

Secondary Bonding. Part 1. Crystal and Molecular Structures of $(C_6H_5)_2IX$ ($X = Cl, Br, \text{ or } I$)

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The structures of the title compounds have been determined. The three compounds are isomorphous, monoclinic, space group $C2/c$, $Z = 8$, with the following cell constants and R values:

X	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$\beta/^\circ$	$N(3\sigma)$	$R/\%$
Cl	20.856(13)	5.695(3)	20.043(4)	102.39(4)*	1 701	4.8
Br	21.483(6)	5.862(2)	20.057(5)	101.64(2)*	1 503	9.1
I	22.122(7)	5.872(2)	20.385(5)	100.98(2)*	1 371	4.3

In the dimeric structures $Ph_2I(\mu-X)_2IPh_2$ mean bond lengths are I-C 2.09, I-Cl 3.09, I-Br 3.25, and I-I 3.44 Å. The I-X bonds are each 0.77 Å longer than in the corresponding IX gas, indicating bond orders of about 0.35. The bonding is interpreted in terms of secondary bonds ($I \cdots X$), holding $[Ph_2I]^+$ and X^- units together.

WEAK interactions, intermediate in length between single bonds and van der Waals distances, have been shown to be of great importance in the crystal structures of many non-metal compounds, and have been given the name *secondary bonds*.¹ Characteristically this is a system $Y-A \cdots X$ in which $Y-A$ is a normal covalent bond, $A \cdots X$ a secondary bond, and the angle $Y-A-X$ is close to 180° . The most plausible explanation for this bonding seems to be (in two equivalent models) either donation from a lone pair on X into the σ^* orbital of the $Y-A$ bond, or as an asymmetric 3-centre system,

can be viewed in three ways. First, X forms one single bond and one dative bond to the two I atoms; this is the normal view of bridged metal halides, and the two bond lengths are usually equal, and close to the standard covalent distance, as in Al_2Br_6 , with terminal Al-Br of 2.21, and bridging Al-Br of 2.33 Å.³ Secondly, they may consist of Ph_2I-X units, in which X forms a weak secondary bond to the second I. Thirdly, they may consist of two $[Ph_2I]^+ + X^-$ units, in which the two halves are held together only by secondary bonds. The published report on diphenyliodonium chloride

TABLE I

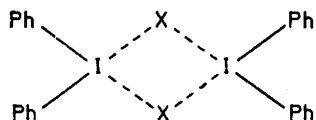
No.	X	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$\beta/^\circ$	$U/\text{\AA}^3$	$D_c/g\text{ cm}^{-3}$	$F(000)$
1	Cl	20.856(13)	5.695(3)	20.043(4)	102.39(4)	2 325	1.81	224
2	Br	21.483(6)	5.862(2)	20.057(5)	101.64(2)	2 474	1.93	242
3	I	22.122(7)	5.872(2)	20.385(5)	100.98(2)	2 583	2.10	260

No.	$\lambda/\text{\AA}$	μ/cm^{-1}	$T/^\circ\text{C}$	$N(3\sigma)$	$2\theta_{\text{max}}/^\circ$	scan width/ $^\circ$ *	minimum scan speed/ $^\circ\text{ min}^{-1}$	$R/\%$
1	Mo- K_α 0.710 69	29.74	-60	1 701	50	1.4	1.5	4.8
2	Cu- K_α 1.5418	245.4	18	1 503	130	1.8	1.0	9.1
3	Mo- K_α	48.93	18	1 371	50	1.8	1.0	4.3

* Plus $\alpha_1 - \alpha_2$ separation.

with three σ orbitals, one on each of Y , A and X , forming molecular orbitals occupied by two electron pairs.

Hitherto, knowledge of secondary bonds has been based on crystal structures studied for other reasons, but in this series of papers it is hoped to examine them



systematically, concentrating on the effects of exchanging two similar atoms (*e.g.* halogens). Of the first compounds chosen, the diphenyliodonium halides, the approximate structure of the chloride has been reported, as has a brief note on the iodide.² These reveal bridged dimeric molecules apparently with significant asymmetry in the two independent $I \cdots X$ distances. Such dimers

¹ N. W. Alcock, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 1.

