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^{129}I Mössbauer Spectroscopic Study of Several n-σ Charge-Transfer Complexes of Iodine with Thioethers

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^{129}I Mössbauer studies have been made of n-σ charge-transfer complexes of iodine with thioethers, such as thiane, 1,4-oxathiane, and 1,4-dithiane. The spectra of these complexes consist of two sets of quadrupole octets, corresponding to the bridging and terminal iodine atoms. The transferred charges from the thioethers are localized on the terminal iodine atoms, and the bridging iodine atoms have slightly positive charges. This result can be well explained in terms of a covalent bond between the sulfur and bridging iodine atoms or the MO treatment of a delocalized three-center four-electron bonding. The contributions of the dative structure to the ground state are estimated to be 36, 28, and 24% for thiane-iodine, 1,4-oxathiane-iodine, and 1,4-dithiane-iodine respectively. The nature of the charge-transfer bond is discussed in comparison with amine-iodine complexes.

The Mössbauer spectroscopy of ^{129}I is a powerful tool for the study of charge-transfer (CT) complexes containing iodine as an electron acceptor. The electronic structure of iodine is directly derived from the Mössbauer spectroscopy parameters, such as the quadrupole coupling constant (e^2Qq) and its sign, the asymmetry parameter (η), and the isomer shift (δ). Actually, many investigations of CT complexes of iodine have been reported to date using ^{129}I Mössbauer spectroscopy.[1—10)] However, these investigations have been mostly concerned with nitrogen-containing compounds (amines) and with aromatic compounds as the electron donors.

Sulfur-containing compounds (thioethers) also act as electron donors and form n-σ type CT complexes with iodine in the same way as do amines. The crystal and molecular structures for some of these complexes (1,4-dithiane–iodine,[11)] dibenzyl sulfide–iodine,[12)] and 1,5-dithiocane–iodine[13)]) have been determined by the X-ray diffraction method. In these complexes, the iodine molecule is bonded to the sulfur atom to give a linear S···I–I arrangement. The intramolecular I–I bond distance is longer than that of the free iodine molecule, whereas the intermolecular S···I bond distance is shorter than the sum of the respective van der Waals radii. Hendra and Sadasivan[14)] measured the far-infrared spectrum of the 1,4-dithiane–iodine complex and found the I–I stretching frequency at 158 cm^{-1}, lower than that of free iodine molecules at 213 cm^{-1}.[15)]

The properties of the CT complexes have been interpreted on the basis of the CT theory developed by Mulliken.[16)] As is well known, the CT interaction between an electron donor (D) and an electron acceptor (A) is to be described in terms of the electronic-wave function of the ground state in this form;

$$\Psi_g = a\psi_0(\mathrm{D,A}) + b\psi_1(\mathrm{D^+{-}A^-}), \qquad (1)$$

where ψ_0 represents the wave function for a non-bond structure and ψ_1, that for a dative structure in which one electron has been completely transferred from the donor to the acceptor molecule. The ground state, Ψ_g, stabilized by a resonance between the non-bond and dative structures. When A is the iodine molecule, the transferred electron may occupy the antibonding molecular orbital (σ_u*) of the iodine molecule. Therefore, the contribution of ψ_1 to Ψ_g gives rise to an increase in the I–I bond distance and a decrease in the stretching frequency of the I–I bond. It is, therefore, important and interesting to estimate the contribution of the dative structure in order to understand the properties of the CT complexes in the electronic ground state.

In this paper we wish to report an ^{129}I Mössbauer spectroscopic study of the crystalline n-σ CT complexes between iodine and thioethers, such as thiane (tetrahydrothiopyrane)–iodine (1:1), 1,4-oxathiane–iodine (1:1), and 1,4-dithiane–iodine (1:2). The charge density and the charge distribution on each iodine atom are determined for these complexes, and the nature of the CT bond is discussed in comparison with amine–iodine complexes.

