

Oxo-bridged Compounds of Iodine(III): Syntheses, Structure, and Properties of μ -Oxo-bis[trifluoroacetato(phenyl)iodine]

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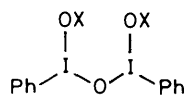
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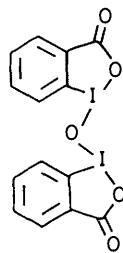
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The title compound has been prepared by using several approaches. It reacts with both strong bases and acids and is an oxidant. Its crystal structure has been determined from four-circle diffractometer data ($R = 0.043$). The primary iodine geometry is T-shaped [$O-I-O = 172.7(3)^\circ$], with shorter $I-O$ (bridge) than $I-O$ (acid) [$2.017(7)$ and $2.272(8)$ Å avg., respectively]. Secondary bonds have $I \cdots O$ of $2.929(8)$ Å to $3.273(8)$ Å.

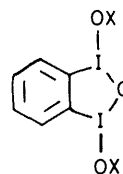
Although organic polyvalent iodine compounds have been known for many years,¹ only in the last two decades have systematic studies of them been undertaken, with the main emphasis on iodonium salts² and (diacyloxyiodo)benzene.³ These compounds show considerable potential as synthetically useful reagents,⁴ although the mechanistic aspects of their reactions are still not well understood. μ -Oxo-di-iodine compounds, in which two trivalent iodine atoms are linked through oxygen provide a further class the chemistry of which is not well understood. Both non-cyclic, (1)–(7), and cyclic (9)–(11), μ -oxo-compounds are known.⁵ We have chosen to



- (1) X = SO₃H
 (2) X = NO₂
 (3) X = ClO₃
 (4) X = SO₂CF₃
 (5), (6) X = COCH₂Hal (Cl, Br)
 (7) X = COCCl₃
 (8) X = COCF₃



(9)



(10) X = Ac

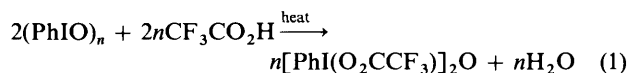
(11) X = Ts (Tosyl)

synthesize and study μ -oxo-bis[trifluoroacetato(phenyl)iodine] (8), because the chemistry of the related bis(trifluoroacetoxy)iodobenzene, $PhI(OCOCF_3)_2$, (12) has been thoroughly studied,³ and thus allows a comparison between the two compounds to be made.

Results and Discussion

Several years ago it was reported that during a preparation of compound (12), by heating iodosylbenzene in trifluoroacetic acid, a yellow oily by-product was isolated, to which structure of (8) was assigned on the basis of i.r. evidence.^{5a} Its formation was attributed to thermal decomposition of (12) or to its interaction with iodosylbenzene. We have found that (12) is thermally stable and does not react with iodosylbenzene. However, since

the structure of iodosylbenzene has been established as being polymeric,⁶ it occurred to us that the formation of (8) might be due to incomplete acidolysis of $(PhIO)_n$. Indeed, heating of a stoichiometric quantity (based on monomer unit) of $(PhIO)_n$ and CF_3CO_2H gave crystalline compound (8) [equation (1)].



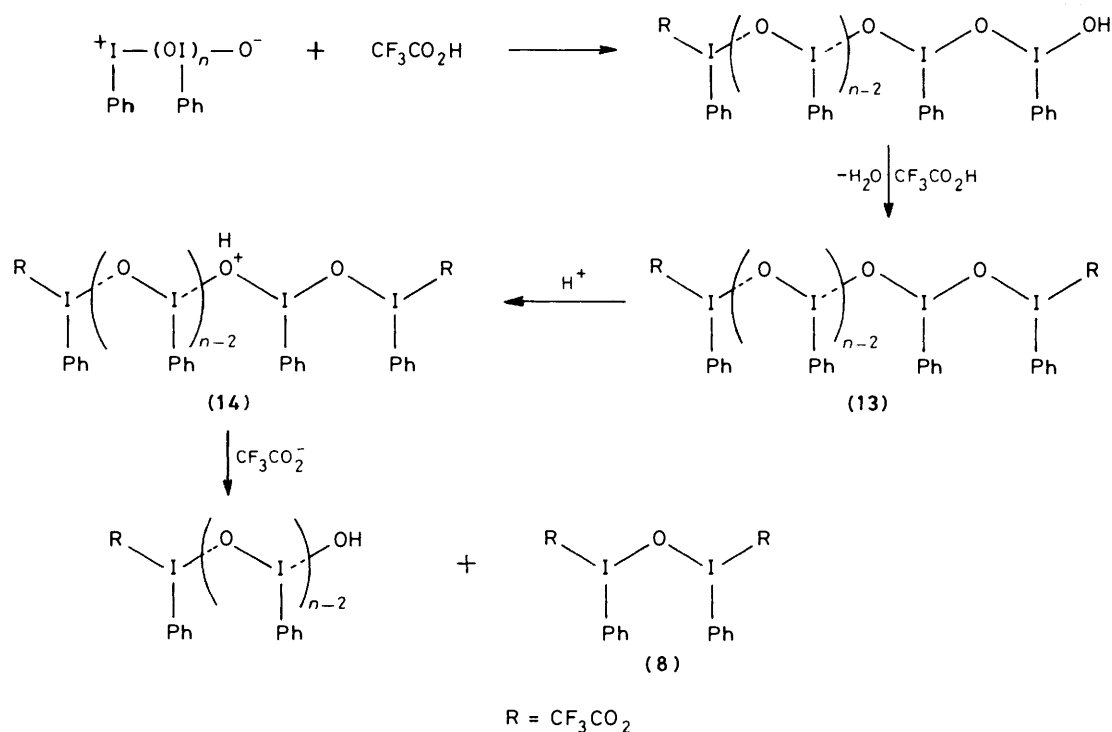
The identification of (8) was based on elemental analysis (C, H) and spectral results; the latter, although similar to those of (12), are different, especially the ¹H n.m.r. spectra. The identification has now been finally confirmed by X-ray analysis. The main spectral features of (8) and (12) are compared in Table 1.

