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^{127}I Mössbauer Spectra of Diphenyliodonium Halides

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The ^{127}I Mössbauer spectra have been obtained at 20 K for the diphenyliodonium halides, Ph_2IX (X=Cl, Br) and their derivatives, (*p*-R–C_6H_4) IPhBr (R=CH_3, CH_3O, Cl, COOH and NO_2). The valence electron populations of iodine are determined by the interactions with carbon atoms but not with bridging halogen atoms. The iodine–carbon bonds, having large *p*-character, are affected scarcely by the substituents at the *para*-position of the phenyl group. The large η values for those compounds are explained in terms of a lone pair electrons on iodine(III) atoms.

Among more than forty Mössbauer elements, iodine Mössbauer spectra provide especially definitive information on the electron configurations of the iodine atoms. The Mössbauer effect has been observed for both the naturally occurring stable isotope ^{127}I and the artificial radioisotope ^{129}I ($T_{1/2}=1.57\times10^7$ y). Although ^{129}I is the superior isotope from the Mössbauer spectroscopic point of view (narrower linewidth, larger $\Delta R/R$, and smaller recoil energy), ^{127}I has the greater advantage that we do not need to prepare the samples to be studied using a radioactive isotope on a small scale.[1)] Hence we have employed ^{127}I Mössbauer spectroscopy in the investigation of the bonding in the organo polyvalent iodine compounds.

Recently organic compounds containing main group elements such as phosphorus, sulfur, silicon, etc. in high valence states have acquired increasing interest because of their novelty and usefulness in synthetic applications. Many organo polyvalent iodine compounds, belonging to such a category, have been synthesized and applied to a variety of reactions, but little is known about their electronic states. We have therefore undertaken to elucidate the bonding in the organo polyvalent iodine compounds by means of ^{127}I Mössbauer spectroscopy. In this article we report the ^{127}I Mössbauer spectra of a series of iodine(III) compounds, i.e. diphenyliodonium halides (Ph_2IX; X=Cl, Br) and their derivatives which are known to be excellent arylating reagents.

Although the ^{127}I Mössbauer spectra of Ph_2ICl and Ph_2IBr have been reported by Birchall and Myers,[2)] their large asymmetry parameters have not been interpreted. Thus we intended to clarify the origin of the asymmetric electron distribution on the *xy* plane which causes the large asymmetry parameters. Furthermore, since substitution effects of the *para*-position in the phenyl ligand on the ^{127}I Mössbauer spectra have not been examined yet, we also measured the ^{127}I Mössbauer spectra for various *p*-substituted derivatives.

Experimental

Materials. Diphenyliodonium halides, Ph_2IX (X=Cl, Br)[3)] and substituted dipheyliodonium bromides, (*p*-R–C_6H_4) IPhBr (R=CH_3, CH_3O, Cl, COOH, NO_2)[3,4)] were prepared according to the literature. The CHN analytical values for the Mössbauer samples agreed with the calculated ones within 0.3%.

Measurements of the ^{127}I Mössbauer Spectra. ^{127}I Mössbauer spectra were recorded as described previously[5)] with the samples and the $Zn^{127m}Te$ source kept at 20 K in a cryostat with a closed-cycle refrigerator.[6)] The source (988 MBq) was prepared by a high-flux neutron (2×10^{14} cm^{-2} s^{-1}) irradiation of $Zn^{126}Te$ at the reactor core of JRR-2 of Japan Atomic Energy Research Institute. The Doppler velocity of the source was measured using a laser interferometer and calibrated by measuring the ^{57}Fe Mössbauer spectrum of an iron foil at 20 K using a ^{57}Co-(Rh) source (1.5 GBq). The spectra were analyzed by using the transmission-integral method developed by Shenoy et al.[7)]

Results and Discussion

The quadrupole-split spectra are all very similar. Typical spectra are shown in Fig. 1 for (*p*-R–C_6H_4)-IPhBr (R=H, CH_3, COOH). The Mössbauer parameters are summarized in Table 1. Agreement between our parameters and those of Birchall and Myers for Ph_2IBr ($\delta=-0.68$ mm s^{-1}, e^2qQ=1970 MHz, η=0.36[2)]) is very good but that for Ph_2ICl ($\delta=-0.54$ mm s^{-1}, e^2qQ=2044 MHz, η=0.31[2)]) is rather poor though they are essentially the same within the experimental error.

