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Structure of Bis(diphenyl iodonium *I*-oxide) Diacetate Trihydrate

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Abstract. $2C_{12}H_{10}IO^+.2C_2H_3O_2^-.3H_2O$, $M_r = 766\cdot36$, triclinic $P\bar{1}$, $a = 12\cdot401$ (2), $b = 12\cdot058$ (2), $c = 11\cdot074$ (1) Å, $\alpha = 106\cdot32$ (2), $\beta = 109\cdot67$ (1), $\gamma = 94\cdot65$ (1)°, $V = 1467\cdot9$ Å^3, $Z = 2$, $D_m = 1\cdot729$, $D_x = 1\cdot733$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å, $\mu = 2\cdot22$ mm^{-1}, $F(000) = 756$, $T = 298$ K, final $R = 0\cdot056$ for 3868 independent non-zero reflections. The coordination around each I atom is distorted octahedral comprising two normal I–C$_{ar}$ [2·13–2·15 (1) Å], one normal I–O [both 1·84 (1) Å] and three secondary I···O bonds [2·45–2·93 (1) Å]. Secondary and H bonds bridge two $C_{14}H_{13}IO_3$ units to form a dimer, which is further linked to a centrosymmetrically equivalent one to form a tetramer. Finally, H bonds link tetramers together into columns along **c**.

Introduction. Diaryliodosyl salts, $Ar_2I^+O.X^-$, constitute a class of little known hypervalent organoiodine compounds in contrast to the well known diaryliodonium salts $Ar_2I^+.X^-$ (Koser, 1983). The hydrated diphenyl iodonium *I*-oxide acetate (DPIA hereafter) is, so far as we know, the only crystalline representative of this structurally unexplored class of compounds. Since spectroscopic data (Beringer & Bodlaender, 1968) could not distinguish among several alternative formulae, a detailed structure investigation was considered necessary.

Experimental. Colourless crystals, $0\cdot5 \times 0\cdot3 \times 0\cdot25$ mm, m.p. 387–389 K. D_m measured by flotation in 1,2-dibromoethane/carbon tetrachloride. Philips PW 1100 computer-controlled single-crystal diffractometer. Cell constants by least-squares analysis of θ angles of 140 strong reflections within the range 9–20°. Graphite-monochromated Mo $K\alpha$, θ–2θ scan mode. Three standard reflections exhibiting the same percentage linear decrease in intensity (20%). 6716 measured reflections, $\theta = 3$–30°, max. $hkl = 16$, ±16, ±13, 3868 with $I > 2\sigma(I)$, $R_{int} = 0\cdot059$ from merging 1184 symmetry-equivalent reflections. Correction for intensity drop, no absorption correction. Space group $P\bar{1}$ from intensity statistics. I atoms located by Patterson synthesis, remaining non-H atoms by Fourier synthesis. Full-matrix least-squares refinement using F, *XRAY*72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). H atoms at calculated positions with isotropic temperature factors equal to those of the atoms to which they are bonded, $w = 1/\{1 + [(F_o - B)/A]^2\}$ with $A = 10$, $B = 50$; final $R = 0\cdot056$, $wR = 0\cdot056$, $S = 1\cdot03$, $(\Delta/\sigma)_{max} = 0\cdot28$, $(\Delta/\sigma)_{mean} = 0\cdot02$, $\Delta\rho = -0\cdot85$ to $1\cdot00$ e Å^{-3}. Atomic scattering factors and anomalous-dispersion correction from *International Tables for X-ray Crystallography* (1974).

Discussion. Final positional parameters and equivalent isotropic temperature coefficients for the non-H atoms are given in Table 1.* Selected interatomic distances and angles are in Table 2. A clinographic projection of

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* Lists of structure amplitudes, anisotropic thermal parameters, H-atom parameters, C—H bond distances, least-squares-plane calculations, selected short intra- and intermolecular distances and bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43274 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and equivalent isotropic temperature factors* (Å^2)