The successful synthesis of (8) from $(PhIO)_n$ indicates that the depolymerisation of the latter is effected by gradual elimination of two iodine units rather than one (see Scheme 1). After attachment of the ionic parts of a CF_3CO_2H equivalent at the ends of the chain, a second equivalent of acid is consumed to form the anhydride (13). This is protonated at the second oxygen bridge, which is less basic because of the CF_3CO_2 group, than the first. The protonated form (14) is attacked by $CF_3CO_2^-$ at the more electrophilic second iodine atom to form (8).

Table 1. Spectroscopic characteristics of (8) and (12).

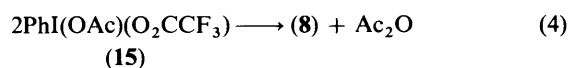
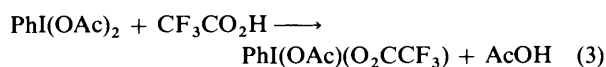
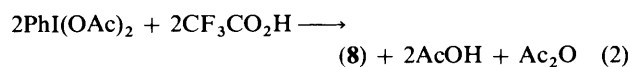
Compd.	$\delta_H(CDCl_3)$	$\delta_C(CDCl_3)$	ν/cm^{-1}	
			(Nujol)	m/z
(8)	7.1–7.5	C-1 124.0,	1 660	317 (5%), 279 (26%)
	(6 H, m)	C-2 133.7,		
	7.7–7.9	C-3 ^a 131.5,	1 705sh	
	(4 H, m)	C-4 132.5,		
(12)		C-5 ^b 162.2(q),		
		C-6 ^b 113.9(q)		
	7.4–7.7	C-1 123.0,	1 700	317, 278, 273
	(3 H, m)	C-2 135.3,		
	8.1–8.3	C-3 ^a 132.1,	1 740	
	(2 H, m)	C-4 133.7,		
	C-5 ^c 161.2(q),			
	C-6 ^c 113.0(q)			

^a The assignment of C-2 and C-3 is not unambiguous, being made by analogy with the spectrum of $PhI(OAc)_2$ (F. Klaus, W. Amann, and H. Fritz, *Chem. Ber.*, 1978, **111**, 2099). ^b Coupling constants: J_{CF} 290 and J_{CCF} 39 Hz. ^c Coupling constants J_{CF} 288 and J_{CCF} 41 Hz.



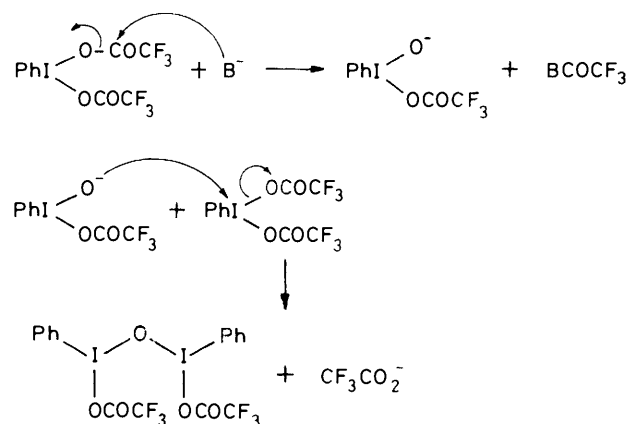
Scheme 1.

Compounds (5), (6), and (7) have been obtained by the reaction of stoichiometric quantities of PhI(OAc)₂ and the corresponding halogenated acetic acid.^{5d} We find that (8) is also formed in high yield from PhI(OAc)₂ and CF₃CO₂H [equation (2)]. The reaction path involves intermediate formation of the mixed trifluoroacetoxy(acetoxy)iodobenzene (15) [equation (3)], which disproportionates into (8) and Ac₂O [equation (4)].



We have shown that (15), prepared independently from (12) and AcONa⁷ or from PhI(OAc)₂ and CF₃CO₂H, also undergoes this reaction.

A further way of obtaining (8) is by heating equimolar amounts of (12) and PhI(OAc)₂, also *via* the mixed compound (15). Among the several pathways that are possible for the conversion of (15) into (8), intermediate formation of the anion PhI(O₂CCF₃)O⁻ is possible; that such an anion can be formed has been shown by a different approach. When (12) in CH₂Cl₂ was treated with strong bases (*e.g.* solid NaOH, Bu^tOK and MeONa) (8) was produced in high yields (Scheme 2). In the case of Bu^tOK the resulting *t*-butyl trifluoroacetate has been isolated and its i.r. and n.m.r. spectra were shown to be identical with those of an authentic sample. By using *p*-tolyl-lithium the reaction was less clean but, among a multitude of products not fully identified, *p*-trifluoroacetyl-toluene was detected. Thus, it is highly probable that attack of the above nucleophiles takes place at the carbonyl centre rather than at iodine, which is normally attacked in all known nucleophilic displacements of



(B = HO, MeO, Bu^tO)

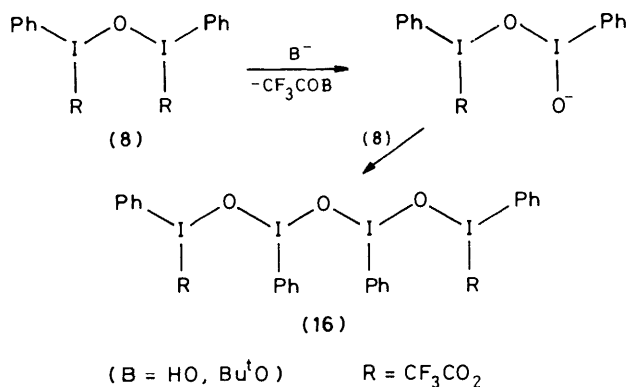
Scheme 2.