Experimental

Materials. The ^{129}I-labeled complexes were prepared on a small scale by mixing approximately stoichiometric amounts of the components in appropriate solvents. The radioisotope ^{129}I was purchased from the New England Nuclear Corporation in the standard form of Na^{129}I in a Na_2SO_3 solution. Molecular iodine ($^{129}I_2$), obtained by oxidizing Na^{129}I with 3 mol dm^{-3} H_2SO_4 and 10% H_2O_2, was extracted with chloroform, hexane, or carbon tetrachloride. Each iodine solution was thoroughly washed with water and passed through a Teflon filter to eliminate any slight amount of water.

The thiane–iodine complex was prepared by adding a stoichiometric amount of thiane to the iodine solution of chloroform. A dark-brown crystalline product was obtained by the subsequent concentration and cooling of the solution. The orange-red 1,4-oxathiane–iodine complex was prepared in hexane in the same manner as the thiane–iodine complex. The purple crystalline complex of 1,4-dithiane–iodine was obtained by adding a saturated iodine solution of carbon tetrachloride to a dithiane solution of the same solvent. Since those complexes slowly decompose in air, the samples obtained were immediately mounted in Teflon sample holders and kept in liq. N_2 until ready for the Mössbauer measurements. The mole ratio of each component for these complexes was checked on nonradioactive (natural iodine) preparation samples by means of iodometry and elemental analysis. The thioether: I_2 ratios determined for the thiane–iodine,1,4-oxathiane–iodine, and 1,4-dithiane–iodine complexes were 1:1, 1:1, and 1:2 respectively. The thichnesses of the absorbers were in the range of 20 to 30 mg ^{129}I/cm^2.

^{129}I Mössbauer Effect Measurement. The ^{66}Zn^{129}Te source ($t_{1/2}$=70 min) was prepared by the irradiation of 150 mg ^{66}Zn^{128}Te at a thermal neutron flux of 2×10^{13} n cm^{-2} s^{-1} for 1 h in the Kyoto University Reactor (KUR). The source activity produced was initially about 10 mCi, which was sufficient to obtain a reasonable spectrum in 3—4 h of data collection. The 27.8 keV Mössbauer γ-ray was detected with a 1 mm-thick NaI(Tl) scintillation counter, and a 100 μm In foil was inserted between the absorber and the detector in order to selectively absorb 29.8 keV X-ray, resulting in the conversion of 39.6 keV Xe γ-ray. The Mössbauer measurement was performed in the transmission geometry by cooling the source and the absorber to 16 K with a closed-cycle helium refrigerator, "Cryodyne 1020." The Mössbauer spectrometer was calibrated using an iron spectrum.

Results and Discussion

In Figs. 1 and 2 the ^{129}I Mössbauer spectra at 16 K of the thiane–iodine, 1,4-oxathiane–iodine, and 1,4-dithiane–iodine complexes are presented. These spectra consist of a superposition of two quadrupole octets, as is to be expected from the molecular structure of the 1,4-dithiane–iodine complex. The spectra were analyzed by the least-squares method using a double set of the fitting parameters, e^2Qq, η, δ, full-width at half-maximum (2Γ), each peak intensity, and a single base line. The solid lines and the stick diagrams in the figures represent the best-fitted Lorentzian curves and the peak positions respectively. The Mössbauer parameters computed are given in Table 1, together with the results for some amine–iodine complexes published elsewhere. The e^2Qq value was converted to that of the ^{127}I nucleus by using the ground-state quadrupole moment ratio, $^{129}Q/^{127}Q$=+0.70121.[17]

The crystallographic data for the 1,4-dithiane–iodine complex suggest that only one atom of the iodine molecule is bonded to the sulfur atom, resulting in a linear S···I–I arrangement (Fig. 3).[11] The Mössbauer spectra shown in Figs. 1 and 2 are similar to each other. The similarity of these spectra suggests that iodine molecules are also bonded equatorially to the sulfur atoms of thiane and 1,4-oxathiane in the thiane–iodine and 1,4-oxathiane–iodine complexes. Since the values of e^2Qq, η, and δ for the 1,4-oxathiane–iodine complex are close to those for the other complexes, the iodine molecule may not interact with the oxygen atom of the 1,4-oxathiane molecule. In the 1,4-oxaselenane–iodine complex, the oxygen atom is also not involved in the intermolecular bonding.[18] These spectra are similar to those of the amine–iodine complexes. By analogy with the pyridine–iodine complex,[3,8] it is appropriate to assign the iodine with the larger quadrupole splitting (I_A) to the iodine atom coordinated to the sulfur atom (the bridging iodine atom), whereas the I_B should be assigned to the terminal iodine atom.