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

	x	y	z	B_{eq}*
I(1)	−0·09908 (5)	0·17122 (5)	0·12710 (6)	2·7
O(1)	0·0125 (5)	0·2170 (6)	0·3003 (7)	3·3
O(3)	−0·2505 (6)	0·1361 (6)	−0·0968 (7)	3·7
C(25)	−0·265 (1)	0·031 (1)	−0·175 (1)	2·8
C(26)	−0·299 (1)	0·010 (1)	−0·320 (1)	3·9
O(4)	−0·2481 (7)	−0·0522 (6)	−0·1283 (8)	4·2
O(W1)	−0·0267 (7)	−0·0366 (7)	0·1300 (8)	4·6
O(W2)	0·1106 (7)	0·1478 (8)	0·5136 (9)	5·2
O(W3)	0·0428 (8)	−0·0973 (8)	0·3654 (9)	5·5
I(2)	0·22448 (5)	0·27303 (5)	0·24953 (6)	2·5
O(2)	0·0982 (5)	0·2448 (6)	0·0900 (7)	3·0
O(5)	0·4098 (6)	0·3175 (7)	0·4433 (7)	3·9
C(27)	0·404 (1)	0·292 (1)	0·545 (1)	3·6
C(28)	0·517 (1)	0·271 (1)	0·638 (1)	5·6
O(6)	0·316 (1)	0·284 (1)	0·572 (1)	5·9
C(1)	−0·2363 (7)	0·1116 (7)	0·1816 (9)	2·3
C(2)	−0·210 (1)	0·057 (1)	0·278 (1)	3·5
C(3)	−0·296 (1)	0·017 (1)	0·317 (1)	4·5
C(4)	−0·409 (1)	0·038 (1)	0·260 (1)	4·2
C(5)	−0·433 (1)	0·094 (1)	0·166 (1)	4·5
C(6)	−0·349 (1)	0·132 (1)	0·123 (1)	3·4
C(7)	−0·138 (1)	0·343 (1)	0·151 (1)	3·4
C(8)	−0·108 (1)	0·414 (1)	0·285 (1)	4·1
C(9)	−0·130 (1)	0·528 (1)	0·312 (1)	4·5
C(10)	−0·177 (1)	0·571 (1)	0·206 (1)	4·8
C(11)	−0·205 (1)	0·500 (1)	0·076 (1)	4·8
C(12)	−0·186 (1)	0·384 (1)	0·045 (1)	3·9
C(13)	0·215 (1)	0·454 (1)	0·326 (1)	2·8
C(14)	0·144 (1)	0·498 (1)	0·227 (1)	3·8
C(15)	0·134 (1)	0·615 (1)	0·276 (1)	4·6
C(16)	0·191 (1)	0·683 (1)	0·410 (1)	5·2
C(17)	0·257 (1)	0·633 (1)	0·501 (1)	5·3
C(18)	0·271 (1)	0·519 (1)	0·461 (1)	4·0
C(19)	0·348 (1)	0·310 (1)	0·161 (1)	2·5
C(20)	0·445 (1)	0·398 (1)	0·237 (1)	3·9
C(21)	0·518 (1)	0·425 (1)	0·172 (1)	4·3
C(22)	0·491 (1)	0·363 (1)	0·037 (1)	4·6
C(23)	0·394 (1)	0·273 (1)	−0·035 (1)	3·8
C(24)	0·317 (1)	0·246 (1)	0·026 (1)	3·2

$$* \ B_{eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

the DPIA dimer is shown in Fig. 1. Two I—C_{ar} bonds and one I—O bond around each of the two I atoms in the asymmetric unit form distorted trigonal pyramids with the I atoms occupying the apices, an arrangement resembling that of the I—O main bonds in the IO^{3-} ion (Alcock, 1972). A further three secondary I⋯O bonds, *trans* to the normal bonds, complete a distorted octahedral coordination around each I atom (see Table 2). Secondary bonds and H bonds bridge the two octahedral arrangements to form a dimer which is further linked by secondary and hydrogen bonds to form a tetramer. The crystal structure of DPIA is made up of columns of such tetramers along c held together by H bonds (see below).

The I—C_{ar} bonds (2·13, 2·13, 2·13, 2·15 Å) differ only slightly and are comparable with the sum (2·05 Å) of the covalent radii (Pauling, 1960). The two covalent I—O bonds [both 1·84 (1) Å] have some double-bond character being significantly shorter than the expected covalent bond of 1·99 Å (Feikema & Vos, 1966). The weak interactions I(1)⋯O(3), I(2)⋯O(5), I(1)⋯O(2), I(2)⋯O(1), I(1)⋯O(W1) and I(2)⋯O(4^i) (see Table 2) are longer than the covalent bond but significantly

shorter than the sum (3·05 Å) of the van der Waals radii (Bondi, 1964). As mentioned above they are aligned *trans* to the corresponding main bonds and may be considered as secondary bonds (Alcock, 1972). The length of the longest bond, I(2)⋯O(1) = 2·93 (1) Å, may be a consequence of O(1) participating in the short