The quadrupole coupling constant, e^2qQ, is positive for all the compounds. Since the ground state nuclear quadrupole moment, eQ, for ^{127}I is negative, the sign of the electric field gradient component eq_{zz} ($=eq$) must thus be negative, implying that the principal z axis has a higher *p*-electron density than the average of those along the x and y axes. According to the X-ray crystal analyses of Ph_2IX (X=Cl, Br, I),[8)] these compounds have planar dimeric structures in which two Ph_2I^+ ions are held together by two bridging X^- ions, the lone pair electrons being located along the out-of-plane direction. The positive signs of e^2qQ are thus those expected from

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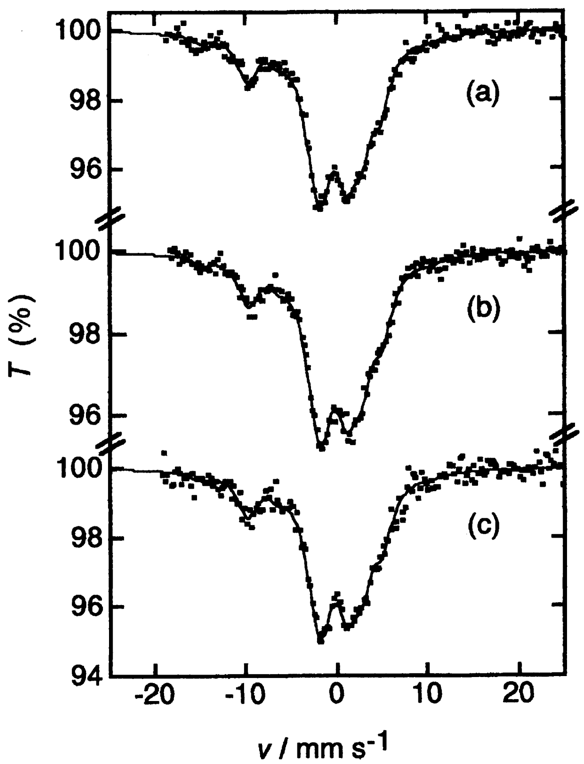


Fig. 1. ^{127}I Mössbauer spectra for diphenyliodonium bromides at 20 K. (a): Ph_2IBr, (b): (p-CH_3–C_6H_4)-IPhBr, (c): (p-HOOC–C_6H_4)IPhBr.

Table 1. ^{127}I Mössbauer Parameters at 20 K for Diphenyliodonium Salts

Compound	$\delta^{a)}$ mm s^{-1} (±0.05)	$e^2qQ^{b)}$ MHz (±25)	η (±0.05)	Γ mm s^{-1} (±0.05)
Ph_2ICl	−0.64	1986	0.40	2.55
(p-R–C_6H_4)IPhBr				
R=H	−0.66	1987	0.38	2.54
CH_3	−0.63	1982	0.40	2.64
CH_3O	−0.67	1990	0.40	2.54
Cl	−0.68	1985	0.40	2.54
COOH	−0.65	2005	0.39	2.54
NO_2	−0.67	1996	0.43	2.73

a) relative to KI at 20 K. b) 1 MHz corresponds to 0.02153 mm s^{-1} for ^{127}I.

the molecular structures, indicating the z axis along the out-of-plane directions.

The non-zero asymmetry parameters, η suggest that there are some differences in the electron densities in the $5p_x$ and $5p_y$ orbitals. The η values for the asymmetrically substituted compounds do not differ much from that of the symmetric salt Ph_2IBr, suggesting that substitution of the *para*-position of the phenyl group hardly influences the electronic state of the iodine atom.

The values of δ, e^2qQ, and η are closely related to the electron configurations of the iodine atoms[1,9]

$$U_p = -\frac{e^2qQ}{(e^2qQ)_{\text{atom}}} = -N_z + \frac{1}{2}(N_x + N_y), \tag{1}$$

$$\eta = \frac{q_{xx} - q_{yy}}{q} = -\frac{3}{2}\frac{N_x - N_y}{U_p}, \tag{2}$$

