Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
Frenz, B. A. (1985). *Enraf–Nonius SDP-Plus Structure Determination Package*. Version 3.0. Enraf–Nonius, Delft, The Netherlands.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Li, N., Maluendes, S., Blessing, R. H., Dupuis, M., Moss, G. R. & De Titta, G. T. (1994). *J. Am. Chem. Soc.* **116**, 6494–6507.
Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Universities of York, England, and Louvain, Belgium.
Peters, J. A. (1979). *Synthesis*, pp. 321–336.
Piacenza, G., Legsaï, G., Blaive, B. & Gallo, R. (1996). *J. Phys. Org. Chem.* **9**, 427–432.
Pierrot, M., Baldy, A., Wimmer, E., Gallo, R. & Boileau, J. (1985). *Eur. Crystallogr. Meet.* **9**, 266.
Vogtle, F. (1992). Editor. *Fascinating Molecules in Organic Chemistry*, pp. 44–57. Chichester: John Wiley.
Xu, S., Gantzel, P. K. & Clark, L. B. (1994). *Acta Cryst.* C**50**, 1988–1989.
Zefirov, N. S. & Palyulin, V. A. (1991). *Top. Stereochem.* **20**, 171–230.

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Dimethyl 2-Iodobenzoylphosphonate, an Unusual Example of a Crystalline α-Ketophosphonate

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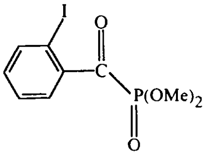
Abstract

The crystal structure analysis of the title compound, $C_9H_{10}IO_4P$, is a rare example of a full structural determination of an α-ketophosphonate ester, a type of compound which normally forms an oil. The P—C(carbonyl) bond is long, there is evidence that steric repulsion between the I and O(carbonyl) atoms is unexpectedly weak and there is a short intermolecular I···O contact linking the molecules in chains. The structure is compared with 2-iodobenzoyl compounds and with a nickel complex of an α-ketophosphonate.

Comment

Acylphosphonates are a particularly interesting group of phosphonates. The proximity of the carbonyl and phosphoryl groups confers special physical, chemical and biological properties on these compounds, while the electron-withdrawing nature of the functional groups results in increased reactivity of both groups and of the bond linking them; for these reasons they are normally considered to be a separate class of phosphonate. Acylphosphonates and their derivatives have been reviewed recently (Breuer, 1996). As these substances normally form oils, dimethyl 2-iodobenzoylphosphonate, (I), represents an unusual example of a crystalline acylphosphonate ester suitable for X-ray structural analysis.



(I)

The molecular structure shows some features of special interest. The P—C7 bond distance is long; the Cambridge Structural Database (Allen & Kennard, 1993; Fletcher, McMeeking & Parkin, 1996) revealed 50 structures with 55 fragments containing phosphonate esters attached to trigonal planar C_{sp^2} atoms. Mean P=O, P—O and P—C distances were 1.461 (2), 1.567 (2) and 1.791 (3) Å, respectively; the P=O and P—O distances of the title compound correspond well with those in the database, but the P—C7 distance is close to the maximum previously found, *i.e.* 1.856 Å in menthylmethyl (R_P)-phenylphosphonate (Donohue & Mandel, 1981), and would be considered somewhat long even for a P—C_{sp^3} bond (Allen, Kennard, Watson, Brammer & Orpen, 1987).

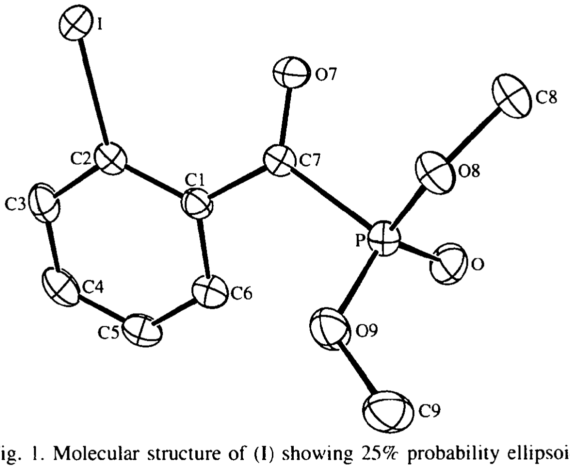


Fig. 1. Molecular structure of (I) showing 25% probability ellipsoids. H atoms are omitted for clarity.

