

## Iodobenzene Diacetate

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**Abstract.**  $C_{10}H_{11}IO_4$ ,  $[\phi I(OAc)_2]$ , orthorhombic, space group  $Pnn2$  ( $C_{2v}^{10}$ , No. 34);  $a = 15.737(5)$ ,  $b = 8.521(5)$ ,  $c = 8.729(5)$  Å;  $Z = 4$ ,  $D_m = 1.786$  (by flotation in  $CHBr_3/CCl_4$ ),  $D_x = 1.814$  g cm $^{-3}$ . The structure was refined to a conventional  $R$  value of 0.04. The molecular shape is a 'bent T' with the benzene ring occupying an equatorial position in the trigonal-bipyramidal arrangement of bonds and lone pairs around the central iodine atom.

**Introduction.** Colorless crystals of  $\phi I(OAc)_2$  in needle form were prepared by the method of Böeseken & Schneider (1931). A crystal ground to a sphere of diameter 0.43 mm was used in the data collection. Unit-cell parameters and intensities were measured at the University of Notre Dame on a Syntex  $P\bar{I}$  automatic diffractometer, with a graphite monochromator and Mo  $K\alpha$  radiation. The data consisted of 1428 independent reflections recorded in the  $\theta$ - $2\theta$  scan mode (scan width  $1.5^\circ$  below  $K\alpha_1$  to  $1.5^\circ$  above  $K\alpha_2$ ; variable scan speed from 2 to  $12^\circ$  min $^{-1}$ ) out to a limit of  $\sin \theta/\lambda \leq 0.648$  Å $^{-1}$ . No absorption correction was applied ( $\mu = 15.1$  cm $^{-1}$ ). After applying the usual Lorentz-polarization factor, 1261 observed data were used in the analysis. The structure was solved by the

heavy-atom method and refined by full-matrix least squares with anisotropic temperature factors for all 15 non-hydrogen atoms. The final  $R$  value based on the observed reflections was 0.04 with weights  $w = 1/\sigma^2(F)$ . Scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). Structure factor calculation and least-squares refinement were carried out with a modification

Table 1. Fractional atomic coordinates ( $\times 10^5$  for I and  $\times 10^4$  for C and O) with e.s.d.'s in parentheses

	x	y	z
I	4924 (3)	23975 (6)	0
C(1)	1613 (6)	1784 (13)	1137 (12)
C(2)	2151 (7)	2984 (14)	1647 (16)
C(3)	2879 (9)	2546 (15)	2421 (17)
C(4)	3063 (7)	943 (18)	2681 (14)
C(5)	2534 (8)	-185 (16)	2132 (15)
C(6)	1771 (7)	209 (13)	1353 (14)
O(1)	89 (5)	2957 (10)	2316 (10)
O(2)	1214 (5)	1619 (10)	-1925 (9)
C(7)	-703 (7)	3408 (13)	2296 (13)
C(8)	731 (9)	1712 (15)	-3155 (15)
O(3)	-1099 (5)	3547 (10)	1105 (11)
O(4)	4 (8)	2134 (15)	-3045 (11)
C(9)	-1092 (9)	3762 (17)	3853 (15)
C(10)	1106 (10)	1183 (18)	-4596 (13)

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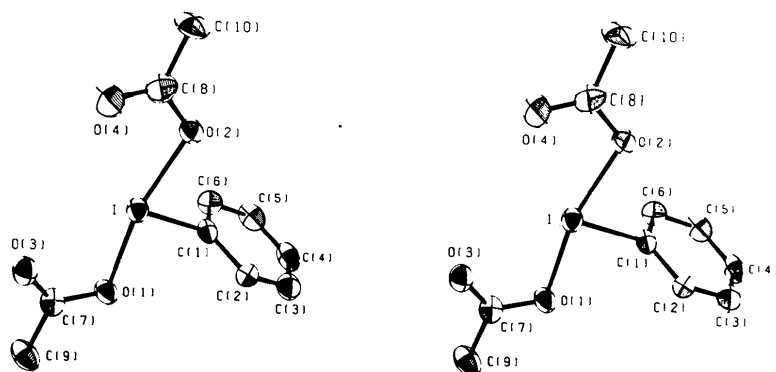


Fig. 1. A stereoview and atom numbering of the iodobenzene diacetate molecule.

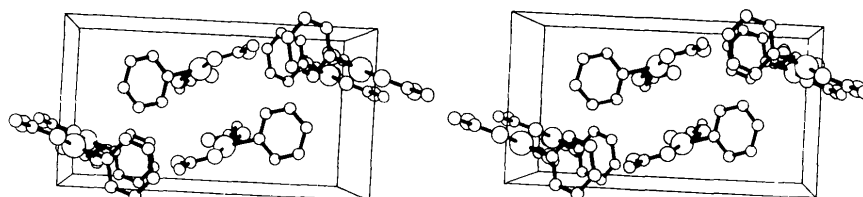


Fig. 2. A stereo-drawing showing the molecular packing viewed approximately along  $c$  towards the origin of the unit cell.

