Secondary Bonding. Part 14.[1] Structural Isomerism in Diaryliodonium Halides and the Structure of Di(*p*-tolyl)iodonium Bromide*

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The *X*-ray structure of di(*p*-tolyl)iodonium bromide has been determined from diffractometer data [3 689 observed reflections, $I \geqslant 3.0\sigma(I)$] and refined to $R = 0.068$. The unit cell contains one centrosymmetric dimer $(R_2IBr)_2$ and one tetramer $(R_2IBr)_4$ (R = *p*-tolyl). The dimer corresponds to that found in $(Ph_2IBr)_2$ but the tetramer is novel. Both contain R_2I^+ groups linked by secondary bonds to Br^- ions. The I–C bonds [av. 2.124(8) Å] are significantly longer than those in $(Ph_2IBr)_2$, but the majority of the I $\cdots$ Br bonds are shorter [range 3.163(2)—3.513(3) Å].

Precision determinations of the crystal structures of the dimeric diphenyliodonium halides, Ph_2IX (X = Cl, Br, or I), were made 10 years ago.[2,3] At that time, the *p*-tolyl analogues were also prepared to examine the effect of an electron-donating substituent on the secondary bonding. In the event, only di(*p*-tolyl)iodonium bromide could be crystallised, and its structure proved impossible to solve from the *X*-ray data. A recent re-examination was more successful, and has revealed a novel tetrameric oligomer.

Experimental

Preparation.—Di(*p*-tolyl)iodonium bromide and iodide were prepared by the method of Beringer *et al.*[4] Recrystallisation from water gave suitable crystals of the bromide, but the iodide could only be obtained as a powder.

Crystal Data.—$C_{14}H_{14}BrI$ (monomer), triclinic, space group $P\bar{1}$, $a = 14.903(6)$, $b = 13.078(7)$, $c = 12.836(7)$ Å, $\alpha = 118.31(3)$, $\beta = 92.07(4)$, $\gamma = 94.18(4)°$, $U = 2\,190(2)$ Å^3, $M = 389.1$, $D_m = 1.75$ g cm^{-3}, $Z = 6$ (monomer units), $D_c = 1.77$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 50.7 cm^{-1}, $F(000) = 1\,116$. Crystal character: pale yellow blocks.

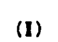
Data were collected with a Syntex $P2_1$ four-circle diffractometer. Maximum 2θ was 42°, with scan range $+1.0°$ (2θ) around the $K\alpha_1$–$K\alpha_2$ angles, scan speed 1—29° min^{-1}, depending on the intensity of a 2-s pre-scan. For $2\theta > 35°$, all data were recorded, but after the first 1 000 reflections of the 35—42° shell, only those reflections exceeding a pre-set count on an 8-s pre-scan were examined; this corresponded approximately to a 2σ rejection criterion. Backgrounds were measured at each end of the scan for 0.25 of the scan time. Three standard reflections were monitored every 100 reflections, and showed no changes during data collection. The density was measured by flotation. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 high-angle reflections. 3 689 Observed reflections [$I/\sigma(I) \geqslant 3.0$] were used in refinement (total 4 440) and corrected for Lorentz, polarisation and absorption effects, the last with ABSCOR;[5] maximum and minimum transmission factors were 0.59 and 0.34. The crystal dimensions were 0.32 × 0.24 × 0.22 mm, with bounding faces {100, 010, 001}. No systematic absences.

Initial attempts at structure solution by Patterson methods were unsuccessful, and direct methods (MULTAN, SHELX, *X*-RAY-76) also failed, as did a prototype of the MITHRIL program (kindly applied for us by Dr. C. Gilmore).[6] The problems encountered with the last were due to the reflections falling into disconnected groups, whose phases could not be linked. With hindsight, this was probably the result of a data-collection strategy that would not have been used, had the need for direct methods been forseen (even though the phase-linking equations are dominated by interactions between the strong reflections). Unsuccessful attempts were also made to find a hexagonal sub-structure based on the tripled contents of the unit cell and its approximately hexagonal dimensions (naturally unsuccessful with hindsight, as no such sub-structure exists).