diacyloxyiodobenzenes. The ambident electrophilic character of (12) is of interest, since only one kind of product is obtained with each nucleophile, *e.g.* (12) and AcONa furnish the mixed (15) exclusively,⁷ whereas with Bu^tOK no mixed* PhI(O₂CCF₃)(OBu^t) has been observed. On the other hand, PhI(OAc)₂ and NaOH react less easily and iodobenzene is formed by attack of HO⁻ on iodine. These differences in reactivity may be explained in terms of HSAB theory; the hard oxygen of the strong bases attacks the hard carbon of the CF₃CO₂ group in the case of (12), while in PhI(OAc)₂ iodine is harder than C and it is attacked selectively. Nucleophiles with a soft oxygen or another soft centre such as the anions of acidic

* Compounds of this type are known (see ref. 8).

amides⁹ attack (12) at iodine and do not react with $\text{PhI}(\text{OAc})_2$, whereas tolyl-lithium must attack both CO and I of (12).

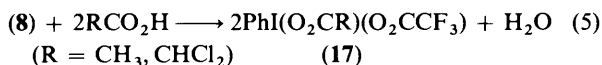
In the reactions of (12) with bases, the stoichiometry of the reactants is important. A 2:1 ratio of (12):base is necessary for Bu^tOK and MeONa and a 1:1 ratio for NaOH ; with the latter $\text{CF}_3\text{CO}_2\text{H}$ is formed, which needs a further equivalent of base for neutralisation. However, with a 2:3 ratio of (12): NaOH or a 4:3 ratio for (12): Bu^tOK , a novel catenated trivalent iodine compound is formed, tri- μ -oxo-*adfi*-tetraphenyl-*bh*-bis(trifluoroacetoxy)tetraiodine (16) (see Scheme 3). Its formation may



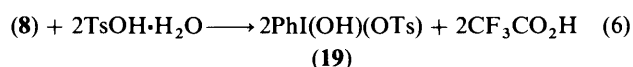
Scheme 3.

be accounted for by attack of the excess of base on the carbonyl C of the initially formed compound (8). Indeed, compound (8) with NaOH (ratio 1:1) or Bu^tOK (ratio 2:1) gave compound (16) quantitatively. The assignment of its structure was based on elemental analysis (C, H), spectral data, and molecular weight determinations; osmometry failed to give satisfactory results, presumably because of dissociation.* Iodometry, however, gave a molecular weight equal to $M = 274.7n$ ($n = 1, 2, 3, 4 \dots$), which for $n = 4$ makes $M = 1099$ (theoretical $M = 1090$). A value of $M = 1140$ has also been obtained by using the n.m.r. method¹¹ and assuming the presence of four phenyl groups.

Apart from its reactions with bases, the chemistry of (8) has also other features of interest. By heating a solution of (8) in CHCl_3 with the appropriate amount of an acid, mixed acyloxy(trifluoroacetoxy)iodobenzenes, (17), are formed in high yields [equation (5)]. With malonic acid the bis-derivative



$[\text{PhI}(\text{O}_2\text{CCF}_3)_2\text{C}]_2\text{CH}_2$, (18), has been obtained, whereas an excess of AcOH was needed to obtain $\text{PhI}(\text{OAc})(\text{O}_2\text{CCF}_3)$. This easy preparation of mixed diacyloxy(iodo)benzenes may be of value for additions of the two acyloxy groups to ethylenic double bonds and other related reactions.³ It is noted that previously only $\text{PhI}(\text{O}_2\text{CCH}_2\text{Cl})(\text{O}_2\text{CCH}_2\text{Br})$ has been prepared¹² from $\text{PhI}(\text{OAc})_2$ by sequential addition of the two acids, while several mixed diacyloxy(iodo)benzenes⁷ result also from (12) and RCO_2Na . The reaction of (8) with toluene-*p*-sulphonic acid gives hydroxy(tosyloxy)iodobenzene,¹³ (19), no doubt resulting from hydrolysis of the initially formed trifluoroacetoxy(tosyloxy)iodobenzene, which appears to be extremely prone to hydrolysis. Acid anhydrides react with compound (8)



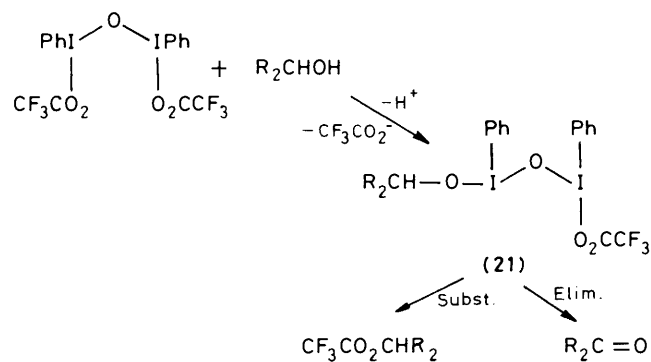
also affording mixed diacyloxy(iodo)benzenes in a reaction [equation (7)] which is the reverse of that described by equation (4).



That an equilibrium exists for this system is evident from the observation that acid anhydrides, such as Ac_2O and $(\text{PhCO})_2\text{O}$, coming from relatively weak acids even in large excess give little or no compound (17), whereas anhydrides from stronger acids, such as $(\text{CH}_2\text{ClCO}_2)_2\text{O}$ react stoichiometrically much more readily. In order to explain the formation of the mixed compounds, (17), it may be tentatively suggested that a species such as $\text{PhI}(\text{O}_2\text{CCF}_3)\text{O}^-$ rather than CF_3CO_2^- is produced and this then attacks the anhydride.

