Iodine-127 Mössbauer Spectra of $[I_2][Sb_2F_{11}]$† and Some Polyhalide Anions

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The ^{127}I Mössbauer spectra of $[I_2][Sb_2F_{11}]$ and some polyhalide anions have been recorded and the Mössbauer parameters discussed in terms of their structures. A reasonable correlation is found between the quadrupole coupling constant and ligand electronegativity. The lack of consistency in reporting isomer-shift data for ^{127}I or ^{129}I is remarked upon and a plea to adopt either $Na_3[H_2IO_6]$ or CuI as a reference standard is made.

THE use of iodine Mössbauer spectroscopy in chemistry and physics has been reviewed by a number of workers.[1-4] The 129 isotope has been favoured over the 127 isotope because of the superior resolution it offers. However, ^{129}I suffers a disadvantage since one must carry out chemical reactions with a radioisotope on a small scale, and it is rare that the products of such reactions are authenticated analytically. This could be a serious problem where complex reactions occur. This disadvantage does not arise for the naturally occurring ^{127}I and the lack of an extensive literature for this isotope is no doubt due to the large natural linewidth ($2\Gamma = 2.54$ mm s^{-1}) and the necessity of carrying out measurements at liquid-helium temperatures. However, the ground-state quadrupole moment is quite large (-0.79 b)[‡] and $^{127}Q_e/^{127}Q_g$ is 0.892,[5] which means that moderate deviation from cubic symmetry results in some splitting of the spectrum into the eight component lines. Even with the large linewidth such spectra can be successfully computer fitted to give reliable hyperfine parameters. This is particularly true if full transmission-integral procedures are incorporated, and indeed Lazarus and Thomas [6] have demonstrated that, in order to obtain reliable data, thickness effects must be taken into account. Now that suitable computer programs are available [7,8] for the analysis of complex spectra it is anticipated that the number of experiments with ^{127}I will increase in the future.

Most of the applications of ^{127}I Mössbauer spectroscopy have centred around the correlation of the Mössbauer parameters with the structure of the molecule and the nature of the bonding to iodine. It has become customary to use empirical relationships to convert isomer shifts and quadrupole coupling constants into *s*- and *p*-orbital populations. For example U_p, the imbalance in the *p* orbitals, is related to the measured quadrupole coupling constant by (1), where $e^2q_{\mathrm{at}}{}^{127}Q_g/h = 2\,293$ MHz; the latter quantity is the value for an iodine atom and is known from n.q.r. measurements.[9] The isomer shift is related to h_s and h_p, the magnitudes of the electron holes in the iodine 5*s* and 5*p* orbitals relative to the closed shell of the iodide ion, by expression (2).

$$U_p = \frac{-e^2q_{\mathrm{mol}}{}^{127}Q_g/h}{e^2q_{\mathrm{at}}{}^{127}Q_g/h} \quad (1)$$

$$\text{Isomer shift} = K[-h_s + \gamma(h_s + h_p)\,(2 - h_s)] \quad (2)$$

In order to use (2) one must first evaluate the constants K and γ. There now appears to be agreement that 0.07 is the best value for γ.[2-4] Perlow and Perlow [10] have used U_p, calculated from the measured quadrupole coupling constants, together with the isomer shifts for HI (anhydrous), I_2, $K[ICl_2]\cdot H_2O$, ICl, and $K[ICl_4]\cdot H_2O$ to obtain a value for $2K\gamma$ of -0.56 mm s^{-1}. This leads to expression (3) for the isomer shift.[2] Expression (3) is

$$^{127}\delta_{\mathrm{ZnTe}} = -4.0[-h_s + 0.07(h_p + h_s)(2 - h_s)] + 0.16 \simeq 3.44\,h_s - 0.56\,h_p + 0.16 \quad (3)$$