Table 2. *Selected interatomic distances* (Å) *and angles* (°)

I(1)–O(1)	1·842 (6)	I(2)–O(2)	1·844 (6)
I(1)–C(1)	2·13 (1)	I(2)–C(13)	2·134 (9)
I(1)–C(7)	2·13 (1)	I(2)–C(19)	2·15 (1)
I(1)⋯O(2)	2·732 (7)	I(2)⋯O(5)	2·451 (6)
I(1)⋯O(W1)	2·735 (9)	I(2)⋯O(1)	2·933 (8)
I(1)⋯O(3)	2·449 (7)	I(2)⋯O(4^i)	2·712 (7)
C(1)–C(2)	1·37 (2)	C(13)–C(14)	1·41 (2)
C(2)–C(3)	1·38 (2)	C(14)–C(15)	1·40 (2)
C(3)–C(4)	1·40 (2)	C(15)–C(16)	1·38 (2)
C(4)–C(5)	1·37 (2)	C(16)–C(17)	1·38 (2)
C(5)–C(6)	1·38 (2)	C(17)–C(18)	1·37 (2)
C(6)–C(1)	1·40 (1)	C(18)–C(13)	1·38 (1)
C(7)–C(8)	1·38 (2)	C(19)–C(20)	1·38 (1)
C(8)–C(9)	1·40 (2)	C(20)–C(21)	1·39 (2)
C(9)–C(10)	1·38 (2)	C(21)–C(22)	1·38 (2)
C(10)–C(11)	1·36 (2)	C(22)–C(23)	1·38 (1)
C(11)–C(12)	1·40 (2)	C(23)–C(24)	1·40 (2)
C(12)–C(7)	1·37 (2)	C(24)–C(19)	1·38 (1)
C(25)–O(3)	1·28 (2)	C(27)–O(5)	1·27 (2)
C(25)–O(4)	1·25 (1)	C(27)–O(6)	1·23 (2)
C(25)–C(26)	1·45 (2)	C(27)–C(28)	1·52 (2)
O(W1)⋯O(2^i)	2·787 (9)		
O(W1)⋯O(W3)	2·78 (1)		
O(W2)⋯O(1)	2·66 (1)		
O(W2)⋯O(6)	2·69 (1)		
O(W2)⋯O(W3)	2·84 (1)		
O(W2)⋯O(W3^ii)	2·79 (2)		
O(1)–I(1)–C(1)	94·8 (3)	O(2)–I(2)–C(13)	93·4 (3)
O(1)–I(1)–C(7)	92·8 (3)	O(2)–I(2)–C(19)	92·9 (3)
O(1)–I(1)⋯O(2)	77·6 (3)	O(2)–I(2)⋯O(1)	72·3 (3)
O(1)–I(1)⋯(W1)	79·6 (3)	O(2)–I(2)⋯O(4^i)	84·2 (3)
O(1)–I(1)⋯O(3)	172·8 (3)	O(2)–I(2)⋯O(5)	171·6 (3)
C(1)–I(1)⋯C(7)	93·6 (4)	C(13)–I(2)⋯C(19)	93·7 (4)
C(1)–I(1)⋯O(3)	85·9 (3)	C(13)–I(2)⋯O(1)	86·6 (3)
C(1)–I(1)⋯O(W1)	87·4 (3)	C(13)–I(2)⋯O(5)	86·8 (3)
C(1)–I(1)⋯O(2)	171·9 (3)	C(13)–I(2)⋯O(4^i)	172·1 (4)
C(7)–I(1)⋯O(2)	89·5 (4)	C(19)–I(2)⋯O(5)	78·7 (3)
C(7)–I(1)⋯O(3)	80·0 (3)	C(19)–I(2)⋯O(4^i)	78·9 (3)
C(7)–I(1)⋯O(W1)	172·4 (3)	C(19)–I(2)⋯O(1)	165·1 (3)
O(2)⋯I(1)⋯O(3)	101·9 (2)	O(5)⋯I(2)⋯O(1)	116·2 (3)
O(2)⋯I(1)⋯O(W1)	88·5 (3)	O(5)⋯I(2)⋯O(4^i)	94·5 (2)
O(3)⋯I (1)⋯O(W1)	107·6 (2)	O(1)⋯I(2)⋯O(4^i)	99·8 (2)

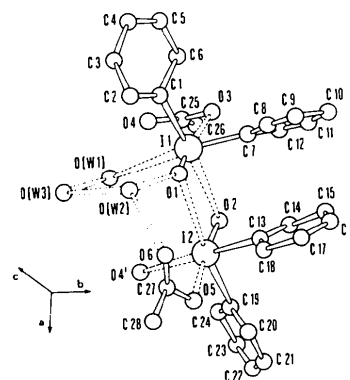Symmetry code: (i) −x, −y, −z; (ii) −x, −y, −z+1.