The values of e^2Qq, η, and δ are closely related to the charge distribution and the charge density on the iodine atom. As is shown in Table 1, these values for the I_A atoms are very close to each other in these complexes, suggesting that they are also similar in S···I_A bond

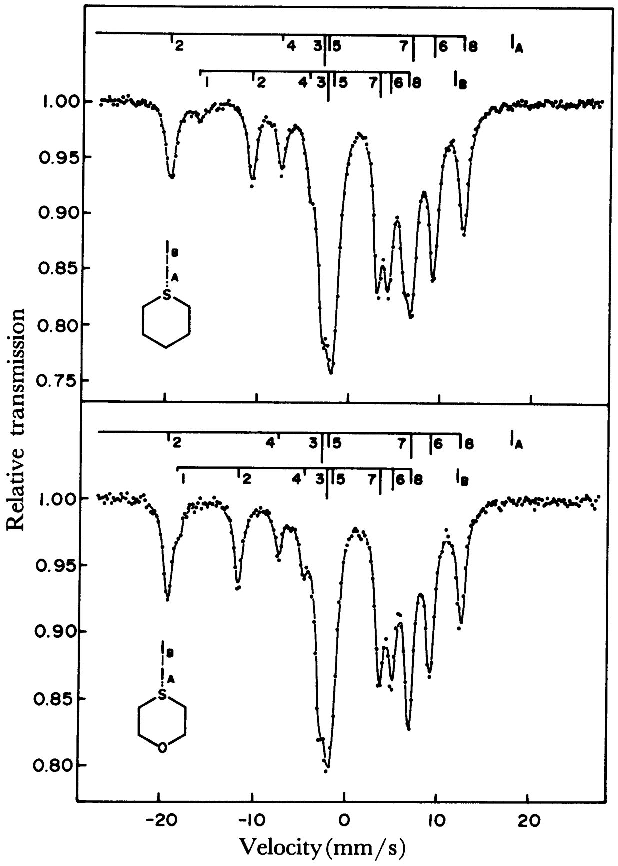

Fig. 1. ^{129}I Mössbauer spectra at 16 K of the thiane–iodine (top) and 1,4-oxathiane–iodine (bottom) complexes.

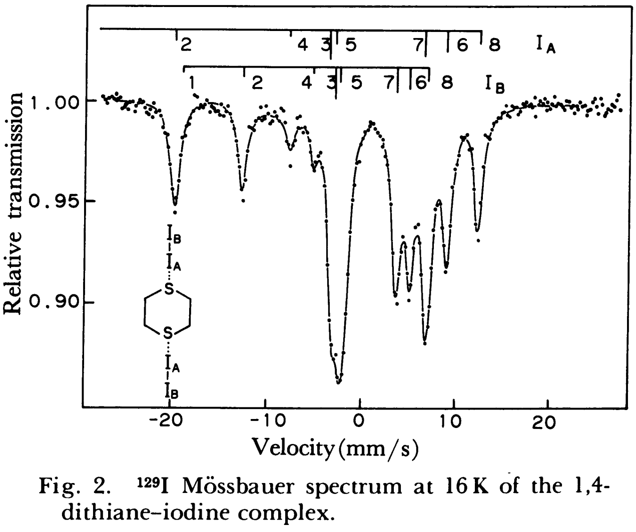

Fig. 2. ^{129}I Mössbauer spectrum at 16 K of the 1,4-dithiane–iodine complex.