then used exclusively to describe the bonding in a wide variety of iodine compounds. Similar expressions are derived for ^{129}I and only occasionally are these simple empirical equations questioned.[11] In establishing (3) it was assumed [10] that there was no involvement of *s* electrons in the bonds to iodine. This may or may not be a good assumption, particularly for HI (anhydrous). There is also some question as to which value for the isomer shift of iodine was used in Figure 2 of ref. 10, in order to obtain the value for $2K\gamma$. The shift used for I_2 relative to I^- was -0.58 mm s^{-1} rather than the -0.74 mm s^{-1} shown in Figure 1 of ref. 10. However, this error may have been partially compensated for by the fact that the isomer shift measured by Perlow and Perlow [10] for $^{127}I_2$ relative to ZnTe appears to be too negative. Greenwood and Gibb [2] have plotted $\delta(^{127}I)$ *versus* $\delta(^{129}I)$ and it is seen that only I_2 deviates seriously from the best fit to the data. A number of workers have measured the spectrum of $^{129}I_2$ and are in reasonable agreement as to its isomer shift relative to ZnTe, namely 0.9 mm s^{-1}.[2,3,11] Conversion of this value into the 127 equivalent, using the data of Jones and Warren,[12] gives -0.31 mm s^{-1} for $\delta(^{127}I_2)$. Relative to the iodide standard of Perlow and Perlow [10] a shift of $-0.31 - (+0.16) = -0.47$ mm s^{-1} is found for $\delta(^{127}I_2)$. This is somewhat closer to the value used to establish equation (3), but is more positive than the measured value. These discrepancies are further complicated by the lack of internal consistency in the original paper. The data using the ZnTe source are claimed to be more reliable than those for the H_6TeO_6 source,[10] yet it is interesting to note that with this latter source $\delta(^{127}I_2) - \delta(^{127}KI)$ is -0.48 mm s^{-1}, in rather good agreement with the value calculated from the ^{129}I data.

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† Di-iodine undecafluorodiantimonate(1−).

‡ Throughout this paper: 1 b (barn) = 10^{-28} m^2.

It is apparent from the above that a number of anomalies exist which need further study. Since data already exist for the $[ICl_2]^-$ (ref. 10) and $[I_3]^-$ (ref. 3) ions we have chosen to examine the $[X{-}I{-}Y]^-$ series of anions, where X and Y can be F, Cl, Br, or I. These linear anions provide us with a series of compounds in which systematic changes made in the ligands surrounding the central iodine can possibly be correlated with Mössbauer parameters. Our data are compared to the existing data for $K[^{127}ICl_2]\cdot H_2O$ and $Cs[^{129}I_3]$. We find systematic trends in quadrupole coupling constants with ligand electronegativity for all except the cases where X = F. An attempt is made to systematize the isomer-shift data and a new isomer-shift expression is derived. The ^{127}I Mössbauer parameters for I_2, $[I_2][Sb_2F_{11}]$, and $[I(py)_2][NO_3]$ (py = pyridine) are also reported and discussed in terms of their known structures.

EXPERIMENTAL

Samples of $[N(CH_3)_4][IBrCl]$, $[N(CH_3)_4][I_2Br]$, $[N(CH_2CH_3)_4][I_2Cl]$, and $[N(CH_2CH_3)_4][IBr_2]$ were prepared according to standard methods [13,14] by mixing tetra-alkylammonium halide salts with the appropriate halogens. The caesium salts of $[IBrF]^-$ and $[IClF]^-$ were prepared by mixing CsF with a large excess of IBr and ICl respectively and warming to *ca.* 50 °C. After allowing the CsF to react completely the excess of IBr or ICl was removed by grinding the material to powder and pumping under high vacuum. All manipulations were carried out under a dry nitrogen atmosphere in a glove-box. The iodine content was determined by addition of a weighed quantity of the polyhalide salt to an excess of aqueous KI and titration with standard $Na_2[S_2O_3]$ solution {Found: I, 30.3. Calc. for $[N(CH_2CH_3)_4][IBr_2]$: 30.45. Found: I, 63.65. Calc. for $[N(CH_3)_4][I_2Br]$: I, 62.25. Found: I, 39.95. Calc. for $[N(CH_3)_4][IBrCl]$: I, 40.1. Found: I, 59.65. Calc. for $[N(CH_2CH_3)_4][I_2Cl]$: I, 60.5. Found: I, 36.8. Calc. for Cs[IBrF]: I, 35.4. Found: I, 45.25. Calc. for Cs[IClF]: I, 40.4%}. The salt $[I_2][Sb_2F_{11}]$ was prepared by the method of Gillespie and co-workers [15] by treating I_2 with SbF_5 in SO_2 solvent. The compound $[I(py)_2][NO_3]$ was prepared by the method of Arotsky and Symons.[16]

