine)-halogen cations. Therefore, we consider only the pure p_σ bond orbitals for the bonding of I atoms in the present compounds. Then we can estimate the charge density on the iodine atoms and, hence the transferred charges from the donor to the acceptor, according to the Townes-Dailey approximation:[14)]

$$\rho = 1 - (e^2q_{zz}Q/h)/(e^2q_{at}Q/h), \tag{1}$$

where $e^2q_{zz}Q/h$ is the observed quadrupole coupling constant, where $e^2q_{at}Q/h$ is the atomic quadrupole coupling constant, which equals the value of 2292.7 MHz for ^{127}I, and where ρ stands for the charge density localized on the iodine atom.

When the frequencies attributable to both the ^{127}I (1/2—3/2) and ^{127}I (3/2—5/2) transitions are obtained, the exact values of the $e^2q_{zz}Q/h$ and the asymmetry parameter (η) are derived from the eigen-value table for a nuclear spin, I=5/2. The $e^2q_{zz}Q/h$ and η values are given in the margin of Table 1 for the I$_B$ atom of TH–I$_2$. In the other cases, where only the ^{127}I(1/2—3/2) transition is observed, we obtain the $e^2q_{zz}Q/h$ value by putting η=0 into the following relation, which holds for $\eta \leq 0.1$:

$$\nu(1/2-3/2) = \frac{3}{20}(e^2q_{zz}Q/h)\left(1+\frac{5}{54}\eta^2\right) \tag{2}$$

It is safe to neglect η in Eq. 2 for the purposes of the present calculation because of the expected small η value and the much smaller contribution to the resonance frequency of the second term than the first. Obviously, the η value is very small for the I$_B$ atom of TH–I$_2$, and also for the iodine atoms of the amine–iodine complexes,[3,15—17)] corresponding to the present type of complexes.

The charge densities on the iodine and sulfur atoms, as calculated from the values of $e^2q_{zz}Q/h$ at 77 K, are listed in Table 2. In accordance with the prediction from the delocalized three-center bonding, the terminal iodine I$_B$ has negative charges, and the bridging iodine I$_A$, small positive charges. The small negative charge on the iodine atom of TT–I$_2$ indicates a weak CT interaction. We may estimate the order of donor strengths toward the iodine molecule from the amounts of the positive charges localized on the donors:

$$\mathrm{TH > TO > DT \gg TT}.$$

The bonding of the complexes is alternatively described in terms of Mulliken's valence-bond expression[18] of a charge-transfer model. As is well known, the ground-state wave function is written as:

$$\Psi_N = a\Psi(\mathrm{D,X_2}) + b\Psi(\mathrm{D^+\text{-}X_2^-}). \tag{3}$$

This equation is satisfactory for a weak CT complex. Bowmaker and Hacobian[1] expanded Eq. 3 in the following form for the strong n-σ complex by considering that the two X atoms in D–X_2 are in inequivalent positions:

$$\begin{aligned}\Psi_N = {} & a\Psi(\mathrm{D,X_2}) + b\alpha\Psi(\mathrm{D^+\text{-}XX^-}) \\ & + b\beta\Psi(\underbrace{\mathrm{D^+X^-X}}) + c\Psi(\mathrm{DX^+X^-})\end{aligned} \tag{4}$$

where the first and fourth terms refer to the no-bond structures, and the second and third, to the dative structures. The fourth structure, regarded as a resonance hybrid with the second structure, is introduced into Eq. 4 because the D^+–X bond must have a partial ionic character if D^+ has a greater affinity than the X atom. This term is more important than the third because the bridging halogen atoms of the complexes have positive charges.

For further discussion, we plot the charges on the I atoms against those on the S donors in Fig. 1. The results of several amine–iodine complexes are also shown in this figure. Unfortunately, the ^{127}I NQR results for the strong n-σ type of amine–iodine complexes have been obtained imperfectly; the frequencies of only the bridging iodine atom are observed, mainly because of the weakness of the resonance intensities of the terminal halogen atoms. However, a few data on the amine–iodine complexes obtained from the ^{129}I Mössbauer-effect measurements[15–17] are available for this purpose.

