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^{129}I Mössbauer Spectroscopic Studies on the Iodine Complexes of *N,N′*-Diphenyl-*p*-phenylenediamine and *N,N′*-Diphenylbenzidine

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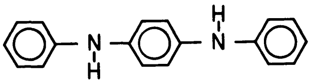
^{129}I Mössbauer and resonance Raman spectroscopy have been applied to the iodine complexes of *N,N′*-diphenyl-*p*-phenylenediamine (DPPD–$I_{2.4}$) and *N,N′*-diphenylbenzidine (DPB–$I_{2.7}$), which exhibit relatively high electrical conductivities. The Mössbauer spectra of these complexes indicate the existence of two unequivalent iodine sites, corresponding to the central and terminal iodine atoms of a linear I_3^- unit. The resonance Raman spectra suggest that the I_3^- unit exists as a successive chain in these complexes. This is consistent with the crystallographic data of the DPPD–$I_{2.4}$ complex. The charge density of the I_3^- unit is slightly different from that of the isolated I_3^- ion because of a weak covalent bond between I_3^- units. It is confirmed that both complexes are partially oxidized mixed-valence compounds, formulated as $(\mathrm{DPPD})^{+0.8}(I_3^-)_{0.8}$ and $(\mathrm{DPB})^{+0.9}(I_3^-)_{0.9}$.

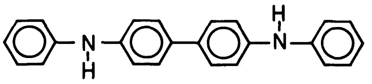
Some iodine complexes of oligoanilinic derivatives show interesting electrical and magnetic properties.[1)] One of these complexes, *N,N′*-diphenyl-*p*-phenylenediamine-iodine (DPPD–I_x, x=1.8—2.4), exhibits relatively high electrical conductivity (≈0.3 S cm^{-1}) at room temperature with a low activation energy (0.07 eV).[2,3)] It is found from measurements of the thermoelectric power that in this complex (x=2.0—2.4) the electron conductivity is slightly more predominant than the hole conductivity near room temperature.[2,4)] The complex is paramagnetic and shows a strong electron-spin resonance signal.[2)] Crystallographic data of the complex (x=2.4) suggest that the iodine atoms are arranged in successive chains consisting of I_3^- units perpendicular to the layer of the planar DPPD molecule.[5)] The iodine chain is coordinated to NH groups of the DPPD molecule. The interatomic distance in the I_3^- unit is approximately 2.99 Å, slightly longer than that of usual triiodide ions (2.92 Å).[6)] The distance of 3.44 Å between I_3^- units along the chain is shorter than twice the van der Waals radius of iodine.

It is interesting to estimate the charge density of each iodine atom in order to understand the electrical and magnetic properties of the complex. The Mössbauer spectroscopy of ^{129}I is a powerful method for this purpose, since the electronic structure of iodine is directly derived from such Mössbauer parameters as the quadrupole coupling constant (e^2Qq) and its sign, the asymmetry parameter (η), and the isomer shift (δ). In this paper we report results of ^{129}I Mössbauer spectroscopy for the *N,N′*-diphenyl-*p*-phenylenediamine-$I_{2.4}$ (DPPD–$I_{2.4}$) and *N,N′*-diphenylbenzidine-$I_{2.7}$ (DPB–$I_{2.7}$) complexes. Furthermore, laser Raman spectra were measured for these complexes in order to clarify the configuration of iodine.

Experimental


N,N′-diphenyl-p-phenylenediamine

(DPPD)


N,N′-diphenylbenzidine

(DPB)

Materials. The commercially available donor molecules, DPPD and DPB, were recrystallized from benzene. The ^{129}I labeled complexes used for measurements of the Mössbauer spectra were prepared from Na ^{129}I in an Na_2SO_3 solution. After oxidizing the iodide with 3 mol dm^{-3} H_2SO_4 and 10% H_2O_2, the resulting molecular iodine ($^{129}I_2$) was extracted with benzene. A dark-green DPPD–I_x complex with metallic luster was obtained upon adding a hot benzene solution of DPPD to the hot benzene solution of iodine. Lustrous, reddish-black crystals of DPB–I_x were obtained by mixing hot benzene solutions of DPB and excess iodine. The samples for measurements of resonance Raman spectra were prepared by using natural iodine in the same manner as the above procedures. The ratio of each component for these complexes was determined to be x=2.4 for DPPD–I_x and x=2.7 for DPB–I_x by iodometry.