² T. L. Khotsyanova, *Kristallografiya*, 1956, **1**, 524; *Chem. Abs.*, 1957, **51**, 4793; 1958, **52**, 4282.

suggested that the I-Cl bonds were significantly asymmetrical, and that it corresponded fairly closely to the second class, but the present work shows that all three compounds are essentially symmetrical.

EXPERIMENTAL

Diphenyliodonium salts were prepared by the method of Beringer *et al.*⁴ and recrystallised from methanol. When pure, all crystallised as white needles.

Crystal Data.— $C_{12}H_{10}IX$ [$X = Cl$ (1), Br(2), I(3)]. The three compounds are isomorphous with $Z = 8$ (monomer units), monoclinic, $C2/c$, systematic absences hkl , $h + k \neq 2n$, $h0l$, $l \neq 2n$. The dimeric units $[Ph_2IX]$ have $\bar{1}$ symmetry. For further data see Table 1. Unit-cell constants and standard deviations were determined by least-squares fit to the reflecting positions of fifteen reflections, using standard Syntex $P2_1$ programs. Reflection data for all three compounds were collected on a Syntex $P2_1$ diffractometer (graphite monochromator, $\theta = 2\theta$ scan)

³ K. J. Palmer and N. Elliott, *J. Amer. Chem. Soc.*, 1938, **60**, 1852.

⁴ F. M. Beringer, M. Drexler, E. M. Gindler, and C. C. Lumpkin, *J. Amer. Chem. Soc.*, 1953, **75**, 2705.

TABLE 2

Atomic co-ordinates ($\times 10^4$) and temperature factors ($\times 10$)* with standard deviations in parentheses

(a) Diphenyliodonium chloride

Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{23}	B_{12}	B_{13}
I	1 784.0(3)	457.1(10)	4 344.1(3)	18.7(2)	18.7(3)	22.1(3)	-0.5(5)	0.4(2)	-3.4(2)
Cl	3 282.3(10)	735.2(43)	4 564.3(13)	20.7(8)	25.2(10)	44.8(11)	-8.7(9)	6.9(8)	-3.6(8)

Atom	X	Y	Z	B	Atom	X	Y	Z	B
C(11)	1 818(4)	-1 989(11)	3 573(3)	26(2)	C(21)	768(3)	278(16)	4 183(5)	31(2)
C(12)	2 286(4)	-3 786(13)	3 703(2)	29(2)	C(22)	385(4)	2 135(13)	3 856(5)	48(3)
C(13)	2 322(3)	-5 436(11)	3 194(3)	36(2)	C(23)	300(4)	2 026(12)	3 748(4)	64(3)
C(14)	1 890(3)	-5 289(10)	2 556(3)	43(2)	C(24)	-603(3)	60(14)	3 965(4)	59(3)
C(15)	1 422(3)	-3 492(12)	2 427(3)	46(2)	C(25)	-220(4)	-180(11)	4 291(4)	52(3)
C(16)	1 386(3)	-1 842(11)	2 935(4)	36(2)	C(26)	466(4)	-1 688(14)	4 400(4)	36(2)
H(12)	2 579(5)	-3 885(19)	4 135(3)	70	H(22)	591(5)	3 468(16)	3 709(6)	70
H(13)	2 640(4)	-6 655(15)	3 282(5)	70	H(23)	560(5)	3 285(15)	3 526(5)	78(45)
H(14)	1 914(5)	-6 409(14)	2 211(4)	125(44)	H(24)	-1 068(3)	-14(17)	3 891(6)	130(44)
H(15)	1 129(4)	-3 393(18)	1 994(3)	131(45)	H(25)	-425(5)	-3 130(14)	4 439(6)	52(49)
H(16)	1 068(4)	-623(15)	2 847(5)	70	H(26)	725(5)	-2 947(2)	4 621(6)	70