Mössbauer spectra (^{127}I) were recorded using an Elscint AME 40 drive system operating in the constant-acceleration mode with automatic folding of the triangular waveform. The transmitted radiation was detected by a Harshaw NaI (Tl) scintillation counter and fed to a Tracor–Northern multichannel analyzer operating in the up–down multiscaling mode. Samples were finely ground powders, intimately mixed with boron nitride, and sandwiched in a copper holder between thin aluminium foils. The samples contained $\simeq 30$ mg of natural iodine per cm^2. The $Zn^{127}Te$ source was purchased from New England Nuclear Corporation. Both sample and source were maintained at liquid-helium temperature (4.2 K), in a detachable-tail research cryostat manufactured by Janis Research Company. Temperatures were monitored by means of a calibrated Allen–Bradley 47-Ω 0.25-W carbon resistor and a temperature controller (Cryogenic Research Company). The velocity scale was calibrated using an iron-foil absorber against a $^{57}Co/Rh$ source. All spectra were computer fitted using a program previously described which incorporates full transmission-integral procedures.[8] The two-site spectra, *i.e.* $[I_2Cl]^-$ and $[I_2Br]^-$, were each fitted to two unique isomer shifts by assigning each iodine site to 50% absorption. This latter constraint was then removed with a resulting moderate improvement in the value of (χ^2/degrees of freedom). For $[N(CH_3)_4][I_2Br]$ and $[N(CH_2CH_3)_4][I_2Cl]$ the value of the (χ^2/degrees of freedom) changed from 0.94 to 0.93 (contribution of central iodine, 0.57) and from 1.14 to 1.09 (contribution of central iodine, 0.62) respectively.

RESULTS AND DISCUSSION

The data from the computer analysis of the spectra are summarized in the Table. We have also included literature data for $K[^{127}ICl_2]\cdot H_2O$,[10] $^{127}I_2$,[10] $Cs[^{129}I_3]$,[3] $^{129}I_2$,[11] and $[^{129}I(py)_2][NO_3]$:[11] the ^{129}I isomer shifts have been converted into ^{127}I shifts by multiplying the ^{129}I data by -0.345.[12] The absorber linewidths, which were allowed to vary in the transmission-integral fitting, are slightly greater than the natural width ($\Gamma_{nat} = 1.25$ mm s^{-1}) except for the two fluoro-complexes which have about twice the natural width. The spectra of these two compounds are also not fitted quite as well as the others.

Our data for iodine are compared to the literature data at 4.2 K. Agreement is quite good for the $e^2q^{127}Q_g/h$ and η parameters but we are in disagreement with the generally accepted value for the isomer shift of $^{127}I_2$, namely -0.58 mm s^{-1} relative to ZnTe or -1.60 mm s^{-1} relative to $Na[H_2IO_6]$.[10] However, we feel that our value is more realistic since it is in excellent agreement with the converted $^{129}I_2$ shifts: $+4.01 \times -0.345 = -1.38$ mm s^{-1}.[11,12] Our shift, namely -1.30 mm s^{-1} (-0.26 mm s^{-1} relative to ZnTe), is the same as that measured by Perlow and Perlow [10] (-1.28 mm s^{-1} relative to $Na_3[H_2IO_6]$) with a telluric acid source.

Oxidation of iodine with antimony pentafluoride produces $[I_2][Sb_2F_{11}]$ whose vibrational spectra and crystal structure have been reported.[15] Analysis of the Mössbauer spectrum of the compound gives an isomer shift which is more positive and a quadrupole coupling constant which is smaller than in I_2. Since $\delta R/R$ is negative for ^{127}I, the more positive shift for $[I_2]^+$ means that the *s*-electron density at iodine has decreased. The most reasonable interpretation of the changes on oxidation is based upon a molecular-orbital (m.o.) description. The m.o. description for I_2 is such that there is one net $\sigma(p_z)$ bond, *i.e.* $\sigma_g{}^2(p_z)\pi_u{}^2(p_x)\pi_u{}^2(p_y)\pi_g{}^{*2}(p_x)\pi_g{}^{*2}(p_y)$. Oxidation results in the removal of a $\pi_g{}^*$ electron and hence an increase in the *p* bond order: the I–I distance shortens from 2.66 to 2.55 Å.[15] The increase in *p*-bonding electron density shields the 5*s* electrons, reduces the *s*-electron density, and the isomer shift becomes more positive. Removal of this antibonding π electron means that the iodine–iodine bond in $[I_2]^+$ has acquired π character. The *p*-electron imbalance U_p is related to the electron occupation numbers U_x, U_y, and U_z of the p_x, p_y, and p_z orbitals by (4).[2,3,9] For each iodine in the

$$U_p = -U_z + \tfrac{1}{2}(U_x + U_y) \qquad (4)$$

iodine molecule U_p becomes equal to $-U_z + 2$, while for $[I_2]^+$, $U_x = -U_y + 1.75$. In our fitting procedure we find that η is essentially zero and hence $U_x = U_y = 1.75$.