Measuremens. A single-line ^{66}Zn^{129}Te Mössbauer source was prepared by irradiating 140 mg ^{66}Zn^{128}Te at a thermal neutron fluence rate of 2×10^{13} n cm^{-2}·s^{-1} for 1 h in the Kyoto University Reactor (KUR). The source activity produced by the ^{128}Te (n,γ) ^{129}Te reaction was initially about 10 mCi, sufficient to obtain a reasonable spectrum in 3—4 h of data collection. The Mössbauer spectra were measured in a transmission geometry by cooling the source and the absorber to 16 K with a closed cycle helium refrigerator. The 27.8 keV Mössbauer γ-rays were detected with a 1 mm-thick NaI(Tl) scintillation counter. The Mössbauer spectrometer was calibrated with a six-line spectrum of an Fe foil.

Laser Raman spectra were recorded with Ar$^+$ (514.5 nm) excitation usig a JEOL-JRS-400T triple monochromator and photon-counting detection. The data were obtained with compressed pellets of powdered samples by the front-surface reflection method using 60 mW laser power and a spinning cell. No decomposition was observed with this laser power.

Results and Discussion

Mössbauer Spectra. ^{129}I Mössbauer spectra of the DPPD–$I_{2.4}$ and DPB–$I_{2.7}$ complexes at 16 K are shown in Fig. 1(a) and (b). The spectra, consisting of two different quadrupole octets, were analyzed by the least-squares method using a double set of fitting parameters such as the quadrupole coupling constant (e^2Qq), the asymmetry parameter (η), the isomer shift (δ), the full-width at half-maximum (2Γ), and the intensity of each peak. The dashed curves in the figure represent the best fitted quadrupole-split octets, and the solid lines indicate the superimposed curves of the two octets. The obtained Mössbauer parameters are summarized in Table 1, together with results of the isolated I_3^- ions in the $[Ru(\eta\text{-}C_5H_5)_2I]I_3$ 7) and β-carotene–I_3 8) complexes. The e^2Qq values are converted to that of the ^{127}I nucleus.

The existence of two unequivalent iodine atoms observed in the Mössbauer spectrum of the DPPD–$I_{2.4}$ complex is consistent with the results of the crystallographic analysis, in which the iodine atoms are arranged in chains of linear I_3^- units.5) The similarity of the spectrum of the DPB–$I_{2.7}$ complex to that of DPPD–$I_{2.4}$ suggested that the iodine atoms build up an I_3^- unit. Later, this speculation was confirmed by the resonance Raman spectrum of the DPB–$I_{2.7}$ complex. It is now appropriate to assign the iodine with the larger quadrupole splitting to the central iodine atom (I_c) of the linear I_3^- unit, whereas the other to the two terminal iodine atoms (I_t). No broadening of the line width has been observed for I_t of the DPPD–$I_{2.4}$ complex, suggesting that the I_3^- unit is symmetric. On the other hand, the line width of I_t is broadened considerably in the DPB–$I_{2.7}$ complex compared with that of I_c and the broadening is enhanced in the region of higher velocity. This implies that the charge densities on the two I_t atoms are slightly different; i.e., the I_3^- unit is slightly asymmetric. Attempts to fit the spectrum with three unequivalent iodine sites were unsuccessful. Therefore, the values of e^2Qq, η, and δ given in Table 1 are

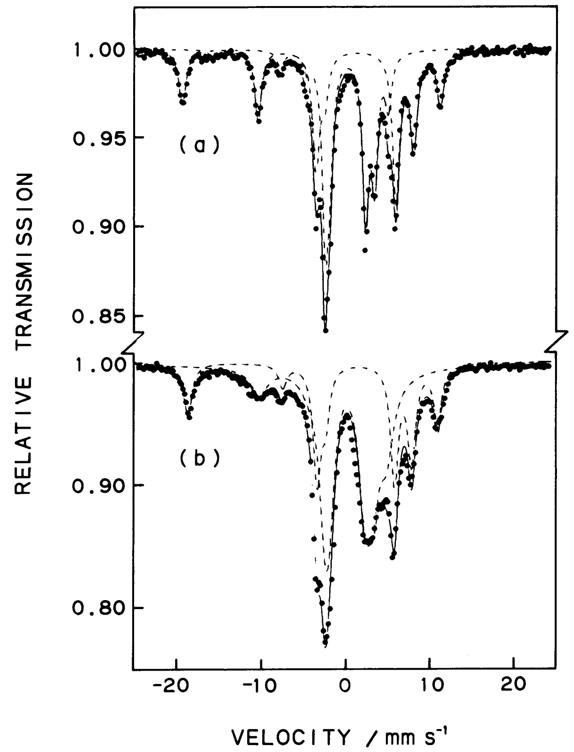


Fig. 1. ^{129}I Mössbauer spectra at 16 K of (a) *N,N'*-diphenyl-*p*-phenylenediamine-$I_{2.4}$ and (b) *N,N'*-diphenylbenzidine-$I_{2.7}$ complexes.