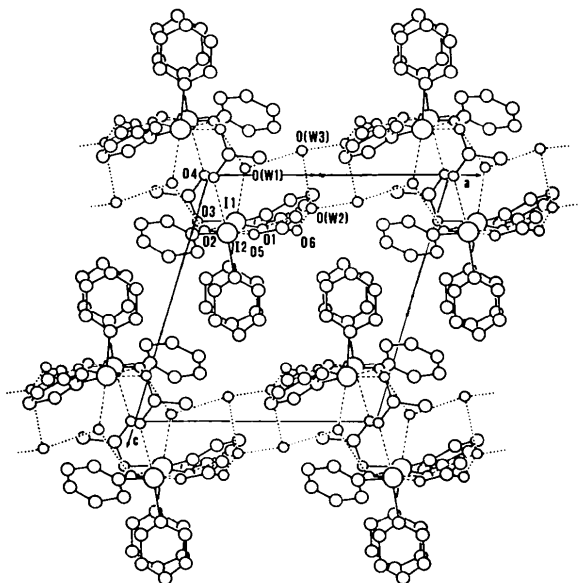Fig. 1. Clinographic projection of the asymmetric unit of DPIA on (001).

Fig. 2. Normal projection of DPIA on (010) showing the packing in the unit cell.

H bond $O(W2)\cdots O(1) = 2.66$ (1) Å. The angle $I(1)-O(1)\cdots I(2) = 101.0$ (3)° is smaller than the corresponding angle $I(2)-O(2)\cdots I(1) = 108.4$ (4)°. To complete the octahedral arrangement of bonds, $I(1)$ requires the O atom of the water molecule $W1$, whilst $I(2)$ requires the centrosymmetrically related acetoxy O atom, $O(4^i)$. The rather short H bonds $O(6)\cdots O(W2) = 2.69$ (1) Å and $O(W2)\cdots O(1) = 2.66$ (1) Å and the two secondary bonds $I(1)\cdots O(2)$ and $I(2)\cdots O(1)$ bridge two formula units to form a dimer. Two such dimers, linked by the

secondary bonds $I(2)\cdots O(4^i)$, $I(1)\cdots O(W1)$, and the H bond $O(2^i)\cdots O(W1) = 2.79$ (1) Å (together with the symmetrically related bonds), form a tetramer around the centre of symmetry at (0,0,0). The tetramer constitutes the true structural unit of the crystal. A network of H bonds, $O(W1)\cdots O(W3)$, $O(W3)\cdots O(W2)$ and $O(W2)\cdots O(W3^{ii})$, links tetramers around centres of symmetry to form columns along c (see also Fig. 2, which shows a projection of the structure). A list of short intra- and intermolecular distances has been deposited.

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Triethylammonium Salt of 1,2,3,4-Tetrahydro-6-hydroxy-4-oxo-N-phenyl-2-thio-5-pyrimidinecarboxamide, Ethanol Solvate

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Abstract. $(C_2H_5)_3NH^+.C_{11}H_8N_3O_3S^-.C_2H_5OH$, $M_r = 410.5$, orthorhombic, $P2_12_12_1$, $a = 11.765$ (3), $b = 12.788$ (3), $c = 15.011$ (3) Å, $U = 2258.4$ Å^3, $Z = 4$, $D_x = 1.21$ g cm^{-3}, $F(000) = 880$, $\lambda(Mo\ K\alpha_1) = 0.70926$ Å, $\mu = 1.4$ cm^{-1}, room temperature, $R = 0.059$ for 1931 'observed' reflections. The molecular dimensions are interpreted in favour of canonical forms in which the formal negative charge on the anion is delocalized over two sites. In addition the double bonds of the $-NH-CS-NH$ and $-CO-NH-$ moieties are