Table 2. Bond lengths (Å) and bond angles ( $^{\circ}$ ) with their estimated standard deviations

C(1)—I	2.093 (9)	C(6)—C(5)	1.422 (17)
O(1)—I	2.186 (9)	C(7)—O(1)	1.304 (14)
O(2)—I	2.143 (8)	C(8)—O(2)	1.324 (16)
C(2)—C(1)	1.402 (16)	O(3)—C(7)	1.224 (14)
C(6)—C(1)	1.379 (16)	C(9)—C(7)	1.528 (17)
C(3)—C(2)	1.383 (18)	O(4)—C(8)	1.203 (19)
C(4)—C(3)	1.414 (20)	C(10)—C(8)	1.468 (18)
C(5)—C(4)	1.360 (19)		
C(1)—I—O(1)	81.6 (0.4)	C(1)—C(6)—C(5)	116.7 (1.1)
C(1)—I—O(2)	81.6 (0.4)	I—O(1)—C(7)	109.2 (0.7)
O(1)—I—O(2)	163.2 (0.3)	I—O(2)—C(8)	108.8 (0.7)
I—C(1)—C(2)	118.7 (0.8)	O(1)—C(7)—O(3)	121.8 (1.1)
C(2)—C(1)—C(6)	123.8 (1.0)	O(1)—C(7)—C(9)	115.4 (1.0)
C(1)—C(2)—C(3)	117.4 (1.1)	O(3)—C(7)—C(9)	122.9 (1.0)
C(2)—C(3)—C(4)	120.7 (1.2)	O(2)—C(8)—O(4)	119.9 (1.3)
C(3)—C(4)—C(5)	120.0 (1.2)	O(2)—C(8)—C(10)	117.1 (1.2)
C(4)—C(5)—C(6)	121.4 (1.2)	O(4)—C(8)—C(10)	122.9 (1.3)

of the program *ORFLS* (Busing, Martin & Levy, 1962). The final positional parameters are listed in Table 1.\*

An *ORTEP* (Johnson, 1965) plot of the molecule with numbering of the atoms is shown in Fig. 1. The bond lengths and angles are given in Table 2. A stereoscopic drawing of the structure viewed along  $c$  towards the origin is shown in Fig. 2.

**Discussion.** Hypervalent iodine compounds have received considerable attention in current chemical literature (Musher, 1969). Recent work includes solid-state chemical studies of benziodole compounds (Etter, 1976*a,b*) and theoretical calculations with CNDO/2 (Hollingworth & Hacopian, 1974) and *ab initio* LCGO—MO—SCF (Rode, 1975) methods. As a contribution to this field, we have undertaken an X-ray analysis of the crystal and molecular structure of iodobenzene diacetate. The compound is of special interest since it reacts with dicarboxylic acids to form polyesters of the type  $[-O-I-(\varphi)-O-CO-(CH_2)_m-CO-]_n$  (Livingston, Sullivan & Musher, 1968) whose unusual solubility behavior and physical properties are attributable to the presence of the iodine(III) atom.

\* Tables of thermal parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32418 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The molecular structure of iodobenzene diacetate is based on a trigonal-bipyramidal arrangement of bonds and lone pairs around the iodine(III) atom, with the acetoxy groups occupying the axial sites and the benzene ring one of the equatorial positions. The gross molecular geometry may be described as a bent T-shape, in accord with those found for  $BrF_3$  (Magnuson, 1957),  $ClF_3$  (Smith, 1953; Burbank & Bensey, 1953), and  $\varphi ICl_2$  (Archer & van Schalkwyk, 1953). The two acetoxy groups, the benzene ring, and the O(1)—I[C(1)]—O(2) grouping are all planar entities within experimental error.

In comparison with the known structure of  $\varphi ICl_2$ , the bulkier acetoxy groups in  $\varphi I(OAc)_2$  are expected to cause greater deviation from the idealized T-shape. This is substantiated by the fact that the  $\varphi-I-OAc$  angle of  $81.6^{\circ}$  is considerably smaller than the corresponding  $\varphi-I-Cl$  angle of  $86.0^{\circ}$ . However, dimensions of the common iodobenzene moiety of both molecules are very similar. In  $\varphi I(OAc)_2$  the dihedral angle between the benzene ring and the planar O(1)—I[C(1)]—O(2) grouping is  $75.4^{\circ}$ , whereas the corresponding angle in  $\varphi ICl_2$  is  $86.2^{\circ}$ .