Table 1. ^{129}I Mössbauer Parameters for the Iodine Complexes of *N,N'*-Diphenyl-*p*-phenylenediamine and *N,N'*-Diphenylbenzidine, $[Ru(\eta\text{-}C_5H_5)_2I]I_3$, and β-Carotene–I_3

		e^2Qq a)	η	δ b)	2Γ	Area Ratio	U_p	h_p	Ref.
		MHz		mm s^{-1}	mm s^{-1}				
DPPD–$I_{2.4}$	I_c	−2347±20	0.05±0.04	1.32±0.04	1.00±0.06	1.0	1.02	1.24	
	I_t	−1183±20	0.04±0.04	0.25±0.04	0.93±0.06	1.6	0.52	0.53	
DPB–$I_{2.7}$	I_c	−2282±20	0.10±0.04	1.35±0.04	1.09±0.06	1.0	1.00	1.26	
	I_t	−1166±20	0.06±0.04	0.22±0.04	1.60±0.06 c)	1.7	0.51	0.51	
$[Ru(\eta\text{-}C_5H_5)_2I]I_3$	I_c	−2460±35	0.06±0.04	1.48±0.05	0.83±0.08	1.0	1.07	1.35	(7)
	I_t	−1152±35	0.06±0.04	0.25±0.05	0.85±0.08	1.6	0.50	0.53	
β-Carotene–I_3	I_c	−2445±20	0.05±0.04	1.59±0.04	1.04±0.10	1.0	1.07	1.42	(8)
	I_t	−1152±20	0.06±0.04	0.23±0.04	1.20±0.10	1.4	0.50	0.51	

a) Quadrupole coupling constants (e^2Qq) are converted to the ^{127}I nucleus. b) Isomer shifts (δ) are relative to the ZnTe source. c) The value is of the line width at zero velocity.

the means of those for the two I_t atoms. The ratios of the absorption areas of I_t and I_c were found to be 1.6:1 and 1.7:1 for the DPPD–$I_{2.4}$ and DPB–$I_{2.7}$ complexes, respectively, as shown in Table 1. The same tendency is found in the I_3^- ions of $[Ru(\eta\text{-}C_5H_5)_2I]I_3$[7] and β-carotene–I_3[8] complexes. The deviation from the composition ratio of 2:1 in I_3^- is explained in terms of the recoilless fraction and the saturation effect. The I_t atom is bonded to one adjacent I_c atom, whereas the I_c atom is bonded to two I_t atoms with the same bond strength. Therefore, the I_t atom is expected to have a lower recoilless fraction than the I_c atom. Since the effective absorber thickness for the I_t atom is twice that for the I_c atom, the saturation for I_t is more dominant than for I_c. These effects result in the decrease in the absorption area of I_t.

The values of e^2Qq, η, and δ are closely related to the charge distribution and the charge density of 5p-electrons localized on the iodine atom as follows:[9,10]

$$U_p = -e^2Qq_{\text{obsd}}/e^2Qq_{\text{atom}} = -N_z + (N_x + N_y)/2, \qquad (1)$$

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

$$\delta = 1.5\,h_p - 0.54\ (\text{mm s}^{-1}, \text{ for ZnTe source}), \qquad (3)$$

$$h_p = 6 - (N_x + N_y + N_z), \qquad (4)$$

where U_p is the number of unbalanced p-electrons, e^2Qq_{atom}, the atomic iodine quadrupole coupling constant, is equal to 2292.7 MHz for ^{127}I, and h_p is the number of 5p-electrons removed from the $5s^25p^6$ (I^-) configuration. N_x, N_y, and N_z are the populations of 5p-electrons in the x, y, and z directions, respectively. When the bonding of iodine is formed by only $5p_\sigma$-electrons, one expects the relationship $U_p = h_p = 1 \pm i$ to be valid; i is the ionic character. When 5s-electrons take part in bond formation (sp hybridization), the relationship $U_p > h_p$ is generally observed because of the decrease in the s-electron density at the nucleus. On the contrary, the participation of the $5p_\pi$-electrons (double bond character or intermolecular bonding in the x or y direction) leads to the relationship $U_p < h_p$. The values of U_p and h_p obtained for each iodine atom are given in Table 1, together with those for the isolated I_3^- ions in the $[Ru(\eta\text{-}C_5H_5)_2I]I_3$ and β-carotene–I_3 complexes.