$$h_p = 6 - (N_x + N_y + N_z), \tag{3}$$

$$\delta = K\gamma[-h_s + \gamma(h_s + h_p)(2 - h_s)], \tag{4}$$

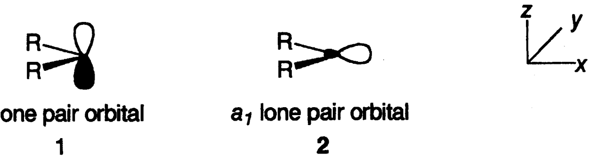
$$h_s = 2 - N_s, \tag{5}$$

where U_p is the p electron imbalance, and $(e^2qQ)_{\text{atom}}$ (i.e. the quadrupole coupling constant of an ^{127}I atom) has the value of 2293 MHz;[10] h_s and h_p are the number of s and p electron holes, respectively. N_s, N_x, N_y, and N_z are the populations in the iodine 5s, $5p_x$, $5p_y$, and $5p_z$ obtitals, respectively. The values of 0.078,[10,11] and −0.50 mm s^{-1} [12,13] are usually adopted for the shielding constant, γ, and the proportionality constant, $2K\gamma$, respectively. Since the $5p_z$ orbital of iodine in diphenyliodonium halides are occupied by the b_1 lone pair electrons (**1** in the Scheme 1), it is reasonable to assume N_z to be 2.00. We can thus estimate N_x and N_y using Eqs. 1 and 2. Applying the h_p values calculated from Eq. 3 to Eq. 4, the h_s values are obtained, which are correlated with N_s values by Eq. 5. The h_s and h_p values, and the valence electron populations thus estimated are presented in Table 2 together with the charge number on the iodine atom, Z_I, which is calculated by the relation

$$Z_I = 7 - (N_s + N_x + N_y + N_z) = -1 + h_s + h_p \tag{6}$$

The x axis is expected from symmetry considerations to coincide with the line that bisects the C–I–C angle.

The populations of the 5s and 5p electrons are essentially invariant among the compounds studied. The sum of the valence electrons, N_t, for Ph_2ICl is less than



Scheme 1.

Table 2. Populations of Valence Electrons and Charge on Iodine Atom for Diphenyliodonium Salts Estimated from ^{127}I Mössbauer Parameters

Compound	h_s	h_p	N_s	N_x	N_y	N_z	N_t	Z_I
Ph_2ICl	0.07	1.73	1.93	1.25	1.02	2.00	6.19	+0.81
(p-R–C_6H_4)IPhBr								
R=H	0.07	1.73	1.93	1.24	1.02	2.00	6.20	+0.80
CH_3	0.08	1.73	1.92	1.25	1.02	2.00	6.19	+0.81
CH_3O	0.07	1.74	1.94	1.25	1.02	2.00	6.20	+0.80
Cl	0.06	1.73	1.94	1.25	1.02	2.00	6.21	+0.79
COOH	0.07	1.75	1.93	1.24	1.01	2.00	6.18	+0.82
NO_2	0.06	1.72	1.94	1.27	1.02	2.00	6.23	+0.78

that for Ph_2IBr by 0.01 e; i.e. the electrons on the iodine atom in Ph_2ICl are more attracted to the bridging halogen atoms than those in Ph_2IBr. Although this agrees with the expectation from the electron withdrawal ability of the bridging atoms, the fact that the difference between Ph_2ICl and Ph_2IBr is quite small suggests that the bridging halogen atoms do not affect the electron configuraions of iodine atoms significantly and interaction between Ph_2I moiety and bridging atoms is thus considered to be quite ionic. This is in accordance not only with the suggestion from the Mössbauer spectra[2)] but also with the results from X-ray structural analyses[8)] and far-infrared spectra.[14)]

Now we consider the relative importance of the 5s and 5p orbitals of iodine in the iodine–carbon bonds. The h_s values are small (0.06—0.08), implying the 5s orbitals are almost completely occupied. In contrast, the rather large h_p values (1.72—1.75) mean that the p_x and p_y electrons are considerably attracted to the carbon atoms. To estimate the degrees of the contribution of s orbitals, the $S\,\%$ values were calculated from[15)]

$$S\% = \frac{100h_s}{h_p + h_s} \tag{7}$$

The $S\,\%$ values obtained are quite small, 3—4%. This implies that the iodine p orbitals essentially dominate the iodine–carbon bonds.

Clearly there are some differences in the populations between the p_x and p_y orbitals. Since the bond angles C–I–C and X–I–X are nearly rectangular, the I $5p_x$ and I $5p_y$ orbitals are expected to interact equally with the C $2p_x$ and C $2p_y$, and p_x and p_y orbitals of halogen atoms. The observed imbalance of the electron populations in $5p_x$ and $5p_y$ orbitals can not be interpreted by the equivalent distribution of the bonding electrons.

