favours the chair–twist equilibrium hypothesis (Chandrasekharan & Bentrude, 1980). The angle between the two rings at N(3) and C(6) is 28°. The packing of the molecules in the unit cell essentially involves van der Waals contacts.

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Structure of Bis(trifluoroacetato)(phenyl)iodine(III), $C_{10}H_5F_6IO_4$

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Abstract. $M_r = 430\cdot04$, triclinic, $P\bar{1}$, $a = 9\cdot824$ (2), $b = 9\cdot111$ (1), $c = 7\cdot688$ (2) Å, $\alpha = 88\cdot75$ (2), $\beta = 99\cdot80$ (2), $\gamma = 90\cdot91$ (1)°, $V = 677\cdot93$ Å^3, $Z = 2$, $D_x = 2\cdot106$, $D_m = 2\cdot076$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 2\cdot48$ mm^{-1}, $F(000) = 408$, $T = 298$ K. Final $R = 0\cdot052$ for 1362 independent non-zero reflections. The molecule shows the characteristic T-shaped coordination geometry of three covalent bonds around the I atom, complemented by two inter- and one intramolecular I···O contacts, which may be considered as secondary bonds. The latter cause the formation of dimers between symmetry-equivalent molecules which, repeated along the b axis, form columns interconnected by O···H—C hydrogen bridging bonds.

Introduction. In the past decade considerable attention was given to compounds containing iodine(III) and a number of crystallographic and solid-state chemical studies appeared in the literature (*e.g.* Gougoutas & Lessinger, 1974; Etter, 1976; Alcock & Countryman, 1977). The main characteristic of almost all these compounds is the slightly distorted T-shaped coordination geometry around the I^{III} atom which forms three covalent bonds to other atoms. In addition, weak inter- and intramolecular coordination contacts between the I atom and its next-nearest neighbours are observed, which may be considered as secondary bonds.

The crystal-structure analysis of the title compound (FAIB) was carried out in order to investigate the features of the iodine coordination in the presence of the trifluoro groups. The compound is of special interest because of its strong oxidative character, which renders it especially effective not only in conventional oxidations but also in the conversion of amides to amines and the cleavage of several kinds of ethers, oxiranes and cyclopropanes (Spyroudis & Varvoglis, 1975, 1979, 1981; Radhakrishna, Parham, Riggs & Loudon, 1979; Shabarov, Pisanova & Saginova, 1981).

Experimental. Transparent, colourless crystals, 0·35 × 0·18 × 0·12 mm, m.p. 388–390 K; D_m measured by flotation in 1,3-dibromobutane/1,2-dibromoethane, computer-controlled Philips PW 1100 four-circle single-crystal diffractomer, three-dimensional data, graphite-monochromated Mo $K\alpha$, ω-scan mode; cell parameters and standard deviations by least-squares analysis of measured θ angles of the 41 strongest reflections; intensity statistics indicated $P\bar{1}$; three standard reflections exhibiting the same percentage linear decrease in intensity; 1663 measured reflections, $\theta = 3$–22°, index

Table 1. *Atomic coordinates and equivalent isotropic temperature factors* (Å^2) *for the non-*H *atoms in FAIB*

Here and throughout this paper e.s.d.'s are given in parentheses and refer to the last digit.

	x	y	z	B_{eq}*
I	0·1977 (1)	0·1196 (1)	0·3963 (1)	4·0
O(1)	0·169 (1)	0·282 (1)	0·589 (1)	4·7
O(2)	0·267 (1)	−0·023 (1)	0·214 (1)	4·8
O(3)	−0·030 (1)	0·166 (1)	0·604 (1)	6·3
O(4)	0·170 (1)	0·111 (1)	−0·018 (1)	5·8
F(1)	−0·030 (2)	0·489 (2)	0·691 (2)	12·9
F(2)	−0·054 (1)	0·336 (1)	0·878 (2)	12·3
F(3)	0·136 (1)	0·431 (1)	0·869 (2)	8·8
F(4)	0·185 (1)	−0·160 (2)	−0·182 (2)	13·5
F(5)	0·370 (2)	−0·049 (2)	−0·153 (2)	14·0
F(6)	0·340 (2)	−0·218 (2)	0·014 (2)	14·0
C(1)	0·374 (1)	0·245 (1)	0·383 (2)	3·8
C(2)	0·372 (2)	0·355 (2)	0·257 (2)	5·1
C(3)	0·490 (2)	0·434 (2)	0·255 (3)	7·1
C(4)	0·609 (2)	0·403 (2)	0·369 (3)	6·9
C(5)	0·611 (1)	0·295 (2)	0·497 (3)	6·2
C(6)	0·493 (1)	0·212 (1)	0·502 (2)	4·9
C(7)	0·055 (1)	0·261 (1)	0·649 (2)	4·0
C(8)	0·027 (1)	0·378 (2)	0·771 (2)	4·3
C(9)	0·230 (2)	0·004 (2)	0·042 (2)	6·3
C(10)	0·285 (2)	−0·110 (2)	−0·065 (2)	6·4

* $B_{eq} = \frac{8}{3}\pi^2 \text{ trace } \tilde{\mathbf{U}}$.