DPPD–$I_{2.4}$ Complex: The U_p value is very close to the h_p value for the I_t atom in the DPPD–$I_{2.4}$ complex, suggesting that the bonding of I_t is mainly due to $5p_\sigma$-electrons. This result is consistent with the small η value of the atom, which implies that the bonding of the I_t atom is almost axially symmetric. Therefore, the I_t atom might not be interacting with the NH group of the DPPD molecule. Even if it should interact, the hydrogen bond with the NH group may be extremely weak. The I_t atom of the complex is found to be negatively charged by 0.48 e^- due to the values of U_p and h_p. It is generally observed that the terminal iodine is negatively charged by 0.50 e^- in the isolated I_3^- ion. The small deviation may be attributable to the weak covalent bond between I_3^- units. That is, the charge on the I_t atom is slightly delocalized along the chain of I_3^- units. This would lead to an increae in the charge density on the I_c atom. Actually, the values of U_p and h_p for I_c in this complex are smaller than those for I_c in the isolated I_3^- ions.

For the I_c atom in the DPPD–$I_{2.4}$ complex, the h_p value is larger than the U_p value. The same tendency is observed for the I_c atoms in the isolated I_3^- ions. This has been generally explained in terms of the presence of π-bonding in which the iodine donates $5p_\pi$-electrons to the neighbor atoms. However, it is quite difficult to consider the presence of a double bond or an intermolecular bond in the isolated I_3^- ion from the crystallographic data of $[Ru(\eta\text{-}C_5H_5)_2I]I_3$.[7] Furthermore, if the discrepancy is due to the π-bonding, the charge density on the I_c atom is estimated to be $+0.24\,e^-$ from the h_p value. This value is unreasonably high compared with the charge density calculated from the molecular orbital treatment of a delocalized three-center four-electron bonding. Lucken[11] has pointed out the contribution of $3d_\sigma$-electrons, on the central atom, to the linear Br_3^- bond formation. In his treatment the electronic structure of trihalide ions are descrided as a mixture of two extreme configurations, i.e., a delocalized three-center four-electron bond using only the valence p-electrons and covalent σ bonds between two $d_\sigma p_\sigma$ hybrid orbitals of the central atom and p_σ orbitals of two terminal atoms. This treatment is applicable to the interpretation of Mössbauer data for the triiodide ion. The contribution of the $4d_\sigma$ hybridization may lead to an increase in the effective s-electron density at the nucleus. This would markedly increase the δ value, but would hardly increase e^2Qq. In our previous paper[12] his treatment on the triiodide ion was concluded to be valid. It is interesting to apply $4d_\sigma$ hybridization to the central iodine atom of the bridging I_3^- unit in the complex, assuming no interaction with the NH group of the donor molecule. Using Eqs 4 and 5 in Ref. 12, the number of $4d_\sigma$ electrons promoted to the $5p_\sigma$-orbital can be easily estimated from the δ and e^2Qq. The h_p and h_d (the number of $4d_\sigma$-electron defect) obtained for the I_c atom are evaluated to be 0.84 and 0.17, respectively. That is, 0.17 e^- of the $4d_\sigma$-electron is promoted to the $5p_\sigma$-orbital. Consequently, the charge localized on the I_c atom is about $+0.01\,e^-$. Thus, the I_c atom has a slight positive charge. If the hydrogen bond exists between the I_c atom and the NH group, the contribution of the $4d_\sigma$ hybridization would decrease and, therefore, the charge density localized on the I_c atom would also decrease slightly. Judging from the small η value of the I_c atom, the hydrogen bond may be considerably weak. In the isolated I_3^- ion of $[Ru(\eta\text{-}C_5H_5)_2I]I_3$ the I_c atom is positively charged by $0.05\,e^-$ (evaluated in Ref. 12). This value is obviously larger than that of the bridging I_3^- unit.

It is concluded from the charge densities of the I_t and I_c atoms that in the bridging I_3^- unit a slight amount of charge is delocalized along the chain, ascribed to a weak covalent bond between the I_3^- units. It is likely that the delocalization of a small amount of charge is responsible for the electron conduction observed for the investigated complex. Furthermore, this complex is concluded to be a partially oxidized mixed-valence compound from the ratio of the iodine atom to the DPPD molecule, and the charge distribution of which is formulated as $(DPPD)^{+0.8}\,(I_3^-)_{0.8}$. A stacking column consisting of the partially oxidized DPPD molecules may govern hole conductivity.

