The ^{127}I Nuclear Quadrupole Resonance of an Iodine Complex with 1,3-Dithiane, $C_4H_8S_2 \cdot 2I_2$

Hiromitsu TERAO* and Hiroshi SAKAI†
Faculty of Integrated Arts and Sciences, Tokushima University,
Minamijosanjima-cho, Tokushima 770
†Research Reactor Institute, Kyoto University, Kumatori-cho, Sennan-gun, Osaka 590-04
(Received August 29, 1987)

Synopsis. The ^{127}I nuclear quadrupole resonance spectrum of 1,3-dithiane-$2I_2$ is reported. Two distinct S···I-I arrangements are present in the crystal. The charge on each iodine atom is obtained; the bonding in the complex is discussed in connection with analogous thioether–iodine complexes. The resonance lines for terminal iodine atoms indicate positive temperature coefficients.

It is well-known that halogen (or interhalogen) molecules act as electron acceptors toward electron-pair donor molecules (such as amines, ethers, and thioeters) and form n-σ-type charge-transfer (CT) complexes with them. In addition, the empirical results obtained from structural investigations show that if CT-bonds in the complexes are comparatively strong, isolated units of complex molecules involving almost linear arrangements of donor atom···halogen–halogen are found in the solid state. In this case, the CT-interaction between donor and acceptor appears to be simple and archetypal. It is, therefore, of great interest to evaluate the charge distributions on the halogen atoms in such complex molecules in order to clarify the nature of the CT-interation.

Many amine–halogen complexes belonging to this class have been investigated for this purpose by means of the halogen[1–3] (and also the nitrogen[4,5]) nuclear quadrupole resonance (NQR) and the ^{129}I Mössbauer effect.[6–8] However, complete results have been obtained for only a small number of complexes, since the NQR signals of the terminal halogen atoms were not detected in many cases and since the ^{129}I Mössbauer effect has been applied to only a few iodine complexes of this class.

Recently we ourselves have applied the ^{127}I NQR[9] and the ^{129}I Mössbauer effect[10] to a series of thioether-iodine complexes (involving a S···I_A–I_B arrangement), such as tetrahydrothiopyran (thiane)–iodine (1:1), 1,4-dithiane–iodine (1:2), and 1,4-thioxane–iodine (1:1), and have estimated the charges on both bridging iodine (I_A) and terminal iodine (I_B) atoms. In the present communication, we with to report the ^{127}I NQR results of 1,3-dithiane-$2I_2$, which has been selected in order to confirm the conclusion deduced in a previous investigation[9] of thioether–iodine complexes.

Experimental

Stoichiometric amounts of iodine and 1,3-dithiane were treated in a carbon tetrachloride solution at room temperature, because the complex had a tendency to decompose in a hot solution. After concentrating the solution under reduced pressure, we filtered the resulting purplish-black crystalline product. The product was extracted in a Soxhlet extractor with dichloromethane to obtain a well-crystallized sample suitable for the NQR measurements. Found: C, 7.72; H, 1.30; I, 81.06%. Calcd for $C_4H_8S_2$–$2I_2$: C, 7.65; H, 1.28; I, 80.85%.

The NQR measurements were carried out using an externally quenched super-regenerative Lecher-line oscillator, as has been described previously.[9]

Results and Discussion

Four resonance lines of the $m=\pm1/2\longleftrightarrow\pm3/2$ transitions by the ^{127}I nuclei were observed for the 1,3-dithiane-$2I_2$ complex between 77 K and room temperature; the frequency values at 77 and 298 K are listed in Table 1, together with the corresponding frequencies for 1,4-dithiane-$2I_2$.[9] The assignment of the resonance lines to the $m=\pm1/2\longleftrightarrow\pm3/2$ transitions was done on the basis of the ^{127}I NQR spectra[9] and the ^{129}I Mössbauer spectra[10] of analogous thioether–iodine complexes.

In the crystal structure of 1,4-dithiane-$2I_2$,[11] each sulfur atom is linked to one iodine moiety, and all the

Table 1. $^{127}I(m=\pm1/2\leftrightarrow\pm3/2)$ NQR Frequencies in 1,3-Dithiane-$2I_2$[a]

Compound	Frequency/MHz		$(d\nu/dT)_{T=273K}$	Assignment[b]
	77 K	298 K	kHz/K	
1,3-Dithiane-$2I_2$	377.34(7)[c]	372.24(2.5)	−28.9	I_A(1)
	371.56(13)	367.20(4.5)	−23.9	I_A(2)
	247.07(4.5)	252.04(2)	26.1	I_B(1)
	243.95(8)	248.67(3.5)	25.0	I_B(2)
1,4-Dithiane-$2I_2$[d]	377.81(6)	374.83(3)	−16.5	I_A
	233.37(2.5)	238.02(2)	25.4	I_B

a) The accuracy of the measurements was estimated to be within ±0.01 MHz in frequency and ±1 K in temperature. b) I_A and I_B denote the bridging and the terminal iodine atoms respectively. c) The numbers in parentheses are the signal-to-noise ratios as measured on an oscilloscope. d) Ref. 9.