Table 1. Values of the Quadrupole Coupling Constant (e^2Qq), the Asymmetry Parameter (η), the Isomer Shift (δ), the Full-Width at Half-Maximum (2Γ), the Relative Intensity, the Unbalanced p-Electron (U_p), and the 5p-Electron Hole (h_p) for the Thioether-Iodine and Amine-Iodine Complexes

		e^2Qq[a)] MHz	η	δ[b)] mm s^{-1}	2Γ mm s^{-1}	Relative[c)] intensity	U_p[d)]	h_p[e)]	Ref.
Thiane–I$_2$	I$_A$	−2513±13	0.02±0.04	1.54±0.04	1.27±0.03	1.23	1.10	1.39	
	I$_B$	−1310±13	0.02±0.04	0.32±0.04	1.22±0.03	1.00	0.57	0.57	
1,4-Oxathiane–I$_2$	I$_A$	−2512±13	0.04±0.04	1.47±0.04	1.20±0.03	1.05	1.10	1.34	
	I$_B$	−1475±13	0.09±0.04	0.43±0.04	1.26±0.03	1.00	0.63	0.65	
1,4-Dithiane–2I$_2$	I$_A$	−2526±13	0.02±0.04	1.47±0.04	1.11±0.03	1.04	1.10	1.34	
	I$_B$	−1553±13	0.06±0.04	0.50±0.04	1.16±0.03	1.00	0.68	0.69	
Hexamethylene-tetramine–I$_2$	I$_A$	−2582±20	0.19	1.51±0.02	—	—	1.13	1.37	(2)
	I$_B$	−1272±20	0.06	0.28±0.02	—	—	0.55	0.55	
Pyridine–I$_2$ in pyridine	I$_A$	−2600±30	—	1.40±0.07	—	—	1.13	1.29	(3)
	I$_B$	−1300±15	—	0.28±0.05	—	—	0.57	0.55	
Pyridine–I$_2$ in CS$_2$	I$_A$	−2631±20	0.10	1.82±0.04	—	—	1.15	1.57	(8)
	I$_B$	−1439±20	—	0.39±0.04	—	—	0.63	0.62	
Triethylamine–I$_2$ in CS$_2$	I$_A$	−2604±20	—	1.56±0.05	—	—	1.14	1.40	(8)
	I$_B$	−1261±20	0.09	0.40±0.05	—	—	0.55	0.62	

a) The e^2Qq values are converted to those of the ^{127}I nucleus by using the $^{129}Q/^{127}Q=0.70121$ ratio. b) The δ values are relative to the ZnTe source. c) The relative intensities are normalized with respect to the I$_B$ atom. d) $U_p=-e^2Qq_{\text{obsd}}/e^2Qq_{\text{atom}}$, $e^2Qq_{\text{atom}}=2292.7$ MHz. e) $\delta=1.5\,h_p-0.54$ (mm/s).

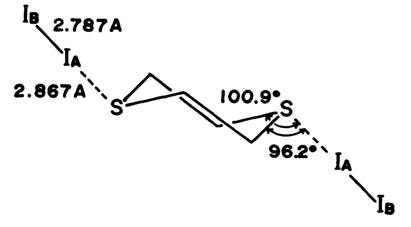

Fig. 3. The structure of the 1,4-dithiane-iodine complex (Ref. 11).

character. The small η values for I$_A$ are consistent with the axially symmetric linear S$\cdots$I$_A$–I$_B$ orientation. On the other hand, the values of e^2Qq and δ for the I$_B$ atoms increase in the order: thiane<1,4-oxathiane<1,4-dithiane. Since an increase in e^2Qq and δ corresponds to a decrease in the p-electrons charge density on the iodine atom, the extent of CT, i.e., the contribution of the dative structure to the ground state, increases in the order of : thiane>1,4-oxathiane>1,4-dithiane in these complexes.

