Acta Cryst. (1990). C**46**, 1300–1303

Structures of Two Phenyliodonium Ylides

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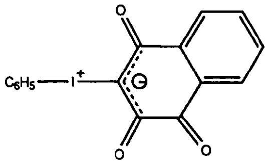
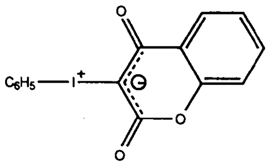
(*Received* 2 *May* 1989; *accepted* 29 *August* 1989)

Abstract. (1) 3-Phenyliodonio-1,2,4-trioxo-1,2,3,4-tetrahydronaphthalenide, $C_{16}H_9IO_3$, $M_r = 376{\cdot}1$, monoclinic, $P2_1/n$, $a = 12{\cdot}503\,(5)$, $b = 7{\cdot}372\,(3)$, $c = 14{\cdot}636\,(6)$ Å, $\beta = 93{\cdot}19\,(3)°$, $V = 1346{\cdot}9\,(9)$ Å^3, $Z = 4$, $D_x = 1{\cdot}86$, $D_m = 1{\cdot}82$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 23{\cdot}2$ cm^{-1}, $F(000) = 1208$, $T = 290$ K, $R = 0{\cdot}039$ for 1383 unique observed $[I/\sigma(I) \geq 2{\cdot}0]$ reflections. (2) 3-Phenyliodonio-2,4-dioxo-1,2,3,4-tetrahydro-1-oxanaphthalenide, $C_{15}H_9IO_3$, $M_r = 364{\cdot}1$, orthorhombic, $Pnc2$, $a = 10{\cdot}842\,(7)$, $b = 13{\cdot}381\,(7)$, $c = 9{\cdot}461\,(1)$ Å, $V = 1373\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}76$ g cm^{-3}, μ(Mo $K\alpha$) = $23{\cdot}1$ cm^{-1}, $F(000) = 1160$, $T = 290$ K, $R = 0{\cdot}054$ for 1179 unique observed $[I/\sigma(I) \geq 2{\cdot}0]$ reflections. Both compounds are best described as iodonium ylides, with nearly equal I—C bonds, and with the negative charge delocalized. Both also form C—I···O secondary bonds with I···O distances of 2·82–2·84 Å.



(1)



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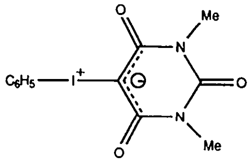

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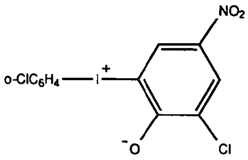

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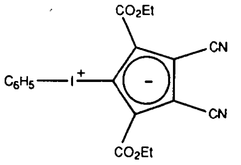

(5)

Introduction. Although crystal structures are available for several diaryliodonium salts, there is a scarcity of data concerning zwitterionic iodonium compounds. Those studied include the phenyliodonium zwitterion of *N,N*-dimethylbarbituride [Martin-Schulz (1984) (3)], a phenolate [Hubbard, Himes, Mighell & Page (1980) (4)] and a cyclopentadienide [Druck & Littke (1978) (5)]. An unusual vinyl iodonium phosphate may be formally considered as belonging to this class (Stang, Wingert & Arif, 1987), whereas diphenyliodonio-2-carboxylate appears to be cyclic rather than zwitterionic (Batchelor, Birchall & Sawyer, 1986); these are not further examined.

The crystal structure analyses of 3-phenyliodonio-1,2,4-trioxo-1,2,3,4-tetrahydronaphthalenide (1) and its 1-oxa analogue (2) were carried out primarily in order to investigate the features of iodine coordination, with the hope that this might correlate with their interesting reactivity patterns (Hatzigrigoriou, Spyroudis & Varvoglis, 1989; Kappe, Korbuly & Stadlbauer, 1978).

Experimental. Compounds (1) and (2) were prepared as described in Hatzigrigoriou *et al.* (1989). Recrystallization from methanol gave yellow block crystals in both cases. D_m by flotation. Data collection details are given in Table 1.