U_p is therefore reduced and we observe a decrease in the quadrupole coupling constant to −1 858 MHz for $[I_2]^+$. This gives a value for U_p of 0.81 (Table) and U_z is therefore 1.75 − 0.81 = 0.94. Using these values for U_x, U_y, and U_p we obtain from (5) [2] a value for h_p, the number of

$$h_p = 6 - (U_x + U_y + U_z) \qquad (5)$$

p holes, of 1.56. Calculation of h_p using equation (3), and our isomer shift relative to ZnTe (−0.08 mm s^{-1}), gives a value of 0.43, not in very good agreement with the h_p value estimated above.

Iodine-127 Mössbauer data and orbital occupation numbers

Compound	Isomer shift mm s^{-1}	$e^2q^{127}Q_g/h$ MHz	η	Γ mm s^{-1}	TA [a]	χ^2/degrees of freedom	U_p	h_p ($h_s = 0$)	h_s ($h_p = U_p$)
I_2	−1.30 ±0.04	−2 193 ±18	0.17 ±0.04	1.85 ±0.15	1.04 ±0.07	1.17	0.96	0.80	0.03
	−1.28 ±0.13 [b]	−2 238 ±20	0.12 ±0.02						
	−1.60 ±0.04 [c]								
	−1.38 ±0.03 [d]	−2 154 ±18	0.16 ±0.03						
$[I_2][Sb_2F_{11}]$	−1.12 ±0.05	−1 858 ±36	0.08 ±0.11	1.67 ±0.18	1.01 ±0.96	1.45	0.81	0.44	0.06
$Cs[I_3]$	−1.64 ±0.04 [e]	−2 515 ±20					1.10	1.48	−0.06
	−1.29 ±0.04 [e]	−1 460 ±14					0.64	0.78	−0.02
	−1.16 ±0.04 [e]	−820 ±25					0.36	0.52	−0.03
$[N(CH_3)_4][BrI_2]$	−1.81 ±0.11	−2 583 ±55		1.43 ±0.20	0.84 ±0.09	0.93	1.13	1.82	−0.11
	−0.64 ±0.13	−1 580 ±75		1.43 ±0.20			0.69	−0.52	0.20
$[N(C_2H_5)_4][I_2Cl]$	−1.40 ±0.07	−2 769 ±37		1.47 ±0.17	1.49 ±0.14	1.09	1.21	1.00	0.03
	−1.22 ±0.12	−1 264 ±75		1.47 ±0.17			0.55	0.64	−0.01
$[N(CH_3)_4][IBrCl]$	−1.42 ±0.05	−3 048 ±18		1.58 ±0.14	1.49 ±0.10	0.99	1.33	1.04	0.05
$K[ICl_2]\cdot H_2O$	−1.28 ±0.04 [b]	−3 189 ±20					1.39	0.76 1.40	0.10 0.0
	−1.60 ±0.04 [c]								
$Cs[IClF]$	−1.64 ±0.05	−3 029 ±36	0.16 ±0.03	2.47 ±0.17	1.45 ±0.07	1.36	1.32	1.48	−0.03
$Cs[IBrF]$	−1.53 ±0.05	−2 769 ±18	0.24 ±0.02	2.25 ±0.16	1.75 ±0.09	1.66	1.21	1.26	−0.01
$[N(C_2H_5)_4][IBr_2]$	−1.36 ±0.05	−2 695 ±36	0.19 ±0.03	1.95 ±0.17	1.21 ±0.08	1.16	1.18	0.92	0.04
$[I(C_5H_5N)_2][NO_3]$	−1.62 ±0.03	−3 159 ±18	0.08 ±0.04	1.42 ±0.10	1.69 ±0.10	1.15	1.38	1.44	−0.01
	−1.64 ±0.03 [d]	−3 239 ±20	0.03 ±0.03						
H_5IO_6	0	0		2.46 ±0.33	0.11 ±0.01	0.87			
	(+1.03 ±0.09) [f]								
$Na_3[H_2IO_6]$	(+1.02 ±0.01) [c]								
I^-	−0.86 [b]								

[a] Dimensionless absorber thickness, see ref. 8. [b] Ref. 10 (H_6TeO_6 source). [c] Ref. 10 (ZnTe source). [d] Ref. 11 (converted from ^{129}I data). [e] Ref. 19 (converted from ^{129}I data). [f] Isomer shift of H_5IO_6 relative to ZnTe source.

