Structure of μ-Oxo-bis[trifluoroacetato(m-tolyl)iodine(III)]

By S. C. Kokkou* and C. J. Cheer

Pastore Chemical Laboratory, Department of Chemistry, University of Rhode Island, Kingston, RI 02881, USA

Abstract. $C_{18}H_{14}F_6I_2O_5$, $M_r = 678 \cdot 11$, triclinic, $P\bar{1}$, $a = 11 \cdot 627$ (2), $b = 10 \cdot 968$ (1), $c = 10 \cdot 488$ (1) Å, $\alpha = 117 \cdot 93$ (1), $\beta = 85 \cdot 39$ (2), $\gamma = 106 \cdot 24$ (1)°, $V = 1132 \cdot 48$ Å^3, $Z = 2$, $D_x = 1 \cdot 988$ g cm^{-3}, λ(Mo Kα) = $0 \cdot 71069$ Å, $\mu = 28 \cdot 9$ cm^{-1}, $F(000) = 644$, $T = 294$ K, final $R = 0 \cdot 068$ for 2011 unique observed reflections. Both I atoms of the molecule have the characteristic T-shaped primary geometry found in most dsp^3 hybridized trivalent iodine compounds but the I—O(oxo) distances are considerably shorter than the I—O(trifluoroacetato) ones. In addition, the two I atoms have different overall coordination. While one forms a single intramolecular secondary bond to O, the second forms both intra- and intermolecular secondary bonds to two O atoms. The latter secondary bond links symmetry-equivalent molecules into dimers.

Introduction. μ-Oxo-diiodine compounds, in which two trivalent I atoms are linked through O, are representative of a class of substances the chemistry of which is neither well understood nor thoroughly investigated. Recently, Gallos, Varvoglis & Alcock (1985) reported the synthesis, structure and properties of μ-oxo-bis-[trifluoroacetato(phenyl)iodine] (OFAPI hereafter). Professor Varvoglis and Dr Papadopoulou have also prepared the title compound, μ-oxo-bis[trifluoroacetato(m-tolyl)iodine] (OFATI hereafter) and have generously provided us with a crystalline sample in order to carry out its X-ray structure analysis as a complement to the reported study of the phenyl derivative, and in order to provide further structural information regarding the electronic influence of substituents on the nature of bonds in hypervalent iodine compounds.

Experimental. Transparent, colourless crystals, $0 \cdot 64 \times 0 \cdot 24 \times 0 \cdot 16$ mm, computer-controlled Philips PW 1100 four-circle diffractometer, three-dimensional data, graphite-monochromated Mo Kα, ω-scan mode; cell parameters and standard deviations by least-squares analysis of measured θ angles of the 160 strongest reflections; intensity statistics indicated $P\bar{1}$;

three standard reflections per hour ($\bar{2}11$, 011, $0\bar{3}2$) exhibiting the same percentage linear decrease in intensity; 2039 (of 4946 possible) measured reflections [with $I_{top} - 2(I_{top})^{1/2} > I_{bck}$, I_{top} = counts s^{-1} at the top of reflections, I_{bck} = mean counts s^{-1} of background at each side of reflection; the minimum observed value for I_{bck} was 12 counts s^{-1}], $\theta = 3$–$27°$, max. $\sin\theta/\lambda = 0 \cdot 6388$ Å^{-1}, index range $h \pm 15$, $k \pm 15$, l $0 \rightarrow 15$, 2011 unique reflections, $R_{int} = 0 \cdot 061$, 28 unobserved with $F_o < 4\sigma(F_o)$, correction for decrease in intensity, no absorption correction; I atoms located by Patterson synthesis, remaining non-H atoms by Fourier synthesis; blocked full-matrix least squares using F with *SHELXTL* (Sheldrick, 1981); atomic scattering factors from *International Tables for X-ray Crystallography* (1974); H atoms at calculated positions (C—H = $0 \cdot 96$ Å) with isotropic temperature factors $1 \cdot 2$ times the equivalent isotropic U of the C atoms to which they are bonded; in the final cycle of refinement m-tolyl groups with adjusted geometry treated as rigid groups and the anisotropic temperature coefficients of their atoms held invariant; the weighting scheme chosen was $w = 1/[\sigma^2(F_o) + gF_o^2]$, where g was fixed at $0 \cdot 00121$, a value which gave the least variation of the mean value of $w(F_o - F_c)^2$ with the magnitude of F_o [$\sigma(F_o)$ from counting statistics]; $R = 0 \cdot 068$, $wR = 0 \cdot 089$, $S = 1 \cdot 500$, $(\Delta/\sigma)_{max} = 0 \cdot 041$, $(\Delta/\sigma)_{mean} = 0 \cdot 005$, $\Delta\rho = -1 \cdot 30$ to $1 \cdot 26$ e Å^{-3} in the region of I atoms.