The quantitative treatment of e^2Qq, η, and δ has been developed by Townes and Dailey[19)] and Hafemeister et al.,[20)] and an additional discussion of the ^{129}I Mössbauer parameters has been given in reviews.[21,22)] According to those reviews, the observed e^2Qq, η, and δ values are related to the population of the 5p-electrons and the number of 5p-electron holes in the iodine atom as follows:

$$U_p = -\,e^2Qq_{\text{obs}}/e^2Qq_{\text{atom}} = -\,N_z + (N_x+N_y)/2 \qquad (2)$$

$$\eta = 3(N_x-N_y)/2U_p \qquad (3)$$

$$\delta = 1.5h_p - 0.54 \quad \text{(mm/s, for ZnTe source)} \qquad (4)$$

where U_p is the number of unbalanced p-electrons and e^2Qq_{atom}, the atomic iodine quadrupole coupling constant, is equal to 2292.7 MHz for ^{127}I. N_x, N_y, and N_z are the populations of the 5p-electrons in the x, y, and z orbitals respectively, and $h_p=6-(N_x+N_y+N_z)$ is the number of p-electron holes in the 5p^6 shell.

The U_p and h_p values obtained for the I$_A$ and I$_B$ atoms of the thioether–iodine complexes are presented in Table 1, together with those for some amine–iodine complexes. It can be observed that all the h_p values are larger than the U_p values for the I$_A$ atoms. The same tendency is found in the I$_A$ atoms of the amine–iodine complexes. This phenomenon has been successfully interpreted in terms of the contribution of 4dσ-electrons to the CT-bond formation.[8)] That is, the S$\cdots$I–I or N$\cdots$I–I bonding can be described as a mixture of two extreme bonding schemes, i.e., a delocalized three-center four-electron bond using only the valence p-electrons and covalent σ bonds of two d$_\sigma$p$_\sigma$ hybrid orbitals of the center atom (I$_A$) with the two terminal atoms (S or N and I$_B$), as was first pointed out by Lucken.[23)] The effect of the 4dσ hybridization leads to an increase in the effective s-electron density and therefore markedly increases the δ value because of the large shielding coefficient, 0.85, for 4d-electrons compared to the value 0.35 for 5p-electrons.[8)] On the contrary, if 5s-electrons take part in the CT-bond formation (sp$_\sigma$ hybridization), the δ value decreases greatly. Using Eqs. 4 and 5 in Ref. 8, the number of the 4d$_\sigma$-electron promotion to the 5p orbital can be easily estimated from the δ and e^2Qq values. The average values of δ and e^2Qq for the I$_A$ atoms lead to 0.19 for h_d (the number of 4d-electron defects) and 0.88 for h_p. The contribution of the d$_\sigma$p$_\sigma$ hybridization to the S$\cdots$I–I bond formation is estimated to be 19%, which is close to the value for the triethylamine-iodine complex. The promotion energy of the 4d$_\sigma$-electron may be compensated for by the stabilization of the CT-bond formation. Consequently, the bridging iodine atom is positively charged by 0.07(=0.19+0.88−1) in the present complexes.

On the other hand, Table 1 shows that the h_p values are in good agreement with the U_p values for the terminal iodine atoms (I$_B$). In the amine–iodine complexes, the h_p values are also close to U_p for the I$_B$ atoms. This agreement implies that the bonding of the I$_B$ atom is mainly due to 5p$_\sigma$-electrons. Therefore, the charge density of the I$_B$ atom can be described with $1-h_p$. From the h_p values in Table 1, the I$_B$ atoms for the thiane–iodine, 1,4-oxathiane–iodine, and 1,4-dithiane–iodine complexes are evaluated to be negatively charged by 0.43, 0.35, and 0.31 respectively.

The experimental fact that the transferred electron is not equally distributed on both I$_A$ and I$_B$, but is strongly localized on I$_B$ in the electronic ground state, can be qualitatively explained in terms of a covalent bond between the sulfur and I$_A$ atoms. The distance of the intermolecular S$\cdots$I$_A$ bond is only 2.867 A for the 1,4-dithiane–iodine complex,[11] compared with the sum of the van der Waals radii of the sulfur and iodine atoms (4.0 A) or the sum of each covalent bond radius (2.37 A). This bond distance strongly suggests that a relatively strong covalent bond exists between the S and I$_A$ atoms. For such strong CT complexes, Eq. 1, used for the weak interaction between a donor and an acceptor, is no longer applicable. Equation 1 may, then, be rewritten as follows:

$$\Psi_g = a\psi_0(>\mathrm{S,I_2}) + b\psi_1(>\mathrm{S,I_A^+I_B^-}) + c\psi_2(>\mathrm{S^+{-}I_AI_B^-}), \tag{5}$$