(b) Diphenyliodonium bromide

Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{23}	B_{12}	B_{13}
I	1 760.7(5)	394.5(20)	4 315.8(5)	36.8(6)	50.9(6)	57.7(6)	-2.0(4)	5.0(4)	-5.8(4)
Br	3 302.8(8)	665.2(38)	4 561.1(1)	39.4(8)	67.1(10)	70.5(11)	-3.5(8)	6.0(7)	-5.7(7)

Atom	X	Y	Z	B	Atom	X	Y	Z	B
C(11)	1 796(7)	-2 011(21)	3 552(6)	49(3)	C(21)	777(5)	350(29)	4 109(8)	48(3)
C(12)	2 241(7)	-3 782(24)	3 688(4)	54(3)	C(22)	433(6)	2 213(24)	3 789(8)	85(6)
C(13)	2 289(6)	-5 372(20)	3 180(6)	69(5)	C(23)	-230(6)	2 247(22)	3 696(7)	94(6)
C(14)	1 892(6)	-5 192(19)	2 536(5)	77(5)	C(24)	-551(5)	415(25)	3 923(7)	93(7)
C(15)	1 447(6)	-3 421(22)	2 401(5)	68(4)	C(25)	-207(6)	-1 449(22)	4 243(8)	81(5)
C(16)	1 399(6)	-1 831(20)	2 909(7)	69(4)	C(26)	457(7)	-1 482(24)	4 336(8)	57(3)
H(12)	2 910(9)	3 903(34)	4 124(5)	100(77)	H(22)	651(8)	3 456(30)	3 636(12)	31(33)
H(13)	2 590(8)	-6 573(27)	3 271(9)	19(36)	H(23)	-463(9)	3 511(27)	3 480(10)	130(100)
H(14)	1 925(9)	-6 271(25)	2 192(7)	115(91)	H(24)	-100(5)	437(34)	3 860(10)	90(80)
H(15)	1 178(8)	-3 300(32)	1 964(5)	149(117)	H(25)	-424(8)	-2 692(27)	4 397(11)	73(61)
H(16)	1 098(9)	-630(27)	2 817(10)	50(48)	H(26)	690(9)	-2 746(30)	4 553(11)	20(29)

(c) Diphenyliodonium iodide

Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{23}	B_{12}	B_{13}
I(1)	1 735.7(4)	350.7(15)	4 269.4(4)	24.7(4)	36.7(4)	37.6(4)	-1.5(3)	4.9(3)	-2.7(3)
I(2)	1 676.6(4)	4 412.2(17)	5 458.9(4)	27.7(4)	48.9(5)	41.8(5)	-2.2(4)	5.8(3)	-2.4(3)

Atom	X	Y	Z	B	Atom	X	Y	Z	B
C(11)	1 767(5)	-2 046(15)	3 510(4)	34(2)	C(21)	772(4)	499(25)	4 065(7)	40(3)
C(12)	2 182(5)	-3 869(18)	3 640(3)	39(3)	C(22)	467(5)	2 388(21)	3 733(7)	70(5)
C(13)	2 233(4)	-5 433(14)	3 133(5)	48(3)	C(23)	-176(6)	2 517(18)	3 625(6)	93(6)
C(14)	1 870(4)	-5 173(13)	2 495(4)	49(3)	C(24)	-515(4)	756(22)	3 849(6)	81(6)
C(15)	1 454(4)	-3 349(16)	2 365(3)	54(4)	C(25)	-210(6)	-1 134(19)	4 181(6)	72(5)
C(16)	1 403(5)	-1 785(15)	2 872(5)	44(3)	C(26)	433(6)	-1 262(21)	4 289(6)	52(3)
H(12)	2 429(7)	-4 046(24)	4 073(4)	70	H(22)	697(7)	3 582(27)	3 581(10)	41(27)
H(13)	2 515(6)	-6 670(19)	3 233(6)	83(62)	H(23)	-383(8)	3 798(23)	3 400(8)	51(16)
H(14)	1 904(6)	-6 233(18)	2 151(5)	104(82)	H(24)	-951(4)	843(30)	3 775(8)	70(23)
H(15)	1 208(6)	-3 172(23)	1 932(4)	152(104)	H(25)	-440(7)	-2 328(24)	4 332(9)	74(64)
H(16)	1 121(6)	-548(19)	2 783(7)	35(30)	H(26)	640(8)	-2 543(26)	4 514(9)	44(35)