Discussion. The final positional parameters are given in Table 1.† An *ORTEP*II (Johnson, 1976) view of the OFATI molecule is shown in Fig. 1. The characteristic structural feature of the molecule is the T-shaped arrangement of three covalent bonds around each I atom familiar from most unbridged compounds of trivalent iodine studied so far. However, as in the case of OFAPI, the I—O distances reflecting the chemically

---

† Lists of structure amplitudes, bond distances and angles, 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 Document Supply Centre as Supplementary Publication No. SUP 43199 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* Permanent address: Applied Physics Laboratory, Department of Physics, Aristotle University of Thessaloniki, Thessaloniki 54006, Greece.

Table 1. *Atom coordinates* ($\times 10^3$, *for* I $\times 10^4$) *and temperature factors* ($\text{Å}^2 \times 10^3$)

	x	y	z	U_{eq}*
I(1)	6075 (1)	2179 (1)	4712 (1)	61
I(2)	3945 (1)	1798 (1)	2262 (2)	73
O(1)	487 (1)	289 (1)	415 (1)	70
O(2)	767 (1)	185 (1)	555 (1)	68
O(3)	640 (1)	10 (1)	591 (2)	88
O(4)	291 (1)	61 (1)	5 (2)	93
O(5)	218 (1)	252 (2)	79 (2)	98
F(1)	844 (1)	−55 (2)	619 (2)	163
F(2)	832 (2)	120 (3)	797 (2)	199
F(3)	946 (1)	135 (2)	634 (3)	217
F(4)	71 (2)	−84 (2)	−139 (2)	173
F(5)	193 (2)	−2 (3)	−252 (2)	199
F(6)	66 (2)	111 (2)	−145 (2)	189
C(1)	737 (1)	84 (2)	592 (2)	62
C(2)	841 (1)	74 (2)	660 (3)	92
C(3)	218 (2)	126 (2)	−3 (2)	83
C(4)	132 (2)	37 (3)	−136 (2)	116
C(5)	746 (1)	377 (1)	457 (1)	42
C(6)	786 (1)	510 (1)	579 (1)	60
C(7)	877 (1)	619 (1)	569 (1)	66
C(8)	927 (1)	595 (1)	437 (1)	66
C(9)	887 (1)	462 (1)	315 (1)	60
C(10)	797 (1)	353 (1)	325 (1)	59
C(11)	937 (1)	433 (1)	166 (1)	86
C(12)	507 (1)	304 (1)	139 (1)	56
C(13)	555 (1)	448 (1)	237 (1)	65
C(14)	631 (1)	540 (1)	189 (1)	82
C(15)	658 (1)	488 (1)	44 (1)	81
C(16)	610 (1)	344 (1)	−53 (1)	96
C(17)	535 (1)	252 (1)	−6 (1)	77
C(18)	693 (1)	702 (1)	276 (1)	98