where the first and second terms refer to the non-bond structures, and the third term, to the dative structure. The fact that the I$_A$ atom has slightly positive charges introduces the second term to the ground-state wave function. Fleming and Hanna[24] pointed out the importance of the second term because the electric field from lone pairs would give rise to an induced dipole in I$_2$ and would polarize partly to I$^+$I$^-$. Although the dative structure is usually described in terms of ψ(>S$^+$–I$_2^-$), in which the two iodine atoms are equivalent, it is reasonable, in the case of strong complexes, to rewrite the dative structure as the third term because of the strong covalent bond between S$^+$ and I$_A$. The positive charge on the thioether is likely to be largely localized on the sulfur atom. Since S$^+$ presumably has a greater electron affinity than I$_A$ in the intermolecular S$^+$–I$_A$ bond, some positive charges may also be localized on I$_A$, resulting in the structure of >S I$_A^+$ I$_B^-$. This structure is the same as that of the second term. Therefore, we include the effect of the ionic character on the second term, which is called "the ionic structure." The contribution of each structure to the ground-state wave function can be evaluated by means of the charge densities on the I$_A$ and I$_B$ atoms obtained from the Mössbauer spectrum, neglecting the overlap between ψ_0 and ψ_1, or between ψ_0 and ψ_2, as follows. Since the I$_A$ atom is positively charged by 0.07, the contribution of the second term, in which I$_A$ is a monocation, is found to be 7%. In both the second and third terms, the I$_B$ atom exists as a monoanion. Therefore, the −0.43 charge localized on the I$_B$ of the thiane complex leads to 43% for the contributions of the second and third terms. We obtain 36% for the contribution of the third term alone. The results for the thioether–iodine complexes are given in Table 2, together with those for some amine–iodine complexes.

Table 2. Contributions of the Non-Bond (a^2), Ionic (b^2), and Dative Structures (c^2) to the Ground-State Wave Function for the Thioether–Iodine and Amine–Iodine Complexes

	a^2/%	b^2/%	c^2/%	Ref.
Thiane–I$_2$	57	7	36	
1,4-Oxathiane–I$_2$	65	7	28	
1,4-Dithiane–2I$_2$	69	7	24	
Hexamethylene-tetramine–I$_2$	55	11	34	(2)
Pyridine–I$_2$ in CS$_2$	62	11	27	(8)
Triethylamine–I$_2$ in CS$_2$	59	11	30	(8)

As is shown in Table 2, there is no great difference in the contribution of the dative structure (c^2) between the thioether and amine complexes. However, it is obvious that the amount of the ionic structure (b^2) for the thioether complexes is less than that for the amine complexes. This result is quite reasonable, for amine cations (N$^+$) have a larger electron affinity than thioether cations (S$^+$) and, therefore, attract more electrons from the bridging iodine atom (I$_A$) than do S$^+$.

It is interesting to interpret the charge densities on the I$_A$ and I$_B$ atoms and the nature of the CT bond on the basis of the simple LCAO-MO theory. The MO treatment of the delocalized three-center four-electron bond has been successfully applied to the halogen NQR results for amine–halogen or –interhalogen complexes.[25] Therefore, we have also applied the same procedure to our thioether–iodine complexes and compared the results with those for the amine–iodine complexes. According to Bowmaker and Hacobian,[25] the secular equation for the S$\cdots$I$_A$–I$_B$ configuration can be written as:

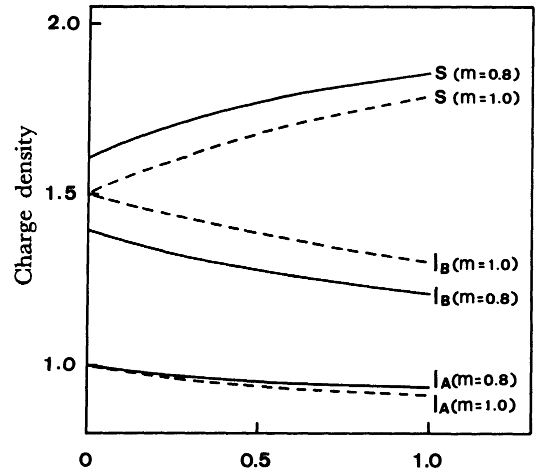

Fig. 4. Charge densities on the sulfur (S), bridging iodine (I$_A$), and terminal iodine (I$_B$) atoms as a function of the Coulomb parameter *n*.