The intramolecular I···O7 distance [3.094 (4) Å] is distinctly less than the sum of van der Waals radii (3.50 Å; Bondi, 1964); allied to this the dihedral angle of the ketophosphorus plane against the benzenoid plane is only 26.2 (2)°. The Cambridge Structural Database (Allen & Kennard, 1993; Fletcher *et al.*, 1996) surprisingly did not reveal any data on 2-iodophenyl ketones, but some carboxylic acids, salts, esters and amides were found. Table 2 summarizes the shortest I···O contact distances and the acute dihedral angles between least-squares planes formed by (*a*) the benzene and carboxylic C atoms and (*b*) the *ipso*-C atom and the three atoms of the carboxylic group. Dihedral angles and I···O distances cover wide ranges and there is a clear correlation between the two. In several cases, the I···O distances are short and the angles small, indicating that in such cases the expected steric repulsion between the I and the carboxylic O atoms does not materialize. The I···O7 distance for the title compound is among the shortest, quite close to those of 2-iodobenzoic and 3-iodo-2-naphthoic acids. It is tentatively suggested that there is an incipient tendency to cyclization with formation of an I—O bond.

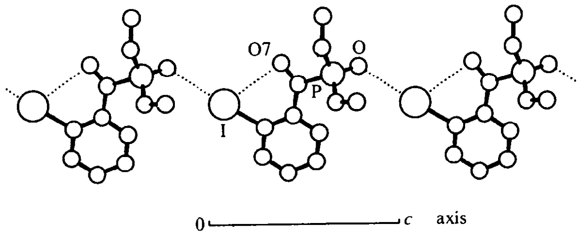


Fig. 2. Packing diagram of (I) along the *c* axis showing the I···O contacts. The view is down the *b* axis.

In addition to this, there is a short intermolecular I···O contact of 3.008 (3) Å, the connected molecules being related by translation along the *c* axis. It is possible that this interaction is responsible for the crystalline nature of this particular ketophosphonate as attempts to crystallize the bromo, chloro and fluoro compounds have not been successful. The I—C2, I···O7 and I···O^{i} vectors are coplanar, and the I···O^{i} and I—C2 vectors almost collinear. The presence of short non-bonded contacts between the I and two O atoms indicates that the I atom carries a partial net positive charge, its own electronegativity being overcome by the higher electronegativity of the ketophosphonate group to which it is conjugated. The I atom is thus able to attract lone-pair electrons from O atoms to build this very unusual arrangement.

Certain ketophosphonate esters form η^2-(CO) complexes with nickel. Although there have been no structural determinations of a complex and the same uncoordinated ligand, it is useful to attempt a comparison of the geometry of the title compound with that of a nickel complex of a ketophosphonate ester (Nakazawa, Nosaka, Kushi & Yoneda, 1990). The complex $[Ni(Ph_3P)_2\{\eta^2\text{-}(CO)EtC(O)P(O)(OMe)_2\}]$ shows P—C and C—O bond lengths of 1.810 (7) and 1.336 (8) Å, respectively. The P—C bond length is shorter than in the title compound but longer than the mean P—C distance quoted above. However, the difference in C—O distances is highly significant, that in the complex being much longer, and the three bonds within the complexed ligand to the carbonyl C atom are not coplanar; taken together these data are definite indications of strong back-bonding from the Ni atom to the C—O group of the ketophosphonate, presumably supported by the electronegative nature of the phosphonate group.

Experimental

Dimethyl 2-iodobenzoylphosphonate, (I), was prepared from 2-iodobenzoyl chloride and trimethyl phosphite. Recrystallization was achieved by layering hexane onto a solution in diethyl ether. Yellow crystals in the form of rectangular plates appeared after 1 d.