Data were collected with a Nicolet $P2_1$ four-circle diffractometer in ω–2θ mode using graphite-monochromatized Mo $K\alpha$ radiation with variable scan speed depending on the intensity of a 2 s prescan; backgrounds were measured at each end of the scan for 0·25 of the scan time. Three standard reflections were monitored every 200 reflections; both crystals showed some decay during data collection (*ca* 5%), and the data were rescaled to correct for this. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 high-angle reflections. Reflections were processed using profile

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Table 1. *Data collection parameters*

	(1)	(2)
Absences	$h0l$, $h+l=2n$; $0k0$, $k=2n$	$0kl$, $k+l=2n$; $h0l$, $l=2n$
Cell det. refl. range (°) (2θ)	20–24	20–22
Angular range (°) (2θ)	3–45	3–50
Scan about $K\alpha_1$–$K\alpha_2$ (°) (2θ)	±1·2	−0·5 + 0·65
Speed ($2\theta^{\circ}$ min^{-1})	8–30	3–30
Cryst. size (mm)	0·26 × 0·27 × 0·16	0·36 × 0·33 × 0·27
Trans. factor range	(Not recorded)	0·56–0·65
Index ranges	0/12; 0/7; −15/15	0/12; 0/15; 0/11
Reflections: total unique	1771	1300
with $I/\sigma(I) \geq 2\cdot0$	1383	1179
R_{int}	0·020	—
Wt parameter (g)	0·0009	0·00066
Final shift/e.s.d.	0·1	0·2
Final R	0·039	0·054
Final wR	0·040	0·063
Final ΔF synthesis maxima (e Å^{-3})	0·6, −0·5	1·25, −0·9

Table 2. *Atomic coordinates* (× 10^4) *and equivalent isotropic displacement parameters* (Å^2 × 10^3)

	x	y	z	U/U_{iso}
(*a*) for (1)				
I	−999·3 (4)	7712·0 (7)	6663·9 (4)	42 (1)*
O(1)	686 (5)	8322 (9)	8271 (4)	55 (2)*
O(2)	−2814 (5)	5600 (9)	9694 (4)	55 (2)*
O(3)	−2718 (5)	5715 (9)	7866 (4)	55 (2)*
C(1)	33 (7)	5564 (12)	6364 (6)	42 (3)*
C(2)	1128 (8)	5855 (14)	6508 (7)	64 (4)*
C(3)	1806 (8)	4441 (18)	6342 (8)	76 (5)*
C(4)	1388 (12)	2743 (19)	6013 (8)	86 (6)*
C(5)	336 (12)	2589 (13)	5877 (7)	71 (5)*
C(6)	−374 (9)	3998 (13)	6047 (6)	56 (4)*
C(7)	−1056 (6)	7217 (10)	8060 (5)	36 (3)*
C(8)	−111 (6)	7739 (10)	8597 (6)	37 (3)*
C(9)	−177 (7)	7479 (10)	9612 (6)	40 (3)*
C(10)	703 (7)	7998 (11)	10179 (6)	47 (3)*
C(11)	661 (9)	7839 (12)	11118 (7)	58 (4)*
C(12)	−239 (10)	7173 (12)	11491 (6)	59 (4)*
C(13)	−1106 (8)	6621 (13)	10936 (6)	52 (3)*
C(14)	−1075 (7)	6784 (10)	9994 (6)	35 (3)*
C(15)	−2011 (7)	6211 (11)	9400 (6)	38 (3)*
C(16)	−1961 (6)	6344 (11)	8356 (5)	33 (3)*
(*b*) for (2)				
I	3406·3 (7)	3457·1 (5)	5000·0	31 (1)*
O(1)	3839 (12)	6186 (10)	2637 (16)	50 (4)*
O(2)	3108 (14)	3231 (8)	1753 (15)	51 (4)*
O(3)	3926 (8)	5837 (6)	5028 (23)	38 (3)*
C(2)	850 (30)	3731 (19)	5806 (33)	87 (10)†
C(3)	−427 (30)	3835 (19)	5703 (33)	67 (9)†
C(4)	−1020 (30)	3642 (19)	4422 (33)	87 (10)†
C(5)	−336 (30)	3346 (19)	3246 (33)	91 (10)†
C(6)	941 (30)	3242 (19)	3350 (33)	52 (8)†
C(1)	1534 (30)	3434 (19)	4630 (33)	71 (11)†
C(22)	735 (18)	2840 (13)	5741 (22)	139 (10)‡
C(33)	−522 (18)	2816 (13)	5548 (22)	157 (10)‡
C(44)	−1058 (18)	3340 (13)	4431 (22)	64 (8)‡
C(55)	−318 (18)	3888 (13)	3507 (22)	347 (11)‡
C(66)	957 (18)	3912 (13)	3699 (22)	121 (10)‡
C(111)	1493 (18)	3388 (13)	4816 (22)	15 (4)‡
C(7)	3456 (13)	4558 (14)	3382 (21)	40 (4)*
C(8)	3742 (13)	5481 (11)	3793 (16)	30 (4)*
C(10)	3713 (9)	6610 (7)	222 (12)	48 (4)
C(11)	3602 (9)	6379 (7)	−1210 (12)	54 (5)
C(12)	3395 (9)	5393 (7)	−1629 (12)	56 (5)
C(13)	3299 (9)	4639 (7)	−617 (12)	43 (4)
C(14)	3410 (9)	4871 (7)	815 (12)	39 (4)
C(9)	3617 (9)	5856 (7)	1235 (12)	29 (3)
C(15)	3318 (14)	4138 (14)	1924 (22)	41 (4)*