DPB–$I_{2.7}$ Complex: The agreement between the U_P and h_P values is good for the I_t atom of the DPB–$I_{2.7}$ complex, although these values represent the mean for the two I_t atoms. Furthermore, the η value is small. These results suggest that the bonding of the I_t atoms is mainly due to the valence $5p_\sigma$-electrons in a similar manner as the I_t atom of the DPPD–$I_{2.4}$ complex. The average charge density for the two I_t atoms was evaluated to be $-0.49\,e^-$. On the other hand, it has been found for the I_c atom of the complex that e^2Qq , i.e, U_p, is smaller and the η is larger than those for the I_c atom of DPPD–$I_{2.4}$. These facts anticipate that an intermolecular bond (a hydrogen bond) exists between the I_c atom and the NH group of DPB in the perpendicular to the linear I_3^- bond. However, since the δ value, i.e., h_p, for the I_c atom of the complex is nearly equal to that of DPPD–$I_{2.4}$ (within experimental error), the charge density localized on the I_c atom might be almost the same as that of the DPPD–$I_{2.4}$ complex. That is, the charge on the I_c atom of the I_3^- unit is slightly positive in the DPB–$I_{2.7}$ complex, but less than that for the isolated I_3^- ion. From the ratio of each composition the present complex is shown to also be a partially oxidized, mixed-valence compound, the charge distribution of which is formulated as $(DPB)^{+0.9}(I_3^-)_{0.9}$ (similar to the DPPD–$I_{2.4}$ complex). If the donor molecule is arranged in a stacking column, whose structure has not been revealed yet, a large electrical conductivity would be expected for the complex. It is not clear from only the Mössbauer data whether the I_3^- unit exists as a successive chain or as an isolated form, although the Mössbauer data of the complex are close to those for the bridging I_3^- unit of the DPPD–$I_{2.4}$ complex rather than the isolated I_3^- ion. This question may be solved by the resonance Raman spectrum of the complex.

Resonance Raman Spectra. In Fig. 2 (a) and (b) are presented resonance Raman spectra of the DPPD–$I_{2.4}$ and DPB–$I_{2.7}$ complexes excited by the Ar^+ 514.5 nm line. Both spectra are very similar to each other, suggesting that the iodine species of these complexes exist in a similar chemical form. This is consistent with the Mössbauer spectra. The Raman bands at 107 and 213 cm^{-1} can be assigned to the symmetric stretching vibration of a linear I_3^- unit and its first overtone, respectively. Teitelbaum et al.[13,14] have reported that the isolated I_3^- ion in $(C_6H_5)_4\,As^+I_3^-$ shows a Raman band of the symmetric stretching vibration at 113 cm^{-1}, whereas the corresponding band is observed at 108 cm^{-1} for the bridging I_3^- unit in $(benzamide)_2H^+I_3^-$. The spectral pattern of the latter compound is similar to those observed for the present complexes. It is, therefore, concluded that the iodine species in the DPPD–$I_{2.4}$ and DPB–$I_{2.7}$ complexes exist as a successive chain of I_3^- units. This is consistent with the crystallographic data of the former.

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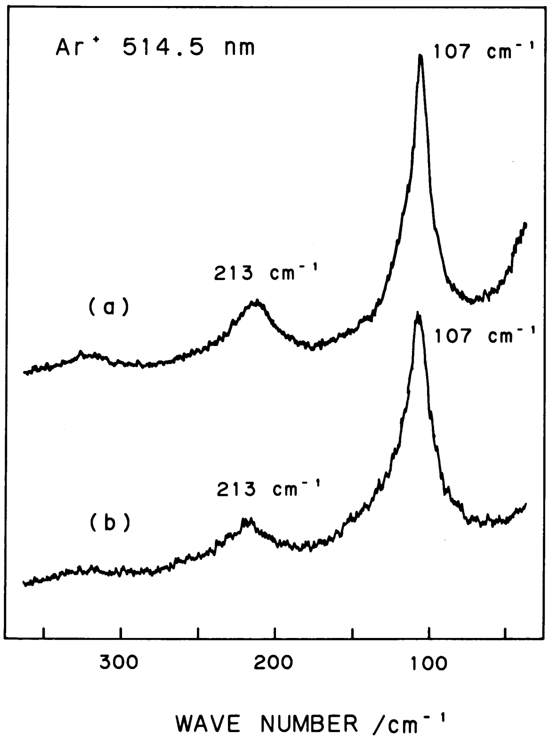

Fig. 2. Resonance Raman spectra excited by the Ar^+ 514.5 nm line of (a) *N,N′*-diphenyl-*p*-phenylenediamine–$I_{2.4}$ and (b) *N,N′*-diphenylbenzidine–$I_{2.7}$ complexes.

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