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

distinct nature of the corresponding bonds are very different. Those to the bridge atom [I(1)—O(1) = 2·02 (2), I(2)—O(1) = 1·98 (1) Å] are considerably shorter than those to the trifluoroacetate O atoms [I(1)—O(2) = 2·30 (2), I(2)—O(4) = 2·29 (2) Å]. The latter are even longer than the corresponding I—O bond distances in the unbridged compound bis(trifluoro-acetato)(phenyl)iodine(III) (FAIB hereafter) (Stergioudis, Kokkou, Bozopoulos & Rentzeperis, 1984; Alcock, Harrison & Howes, 1984) as a result of the differentiation of their strength caused by the substitution of an I—O—I bridge for an I—O(oxyacetato) bond. As expected from the structure of I^{III} oxy-compounds so far investigated (Varvoglis, 1982; Musher, 1969), the coordination geometry of both I atoms is complemented by I···O secondary bonds (Alcock, 1972), i.e. I···O contacts significantly shorter than 3·46 Å, the sum of the van der Waals radii of the corresponding atoms (Bondi, 1964). I(1) forms one intra- and one intermolecular secondary bond [I(1)···O(3) = 3·18 (12), I(1)···O(3^i) = 3·12 (2) Å respectively], coplanar to a good approximation with its covalent bonds so that its overall geometry can be described as approximately pentagonal planar. The T-shaped group I(1), O(1)O(2), C(5) is planar to within 0·07 (1) Å with O(3) and O(3^i) at distances 0·06 (1) and 0·48 (1) Å from its mean plane. The intermolecular secondary bond I(1)···O(3^i) links the molecules with inversion equivalent ones into dimers

(*cf.* Fig. 2). I(2) on the contrary, forms only one intramolecular secondary bond [I(2)···O(5) = 3·13 (2) Å] distinctly non-coplanar with its covalent bonds. Owing to the twisted orientation of the corresponding trifluoroacetoxy group, O(5) is at a distance −2·19(2)Å from the mean plane of the T-group I(2), O(1),O(4),C(12) which is planar to within 0·01 (1) Å.

Noticeable differences concerning the I···O secondary bonding in OFATI are observed in comparison with OFAPI and FAIB. In the oxo-bridged compound OFAPI one of the I atoms also forms one intra- and one intermolecular I···O secondary bond. The O atoms, however, are at 2·22 and 0·96 Å from the mean plane of the corresponding T-group so that the I···O bonds are not coplanar with it and consequently the overall coordination geometry of this I atom is not planar. In addition, the lengths of these two secondary bonds [3·273 (8), 3·084 (9) Å] are unequal with a considerable difference (15·7σ). The other I atom again
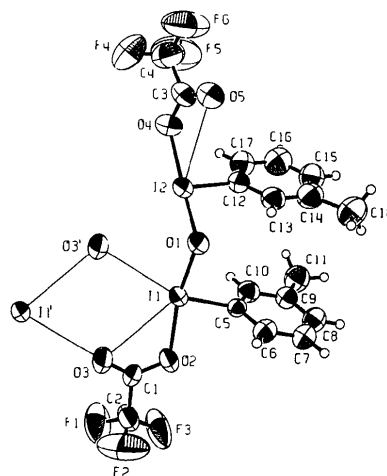

Fig. 1. *ORTEPII* drawing (Johnson, 1976) of the OFATI molecules. Thermal ellipsoids are drawn at 50% probability level while isotropic hydrogen thermal parameters are represented by spheres of arbitrary size.
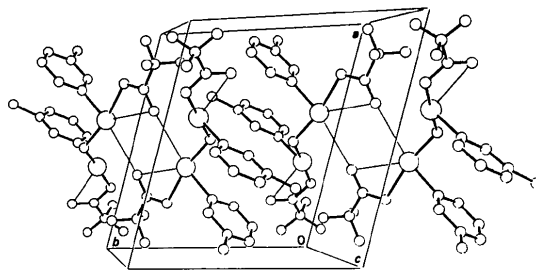

Fig. 2. Perspective view of the unit cell showing the molecular packing.

forms only one intramolecular I⋯O secondary bond [2·939 (8) Å]. But this is precisely coplanar with its primary bonds and has a length significantly shorter than any other I⋯O distance in OFAPI or OFATI. In the unbridged compound FAIB the I atom forms two intra- [3·00 (1), 3·16 (1) Å] and one intermolecular [3·06 (1) Å] secondary I⋯O bonds, *i.e.* three in all instead of two. One of the former is approximately coplanar with its primary bonds but the other two lie well out of the plane of the covalent bonds. Their lengths are unequal with differences less than those in the case of OFAPI but still greater than those in the case of the present compound OFATI.