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

† Occupancy 0·60 (1).

‡ Occupancy 0·40 (1).

Table 3. *Bond lengths* (Å) *and angles* (°)

(*a*) for (1)			
I—C(1)	2·104 (9)	I—C(7)	2·081 (8)
O(1)—C(8)	1·207 (10)	O(2)—C(15)	1·202 (10)
O(3)—C(16)	1·245 (9)	C(1)—C(2)	1·391 (13)
O(1)—C(6)	1·334 (13)	C(2)—C(3)	1·374 (14)
C(3)—C(4)	1·430 (17)	C(4)—C(5)	1·324 (17)
C(5)—C(6)	1·397 (15)	C(7)—C(8)	1·435 (11)
C(7)—C(16)	1·391 (11)	C(8)—C(9)	1·506 (12)
C(9)—C(10)	1·394 (11)	C(9)—C(14)	1·379 (12)
C(10)—C(11)	1·384 (14)	C(11)—C(12)	1·368 (15)
C(12)—C(13)	1·380 (13)	C(13)—C(14)	1·387 (12)
C(14)—C(15)	1·481 (11)	C(15)—C(16)	1·536 (11)
C(7)—I—C(1)	97·3 (3)	C(2)—C(1)—I	117·5 (7)
C(6)—C(1)—I	119·8 (7)	C(6)—C(1)—C(2)	122·6 (9)
C(3)—C(2)—C(1)	118·0 (10)	C(4)—C(3)—C(2)	120·4 (10)
C(5)—C(4)—C(3)	117·8 (11)	C(6)—C(5)—C(4)	123·0 (11)
C(5)—C(6)—C(1)	118·1 (10)	C(8)—C(7)—I	114·7 (6)
C(16)—C(7)—I	117·4 (6)	C(16)—C(7)—C(8)	127·8 (8)
C(7)—C(8)—O(1)	123·6 (8)	C(9)—C(8)—O(1)	121·8 (7)
C(9)—C(8)—C(7)	114·6 (7)	C(10)—C(9)—C(8)	117·8 (8)
C(14)—C(9)—C(8)	122·5 (7)	C(14)—C(9)—C(10)	119·6 (8)
C(11)—C(10)—C(9)	119·7 (10)	C(12)—C(11)—C(10)	120·3 (9)
C(13)—C(12)—C(11)	120·5 (9)	C(14)—C(13)—C(12)	119·7 (10)
C(13)—C(14)—C(9)	120·2 (8)	C(15)—C(14)—C(9)	120·2 (8)
C(15)—C(14)—C(13)	119·6 (8)	C(14)—C(15)—O(2)	123·1 (8)
C(16)—C(15)—O(2)	117·5 (8)	C(16)—C(15)—C(14)	119·4 (8)
C(7)—C(16)—O(3)	126·8 (8)	C(15)—C(16)—O(3)	116·5 (7)
C(15)—C(16)—C(7)	114·7 (7)		
(*b*) for (2)			
I—C(1)	2·060 (33)	I—C(111)	2·084 (19)
I—C(7)	2·125 (19)	O(1)—C(8)	1·448 (21)
O(1)—C(9)	1·419 (19)	O(2)—C(15)	1·246 (22)
O(3)—C(8)	1·277 (25)	C(7)—C(15)	1·497 (28)
C(7)—C(8)	1·331 (24)	C(14)—C(15)	1·440 (22)
C(1)—I—C(7)	85·0 (9)	C(111)—I—C(7)	89·8 (7)
I—C(7)—C(8)	116·0 (13)	I—C(7)—C(15)	113·6 (12)
C(8)—C(7)—C(15)	129·9 (17)	O(1)—C(8)—O(3)	115·9 (13)
O(1)—C(8)—C(7)	113·6 (15)	O(3)—C(8)—C(7)	130·5 (16)
C(9)—C(14)—C(15)	116·6 (9)	O(1)—C(9)—C(10)	113·8 (7)
O(1)—C(9)—C(14)	126·0 (7)	O(2)—C(15)—C(14)	125·6 (17)
O(2)—C(15)—C(7)	120·3 (17)	C(8)—O(1)—C(9)	119·4 (12)
C(7)—C(15)—C(14)	114·1 (15)		