* Anisotropic temperature factors in the form: $\exp\{-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{23}k lb^{*}c^{*} + 2B_{13}h la^{*}c^{*} + 2B_{12}h ka^{*}b^{*})\}$.

with conditions as in Table 1. The scan rates varied between 29.5° min⁻¹ and a set minimum depending on the intensity of a pre-scan count. Background counts (each 0.25 of scan time) were recorded at each end of the scan. The intensities of standard reflections were monitored every 75 reflections, and for all compounds remained essentially constant during data collection. Data for (1) were taken at -60 °C to find the effect of low temperature on the accuracy of the determination.

Lorentz, polarisation, and absorption corrections were applied, the last with the program ABSCOR.⁵ Trial structures were derived from the published co-ordinates for PH₂ICI,³ from which all the structures were readily refined. In final refinement (with the SFLSR program of Dr. D. R. Russell), the phenyl rings were held as rigid hexagons, with symmetrically disposed hydrogen atoms (C-C 1.40, C-H 0.95 Å), in order to obtain maximum

* For details, see Notice to Authors No. 7, in *J.C.S. Dalton*, 1976, Index issue.

accuracy in I-C distances. Anisotropic temperature factors were used for heavy atoms only; a few hydrogen atoms had temperature factors that did not refine satisfactorily, and were fixed at 7.0 Å². Scattering factors were from ref. 6 and anomalous dispersion was included. Computing was on an ICL 4130 computer. Final co-ordinates and temperature factors are in Table 2. Structure factors are listed in Supplementary Publication No. SUP 21887 (29 pp., 1 microfiche).*

RESULTS AND DISCUSSION

All three compounds are isomorphous showing the overall structure reported by Khotsyanova,² of centrosymmetric dimers, held together by halogen bridges

⁵ N. W. Alcock, 'The Analytical Method for Absorption Correction,' in 'Crystallographic Computing,' ed. F. Ahmed, Munksgaard, Copenhagen, 1970, p. 271.

⁶ 'International Tables for X-ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

(Figure 1). However, the detailed dimensions (Table 3) are rather different from those originally published,² and, in particular for (1), the two I-Cl distances differ by

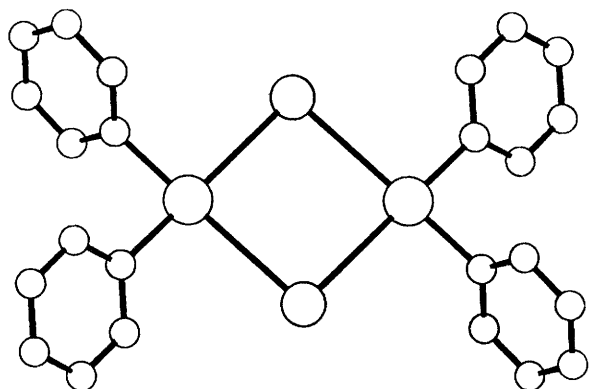
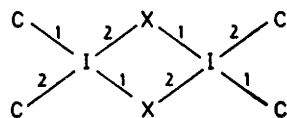


FIGURE 1 The molecule $[(C_6H_5)_2IBr]_2$, viewed perpendicular to the I_2Br_2 plane

only 0.04 Å. The dimers are precisely planar and all six I-C bonds are equal to within experimental error (mean 2.090 Å). The two I-X bonds in each molecule

TABLE 3

Bond lengths (Å) and angles (°) with standard deviations in parentheses. Bonds 1 and 2 are arranged as follows, with $(C-I)_1$ shorter than $(C-I)_2$