Molecular orbital calculations for $I(CH_3)_2^+$ and its salt $I_2(CH_3)_4Cl_2$ as model compounds[16)] were carried out to obtain further information on the electronic states of the dipheyliodonium halides. The extended Hückel calculations showed that the electronic structure of $I(CH_3)_2$ moiety in $I_2(CH_3)_4Cl_2$ was essentially the same as that of $I(CH_3)_2^+$, suggesting the interactions between the iodine and bridging chlorine atoms are fairly small and ionic. This supports the bonding model of $(Ph_2I)^+X^-$ mentioned above. Thus we may discuss the electronic structure of diphenyliodonium halides by examining the electronic structure of $I(CH_3)_2^+$. The highest occupied orbital (HOMO) of $I(CH_3)_2^+$ was a b_1 lone pair orbital (**1** in Scheme 1) and second HOMO was an a_1 lone pair (**2** in Scheme 1). The Mulliken population analysis showed that the valence electron population of iodine was $5s^{1.77}$ $5p_x^{1.46}$ $5p_y^{1.13}$ $5p_z^{1.99}$, showing the non-equivalent distribution of the $5p_x$ and $5p_y$ orbitals. The atomic orbital bond populations indicate that the a_1 lone pair orbital contributes to the large $5p_x$ population.

The a_1 lone pair orbital may arise from the fact that two lobes of the I $5p_x$ orbital interact differently, one with two carbon atoms, the other with none. If the bridging halogen atoms would interact with I $5p_x$ orbital strongly so that two lobes might interact equally to four coordinating atoms (thus producing no a_1 lone pair orbital), the η value would be diminished. Actually planar I_2Cl_6, in which the interaction between the iodine and bridging chlorine atoms is stronger than that in Ph_2ICl, gives a quite small η value of 0.09.[2)] The average bond length of I–Cl (bridge) in I_2Cl_6 (270 pm)[17)] is substantially smaller than that in Ph_2ICl (308.5 pm).[8)] Hence the large η values of 0.4 for diphenyliodonium halides are further evidence for the weak interaction between the iodine and halogen atoms.

Finally we will examine the substitution effect. The electron populations for the asymmetrically substituted diphenyliodonium bromides differ scarcely from one another. Both the variation of the populations and the charge on iodine atom are smaller in the compounds studied than those for the corresponding *para*-substituted (dicholroiodo)benzenes, $PhICl_2$.[18)] The effects of phenyl-group substituents on the ^{127}I Mössbauer parameters of organoiodine compounds have been rarely studied. The only study is the investigation by Lazarus and Thomas.[15)] They have compared the ^{127}I Mössbauer spectra of fluorosubstituted iodobenzenes and found that h_p increased slightly on substitution of a phenyl hydrogen atom. According to their results, the increment of h_p is especially small (0.010) for the *para*-substituted derivative. The degree of variation of the h_p values in diphenyliodonium halides is of the same magnitude as that for the *para*-substituted fluorobenzene. The small variation of h_p for *para*-substitution would arise from the fact that the substituents are furthest from the iodine atom. The effects of the substitution upon the valence electron population of an iodine atom are considered to be weakened appreciably by the carbon–carbon bonds in the phenyl group, and the substituents consequently do not significantly affect the iodine–carbon interactions, which are dominant in determining the Mössbauer parameters. We intended to obtain further information on the electronic states of these compounds from the ^{13}C NMR spectra, but such attempts were unsuccessful because of the highly reactive nature of the compounds towards the usual NMR solvents.

The substituent effects of diphenyliodonium salts in the arylation reactions

$$\text{R–C}_6\text{H}_4\text{IPh}^+ + \text{X}^- \rightarrow \text{R–C}_6\text{H}_4\text{X} + \text{PhI}$$

have been studied.[19,20)] The mechanistic studies have shown that nucleophilic and radical process operate competitively.[19)] In the nucleophilic displacement reaction, the nucleophilic attack of X^- at *ipso*-carbon atom is involved, so the reaction rate depends on the *p*-substituents, which affect the electron densities of *ipso*-

carbons. On the other hand, radical process is initiated by electron transfer from X^- to iodine atom and would be affected by charges on the iodine atoms. However this process is expceted to be independent on the substituents because the charges on iodine atoms are merely changed by substituents as judged from this ^{127}I Mössbauer study. Indeed no substituents effect has been observed in the radical processes.[20] Thus the present Mössbauer spectroscopic study is consistent with these mechanistic studies.

In summary, the electronic state of diphenyliodonium halides has been made clear by the Mössbauer spectra; the electron configurations of iodine atoms are determined by the iodine–carbon bonding, having a large *p*-character, whereas the bonding between the iodine and bridging halogen atoms are very weak. The large η values attributed to the lone pair character of the iodine $5p_x$ orbital are further evidence for the ionic nature of the compounds. The populations of the valence electrons of the iodine atoms are scarcely affected by *para*-substituents on the phenyl ring.

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