analysis and those with $I/\sigma(I) \geq 2\cdot0$ were considered observed and used in refinement; they were corrected for Lorentz, polarization and absorption effects, the last by the Gaussian method. Heavy atoms were located by the Patterson interpretation section of *SHELXTL* and the light atoms then found on successive Fourier syntheses. Anisotropic temperature factors were used for all non-H atoms in (1), but for I, O and C(7), C(8), C(15) only in (2). H atoms were placed in calculated positions with fixed U_{iso} = 0·07 Å^2 (1) and 0·08 Å^2 (2). Final refinement was on F by least-squares methods. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ was used and shown to be satisfactory by a weight analysis. Computing with *SHELXTL-PLUS* (Sheldrick, 1986) on a DEC MicroVAX II. Scattering factors in the analytical form and anomalous-dispersion factors were taken from *International Tables for X-ray Crystallography* (1974). Final atomic coordinates are given in Table 2,* and bond lengths and angles in Table 3.

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* Lists of structure factors, anisotropic thermal parameters and full bond lengths and angles have been deposited with the British Library Document Supply Centre Supplementary Publication No. SUP 52558 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

For (1), the structure determination and refinement proceeded smoothly. For (2), the phenyl ring was found to be disordered, and was treated as two rigid hexagons with linked occupancies [refined to 0·60 and 0·40 (1)]; the fused C_6 ring was also treated as a rigid hexagon. The structural chirality of the individual crystal of (2) was checked by refinement of a $\delta f''$ multiplier, and the iodine z coordinate was held fixed to define the origin. The largest residual peaks lay close to the I atom.

Discussion. The structures of (1) and (2) are shown in Figs. 1 and 2, and the principal dimensions are compared with those of the related compounds (3)–(5) in Table 4. Although the precision of structure (2) is limited, it is clear that both (1) and (2) conform to the same overall pattern. They are best formulated as zwitterions, with a positive charge on I, and the negative charge delocalized over the three adjoining C atoms. In the two unsymmetrical compounds (2) and (5), this C—C—C unit shows substantial asymmetry. The I—C bond on this side [I—C(7) in Table 4] is slightly shortened compared to the I—C (phenyl) bond, indicative of a slight double-bond character.* Although the normal C—I—C angle is clearly about 98°, the two values found for (2) differ significantly from this and from each other. This indicates that the angle is relatively 'soft', and able to distort under packing forces [which must be the main difference between the alternative positions of the phenyl ring in (2)].