A study of the oxidative properties of (8) at room temperature showed that it is more effective in this respect than compound (12) (see Table 2). Thus, yields are always better with (8), even though reaction times are sometimes quite long. It is noted that from anthracene and diphenylacetylene the primary oxidation products³ are acylals and enol esters, respectively, which are further hydrolysed.

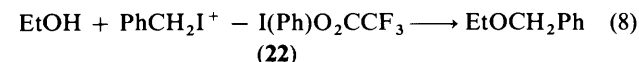
The oxidation of benzopinacol and benzhydrol with (8) takes 1 and 5 days, respectively, affording solely benzophenone. Primary alcohols are more resistant to oxidation and it took 45 days for benzyl alcohol to be converted into a mixture of benzaldehyde and benzyl trifluoroacetate; *n*-heptanol gave exclusively *n*-heptyl trifluoroacetate. The formation of this unexpected reaction product may be explained taking into account that the initially formed intermediate (21) (Scheme 4)



Scheme 4.

undergoes a proton elimination when the alcohol bears electron-withdrawing groups to form ketones either exclusively (two phenyl groups) or predominantly (one phenyl), whereas with aliphatic alcohols, (21) is attacked by CF_3CO_2^- to give the ester.

The reaction of alkyl iodides with (12) has been the subject of a separate study¹⁴ and it has been found that primary alkyl iodides give alkyl trifluoroacetates. A similar reaction is observed with compound (8). When the reaction was performed in CHCl_3 containing EtOH , the major product was benzyl ethyl ether (65%). Its formation must be due to a nucleophilic attack by the alcohol rather than CF_3CO_2^- on the intermediate (22), formed from benzyl iodide and (8). Efforts are under way to



investigate the details and the synthetic utility of the above reaction which is also given with (12).

* Compound (12) also gave a lower value of M osmotically. Analogous anomalies have been reported for related compounds (ref. 10).

Table 2. Oxidations with (8) and (12)

Substrate	Product(s) with (8)	(yield %)	(Time, d)	Product with (12)	(yield %)
Anthracene	Anthraquinone	(58)	(3)		
9,10-Dihydroanthracene	Anthraquinone	(68)	(3)	Anthracene	(20) ^{a,b}
PhC≡CPh	PhCOCOPh	(94)	(7)	PhCOCOPh ^c	(74)
Ph ₂ C(OH)C(OH)Ph ₂	Ph ₂ CO	(99)	(1)	Ph ₂ CO ^a	(90)
Ph ₂ CHOH	Ph ₂ CO	(86)	(5)	Ph ₂ CO ^{a,b}	(65)
PhCH ₂ OH	PhCHO(54) + PhCH ₂ O ₂ CCF ₃	(36)	(45)	PhCHO ^{a,b}	(50)
n-C ₇ H ₁₅ OH	n-C ₇ H ₁₅ O ₂ CCF ₃	(100) ^d	(45)		
PhCH ₂ I	PhCH ₂ O ₂ CCF ₃	(100) ^d	(0.1)	PhCH ₂ O ₂ CCF ₃	(54) ^e
I ₂	PhI	(88)	(1)	1,4-Di-iodobenzene	(80) ^f

^a Data taken from S. Spyroudis and A. Varvoglis, *Synthesis*, 1975, 445. ^b Heated at 80 °C with pyridine. ^c Datum taken from E. B. Merkushev and M. C. Schwarzberg, 'Organiodine Compounds in Synthesis' (in Russian), Tomsk Pedagog. Inst., Tomsk, USSR, 1978. ^d By n.m.r. ^e Ref. 14. ^f Datum from J. Gallos and A. Varvoglis, *J. Chem. Res.*, 1982 (S), 150; (M), 1649.

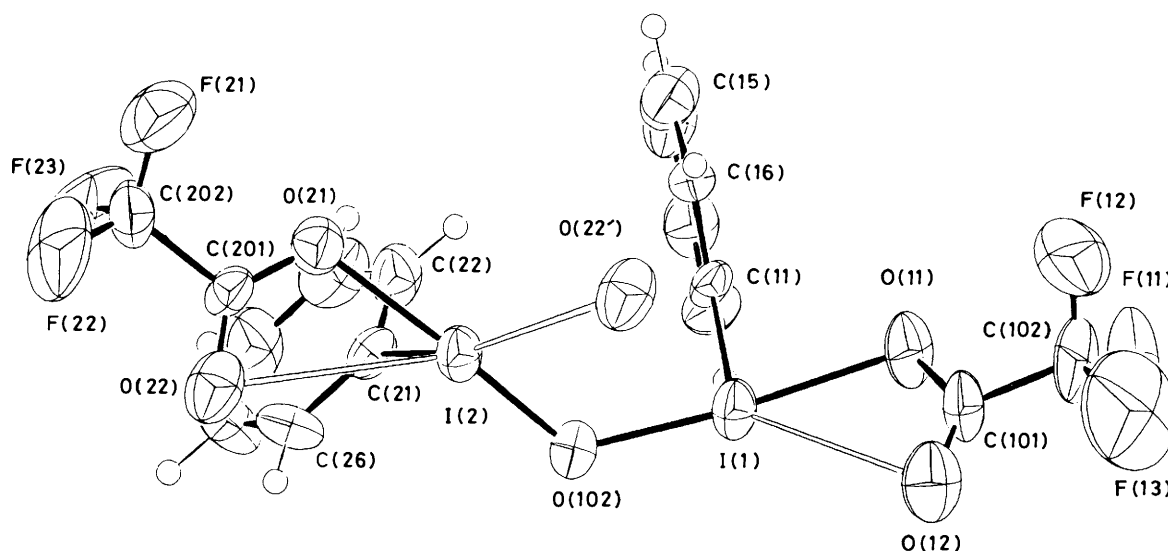


Figure 1. View of (8), showing the atomic numbering. Long I...O interactions are shown with outline bonds; O(22') is related to O(22) by $(1 - x, \frac{1}{2} + y, \frac{1}{2} - z)$.