Though the quantity of data is restricted, it is found from the charges on the donors that the S donor is almost as strong as the N donor in its donor strength toward the iodine molecule. When the donor strength increases in each set of the S···I_A–I_B and N···I_A–I_B complexes, the negative charge on the I_B atoms increases linearly, whereas the charge on the I_A atoms is maintained at an almost constant value. It is, therefore, obvious that transferred charges from the donor are mostly localized on the terminal iodine atom. This shows that the weight of the fourth term in Eq. 4 is maintained to about a constant value from complex to complex in each set of complexes, while the third term is practically negligible. Thus, we can calculate the weight of each structure in Eq. 4 from the charge densities, neglecting the third structure. The weights of the first (no-bond covalent), the second (dative), and the fourth (no-bond ionic) structures are 68, 22, and 10% for DT-2I_2, 57, 33, and 10% for TH-I_2, and 64, 27, and 9% for TO-I_2, respectively. Both positive charges on I_A and negative ones on I_B are larger in their absolute values for the N-atom donors than for the S-atom donors when the donor strengths are about the same. Those results indicate that the contribution of the fourth term in Eq. 4 is smaller for the S-atom donor-iodine complexes than for the N-atom donor-iodine complexes. The ionic structure of the ground state is less important in the former than in the latter. This is reasonable, because the N^+ has a larger electron affinity than the S^+.

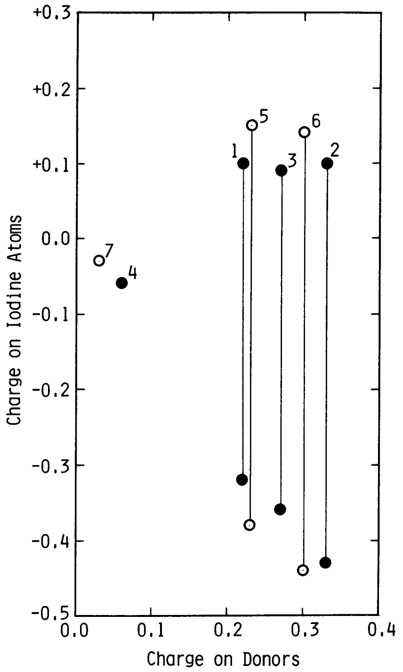

Fig. 1. Plot of the charges on I atoms *vs.* the charges on donors. ●: S donor; ○: N donor. 1) 1,4-Dithiane-2I_2, 2) Thiane-I_2, 3) 1,4-Thioxane-I_2, 4) 1,3,5-Trithiane-I_2, 5) Pyridine-I_2,[15,17] 6) Triethylamine-I_2,[17] 7) Phenazine-I_2.[3,16]

The temperature dependence of the resonance frequency due to the ^{127}I (1/2—3/2) transition was observed in the range of from the temperature of liquid N_2 to room temperature. The results for the present complexes are shown in Figs. 2 and 3, while the temperature coefficients at 273 K of the frequency curves are listed in the fourth column of Table 1. It is found that all terminal iodine atoms of DT-2I_2, TH-I_2, and TO-I_2 have positive temperature coefficients; this is in accordance with the results previously reported for the terminal halogens of pyridine-ICl,[2] 4-methylpyridine-ICl,[2] and 3,5-dibromopyridine-Br_2.[1]

This tendency can be qualitatively realized from Eq. 4. As the temperature is raised, the increasing excitation of molecular vibrations will weaken the weaker intermolecular CT-bond rather than the intramolecular I–I bond; the contribution of the dative