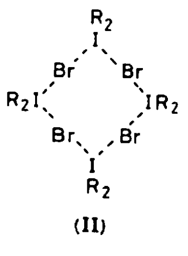
Finally, the heavy atoms were located from the Patterson solution routine of SHELX 84 (kindly applied by Professor G. Sheldrick). The substantial overlap of the Patterson peaks revealed by the solution was probably the cause of the previous failure of manual solution methods. The light atoms were then found on successive Fourier syntheses. Hydrogen atoms were given fixed isotropic thermal parameters, $U = 0.07$ Å^2. Those defined by the molecular geometry were inserted at calculated positions and not refined; methyl groups were treated as rigid units, with their initial orientation taken from the strongest peak on a difference Fourier synthesis. Final refinement was by cascaded least-squares methods with anisotropic thermal parameters for all atoms other than hydrogen. The largest peak on a final difference Fourier synthesis was of height 0.8 Å^{-3}. Unit weights were used and shown to be satisfactory by a weight analysis. The final *R* value was 0.068. Computing was with the SHELXTL system[7] on a Data General DG30, following initial processing on an ICL 4130 and a Burroughs B6800. Scattering factors in the analytical form and anomalous dispersion factors were taken from ref. 8. Final atomic co-ordinates are given in Table 1, and selected bond lengths and angles in Table 2.

Results

The six molecules of $(p\text{-}MeC_6H_4)_2IBr$ in the unit cell comprise two different centrosymmetric aggregations. Two molecules make up a dimer (**I**) of the standard form found for the phenyl derivatives (Figure 1). However, the remaining molecules form a novel tetramer (**II**) (Figure 2). The hitherto unobserved ability shown by this diaryliodonium compound to exist in alternative



(**I**)



(**II**)

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.* 1987, Issue 1, pp. xvii—xx.

Table 1. Atomic co-ordinates (× 10^4)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
I(1)	564.0(9)	585.6(10)	1 800.0(10)	C(25)	7 259(16)	−1 789(18)	2 410(18)
I(2)	6 624.6(9)	−218.5(10)	175.5(10)	C(26)	6 827(18)	−1 267(20)	1 859(21)
I(3)	5 493.7(10)	3 797.6(11)	1 201.4(11)	C(201)	8 615(23)	−2 571(26)	2 903(27)
Br(1)	−537(2)	1 839(2)	590(2)	C(27)	6 626(14)	1 373(15)	1 862(16)
Br(2)	6 475(2)	−2 833(2)	−2 042(2)	C(28)	5 788(14)	1 621(16)	2 292(15)
Br(3)	5 694(2)	1 321(2)	−976(2)	C(29)	5 787(15)	2 614(17)	3 436(17)
C(11)	552(13)	2 143(13)	3 426(14)	C(210)	6 594(15)	3 284(15)	4 065(17)
C(12)	−233(14)	2 349(16)	4 017(14)	C(211)	7 387(15)	2 993(15)	3 528(17)
C(13)	−213(15)	3 346(18)	5 138(17)	C(212)	7 405(14)	2 059(16)	2 414(19)
C(14)	543(14)	4 120(15)	5 638(16)	C(202)	6 480(17)	4 303(17)	5 318(15)
C(15)	1 331(15)	3 883(16)	4 990(18)	C(31)	6 652(14)	4 256(16)	523(17)
C(16)	1 349(13)	2 915(15)	3 887(16)	C(32)	6 606(13)	5 109(18)	174(15)
C(101)	607(19)	5 168(19)	6 832(20)	C(33)	7 315(19)	5 359(18)	−359(18)
C(17)	1 212(14)	−199(16)	2 680(17)	C(34)	8 078(20)	4 778(20)	−544(18)
C(18)	1 980(15)	−778(18)	2 266(17)	C(35)	8 127(16)	4 016(22)	−102(22)
C(19)	2 402(17)	−1 283(21)	2 858(19)	C(36)	7 423(15)	3 738(17)	450(20)
C(110)	2 090(16)	−1 256(19)	3 841(21)	C(301)	8 847(22)	5 102(27)	−1 100(32)
C(111)	1 324(18)	−669(24)	4 273(23)	C(37)	5 540(15)	5 555(16)	2 666(15)
C(112)	903(18)	−196(24)	3 681(24)	C(38)	5 014(14)	6 353(17)	2 564(17)
C(102)	2 563(17)	−1 788(27)	4 509(26)	C(39)	5 095(16)	7 475(18)	3 511(21)
C(21)	7 244(14)	−1 019(14)	1 059(16)	C(310)	5 662(18)	7 816(18)	4 567(18)
C(22)	8 168(13)	−1 308(17)	881(18)	C(311)	6 160(18)	6 955(21)	4 566(19)
C(23)	8 576(14)	−1 797(20)	1 459(21)	C(312)	6 079(16)	5 852(18)	3 657(17)
C(24)	8 148(15)	−2 003(19)	2 286(18)	C(302)	5 693(20)	9 025(20)	5 541(22)