The only significant difference between (8) and (12) is their behaviour towards iodine. Thus (12) affords *p*-di-iodobenzene almost quantitatively, whereas (8) gives only iodobenzene. No satisfactory explanation for this differentiation can be advanced at present.

Crystal Structure Determination.—The determination confirms the chemical identification of (8) as the μ -oxo species (Figure 1). Each iodine atom has the expected T-shaped geometry for its primary bonds, with a standard I—C distance^{5b} of 2.067(8) Å avg. (Table 3). The I—O distances are very different, 1.999(7), 2.033(7) Å to the bridge oxygen, and 2.258(8), 2.287(7) Å to the trifluoroacetate oxygen atoms; closely comparable distances [average 2.00(5) and 2.32(3) Å] occur in the μ -oxo nitrate.^{5b} The O—I—O angles are both somewhat below 180° [averages 172.7(3) and 169(1)° respectively]; the bridge angles in the two compounds are also similar [120.8(4) and 123.7(6)° respectively], both suggesting approximately sp^2 hybridisation. The most significant comparison is with the unbridged compound $C_6H_5I(O_2CCF_3)_2$.¹⁵ This has an identical I—C distance [2.074(4) Å] but the I—O distances are considerably shorter than those to the acid groups in the bridged compounds [average 2.164 Å with a range from 2.138(5) to 2.186(3)]. The O—I—O angle is also somewhat reduced [168.5(1)°]. However, the dimensions of the acid groups themselves are essentially identical, with the expected differences in O—C distances

[1.287(10) and 1.200(11) Å (avg.) in the bridged species, 1.277(5) and 1.192(5) Å in the unbridged one].

The variation in I—O distance undoubtedly results from the changing ionicity of these bonds. The effect on this of substituting an I—O—I bridge for an I—O (acid) bond correlates closely with the chemical evidence already described. In the unbridged compound, both I—O bonds are of equal, moderate polarity, but in the bridged species, the I—O bridge bonds are strong and of low polarity, while the I—O (acid) bonds have come closer to dissociation $I^+ O^-$, giving a framework $\delta^- \dots \delta^+ I \dots \delta^+ O \dots \delta^-$. The system can also be viewed in terms of multi-centre bonding. The O—I—O system is seen to exist either in a symmetrical or an unsymmetrical O—I...O form. This is comparable, for example, with the I_3^- and O—H—O systems, and suggests a description in terms of 3-centre-4-electron bonding without substantial d-orbital involvement.

Iodine(III) oxycompounds characteristically form secondary bonds,¹⁶ and in $[C_6H_5I(O_2CCF_3)_2]_2$ these form a pentagonal planar pattern around I, with three primary bonds in T-shaped arrangement, and two secondary bonds. In the present compound, I(1) has this geometry in the modified form of a half-pentagonal plane (in which only one secondary bond is present); this has previously been observed in tellurium(IV) aryl oxy-salts.¹⁵ For I(1), the secondary bond is formed by O(12), *i.e.* asymmetrical chelation from the trifluoroacetate group, and

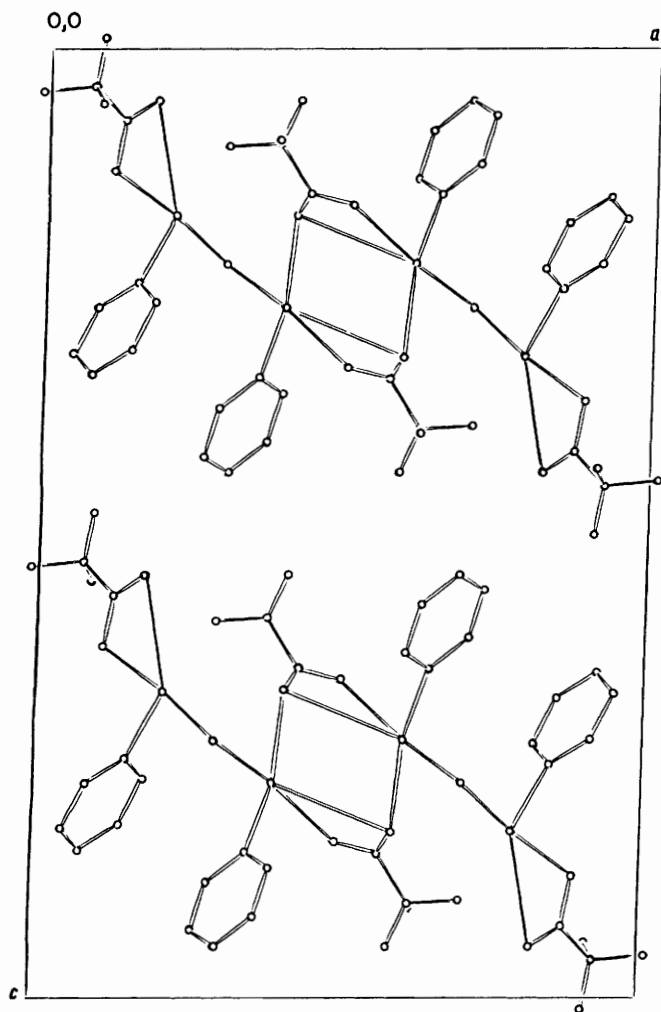


Figure 2. Packing diagram, viewed down *b*.