The measured C—I and O—I distances (Table 2) are in good agreement with the appropriate sums of covalent atomic radii, and are also similar to those found in 1-acetoxy-1,2-benziodoxolin-3-one (Gougoutas & Clardy, 1972*a*) and related compounds (Gougoutas & Clardy, 1972*b*; Gougoutas & Lessinger, 1974).

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## Tétrafluoroborate de *N,N*-Diméthyl-(*O*-éthyl)phénylpropiolamidium

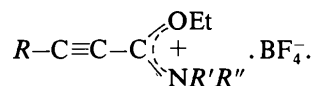
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**Abstract.**  $[C_{13}H_{16}NO]^+BF_4^-$ ; monoclinic, space group  $P2_1/m$ ;  $a = 12.072$  (5),  $b = 6.866$  (3),  $c = 8.912$  (4) Å;  $\beta = 93.22^\circ$ ;  $Z = 2$ ;  $V = 737.5$  Å<sup>3</sup>;  $D_x = 1.30$  g cm<sup>-3</sup>. The structure was solved by direct methods and refined by block-diagonal least squares to an  $R$  of 0.127. Organic cations lie in the symmetry planes. Strong interaction occurs between the short triple bond and the aromatic ring.

**Introduction.** Baum & Viehe (1976) ont émis l'idée que la fonction iminium  $>C=N^+<$  directement implantée sur une liaison multiple doit exercer sur celle-ci un effet inductif et mésomère important, susceptible de se manifester par des additions de Diels–Alder ou des cycloadditions dipolaires-1,3 faciles. Ils ont vérifié cette hypothèse sur une série originale de dérivés



Nous avons, de notre côté, vérifié et analysé la structure du dérivé dans lequel  $R = C_6H_5$ , et  $R' = R'' = CH_3$ . Les conditions d'enregistrement du spectre de diffraction sont données au Tableau 1.

Les extinctions systématiques du spectre de diffraction donnent le choix entre les groupes spatiaux  $P2_1$  et

$P2_1/m$ . Afin de ne pas préjuger de l'existence de plans de symétrie dans la structure, celle-ci a été résolue, par application de la chaîne de programmes *MULTAN* 74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974), dans l'hypothèse d'une symétrie  $P2_1$ . La première synthèse de Fourier, calculée au moyen des 250 coefficients  $E$  les plus élevés, a fait apparaître la position de tous les atomes, hormis les hydrogènes. A l'exception de deux atomes de fluor de l'ion  $BF_4^-$ , tous les atomes de l'unité asymétrique du motif présentent des coordonnées  $y$  très voisines, de telle sorte qu'on peut, en bonne approximation, les localiser dans un plan moyen unique, perpendiculaire à l'axe binaire. L'écart moyen des positions individuelles par rapport à

Tableau 2. *Coordonnées des atomes* ( $\times 10^4$ ) *avec écarts-type*

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	−23 (6)	7500 (0)	7238 (8)
C(2)	−973 (7)	7500 (0)	8093 (8)
C(3)	−2003 (6)	7500 (0)	7326 (8)
C(4)	−2086 (6)	7500 (0)	5752 (8)
C(5)	−1210 (6)	7500 (0)	4901 (8)
C(6)	−161 (6)	7500 (0)	5648 (8)
C(7)	830 (5)	7500 (0)	4795 (7)
C(8)	1624 (5)	7500 (0)	4142 (7)
C(9)	2685 (5)	7500 (0)	3458 (6)
N(10)	2750 (5)	7500 (0)	1990 (6)
C(11)	1707 (6)	7500 (0)	919 (8)
C(12)	3791 (6)	7500 (0)	1288 (8)
O(13)	3588 (4)	7500 (0)	4287 (4)
C(14)	3553 (6)	7500 (0)	5950 (8)
C(15)	4738 (7)	7500 (0)	6532 (8)
B(16)	7038 (9)	7500 (0)	1434 (11)
F(17)	6356 (5)	7500 (0)	143 (5)
F(18)	7617 (3)	9050 (6)	1462 (4)
F(19)	6400 (4)	7500 (0)	2695 (5)

Tableau 1. *Conditions expérimentales*

Spectre relevé sur un diffractomètre Picker à quatre cercles commandé par cartes perforées  
 Source Cu  $K\alpha$ ,  $\lambda = 1,5418$  Å; filtre Ni  
 Balayage  $\omega-2\theta$ ;  $\theta_{max} = 50^\circ$   
 Nombre de réflexions indépendantes mesurées: 826  
 Nombre de réflexions observées: 668  
 Critère d'observation  $I/\sigma(I) \geq 2,5$