Table 2. Principal bond lengths (Å) and angles (°)*

I(1)–Br(1)	3.227(3)	I(1)–C(11)	2.117(13)
I(1)–C(17)	2.104(26)	I(1)–Br(1′)	3.197(2)
I(2)–Br(2)	3.234(2)	I(2)–Br(3)	3.353(3)
I(2)–C(21)	2.103(23)	I(2)–C(27)	2.178(15)
I(3)–Br(3)	3.163(2)	I(3)–C(31)	2.133(22)
I(3)–C(37)	2.166(15)	I(3)–Br(2′)	3.513(3)
Br(1)–I(1′)	3.197(2)	Br(2)–I(3′)	3.513(3)

Br(1)–I(1)–C(11)	86.9(6)	Br(1)–I(1)–C(17)	175.9(6)
C(11)–I(1)–C(17)	90.5(7)	Br(1)–I(1)–Br(1′)	94.9(1)
C(11)–I(1)–Br(1′)	177.0(6)	C(17)–I(1)–Br(1′)	87.6(4)
Br(2)–I(2)–Br(3)	103.5(1)	Br(2)–I(2)–C(21)	82.5(4)
Br(3)–I(2)–C(21)	174.1(4)	Br(2)–I(2)–C(27)	168.7(6)
Br(3)–I(2)–C(27)	84.5(6)	C(21)–I(2)–C(27)	89.7(7)
Br(3)–I(3)–C(31)	81.1(4)	Br(3)–I(3)–C(37)	172.4(6)
C(31)–I(3)–C(37)	91.7(7)	Br(3)–I(3)–Br(2′)	94.1(1)
C(31)–I(3)–Br(2′)	174.6(4)	C(37)–I(3)–Br(2′)	93.2(6)
I(1)–Br(1)–I(1′)	85.1(1)	I(2)–Br(2)–I(3′)	94.5(1)
I(2)–Br(3)–I(3)	105.9(1)		

* Primed atoms are related to unprimed atoms by a centre of symmetry.