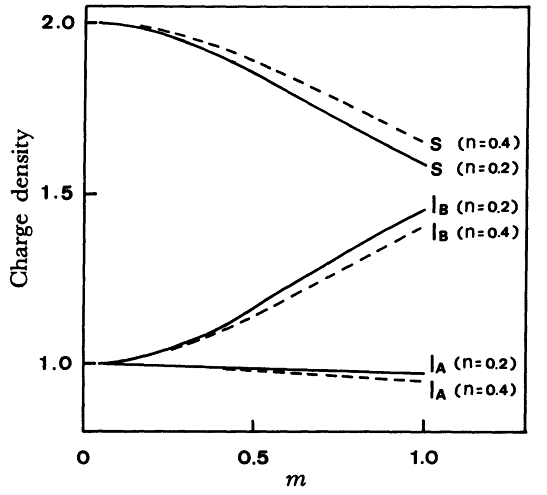

Fig. 5. Charge densities on the sulfur (S), bridging iodine (I$_A$), and terminal iodine (I$_B$) atoms as a function of the resonance integral parameter *m*.

$$\begin{vmatrix} \alpha + n\beta - \mathrm{E} & m\beta & 0 \\ m\beta & \alpha - \mathrm{E} & \beta \\ 0 & \beta & \alpha - \mathrm{E} \end{vmatrix} = 0$$

where α is the Coulomb integral for the valence p_z orbital of iodine and β, the resonance integral between two valence p_z orbitals of iodine; *n* refers to the Coulomb parameter of sulfur and *m*, to the resonance integral parameter for the S···I$_A$ bond.

The charge densities on each atom calculated are shown in Fig. 4 as a function of *n* in the cases of 0.8 (—) and 1.0 (----) for *m*. The charge density on the sulfur atom increases with an increase in the *n* value, which depends on the difference in electronegativity between the donor (sulfur) and iodine atoms. In the amine-iodine complexes, the *n* value for nitrogen is estimated to be 0.9 from the charge densities on the bridging and terminal iodine atoms.[25] Since the electronegativity of sulfur is smaller than that of nitrogen, a smaller *n* value for sulfur is required. When the *n* values are taken to be 0.2 (—) and 0.4 (---), the charge densities calculated as a function of *m* are shown in Fig. 5. It is found that an increase in the *m* value causes a decrease in the charge density on sulfur. The transferred charges from sulfur are localized on the terminal iodine atom (I$_B$), and the bridging iodine atom (I$_A$) has slightly positive charges. Judging from the charge densities on the I$_B$ atoms obtained from the Mössbauer results, the appropriate value of the Coulomb parameter *n* seems to be about 0.2 for the sulfur atoms in the thioethers. This value seems reasonable, because the electronegativity of sulfur is only slightly larger than that of iodine. In the range of 0.75 to 0.95 for the *m* value, the charge densities on the I$_B$ atoms calculated are in good agreement with those obtained experimentally. The appropriate *m* value is estimated to be 0.9 for the amine–iodine complexes.[25] When the *n* and *m* values are 0.2 and 0.9 respectively, the charge density on the I$_A$ atom is calculated to be 0.97 (positively charged by 0.03). Considering that the simple LCAO-MO calculation is used for these complexes, the *n* and *m* values which seem chemically reasonable give a good agreement between the calculated and experimentally observed charge densities on each atom. Therefore, the S···I–I bonding is described mainly in terms of the delocalized three-center four-electron bond in the electronic ground state, such as the bonding in the triiodide anion. The quantity of the transferred charges depends strongly on the Coulomb integral of the donor atom and the resonance integral of the bond between the donor and the bridging iodine atoms.

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