As expected from iodine's propensity for forming secondary bonds (Alcock, 1972), the I atoms make a series of short I···O contacts. In (4) and (5) the shortest contacts are intramolecular, but in (1) and (2) the intramolecular contacts to the C=O O atoms are in the range 3·1–3·2 Å, and shorter intermolecular contacts are found. In (1) a nearly linear C—I···O secondary bond is found with I···O of 2·84 Å, while (2) achieves similar interactions involving both C(1) and C(7), though neither is as close to linear as in

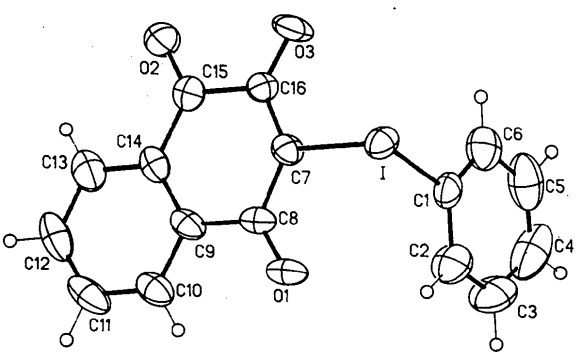

Fig. 1. View of (1) showing the atomic numbering (50% probability ellipsoids).

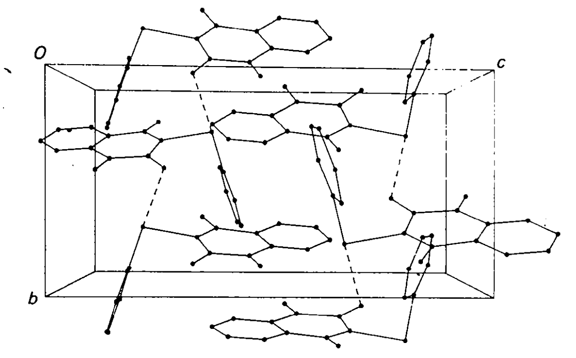

Fig. 3. Packing diagram for (1) viewed down **a** showing I···O interactions.

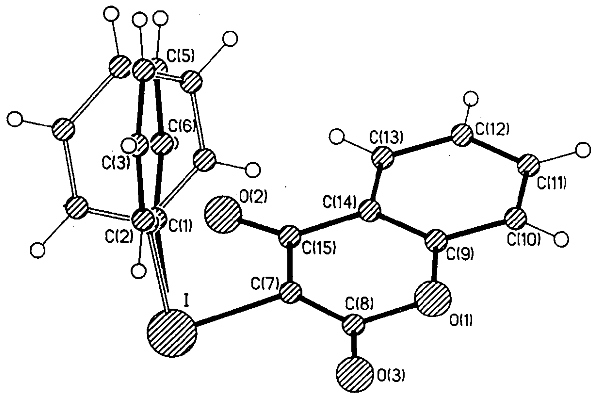

Fig. 2. View of (2) showing the atomic numbering (apart from the second positions of the disordered phenyl ring).

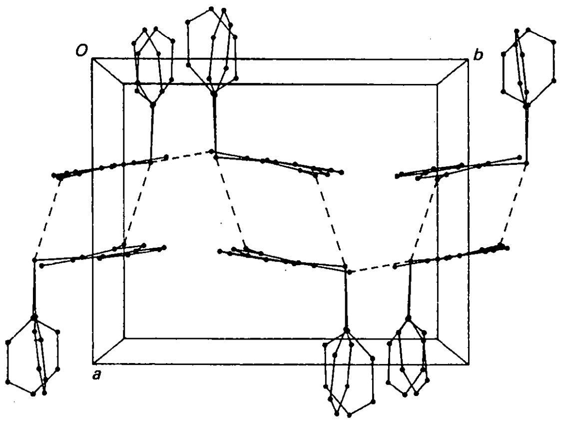

Fig. 4. Packing diagram for (2) viewed down **c** showing I···O interactions.