The empirical equation (3) is widely used to calculate h_p, or h_s if the assumption is made that $U_p = h_p$. However, in the introduction we have cast some doubt upon the validity of this expression. The expression obviously is satisfactory for $[ICl_2]^-$, since this was used to establish equation (3), but for the structurally related $[I_3]^-$ the values of h_p for the central iodine, calculated from e^2qQ_g/h and the isomer shift, are 1.10 and 1.29 respectively. Here the agreement is not as good. In an attempt to verify these simple relationships we have examined a series of compounds containing the $[X–I–Y]^-$ anion. Like the anions in $K[ICl_2]\cdot H_2O$ [10] and the $[I_3]^-$ salts,[17–19] these anions are essentially linear. The structures of $Cs[I_3]$,[20] $Cs[I_2Br]$,[21] and $Cs[IBr_2]$ [22] have been reported, and vibrational spectroscopy has been used to infer linearity in a number of the other anions.[23]

We have examined compounds containing all of the possible $[X–I–Y]^-$ anions for which Mössbauer data did not previously exist. The Mössbauer data for Cs[F–I–Cl] and Cs[F–I–Br] are the first spectroscopic evidence for these species which have not been prepared before. We are unable to synthesize pure Cs[F–I–I]. Figure 1 shows spectra of $[N(CH_3)_4][IBrCl]$ and $[N(C_2H_5)_4][I_2Cl]$.

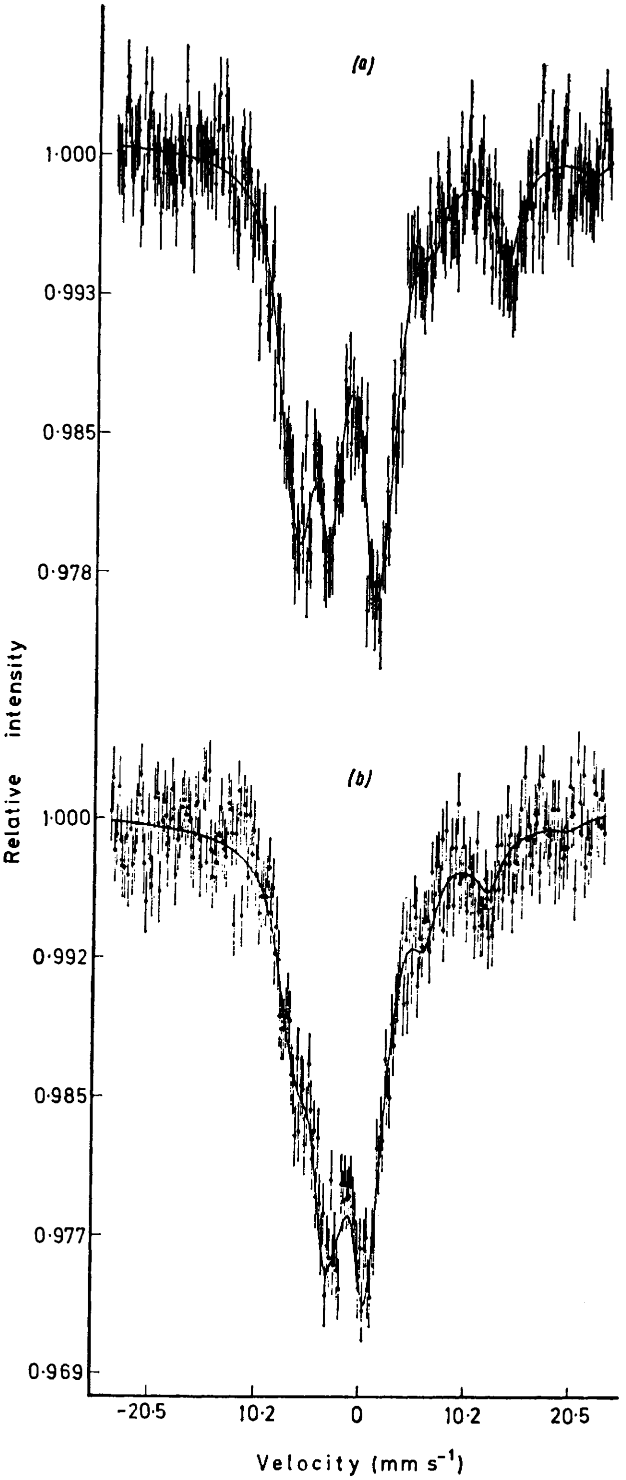

FIGURE 1 Iodine-127 Mössbauer spectrum at 4.2 K of (*a*) $[N(CH_3)_4][IBrCl]$ and (*b*) $[N(C_2H_5)_4][I_2Cl]$. The solid lines are the best fits to the data

All of the spectra are similar with the line due to transition number 2 [1,2] being well resolved at high positive velocity. This means that e^2qQ_g/h is negative for all of the compounds as would be expected for a central iodine with the X and Y halogens along the internuclear axis, taken as z, and the non-bonding electron pairs in the xy plane.