S$\cdots$I$_A$–I$_B$ arrangements are identical. In accordance with this, only two resonance lines, corresponding to the bridging iodine (I$_A$) and the terminal iodine (I$_B$) atoms, have been observed. However, the observation of four resonance lines, though no crystallographic data is known, indicates that two distinct S$\cdots$I$_A$–I$_B$ arrangements are present in the 1,3-dithiane-2I$_2$ crystal. Presumably the respective S atoms at the 1- and 3-positions of the C$_4$S$_2$ ring are linked to one iodine moiety in such a way that these atoms are no longer equivalent to each other in the crystal.

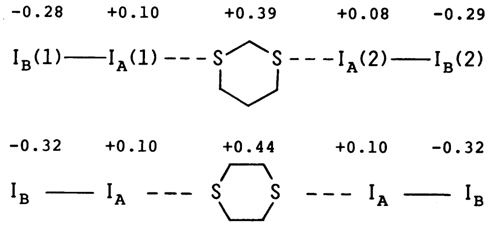
The assignment of the resonance lines to the I$_A$ or the I$_B$ atoms can be done unambiguously, since it is well-established that the lines for the I$_B$ atoms have lower frequency values than those for the I$_A$ atoms and that the frequency difference between them is very large. Further, considering that the signal-to-noise ratios of each two lines for the I$_A$ and the I$_B$ atoms are evidently different (ca. 1:1.8), we have tentatively made pairs of the weaker I$_A$ line and the weaker I$_B$ line and of the stronger I$_A$ line and the stronger I$_B$ line (Table 1).

A simple three-center four-electron bonding theory,[1,3,10] using only the valence p-orbitals of halogens, has been successfully applied to the donor atom$\cdots$halogen–halogen systems. The charges on the halogen atoms can be well-explained with the theory.[12] By considering only the p-orbitals for the bondings of iodine atoms, therefore, we estimate the charges on both I$_A$ and I$_B$ atoms according to the Townes–Dailey approximation (in the previous paper[9] we reported this equation incorrectly):

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

where ρ is the charge on the iodine atom, where $e^2q_{zz}Q/h$ is the observed quadrupole coupling constant, and where $e^2q_{at}Q/h$ is the atomic quadrupole coupling constant (2292.7 MHz for ^{127}I).

As the arrangement of S$\cdots$I$_A$–I$_B$ is considered to be almost linear, the asymmetry parameters (η) are expected to be small for both I$_A$ and I$_B$ atoms. In fact, practically zero values of η were observed from the ^{127}I NQR measurements for the I$_A$ atoms of several amine–I$_2$ complexes[3] and for the I$_B$ atom of the thiane–I$_2$ complex.[9] By neglecting the expected small η value, the relation between the $e^2q_{zz}Q/h$ and the frequency (ν) are simplified to $e^2q_{zz}Q/h=20/3\cdot\nu$ for the ^{127}I ($m=\pm1/2\longleftrightarrow\pm3/2$) transitions. Then, the ρ on the iodine atoms (and also the charges on the donors) are obtained from Eq. 1, by using the ν values at 77 K, as follows:



The charge transferred from the donor to the iodine moiety is slightly less in 1,3-dithiane-2I$_2$ than in 1,4-dithiane-2I$_2$. This is consistent with the observation that the former complex is more labile than the latter.

For comparison, in Fig. 1 the present data for the charge distributions in 1,3-dithiane-2I$_2$ are added to a previous figure[9] representing the relation of the charges on the I$_A$ and the I$_B$ atoms to the charges (per donor atom) on the donors. In the figure, the average values were used as the respective charges on the I$_A$

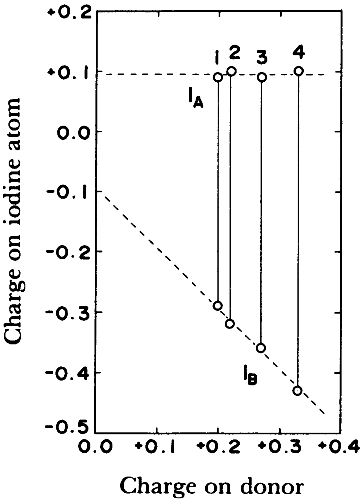


Fig. 1. Plot of the charges on I atoms vs. the charges on donors. (1) 1,3-Dithiane-2I$_2$, (2) 1,4-dithiane-2I$_2$,[9] (3) 1,4-thioxane-I$_2$,[9] (4) thiane-I$_2$.[9]