this atom is precisely coplanar with the other atoms around I(1) (Table 4). The secondary bond distance [2.929(8) Å] is slightly shorter than those in the unbridged compound [3.017(4) Å avg.] perhaps reflecting the greater positive character of the iodine atom. Surprisingly, for I(2), the oxy acid is twisted so that O(22) is as far out of plane as possible, and a weaker interaction is formed with O(22') from another molecule. This makes up a virtually linear secondary bond C(21)–I(2)···O(22'), and links the molecules into dimers around a centre of symmetry (Figure 2). The twist presumably results from some steric constraint, although its origin is not obvious. Curiously, in the unbridged compound, one of the two trifluoroacetate groups (here both attached to the same iodine) is twisted in an identical fashion. Similar behaviour, involving both pentagonal planar and linear secondary bonds has been found for [(MeC₆H₄)₂Te(O₂C-Me)₂].¹⁵

Experimental

¹H and ¹³C N.m.r. spectra were obtained on Varian spectrometers, A-60A and CFT-20, respectively, in CDCl₃ with SiMe₄ as internal standard. I.r. spectra were recorded on a Perkin-Elmer 297 spectrophotometer (Nujol mulls). Mass spectra were obtained from a Hitachi-Perkin-Elmer RMU-6L (single focussing) spectrometer at 70 eV.

All known compounds were characterised by comparison of their m.p. and spectral data with those of authentic samples. All

new compounds were recrystallised from CHCl₃–hexane. Chromatographic separations refer to column chromatography with silica gel as adsorbent and mixtures of light petroleum–chloroform as eluant.

μ-Oxo-bis[trifluoroacetato(phenyl)iodine] (**8**).—(a) To a suspension of (PhIO)_n (440 mg, 2 mmol) in CHCl₃ (15 ml) was added CF₃CO₂H (228 mg, 2 mmol) and the mixture was refluxed for 2 h. The filtered reaction mixture was evaporated and the residue crystallised upon addition of hexane (5 ml), to afford (**8**) (485 mg, 75%), m.p. 110–112 °C (Found: C, 29.6; H, 1.45. Calc. for C₁₆H₁₀F₆I₂O₅: C, 29.56; H, 1.55%).

(b) To a stirred solution of (**12**) (1.72 g, 4 mmol) in CH₂Cl₂ (20 ml) was added Bu^tOK (224 mg, 2 mmol). After the mixture had been stirred at room temperature for 1 h, CF₃CO₂K was filtered off and the solvent removed to leave (**8**) 1.264 g, 97%. A similar yield was obtained with MeONa, whereas NaOH (ratio 1:1) gave a yield of 79%.

(c) Other methods of preparing (**8**) involved the heating of PhI(OAc)₂ and CF₃CO₂H (1:1) in refluxing CHCl₃ (yield 97%); heating of PhI(OAc)(O₂CCF₃) in CHCl₃ (yield 95%); and heating of PhI(OAc)₂ and (**12**) in refluxing CHCl₃ (yield 78%).

Tri-μ-oxo-adfi-tetraphenyl-bh-bis(trifluoroacetoxy)tetraiodine (**16**).—(a) To a stirred solution of (**12**) (2.15 g, 5 mmol) in CH₂Cl₂ (20 ml) was added Bu^tOK (420 mg, 3.75 mmol). After 1 h CF₃CO₂K was filtered off and the CH₂Cl₂ removed to give (**16**) (1.15 g, 85%), m.p. 125–126 °C; δ 7.1–7.5 (12 H, m) and 7.7–7.9 (8 H, m); ν_{max}. 1 665 cm⁻¹; *m/z* 317 (5), 263 (3), and 204 (100) (Found: C, 30.5; H, 1.65. Calc. for C₂₈H₂₀F₆I₄O₇: C, 30.85; H, 1.85%).

(b) By the same procedure as in (a), (**8**) and Bu^tOK (2:1) and also (**12**) and NaOH (2:3) gave (**16**) (81 and 90% yield, respectively).

Mixed Diacyloxy(iodo)benzenes.—(a) *Acetoxy(trifluoroacetoxy)iodobenzene* (**15**). A solution of (**8**) (1.3 g, 2 mmol) and AcOH (480 mg, 8 mmol) in CHCl₃ (10 ml) was heated under reflux for 4 h. Evaporation of the solvent and addition of hexane to the oily residue gave crystalline (**15**) (1.147 g, 76%), m.p. 129–130 °C; δ 2.02 (3 H, s) and 7.22–7.97 (5 H, m); ν_{max}. 1 670 and 1 705 cm⁻¹; *m/z* 317 (5) and 204 (100) (Found: C, 31.45; H, 2.05. Calc. for C₁₀H₈F₃IO₄: C, 31.93; H, 2.14%).

(b) *Dichloroacetoxy(trifluoroacetoxy)iodobenzene* (**17**). By the same procedure as in (a), with a 1:2 ratio of (**8**):acid, (**17**) was obtained in 94% yield, m.p. 94–96 °C; δ 5.9 (1 H, s) and 7.6 (3 H, m); ν_{max}. 1 640–1 720br cm⁻¹; *m/z* 448, 446, 444 (*M*⁺), 333, 331, and 317 (Found: C, 26.8; H, 1.45. Calc. for C₁₀H₆Cl₂F₃IO₄: C, 26.09; H, 1.36%).

(c) *μ*-Malonato-bis[trifluoroacetato(phenyl)iodine] (**18**). By the same procedure as described above, with a 1:1 ratio of (**8**) malonic acid gave (**18**) (50%), m.p. 109–110 °C; δ 3.47 (2 H, s) and 7.95 (10 H, m); ν_{max}. 1 710 and 1 670 cm⁻¹; *m/z* 403 (trace) and 317 (8) (Found: C, 30.75; H, 1.65. Calc. for C₁₉H₁₂F₆I₂O₈: C, 30.98; H, 1.63%).

(d) *Chloroacetoxy(trifluoroacetoxy)iodobenzene* (**20**). The same procedure as described above was used but with (**8**) and (ClCH₂CO)₂O rather than the acid (ratio 1:1); yield of (**20**) 74%, m.p. 85–88 °C, δ 4.0 (2 H, s), 7.6 (3 H, m), and 8 (2 H, m); ν_{max}. 1 640–1 720br cm⁻¹; *m/z* 317 (1), 299, and 297 (trace) (Found: C, 28.8; H, 1.75. Calc. for C₁₀H₇ClF₃IO₄: C, 29.26; H, 1.72%).