It is apparent from the Table that the quadrupole coupling constant for the central iodine increases with the electronegativities of the terminal halogens. For example $e^2q^{127}Q_g/h$ for $[I_3]^- < [IBr_2]^- < [ICl_2]^-$, and $[I_3]^- < [I_2Br]^- < [I_2Cl]^-$. Only the fluoro-anions do not follow this trend. These trends are further illustrated in Figure 2 where U_p is plotted against the sum of the electronegativities of the terminal halogens. We have used Pauling electronegativities, although a similar correlation is obtained using the Allred–Rochow values. The fluoro-anions $[FICl]^-$ and $[FIBr]^-$ both deviate markedly from the least-squares fit, having much lower quadrupole coupling constants and hence U_p values than would have been expected. In fact their quadrupole coupling constants are *ca.* 100 MHz smaller than those of the parent ICl and IBr molecules.[24] In β-ICl there is, in addition to the short I–Cl bond (2.351 Å), another longer I–Cl bond (2.939 Å) which is almost collinear with the first. Other I–Cl molecules in the crystal have an iodine atom, rather than a chlorine atom, collinear with the ICl bond and there are therefore two iodine environments in this crystal.[25] A similar situation applies in α-ICl.[26] The first of these iodine sites should have a quadrupole coupling constant similar to that in $[ICl_2]^-$ while the other should resemble that of the central iodine in $[I_2Cl]^-$. In the ^{129}I Mössbauer spectrum of ICl Pasternak and Sonnino [24] attribute additional lines to impurities, but perhaps these were in fact from the other site. A similar interaction, although probably weaker, is also likely in IBr. The diatomic molecule IF is not isolable probably because of the weakness of the I–F bond and the stability of the disproportionation products. Thus when the reaction between ICl and CsF takes place to produce Cs[ClF], the secondary (· · ·) bond in [Cl–I · · ·

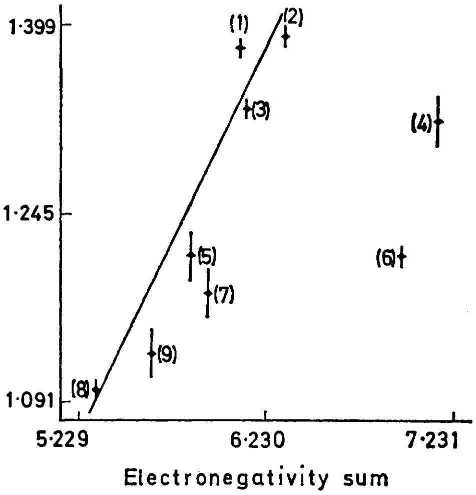

FIGURE 2 Plot of U_p against the sum of the Pauling electronegativities of the terminal halogens in $[X–I–Y]^-$. The line drawn is the best least-squares fit to the data excluding the fluoro-anions. Ions: (1) $[I(py)_2]^+$; (2) $[ICl_2]^-$; (3) $[IBrCl]^-$; (4) $[IClF]^-$; (5) $[I_2Cl]^-$; (6) $[IBrF]^-$; (7) $[IBr_2]^-$; (8) $[I_3]^-$; (9) $[I_2Br]^-$

Cl]$^-$ is replaced by a much weaker I $\cdots$ F$^-$ interaction. It is also likely that the F$^-$ would interact with more than one ICl molecule so that its potential electronegativity is not reached and the withdrawal of electron density along the bonding axis is less then expected. A similar situation probably pertains in Cs[IBrF]. The fluoro-anions also show significantly higher asymmetry parameters than the other compounds. This could mean that these fluoro-anions are not linear or that additional interactions to the iodine atom exist which are off the *z* axis. These latter interactions could arise from the the fluorine bridging suggested above. However, because the quadrupole coupling constant is still large and negative we can take this as good evidence that the F$^-$ $\cdots$ IX (X = Cl or Br) interaction is predominantly linear as in the well characterized anions $[I_3]^-$,[20] $[I_2Br]^-$,[21] and $[IBr_2]^-$.[22]

In the iodine–chlorine series of compounds it was suggested that $e^2q^{127}Q_g/h$ was a property of the I–Cl bond.[24] Jones [11] has already commented upon this and our results clearly show that the quadrupole coupling depends upon the nature of all co-ordinated ligands. For example, quadrupole couplings for anions containing an I–I bond range from −2 515 to −2 769 MHz, for an I–Br bond from −2 585 to −3 048 MHz, and for an I–Cl bond from −2 765 to −3 189 MHz.