It is worthwhile to note that in all three compounds one of the acetoxy groups is twisted in an indentical way so that the deviations of respective O atoms from the mean planes of the corresponding T-groups are almost the same [2·19 (1) in OFATI, 2·19 (1) in FAIB, 2·22 Å in OFAPI]. In no case are there obvious steric constraints to which this twist may be attributed.

Fig. 2 shows the molecular packing of OFATI in the unit cell. The centrosymmetrical dimers repeat along the *c* axis to form columns. A short intermolecular contact $[O(5)\cdots H(6^i) = 2\cdot6\ (2)$ Å, $O(5)\cdots C(6^i) = 3\cdot31\ (2)$ Å, angle $O(5)\cdots H(6^i)-C(6^i) = 133\cdot8\ (5)°$, with the symmetry code (i) $1-x$, $1-y$, $1-z$] suggests that they may be interconnected by a possible weak O⋯H—C hydrogen bond.

References

ALCOCK, N. W. (1972). *Adv. Inorg. Chem. Radiochem.* **15**, 1–58.
ALCOCK, N. W., HARRISON, W. D. & HOWES, C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1709–1716.
BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.
GALLOS, J., VARVOGLIS, A. & ALCOCK, N. W. (1985). *J. Chem. Soc. Perkin Trans.* pp. 757–763.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 71–151. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
JOHNSON, C. K. (1976). *ORTEPII.* ORNL-5138. Oak Ridge National Laboratory, Tennessee.
MUSHER, J. (1969). *Angew. Chem. Int. Ed. Engl.* **8**, 54–68.
SHELDRICK, G. M. (1981). *Nicolet SHELXTL* Operations Manual, revision 3. Nicolet XRD Corporation, Cupertino, California.
STERGIOUDIS, G. A., KOKKOU, S. C., BOZOPOULOS, P. A. & RENTZEPERIS, P. J. (1984). *Acta Cryst.* C40, 877–879.
VARVOGLIS, A. (1982). *Chem. Soc. Rev.* **10**, 377–407.

Structure of 5,7-Dibromo-3-phenyl-1,2-benzisoxazole 2-Oxide

BY S. C. KOKKOU*

Pastore Chemical Laboratory, Department of Chemistry, University of Rhode Island, Kingston, RI 02881, USA

Abstract. $C_{13}H_7Br_2NO_2$, $M_r = 369\cdot02$, monoclinic, $P2_1/n$, $a = 13\cdot362\ (3)$, $b = 23\cdot544\ (4)$, $c = 3\cdot8893\ (8)$ Å, $\beta = 96\cdot10\ (2)°$, $V = 1216\cdot59$ Å^3, $Z = 4$, $D_x = 2\cdot014$ Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0\cdot71069$ Å, $\mu = 7\cdot05$ mm^{-1}, $F(000) = 712$, $T = 298$ K, $R = 0\cdot062$ for 970 independent non-zero reflections. In the isoxazole 2-oxide ring the acyclic N—O bond distance compares well with that of a nitro group while the cyclic one is longer. Both compare very well with the corresponding bond distances in furoxans. These features may be used to interpret some aspects of the mass spectra of benzisoxazole *N*-oxides.

Introduction. Recently, Tsiamis & Tsoungas (1985) reported the electron-impact mass spectra of a series of 1,2-benzisoxazole *N*-oxides. They are representative of a new class of heterocyclic *N*-oxides, the molecular structure of which has already been confirmed by X-ray analysis of 5-chloro-3-methyl-1,2-benzisoxazole 2-oxide (CMBO hereafter)·(Chiari & Viterbo, 1982). In order to have further evidence for those structural features of these compounds which are correlated with their mass spectra, we have elected to carry out the X-ray crystal structure determination of the title compound, suitable crystals of which were generously supplied by Professor C. Tsiamis.

Experimental. Transparent crystals, 0·54 × 0·48 × 0·37 mm, computer-controlled Philips PW 1100 four-

* Permanent address: Applied Physics Laboratory, Department of Physics, Aristotle University of Thessaloniki, Thessaloniki 54006, Greece.