Hydroxy(tosyloxy)iodobenzene (**19**). A mixture of (**8**) (1.3 g, 2 mmol) and toluene-*p*-sulphonic acid hydrate (760 mg, 4 mmol) in CHCl₃ (15 ml) was refluxed for 1 h. As the mixture cooled, (**19**) crystallised out (1.365 g, 87%), m.p. 133–135 °C (lit.¹³ m.p. 136–138 °C).

Oxidations with Compound (8).—All reactions were performed

Table 3. Bond lengths (Å) and bond angles (°)

I(1)–O(102)	2.033(7)	I(1)–O(11)	2.258(8)
I(1)–C(11)	2.064(10)	I(2)–O(102)	1.999(7)
I(2)–O(21)	2.287(7)	I(2)–C(21)	2.069(10)
O(11)–C(101)	1.295(13)	O(12)–C(101)	1.193(15)
O(21)–C(201)	1.281(13)	O(22)–C(201)	1.206(14)
F(11)–C(102)	1.321(18)	F(12)–C(102)	1.315(18)
F(13)–C(102)	1.244(15)	F(21)–C(202)	1.300(16)
F(22)–C(202)	1.324(17)	F(23)–C(202)	1.282(16)
C(101)–C(102)	1.512(19)	C(201)–C(202)	1.529(16)
C(11)–C(12)	1.372(15)	C(11)–C(16)	1.370(15)
C(12)–C(13)	1.392(17)	C(13)–C(14)	1.378(20)
C(14)–C(15)	1.387(20)	C(15)–C(16)	1.387(17)
C(21)–C(22)	1.387(16)	C(21)–C(26)	1.365(16)
C(22)–C(23)	1.382(17)	C(23)–C(24)	1.372(21)
C(24)–C(25)	1.346(20)	C(25)–C(26)	1.402(18)
I(1)⋯O(12)	2.939(8)	I(2)⋯O(22)	3.273(8)
I(2)⋯O(22')	3.084(9)		
O(102)–I(1)–O(11)	173.3(3)	O(102)–I(1)–C(11)	91.0(3)
O(11)–I(1)–C(11)	82.3(3)	O(102)–I(2)–O(21)	172.1(3)
O(102)–I(2)–C(21)	90.9(4)	O(21)–I(2)–C(21)	81.3(3)
I(1)–O(102)–I(2)	120.8(4)	I(1)–O(11)–C(101)	107.2(7)
I(2)–O(21)–C(201)	118.1(7)	O(11)–C(101)–O(12)	126.8(11)
O(11)–C(101)–C(102)	112.6(10)	O(12)–C(101)–C(102)	120.5(10)
F(11)–C(102)–F(12)	103.7(13)	F(11)–C(102)–F(13)	107.2(12)
F(12)–C(102)–F(13)	108.9(13)	F(11)–C(102)–C(101)	110.3(12)
F(12)–C(102)–C(101)	112.0(11)	F(13)–C(102)–C(101)	114.1(13)
O(21)–C(201)–O(22)	127.3(10)	O(21)–C(201)–C(202)	113.0(10)
O(22)–C(201)–C(202)	119.2(10)	F(21)–C(202)–F(22)	104.9(11)
F(21)–C(202)–F(23)	108.0(11)	F(22)–C(202)–F(23)	109.8(12)
F(21)–C(202)–C(201)	112.9(10)	F(22)–C(202)–C(201)	109.7(10)
F(23)–C(202)–C(201)	111.3(11)	I(1)–C(11)–C(12)	118.3(8)
I(1)–C(11)–C(16)	119.9(7)	C(12)–C(11)–C(16)	121.7(10)
C(11)–C(12)–C(13)	119.2(11)	C(12)–C(13)–C(14)	119.9(12)
C(13)–C(14)–C(15)	120.1(12)	C(14)–C(15)–C(16)	120.0(12)
C(11)–C(16)–C(15)	119.1(10)	I(2)–C(21)–C(22)	119.1(8)
I(2)–C(21)–C(26)	119.9(8)	C(22)–C(21)–C(26)	121.0(10)
C(21)–C(22)–C(23)	118.8(12)	C(22)–C(23)–C(24)	119.4(12)
C(23)–C(24)–C(25)	122.1(13)	C(24)–C(25)–C(26)	119.1(12)
C(21)–C(26)–C(25)	119.4(11)		
O(11)–I(1)⋯O(12)	48.5(3)	O(21)–I(2)⋯O(22)	42.9(2)
C(21)–I(2)⋯O(22')	161.8(3)		

O(22') is related to O(22) by $(1 - x, \frac{1}{2} + y, \frac{1}{2} - z)$

Table 4. Deviations from mean planes (Å) (defining atoms asterisked)

Plane 1: I(1),* 0.006; C(11),* 0.000; O(102),* –0.003; O(11),* –0.003; O(12), 0.07.

Plane 2: I(2),* 0.000; C(21),* 0.000; O(102),* 0.000; O(21), 0.000; O(22), 2.22; O(22'), –0.96.

in CHCl₃ at room temperature in the dark. The products were separated chromatographically.

Reaction of (8) with benzyl iodide in the presence of ethanol. To a solution of PhCH₂I (436 mg, 2 mmol) in CHCl₃ (15 ml) containing ethanol (1%) was added (8) (650 mg, 1 mmol). The mixture was then allowed to stand in the dark for 2 h after which it was washed with 5% aqueous NaHSO₃, and water, dried (Na₂SO₄), evaporated to dryness, and chromatographed. After phenyl iodide, benzyl trifluoroacetate (45 mg, 11%), benzyl ethyl ether (150 mg, 65%), and benzyl alcohol (40 mg, 18%) were sequentially eluted. Under the same conditions but with pure CHCl₃ only the ester was produced (by n.m.r.).