Dipyridineiodine(I) nitrate shows the highest quadrupole coupling constant of any of the compounds we examined. Our value is slightly smaller than that measured by Jones [11] using the ^{129}I isotope. The *p*-electron imbalance is very large at 1.38 and is what one would expect for an iodine cation linearly bonded between two electronegative pyridine nitrogens. In all of this discussion it has been assumed that the lattice contribution can be ignored. This is probably not unreasonable for the systems reported here since they are all linear ions.

The isomer-shift data are much less easy to interpret than are the quadrupole coupling constants. Unlike the latter, the shifts are dependent upon the source, upon the reference compound used, if any, and upon whether the source and absorber are at the same temperature. Agreement on the reporting of shift data for ^{57}Fe, ^{119}Sn, and ^{121}Sb is virtually universal but no standard appears to be used for either ^{127}I or ^{129}I data. Rather, each group of workers refers its shifts to the source used and although the sources may nominally be the same (*e.g.* ZnTe) the quality might vary considerably. This makes it very difficult to compare data from one group to another particularly for ^{127}I where shifts much smaller than the natural linewidth are usual. Earlier we commented upon the inconsistencies in the data of Perlow and Perlow [10] and believe that the much quoted data relative to the ZnTe source are less reliable than those from the H_6TeO_6 source. It is important that these anomalies be cleared up and a reference substance adopted before relationships such as (3) can be used to estimate *s* and *p* occupation numbers. In order to test the internal consistency of our shifts we have compared our ^{127}I chemical shifts for H_5IO_6, I_2, and $[I(py)_2][NO_3]$ with the literature data for their ^{129}I equivalents.[3,11] We find a linear relationship within the errors quoted and allowing for the possible shift between H_5IO_6 and its trisodium salt. We believe our results are internally consistent and have chosen H_5IO_6 as our reference compound, *i.e.* its isomer shift is taken as zero relative to the source. All shifts (Table) are relative to this standard. We have included two values for the isomer shift of $K[ICl_2]\cdot H_2O$ measured by Perlow and Perlow.[10] One (−1.60 mm s^{-1}) was measured using the ZnTe source, the other value (−1.28 mm s^{-1}) we have arrived at by assuming that, since $K[ICl_2]\cdot H_2O$ and I_2 have the same shift (ZnTe source) and since the shift for I_2 using a telluric acid source appears more reliable, we assign $K[ICl_2]\cdot H_2O$ an identical shift. For $Cs[I_3]$ we have taken the iodine-129 data of de Waard and Spanhoff,[19] relative to $Na_3[H_2IO_6]$, and converted them into their 127 equivalents by multiplying by − 0.345.[12]

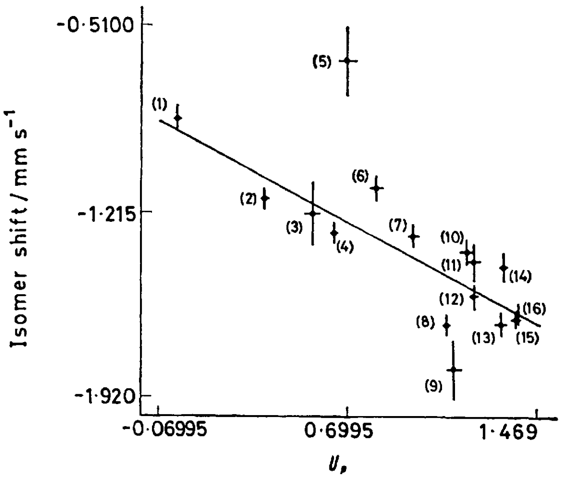

FIGURE 3 Plot of isomer shift against U_p. The line drawn is the best least-squares fit to the data. Ions (1) I^-; (2) $[\mathrm{I{-}I{-}}I]^-$; (3) $[\mathrm{Cl{-}I{-}}I]^-$; (4) $[I\mathrm{{-}I{-}I}]^-$; (5) $[\mathrm{Br{-}I{-}}I]^-$; (6) $[I_2]^+$; (7) I_2; (8) $[\mathrm{I{-}}I\mathrm{{-}I}]^-$; (9) $[\mathrm{Br{-}}I\mathrm{{-}I}]^-$; (10) $[IBr_2]^-$; (11) $[\mathrm{Cl{-}I{-}}I]^-$; (12) $[\mathrm{Br{-}I{-}F}]^-$; (13) $[\mathrm{Cl{-}I{-}F}]^-$; (14) $[\mathrm{Br{-}I{-}Cl}]^-$; (15) $[I(py)_2]^+$; (16) $[ICl_2]^-$