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* The reversal of this trend in (2) is likely only to be a result of the need to constrain the phenyl ring to be a regular hexagon.

Table 4. *Comparative dimensions* (Å *and* °) *of iodonium ylides*

Cpd	C—I—C	I—C(Ph)	I—C(7)	C—C(*)	C(*)—O	I···O	C—I···O
(1)	97·3 (3)	2·104 (9)	2·081 (8)	1·42 (1)	1·20 (1)	2·841 (9)^{i}	176·4 (3)^{i}
						2·82 (2)^{ii}	169 (1)^{ii}
(2)	85·0 (9)/89·8 (7)	2·07 (2)	2·13 (2)	1·41 (4)	1·26 (2)	3·23 (2)^{iii}	160 (1)/164 (1)^{iii}
(3)	98·8	2·090	2·039	1·37	1·233	—	
(4)	98·7	2·089	2·078	1·40	—	2·755	148·9
(5)	98·4	2·106	2·105	1·412/1·356	1·26	*a*	

Notes: (1), (2) this work; (3) Martin-Schultz (1984) (intermolecular distances not reported); (4) Hubbard *et al.* (1980); (5) Druck & Littke (1978). (i) O at $-x-0·5$, $0·5+y$, $1·5-z$; (ii) O at x, $0·5-y$, $0·5+z$; involves C(7); (iii) O at $1-x$, $1-y$, z; involves C(1)/C(111). (*a*) Intramolecular distances to O of C=O group 2·965; 3·138 Å.

* Average distances involving C atoms adjoining C(7)[C(8), C(16) for (1), C(8), C(15) for (2)].

(1). These interactions dominate the packing (Figs. 3, 4).

In both (1) and (2), the I—C (phenyl) bond is about 15° off the perpendicular to the naphthalene plane [dihedral angles: C(ph)—I—C(7) to I—C(7)C_2O_2 of 103 (1)° and 108 (1)/106 (1)° respectively]; this is similar to (3) and (4) but contrasts with the 161° angle in (5) resulting from its close intramolecular contact.

Regioselectivity has been observed in some reactions of (1) with alkenes, leading to the formation of 1,4- rather than 1,2-naphthoquininic furan derivatives (Hatzigrigoriou *et al.*, 1989). This may now be explained from the crystal structure if it is assumed that the conformation of (1), with the phenyl group in an '*anti*' position in relation to O(3), is maintained in solution. The approach of the alkene from the side of O(1) will then be sterically hindered. This is probably the reason why (2) fails to undergo an analogous reaction, since the approach of the alkene from the side of the carbonyl group is hindered, whereas its lactonic carbonyl is unreactive on electronic grounds.

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Acta Cryst. (1990). **C46**, 1303–1305

Structure of N^{α}-Acetyl-*N*-methyl-L-tryptophanamide

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(*Received* 2 *June* 1989; *accepted* 3 *July* 1989)

Abstract. $C_{14}H_{17}N_3O_2$ (Ac-L-Trp), $M_r = 259·14$, orthorhombic, $P2_12_12_1$, $a = 8·157$ (1), $b = 11·185$ (1), $c = 15·081$ (2) Å, $V = 1376$ Å^3, $Z = 4$, $D_x = 1·25$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 0·8$ cm^{-1}, $F(000) = 552$, $T = 295$ K. Final R value 0·036 for 1407 [$I \geq 1·5\sigma(I)$] observed reflections, GOF = 1·06. The conformational angles are: $\varphi = -81·5$ (2), $\psi = 167·9$ (2), $\chi_1 = -67·1$ (2), $\chi_2 = 94·8$ (3)°. Each molecule is hydrogen bonded to six other molecules. The N-terminal carbonyl group accepts two hydrogen bonds and the H···O···H plane is approximately perpendicular to the peptide group.