Crystal data

$C_9H_{10}IO_4P$
$M_r = 340.04$
Monoclinic
$P2_1/n$
$a = 7.642\ (4)$ Å
$b = 19.928\ (8)$ Å
$c = 8.388\ (4)$ Å
$\beta = 113.23\ (2)°$
$V = 1173.8\ (9)$ Å^3
$Z = 4$
$D_x = 1.924$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 23.0\text{–}25.9°$
$\mu = 2.856$ mm^{-1}
$T = 291\ (1)$ K
Plate
0.60 × 0.45 × 0.15 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega\text{–}2\theta$ scans
Absorption correction: 9 ψ scans (*MolEN*; Fair, 1990)
$T_{min} = 0.292$, $T_{max} = 0.651$
2709 measured reflections
2302 independent reflections

1960 reflections with $I > 2\sigma(I)$
$R_{int} = 0.014$
$\theta_{max} = 25.97°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 24$
$l = -10 \rightarrow 9$
3 standard reflections frequency: 60 min intensity decay: 9.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.097$
$S = 1.147$
2302 reflections
136 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0571P)^2 + 0.9P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max} = 1.150$ e Å^{-3}
$\Delta\rho_{min} = -0.759$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

I—C2	2.100 (4)	P—C7	1.850 (4)
I···O7	3.094 (4)	O7—C7	1.214 (5)
I···O^{i}	3.008 (3)	O8—C8	1.439 (5)
P—O	1.457 (3)	O9—C9	1.445 (5)
P—O8	1.564 (3)	C1—C7	1.482 (5)
P—O9	1.560 (3)		

O—P—O8	114.9 (2)	C1—C2—I	123.4 (3)
O—P—O9	118.8 (2)	C3—C2—I	117.3 (3)
O—P—C7	112.2 (2)	O7—C7—C1	124.0 (4)
O8—P—O9	102.9 (2)	O7—C7—P	114.2 (3)
O8—P—C7	104.0 (2)	C1—C7—P	121.7 (3)
O9—P—C7	102.3 (2)	I···O^{i}—P^{i}	129.3 (2)
P—O8—C8	121.1 (3)	O^{i}···I—C2	176.7 (1)
P—O9—C9	121.9 (3)	O^{i}···I···O7	109.96 (8)
C2—C1—C7	123.3 (3)	O7···I—C2	66.9 (1)
C6—C1—C7	117.7 (4)		
O—P—C7—O7	−94.6 (3)	C6—C1—C7—P	−25.4 (5)
O—P—C7—C1	82.7 (3)	C6—C1—C7—O7	151.7 (4)
O8—P—C7—O7	30.1 (3)	O7···I···O^{i}—P^{i}	−131.6 (2)
O8—P—C7—C1	−152.6 (3)	C2—I···O^{i}—P^{i}	−115 (2)
O9—P—C7—O7	137.0 (3)	O^{i}···I···O7—C7	157.5 (3)
O9—P—C7—C1	−45.7 (3)	C2—I···O7—C7	−21.5 (3)
C2—C1—C7—P	156.3 (3)	O^{i}···I—C2—C1	−5 (2)
C2—C1—C7—O7	−26.6 (6)	O^{i}···I—C2—C3	172 (2)

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

Table 2. *Comparative I···O distances and acute dihedral angles (δ) in 2-iodobenzoyl derivatives*

CODE[a]	*R* factor	*d*(I···O) (Å)	δ (°)
IBBIOX01[b]	0.09	3.07	6.1
OIBZAC[c]	0.08	3.09	16.7
Title compound	0.03	3.09	26.2
INPHAC[d]	0.06	3.10	19.4
IBRBPX[e]	0.05	3.18	28.8
IBBIOX[f]	0.13	3.20[l]	43.7
DIBZPO[g]	0.13	3.25	48.3
DIBZPO[g]	0.13	3.25	21.5
IBNZAM[h]	0.10	3.27	46.7
FUMZES[i]	0.09	3.28	62.0
IBBIOX[f]	0.13	3.30[l]	53.2
ICBOYP[j]	0.14	3.33	53.3
FUMZES[i]	0.09	3.64	84.9
LSDIBZ[k]	0.04	3.71	84.1