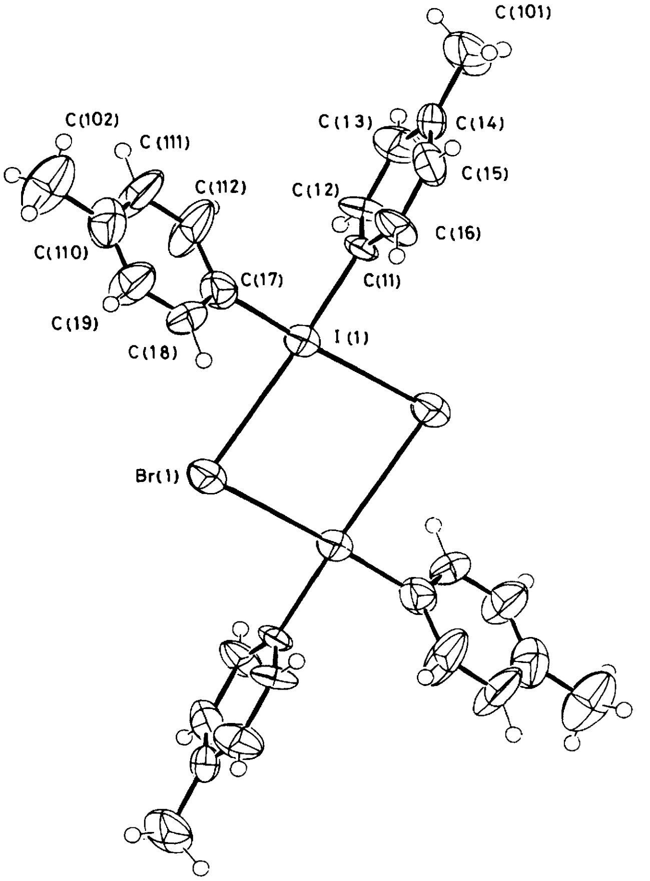

Figure 1. The dimer in $(p\text{-MeC}_6H_4)_2IBr$, showing the atomic numbering

forms indicates clearly that the chemistry of these species must be more complex than had been supposed from the evidence of the phenyl derivatives. A close parallel[9] can be seen in the structural isomers of XeF_6. This contains XeF_5 units held together in different ways by secondary bonds to F^- ions; it thus resembles the R_2I^+ units held together by secondary bonds to Br^- in the present compound. Further studies will be required to establish what controls the oligomerisation of the iodonium compounds and whether they can also form polymer chains. However, the existence of two isomers in the crystals of $(p\text{-MeC}_6H_4)_2IBr$ suggests that interconversions are fairly easy and that a major influence is the crystal packing. Figure 3 shows this. The dimer units are centred at the corners of the unit cell, alternating in stacks with the tetramers centred at $[\frac{1}{2},0,0]$.

Inspection of the packing diagram suggests that π interactions between parallel aromatic rings in the stacks are important, while methyl–methyl contacts occur between stacks. However,

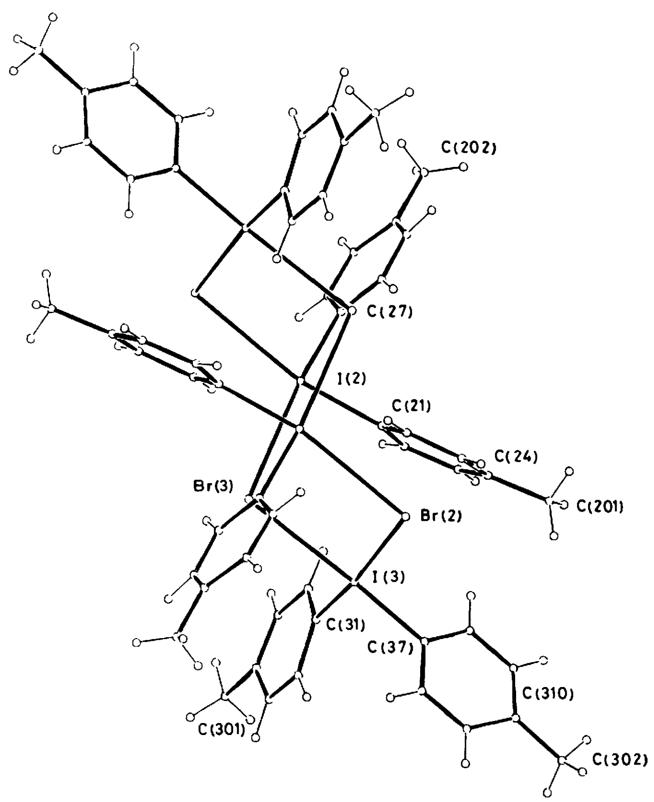

Figure 2. The tetramer in $(p\text{-MeC}_6H_4)_2IBr$, showing selected atomic numbers

no obvious cause can be seen for the stabilisation of the tetramer as well as the dimer.

The tetramer retains the dimer's planar geometry at iodine, resulting from the formation of two linear secondary bond systems. However, the molecule is twisted at each bromine atom so that the next R_2I unit is perpendicular to the previous one (rather than coplanar as in the dimer). The result is a stepped I_4Br_4 framework which, from geometric considerations, could be extended indefinitely, turning through 90° at each Br. This framework is broadly similar to the chair isomers of $M_4(PR_3)_4X_4$ (M = Cu or Ag, X = halide), which also consist of three linked parallelograms each perpendicular to the next.[10] However, the similarity extends only to the spatial arrangement, as the metal complexes are cross-connected [corresponding to links between Br(3) and I(2′) in the present structure].