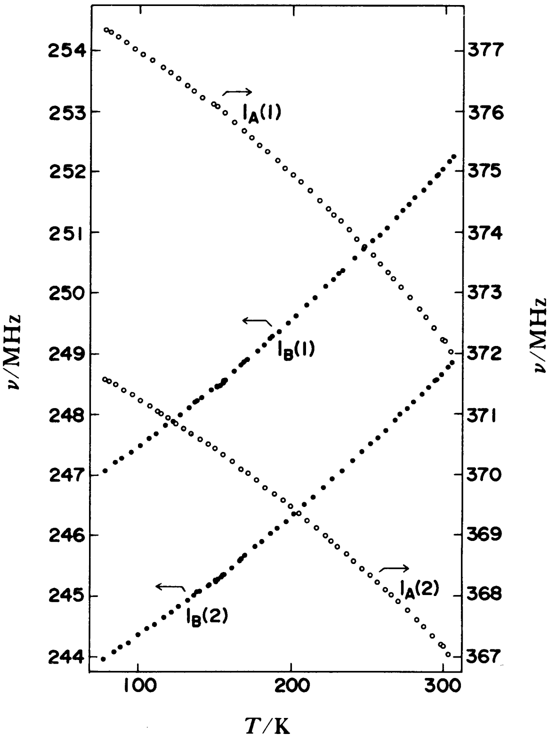


Fig. 2. Temperature dependence of the ^{127}I ($m=\pm 1/2\leftrightarrow\pm3/2$) NQR frequencies in 1,3-dithiane-2I$_2$.

and the I_B atoms in 1,3-dithiane–$2I_2$.

Obviously, our previous finding is confirmed in Fig. 1:[9] The charges on the I_A atoms are almost independent of the charges on the donors, and hence the negative charges on the I_B atoms increase linearly with the increase in the charges on the donors. This observation suggests that the formation of the complex is followed by two effects: One is the polarization[2] of the iodine moiety by the donor, $I^{\delta+}\,I^{\delta-}$ (represented as a no-bond ionic structure[1,9] in the valence-bond expression), and the other is the CT from the donor to the iodine moiety. Further, Fig. 1 shows that (1) the polarization effects are maintained at an almost constant value for the same donor atom[9] (ca. ±0.1 *e* charges are polarized on the respective I_A and I_B atoms of an iodine moiety in the case of the S donors) and (2) the charges (ca. 0.2—0.3 *e*) transferred from the donors to the iodine moieties are mostly piled up on the I_B atoms.

The temperature dependence of the resonance frequencies measured between 77 K and room temperature is shown in Fig. 2. In accordance with the previous observations[1,2,4,9] the resonance lines of terminal iodine atoms have positive temperature coefficients (Table 1). This trend is qualitatively realized by considering the weakening of the CT-bond with the increasing temperature.[9]

References

1) G. A. Bowmaker and S. Hacobian, *Aust. J. Chem.*, **22**, 2047 (1969).

2) H. C. Fleming and M. W. Hanna, *J. Am. Chem. Soc.*, **93**, 5030 (1971).

3) R. Brüggemann, F. Reiter, and J. Voitländer, *Z. Naturforsch., A,* **27**, 1525 (1972).

4) G. A. Bowmaker, *J. Chem. Soc., Faraday Trans. 2,* **72**, 1964 (1976).

5) G. V. Rubenacker and T. L. Brown, *Inorg. Chem.*, **19**, 392 (1980); **19**, 398 (1980).

6) S. Bukshpan, C. Goldstein, T. Sonnino, L. May, and M. Pasternak, *J. Chem. Phys.*, **62**, 2606 (1975).

7) S. Ichiba, H. Sakai, H. Negita, and Y. Maeda, *J. Chem. Phys.*, **54**, 1627 (1971).

8) H. Sakai, Y. Maeda, S. Ichiba, and H. Negita, *J. Chem. Phys.*, **72**, 6192 (1980).

9) H. Terao, H. Sakai, and H. Negita, *Bull. Chem. Soc. Jpn.*, **58**, 2318 (1985).

10) H. Sakai. T. Matsuyama, and Y. Maeda, *Bull. Chem. Soc. Jpn.*, **59**, 981 (1986).

11) G. Y. Chao and J. D. McCullough, *Acta Crystallogr.*, **13**, 727 (1960).

12) Recently, Sakai et al.[8,10] found, in their ^{129}I Mössbauer investigations, that the quadrupole coupling constants ($e^2q_{zz}Q/h$) obtained from the quadrupole splittings are always smaller than the values to be expected from the isomer shifts (δ) in the case of the I_A atoms, whereas the two values were in fair agreement in the case of the I_B atoms. Those facts may indicate that the model using only the valence p-orbitals is oversimplified for the I_A atoms apart from the I_B atoms.