Table 2. *Interatomic distances* (Å) *and angles* (°)

I–O(1)	2·17 (1)	C(8)–F(1)	1·25 (2)
I–O(2)	2·13 (1)	C(8)–F(2)	1·29 (2)
I–C(1)	2·08 (1)	C(8)–F(3)	1·29 (2)
$I\cdots O(3)$	3·00 (1)	C(10)–F(4)	1·30 (2)
$I\cdots O(4)$	3·16 (1)	C(10)–F(5)	1·27 (3)
$I\cdots O(3^{i})$	3·06 (1)	C(10)–F(6)	1·23 (2)
O(1)–C(7)	1·29 (2)	C(1)–C(2)	1·37 (2)
O(2)–C(9)	1·33 (2)	C(2)–C(3)	1·36 (3)
O(3)–C(7)	1·20 (2)	C(3)–C(4)	1·36 (3)
O(4)–C(9)	1·19 (2)	C(4)–C(5)	1·37 (3)
C(7)–C(8)	1·50 (2)	C(5)–C(6)	1·38 (2)
C(9)–C(10)	1·50 (3)	C(6)–C(1)	1·39 (2)
		$C(4)–H(C4)\cdots O(1^{ii})$	3·56 (2)

O(1)–I–O(2)	168·3 (0·3)	F(1)–C(8)–F(2)	105·1 (1·5)
O(1)–I–C(1)	82·2 (0·4)	F(1)–C(8)–F(3)	104·2 (1·4)
O(2)–I–C(1)	86·5 (0·4)	F(2)–C(8)–F(3)	105·8 (1·3)
O(1)–I–O(3)	47·8 (0·3)	C(9)–C(10)–F(4)	108·9 (1·8)
O(2)–I–O(4)	44·8 (0·3)	C(9)–C(10)–F(5)	109·3 (1·6)
O(3)–I–O(3)	71·9 (0·3)	C(9)–C(10)–F(6)	117·7 (1·6)
$O(4)–I–O(3^{i})$	90·4 (0·3)	F(4)–C(10)–F(5)	105·3 (1·6)
I–O(1)–C(7)	111·7 (0·8)	F(4)–C(10)–F(6)	106·2 (1·7)
I–O(2)–C(9)	119·1 (1·0)	F(5)–C(10)–F(6)	108·7 (2·0)
O(1)–C(7)–O(3)	126·3 (1·3)	I–C(1)–C(2)	120·3 (0·9)
O(1)–C(7)–C(8)	113·0 (1·1)	I–C(I)–C(6)	117·6 (1·0)
O(3)–C(7)–C(8)	120·4 (1·3)	C(2)–C(1)–C(6)	122·1 (1·2)
O(2)–C(9)–O(4)	123·6 (1·5)	C(1)–C(2)–C(3)	117·8 (1·4)
O(2)–C(9)–C(10)	111·3 (1·4)	C(2)–C(3)–C(4)	121·4 (1·7)
O(4)–C(9)–C(10)	124·8 (1·5)	C(3)–C(4)–C(5)	121·2 (1·8)
C(7)–C(8)–F(1)	112·9 (1·3)	C(4)–C(5)–C(6)	118·9 (1·5)
C(7)–C(8)–F(2)	113·4 (1·3)	C(5)–C(6)–C(1)	118·7 (1·4)
C(7)–C(8)–F(3)	114·5 (1·3)	$C(4)–H(C4)\cdots O(1^{ii})$	146·9

Symmetry code: (i) $-x, -y, 1-z$; (ii) $1-x, 1-y, 1-z$.

range h 0→10, h −9→9, l −8→7, 1362 with $I > 2\sigma(I)$; correction for decrease in intensity, no absorption correction; I atom located by Patterson synthesis; remaining non-H atoms by Fourier synthesis; full-matrix least squares using F, *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976); H atoms at calculated positions (C—H = 1·09 Å) with isotropic temperature factors as those of bonded C atoms but not refined, $w = x \times y$ with $x = 1$ if $\sin\theta > B$, else $x = \sin\theta/B$ and $y = 1$ if $F_{obs} < C$, else $y = C/F_{obs}$ where $B = 0{\cdot}25$, $C = 60{\cdot}0$; $R = 0{\cdot}052$, $R_w = 0{\cdot}600$, $S = 1{\cdot}87$, $(\Delta/\sigma)_{max} = 0{\cdot}143$, $(\Delta/\sigma)_{mean} = 0{\cdot}024$, $\Delta\rho = -1{\cdot}06–1{\cdot}23$ e Å^{-3} in the region of the I atom.