X		C-I	I-X	$(I-X)_{single}$	Ref.	$(I-X)_{obs.} - (I-X)_{single}$
Cl	1	2.078(6)	3.064(3)			
	2	2.096(7)	3.105(3)			
	Mean	2.087	3.085	2.321	a	0.764
Br	1	2.071(10)	3.253(2)			
	2	2.095(13)	3.248(3)			
	Mean	2.083	3.250	2.485	b	0.765
I	1	2.095(9)	3.453(2)			
	2	2.103(9)	3.421(2)			
	Mean	2.099	3.437	2.667	c	0.770
		C-I-C	X-I-X	I-X-I		X-I-C
Cl		92.6(3)	93.48(7)	86.52(7)		179.3(3) 177.3(2)
Br		91.8(6)	92.54(6)	87.46(6)		177.0(4) 176.5(5)
I		93.2(5)	91.91(3)	88.10(3)		177.8(3) 174.8(4)

^a E. Hulthen, N. Johansson, and U. Pilsäter, *Arkiv. Fys.*, 1959, **14**, 31. ^b T. S. Jaseja, *J. Mol. Spec.*, 1960, **5**, 445. ^c D. H. Rank and W. M. Baldwin, *J. Chem. Phys.*, 1951, **19**, 1210.

do differ significantly (for X = Cl and I) but the differences are so small in absolute terms that they cannot be regarded as important. There are small systematic changes in the X-I-X and I-X-I angles, as X becomes larger, and the average *trans*-X-I-C angle decreases

slightly (178.3 to 175.3°) while remaining very close to 180°.

The most important trend in the series is in the I-X distances themselves, as indications of the strength of the secondary bond. Here, fortunately, very good standard I-X distances are available with no intermolecular interactions, from the gaseous IX molecules.

In ref. 1 it was proposed that the best measure of 'weak' bond strength was the difference between the observed bond length and the normal single bond length. This is strongly supported by the present results. This difference is constant (to 0.006 Å) for all these three compounds which might be expected to show the same bond order. From the curve of ref. 7 this corresponds to bond orders of about 0.35. The I-Cl distance can also be compared directly with the covalent $I^{III}-Cl$ bond length of 2.45 Å in $PhICl_2$.⁸

These I-X distances are so much longer than the single bond distances that an explanation in terms of one covalent and one dative bond is implausible. However, the interpretation as a $\{[Ph_2I]^+[X]^- \}_2$ system held

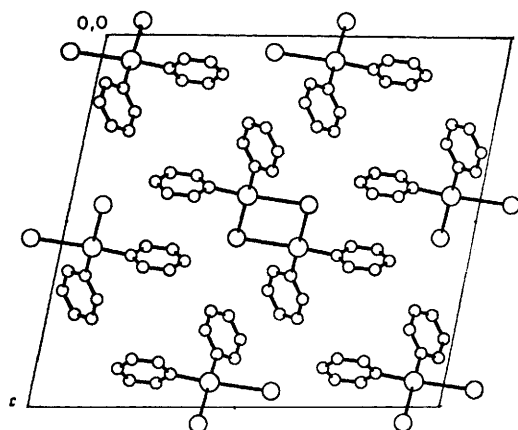


FIGURE 2 Packing diagram viewed down b , for $[(C_6H_5)_2IBr]_2$

together with secondary bonds does seem satisfactory; it is also consistent with the very closely linear X-I-C systems. The systematic trend, or rather *lack* of any trend, in bond order with change in halogen is unexpected; it contrasts, for example, with the marked increase in secondary bond order when the *central* atom is changed from Cl to Br in $[ClF_2][SbF_6]$ and $[BrF_2][SbF_6]$.¹

Packing (Figure 2) is dominated by contacts between the phenyl rings, each dimer unit being inclined at about 30° to the ac plane.

We thank the S.R.C. for a grant for the diffractometer (N. W. A.) and for a post-doctoral fellowship (R. M. C.).

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⁷ E. H. Wiebenga and D. Kracht, *Inorg. Chem.*, 1969, **8**, 738.
⁸ E. M. Archer and T. G. D. van Schalkwyk, *Acta Cryst.*, 1953, **6**, 88.