The comparison of the dimensions of the two units of $(p\text{-MeC}_6H_4)_2IBr$ (**1**) with each other and with $(Ph_2IBr)_2$ (**2**) show systematic effects. The presence of the CH_3 group produces a significant lengthening of the I–C bond [av. 2.083(8) in (**2**) and 2.124(8) Å in (**1**)]. This presumably results from electron donation, increasing the electron density at the *p*-carbon and hence repelling the iodine atom slightly. A more substantial effect is seen on the I ··· Br secondary bonds which are shortened [av. 3.250(2) in (**2**), 3.212(2) Å in the dimer of (**1**)]; this inverse correlation is as expected[11] for donation by Br^- into the π^* orbital of the C–I bond. The effect on the tetramer of (**1**) is more complex. Unlike the dimer, this shows some asymmetry, each iodine having a long and shorter I ··· Br bond; both shorter bonds are shorter than those in (**2**) and in the dimer [av. 3.198(2) Å], but the other bonds are considerably longer [3.353(3) and 3.513(3) Å]. Considered individually, these bonds are paired, so that the shortest and the longest I ··· Br are formed by the same iodine atom [I(3)]; the bonds at I(2) are of intermediate length and, as already noted, those in the dimer [I(1)] are almost equal. As well as this correlation between the I ··· Br bonds of individual iodine atoms, a correlation can be suggested between an I–C bond length and the I ··· Br bond length opposite it. For each iodine, the longer I–C and shorter I ··· Br bonds are *trans*. However, the errors in the I–C bond lengths are too great to show this effect with confidence (with deviations of about 3σ from the mean value). These correlated changes in bond lengths can be compared to those in the tri-iodides,[12] where changes in packing forces cause one I–I bond to shorten and the *trans* bond to lengthen, and the underlying cause must be the same: the correlation in a partly delocalised set of bonding electrons of changes in one portion of the molecule with those in another.

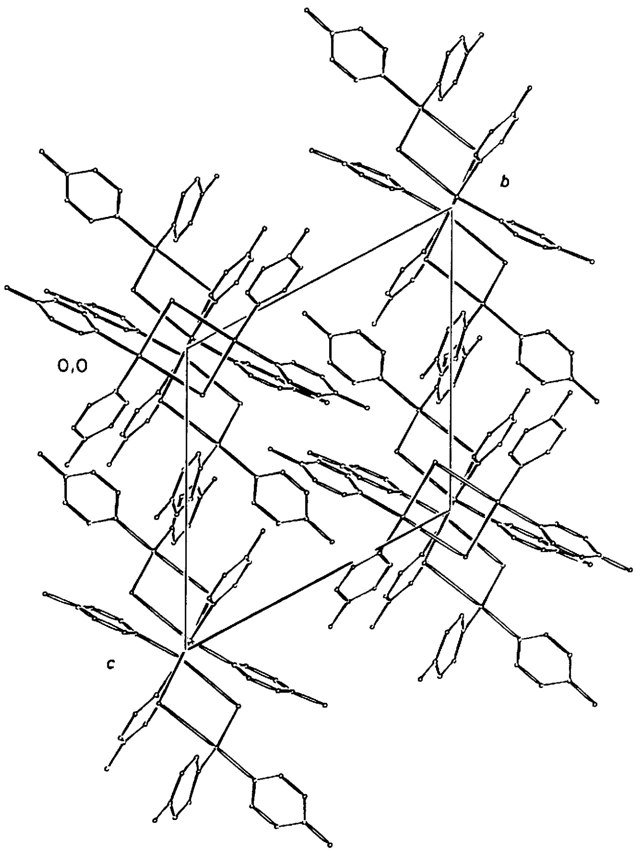

Figure 3. Packing of $(p\text{-MeC}_6H_4)_2IBr$ viewed down *a*. The dimers centred at (1,1,0) and (1,0,1) have been omitted for clarity

Acknowledgements

We thank the S.E.R.C. for support.

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Received 31*st January* 1986; *Paper* 6/215