Table 5. Atom co-ordinates ($\times 10^4$)

Atom	x	y	z
I(1)	2 115.6(5)	3 872.1(15)	1 764.2(3)
I(2)	3 942.1(5)	3 537.7(13)	2 728.9(3)
O(102)	2 962(5)	2 003(13)	2 275(3)
O(11)	1 100(5)	6 086(15)	1 292(3)
O(12)	1 774(6)	4 650(16)	539(3)
O(21)	4 990(5)	5 031(13)	3 354(3)
O(22)	5 908(5)	2 054(15)	3 248(4)
F(11)	–126(6)	7 359(20)	447(4)
F(12)	876(7)	9 771(15)	580(4)
F(13)	893(8)	7 577(22)	–122(3)
F(21)	6 217(6)	6 903(14)	4 046(4)
F(22)	7 053(6)	4 070(19)	3 972(4)
F(23)	5 879(8)	3 852(22)	4 459(4)
C(101)	1 253(7)	5 907(22)	753(4)
C(102)	740(10)	7 658(28)	396(5)
C(201)	5 687(7)	3 827(19)	3 471(4)
C(202)	6 205(9)	4 673(23)	4 002(5)
C(11)	1 524(7)	5 278(18)	2 466(4)
C(12)	870(7)	4 040(21)	2 723(5)
C(13)	487(8)	4 918(24)	3 210(5)
C(14)	775(9)	6 997(25)	3 431(5)
C(15)	1 439(9)	8 220(23)	3 167(5)
C(16)	1 805(7)	7 368(19)	2 674(4)
C(21)	3 544(7)	1 923(19)	3 465(4)
C(22)	2 897(8)	2 954(23)	3 788(4)
C(23)	2 669(9)	1 933(25)	4 296(5)
C(24)	3 064(10)	–104(26)	4 458(6)
C(25)	3 686(9)	–1 128(23)	4 144(5)
C(26)	3 930(8)	–107(18)	3 630(5)

Crystal Structure Analysis.—Colourless lath-shaped crystals of (8), obtained as (a) above were suitable for X-ray study. Because of previous experience of crystal decomposition, the chosen crystal was held at –100 °C (with the Syntex LT-1 attachment), during data collection. Despite this, small intensity changes occurred in the three standard reflections (monitored every 100 reflections) and the data were adjusted using a sliding scale factor. These changes were partly due to some crystal movement, corrected by recentring every 300 reflections. A failure in the cooling system caused the loss of the crystal 200 reflections short of completion of the data set. Despite the problems, the final refinement proved fully satisfactory.

Crystal Data.—C₁₆H₁₀F₆IO₅, monoclinic, space group $P2_1/c$, $a = 15.013(5)$, $b = 5.809(4)$, $c = 23.455(8)$ Å, $\beta = 91.80(3)^\circ$, $U = 2 044(2)$ Å³, $M = 650.04$, $Z = 4$, $D_c = 2.12$ g cm^{–3}, Mo-K α radiation, $\lambda = 0.71 069$ Å, $\mu(\text{Mo-K}\alpha) = 31.2$ cm^{–1}, $F(000) = 1 012$. Data were collected with a Syntex $P2_1$ four-circle diffractometer. Maximum 2θ was 50° with scan range $\pm 1.05^\circ(2\theta)$ around the $K_{\alpha 1}$ – $K_{\alpha 2}$ angles, scan speed 3–29° min^{–1}, depending on the intensity of a 2 s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. Unit cell dimensions and standard deviations were obtained by least-squares fit to 15 high angle reflections. 1 787 Unique observed reflections ($I/\sigma(I) > 3.0$) were used in refinement, and corrected for Lorentz, polarisation, and absorption effects, the last with ABSCOR;¹⁷ maximum and minimum transmission factors were 0.93 and 0.64. The crystal dimensions were $0.17 \times 0.85 \times 0.095$ mm. Systematic absences $h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$, indicated space group $P2_1/c$. However, the automatic Patterson solution routine of SHELXTL¹⁸ did not show the expected two heavy atoms, and attempted solutions were unsuccessful in both this space group and in $P2/c$. In Pc , the Patterson solution routine showed four peaks, and the structure was readily solved starting from these as four iodine

atoms (*i.e.* two independent molecules in the asymmetric unit). After some refinement, with most light atoms located from Fourier synthesis, examination of the co-ordinates showed that the correct space group was $P2_1/c$ as originally expected. Final refinement in this space group was by cascaded least-squares methods. All non-hydrogen atoms were given anisotropic temperature factors, while hydrogen atoms were inserted at calculated positions with fixed isotropic temperature factors, $U = 0.07 \text{ \AA}^2$, and were not refined. The largest peaks on a final difference Fourier synthesis were of height 1 el. \AA^{-3} in the vicinity of the iodine atoms. A weighting scheme of the form $W = 1/(\sigma^2(F) + gF^2)$ with $g = 0.002$ was used, and this was shown to be satisfactory by weight analysis. The final R value was 0.043. Computing was with the SHELXTL system¹⁸ on a Data General NOVA3, following initial processing on a Burroughs B6700. Scattering factors in the analytical form and anomalous dispersion factors were taken from ref. 19. Final atomic co-ordinates are given in Table 5 and Figure 1 shows the atomic numbering. Thermal parameters and hydrogen atom co-ordinates are available as a Supplementary publication [SUP No. 56137 (2 pp)]* and the structure factors may be obtained on request from the editorial office.

* For details of the Supplementary publications Scheme, see Instructions for Authors (1985), *J. Chem. Soc., Perkin Trans. I*, 1985, Issue 1.

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