Notes: (*a*) Cambridge Structural Database reference codes; (*b*) 1-(2′-iodobenzoyloxy)-1,2-benziodoxolin-3-one, β-form (Gougoutas & Clardy, 1972); (*c*) *o*-iodobenzoic acid (Gougoutas, 1977); (*d*) 3-iodo-2-naphthoic acid (Gougoutas & Toeplitz, 1977); (*e*) 2-iodo-3′-bromodibenzoyl peroxide, β-form (Gougoutas & Chang, 1979); (*f*) 1-(2′-iodobenzoyloxy)-1,2-benziodoxolin-3-one, α-form (Gougoutas & Clardy, 1972); (*g*) 2,2′-diiododibenzoyl peroxide (Gougoutas & Clardy, 1970); (*h*) *o*-iodobenzamide (Nakata, Tateno & Sakurai, 1976); (*i*) (3*S*)-(−)-*N*-(2,3-dihydro-1-methyl-2-oxo-5-phenyl-1*H*-1,4-benzodiazepin-3-yl)-2-iodobenzenecarboxamide (Bock *et al.*, 1987); (*j*) 2-iodo-3′-chlorodibenzoyl peroxide (Gougoutas & Lessinger, 1973); (*k*) lysergic acid diethylamide *o*-iodobenzoate (Baker, Chothia, Pauling & Weber, 1972); (*l*) contact to singly bound oxygen.

The final Fourier difference map showed four positive and three negative peaks lying near the I atom (distances 0.91–0.99 Å for positive and 1.07–1.69 Å for negative peaks) in an approximate plane perpendicular to the phenyl–iodine plane. All other peaks were of height < 0.5 e Å^{-3}.

Data collection: *CAD*-4 *Manual* (Enraf–Nonius, 1988). Cell refinement: *CAD*-4 *Manual*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MolEN*. Program(s) used to refine structure: *MolEN* and *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *MolEN*. Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1305). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.
Baker, R. W., Chothia, C., Pauling, P. & Weber, H. P. (1972). *Science*, **178**, 614–615.
Bock, M. G., DiPardo, R. M., Evans, B. E., Rittle, K. E., Veber, D. F., Freidinger, R. M., Hirshfield, J. & Springer, J. P. (1987). *J. Org. Chem.* **52**, 3232–3239.
Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Breuer, E. (1996). *The Chemistry of Organophosphorus Compounds*, Vol. 4, edited by F. R. Hartley, ch. 7, pp. 656–729. New York: Wiley.
Donohue, J. & Mandel, N. (1981). *J. Cryst. Mol. Struct.* **11**, 189–196.
Enraf–Nonius (1988). *CAD*-4 *Manual*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
Fletcher, D. A., McMeeking, R. F. & Parkin, D. (1996). *J. Chem. Inf. Comput. Sci.* **36**, 746–749.
Gougoutas, J. Z. (1977). *Cryst. Struct. Commun.* **6**, 703–706.
Gougoutas, J. Z. & Chang, K. H. (1979). *Cryst. Struct. Commun.* **8**, 977–980.
Gougoutas, J. Z. & Clardy, J. C. (1970). *Acta Cryst.* B**26**, 1999–2008.
Gougoutas, J. Z. & Clardy, J. C. (1972). *J. Solid State Chem.* **4**, 230–242.
Gougoutas, J. Z. & Lessinger, L. (1973). *J. Solid State Chem.* **7**, 175–185.
Gougoutas, J. Z. & Toeplitz, B. K. (1977). *Cryst. Struct. Commun.* **6**, 331–334.
Nakata, K., Tateno, T. & Sakurai, K. (1976). *Mem. Osaka Kyoiku Univ.* **25**, 61–64.
Nakazawa, H., Nosaka, H., Kushi, Y. & Yoneda, H. (1990). *Organometallics*, **9**, 1958–1963.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

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2-(3-Nitrophenyl)-1,3-dioxolane at 150 K

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Abstract

The title compound, $C_9H_9NO_4$, is an intermediate in the synthesis of polyvinylaminobenzaldehyde azo dyes. The dioxolane ring displays an envelope conformation