Discussion. Final positional parameters and equivalent isotropic temperature coefficients for the non-H atoms are given in Table 1.* Interatomic distances and angles are in Table 2. A clinographic projection of the FAIB molecule is shown in Fig. 1. The characteristic feature of the molecule is the T-shaped arrangement of three covalent bonds around the I atom familiar from most compounds of I^{III} investigated. The angles C(1)—I—O(1), C(1)—I—O(2) and O(1)—I—O(2) are 82·2 (4), 86·5 (4) and 168·3 (3)°, respectively. The two bond lengths I—O(1) = 2·17 (1) and I—O(2) = 2·13 (1) Å differ slightly. They and the bond distance I—C(1) = 2·08 (1) Å are comparable with the sums, 1·94 and 2·05 Å, of the corresponding covalent radii (Pauling, 1960). As in the case of bis(dichloroacetato)(phenyl)iodine(III) (Alcock, Countryman, Esperas & Sawyer, 1978) apart from these covalent bonds, three I···O contact distances are also observed. They are significantly less than 3·46 Å, the sum of the van der Waals radii of the corresponding atoms (Bondi, 1964), and may be considered as secondary bonds (Alcock, 1972). Two of them, I···O(3) = 3·00 (1) and I···O(4) = 3·16 (1) Å, are intermolecular contacts, while the third, I—O(3^{i}), is an intramolecular contact between the I atom and the free

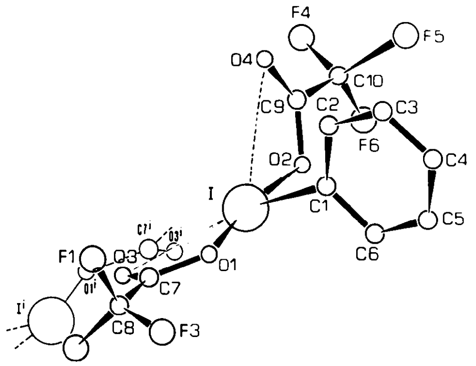

Fig. 1. Clinographic projection of the FAIB molecule.

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* Lists of structure factors, anisotropic thermal parameters of the non-H atoms, coordinates and isotropic temperature factors for H atoms and least-squares-planes' calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39185 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

oxygen of the acetoxy groups of an inversion equivalent molecule. In this way, O(3) is involved in both inter- and intramolecular contacts causing dimerization of the molecules (*cf.* Fig. 2). The T-shaped group I,O(1),O(2),C(1) is planar to within 0·04 (3) Å with O(3), O(3^{i}) and O(4) at distances of 0·15 (1), −0·67 (<1) and 2·19 (1) Å from the mean plane. Consequently, the dihedral angles which the T-group plane forms with the planes of the two acetoxy groups, involving O(3) and O(4), and the plane of the I,O(1),O(2),O(3^{i}) group are 4·6 (<1), 84·6 (3) and 12·9 (2)°, respectively. The planar phenyl ring is almost perpendicular to the T-group plane, dihedral angle 87·8 (1)°. The structural and conformation details given so far agree very well with those of bis(dichloroacetato)(phenyl)iodine(III) mentioned above. However, there is a considerable deviation from the structure of diacetato(phenyl)iodine(III) (Lee, Mak, Li & Kirner, 1977; Alcock *et al.*, 1978), in which only two secondary I···O bonds are observed in a pentagonal-planar arrangement with the three covalent I—O bonds of the T-group.

The bond lengths and angles in the two acetoxy groups, apart from the difference between the O(1)—C(7) and O(2)—C(9) distances, are within acceptable values. In the two $-CF_3$ groups the F atoms have relatively large thermal parameters and the C—F bond lengths show significant differences. Since there was no indication of disorder, these may be attributed to the high degree of libration of the $-CF_3$ groups about the corresponding C—C bonds, which prevents accurate determination of the F-atom positions. The mean values of the bond angles in the two groups, 109·3 and 109·4°, are normal for a tetrahedral arrangement. The mean values of the F—C—F angles, 105·0 and 106·7°, and those of the C—C—F angles, 113·6 and 112·0°, agree satisfactorily with the corresponding values given in the recent literature (*e.g.* Doesburg, Petit & Merckx, 1982; Stenkamp & Ko, 1982).

A projection of the structure illustrating the molecular packing of FAIB in the unit cell is shown in Fig. 2. The centrosymmetrical dimers, repeated along the *b* axis, form columns interconnected by O···H—C hydrogen bridging bonds (Table 2).

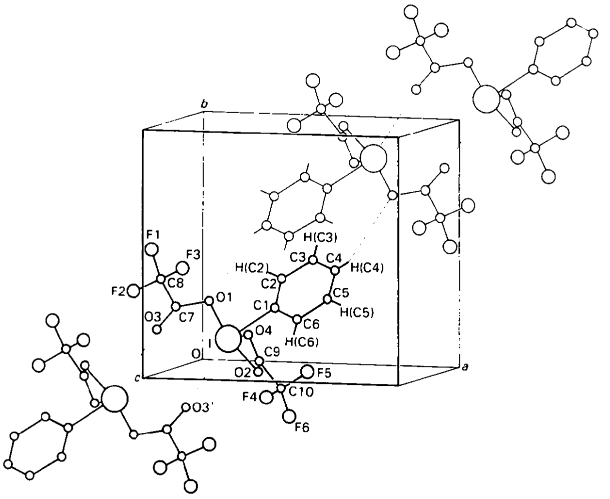

Fig. 2. Clinographic projection showing the molecular packing.

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