In order to evaluate the constants in equation (2) it is usual to plot isomer shift against U_p for a series of compounds. If the bonding is of *p* character only then $U_p \equiv h_p$, (2) reduces to (6), and a plot of δ *versus* h_p (*i.e.* U_p)

$$\delta = 2K\gamma h_p \qquad (6)$$

gives a line of slope = $2K\gamma$. Since $\gamma = 0.07$,[2,4,27] the value for *K* may be calculated. We have plotted the isomer-shift data against U_p in Figure 3, where the straight line represents a least-squares fit to all the data. The slope of this line is −0.50 ± 0.09 mm s^{-1} with an intercept of −0.90 ± 0.1 mm s^{-1}. In view of the scatter of the data the intercept is gratifyingly close to the measured shift for I$^-$, namely −0.86 mm s^{-1} relative to $[IO_6]^{5-}$.[10] The slope of the line is more positive than that usually accepted, −0.56 mm s^{-1},[10] but identical to Ehrlich and Kaplan's value of −0.50 mm s^{-1}.[27] A slightly smaller value, -0.48 mm s^{-1}, has also been used by Pasternak and Sonnino.[24] Hence the value of K is -3.57 mm s^{-1} and equation (2) becomes (7) or (8).

$$
\begin{aligned}
{}^{127}\delta_{\mathrm{I}^-} &= -3.57\,[-h_s + 0.07(h_p + h_s)(2 - h_s)] \\
&= 3.07\,h_s - 0.50\,h_p \qquad (7) \\
{}^{127}\delta_{[\mathrm{IO}_6]^{5-}} &= 3.07\,h_s - 0.50\,h_p - 0.90 \qquad (8)
\end{aligned}
$$

It is apparent from Figure 3 that there is considerable scatter of these data. For $[I_3]^-$ and $[ICl_2]^-$, uncertainty either in the referencing of the literature shifts and/or their conversion from ^{129}I data could be the cause of their deviation from the straight line, but it would appear that -1.60 mm s^{-1} is the more correct value for $K[ICl_2]\cdot H_2O$. The largest deviations are observed for the two sites in $[Br{-}I{-}I]^-$ where the two isomer shifts are strongly correlated in the fitting procedure. If these two isomer shifts are constrained to be equal an isomer-shift value of -1.36 mm s^{-1} is found which correlates better with the line drawn. However, there is no reason to expect these two shifts to be the same and indeed a lower χ^2 is obtained when the two isomer shifts are allowed to vary in the fitting procedure. Perhaps a ^{129}I spectrum should be recorded for this anion in order to obtain better resolution and so check this point. The fluoro-anions also deviate slightly, but this probably can be attributed to additional interactions between anions *via* fluorine bridges as discussed above for the quadrupole coupling constants. Equation (8) can then be used to calculate h_p, assuming that $h_s = 0$, or to estimate h_s by equating h_p and U_p, and these calculated values are listed in the Table. One can see that there is little agreement between the values for U_p and h_p calculated in this way. The difference between these two parameters can not be accounted for by inclusion of either s involvement or of π character to the bonds. Negative values for h_s can have no meaning, while π character to the bonding is usually invoked when $h_p > U_p$, yet the only compound studied where π character is clearly involved, *i.e.* $[I_2][Sb_2F_{11}]$, has $h_p < U_p$. Further discussion along these lines does not appear to be worthwhile until some of the anomalies discussed earlier are cleared up.

Conclusions.—The ^{127}I Mössbauer spectra of $[I_2][Sb_2F_{11}]$ and a number of halogen anions of the form $[X{-}I{-}Y]^-$ have been recorded and compared with literature data for related compounds. A reasonable correlation is found between the quadrupole coupling constants and the electronegativities of the attached ligands, except for the fluoro-anions. In these cases it is suggested that the data indicate that intermolecular interactions between anions are present *via* fluorine bridges. A value for the constant K is proposed which leads to a new correlation between the isomer shift h_s and h_p. The problems of establishing such an equation are discussed and depend heavily upon the care with which measurements are made, particularly with regard to the choice of a reference compound. No attempt appears to have been made to establish a reference substance for either iodine isotope. There would appear to be two suitable compounds namely $Na_3[H_2IO_6]$ and CuI. The iodine in the former is quite rigidly bound in an octahedral environment of oxygens and has a large positive isomer shift (negative for ^{129}I). Copper(I) iodide also has the iodine in a symmetric environment (tetrahedral), has an isomer shift in the middle of the measured range, is easily prepared, and is very stable. It seems imperative that one of these standards be adopted before further correlations are attempted.

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