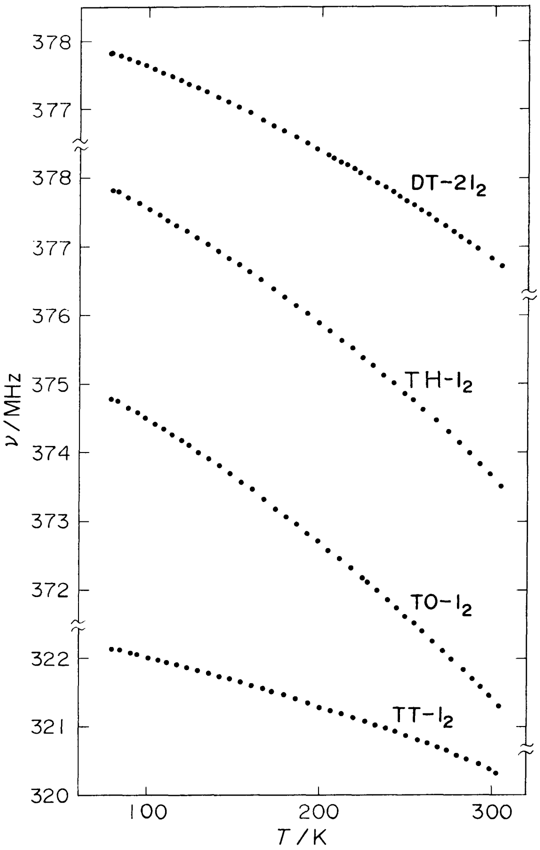

Fig. 2. Temperature dependence of the ^{127}I(1/2—3/2) NQR frequencies of the bridging iodine atoms. DT: 1,4-dithiane, TH: Thiane, TO: 1,4-thioxane, TT: 1,3,5-trithiane.

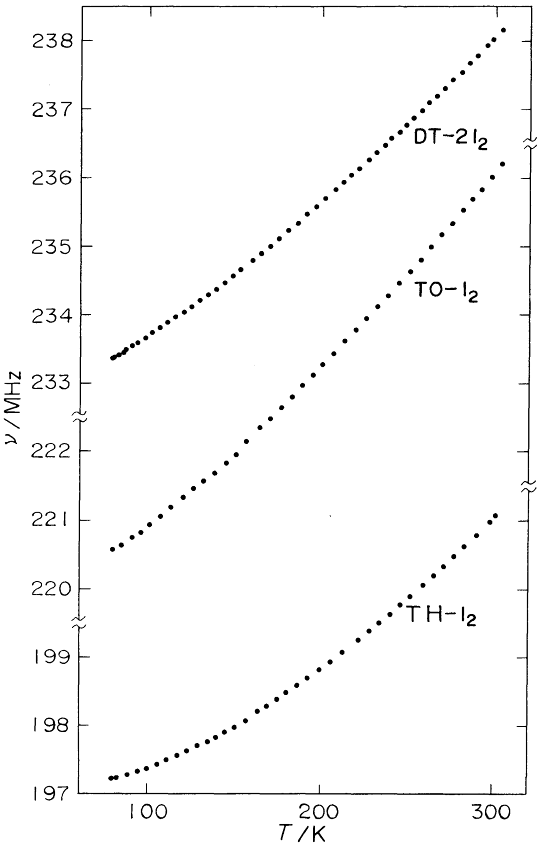

Fig. 3. Temperature dependence of the ^{127}I(1/2—3/2) NQR frequencies of the terminal iodine atoms. DT: 1,4-dithiane, TH: Thiane, TO: 1,4-thioxane.

structure will, consequently, decrease with the increase in the temperature. As has been seen previously, the dative structure is approximated by the second structure in Eq. 4, while neglecting the third structure. The contribution of the no-bond covalent structure is larger than that of the no-bond ionic one. Further, the contribution of the no-bond ionic structure is kept at about a constant value even if the donor strength is changed. Accordingly, it is mainly the no-bond covalent structure that increases its contribution with an increase in the temperature. The conversion of the second structure to the first one reduces the negative charge (and hence the p_z-electron populations) of the I$_B$ atom, holding the charge density of the I$_A$ atom constant. Since the decrease of p_z-electron populations of the iodine atom results in the increase of the value of its electric-field gradient (eq_{zz}), the resonance frequency increases from Eq. 2. The frequency of the I$_B$ atom thus increases with the temperature, as in the present case, if the frequency increase due to the decrease of the dative structure described above overcomes the normal decrease in frequency$^{19)}$ which is caused by the averaging of eq_{zz} following the increasing molecular vibrations.

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