Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.121$
$S = 1.093$
2334 reflections
185 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0514P)^2 + 0.3355P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.014$
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.22$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.101 (8)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

C6—N7	1.257 (3)	C9—C10	1.520 (3)
N7—C8	1.462 (3)	C10—N11	1.464 (3)
C8—C9	1.520 (3)	N11—C12	1.270 (3)
C9—O18	1.422 (3)		
O18—C9—C8	111.5 (2)	C8—C9—C10	112.9 (2)
O18—C9—C10	105.4 (2)		

Refinement was on F^2 for all reflections except for 103 with very negative F^2 or flagged by the user for potential systematic errors. The H18 atom was located from a $\Delta\rho$ map and refined positionally with fixed $U = 0.05$ Å^2. All other H atoms were placed in calculated positions using a riding model [C—H = 0.93 Å, $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for C_{sp^2}; C—H = 0.96 Å, $U(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for C_{sp^3}]. All calculations were performed on a DEC 3000 AXP and PC/486 computer.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *SET*4 in *CAD*-4 *EXPRESS*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1996). 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: FR1056). Services for accessing these data are described at the back of the journal.

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2,2,6,6-Tetramethyl-4-oxopiperidinium Bis(pentafluorophenyl)phosphinate

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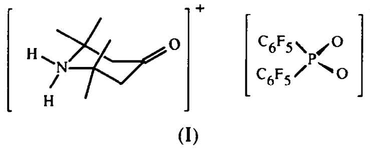
Abstract

The structure consists of centrosymmetric $\{(\text{C}_9\text{H}_{18}\text{NO})^+\text{-}[(\text{C}_6\text{F}_5)_2\text{PO}_2]^-\}_2$ units linked by N—H···O hydrogen bonds to form 12-membered [H—N—H···O—P—O···H—N—H···O—P—O···] rings.

Comment

As part of a general study of metal phosphinate compounds (Du, Rettig, Thompson & Trotter, 1991), we attempted the preparation of a formamide complex of cobalt(II) bis(pentafluorophenyl)phosphinate (see *Experimental*). Instead of the target complex, crystals of the title complex, (I), were isolated. The reaction to produce this salt likely involves the acid-catalyzed condensation of acetone with formamide.



(I)

The asymmetric unit consists of two independent sets of cations and anions. The structure of the piperidonium cation is as expected and does not differ significantly from those reported previously (Rees & Weiss, 1971; Simpson, 1992; Conary *et al.*, 1993), although the structural parameters resulting from this study are considerably more precise. Metrical data for one of the two independent cations are given in Table 1.

This constitutes only the second structure containing the bis(pentafluorophenyl)phosphinate anion to be reported; the first, that of the simple oxonium salt, was reported only recently (Oliver *et al.*, 1997). The structure consists of centrosymmetric $\{(C_9H_{18}NO)^+[(C_6F_5)_2PO_2]^-\}_2$ units, symmetrically linked by N—H···O hydrogen bonds to form 12-membered [H—N—H···O—P—O···H—N—H···O—P—O···] rings (details are given in Table 2). The most significant contacts between these units are weak C—H···F interactions, summarized in Table 2. Oxonium bis(pentafluorophenyl)phosphinate (Oliver *et al.*, 1997) has a polymeric structure in which each phosphinate O atom is involved in one intermediate-strength O—H···O hydrogen bond and one of the phosphinate O atoms is also involved in a very strong hydrogen bond to the oxonium cation. This results in significantly different P—O bond lengths for each of the two crystallographically independent anions (mean P—O = 1.479 [2] and 1.490 [2] Å). In the present structure, with very symmetric hydrogen bonding, the P—O distances are equal within the limits of experimental error, averaging 1.480 [1] Å. The P—C distances in these two salts compensate for the differences in the P—O bonding, being shorter in the oxonium salt by about 0.02 Å. In both of the bis(pentafluorophenyl)phosphinate salts, the P—C distances show significant variation, ranging from 1.811 (3) to 1.820 (3) Å for the oxonium salt and from 1.825 (2) to 1.847 (2) Å for the 2,2,6,6-tetramethyl-4-piperidonium salt. The perfluorophenyl groups display normal substituent-induced geometric distortions: C_{ar}—F = 1.336 (2)–1.354 (2), mean 1.343 [5] Å; and C_{ar}—C_{ar} = 1.363 (3)–1.395 (2), mean 1.379 [9] Å.

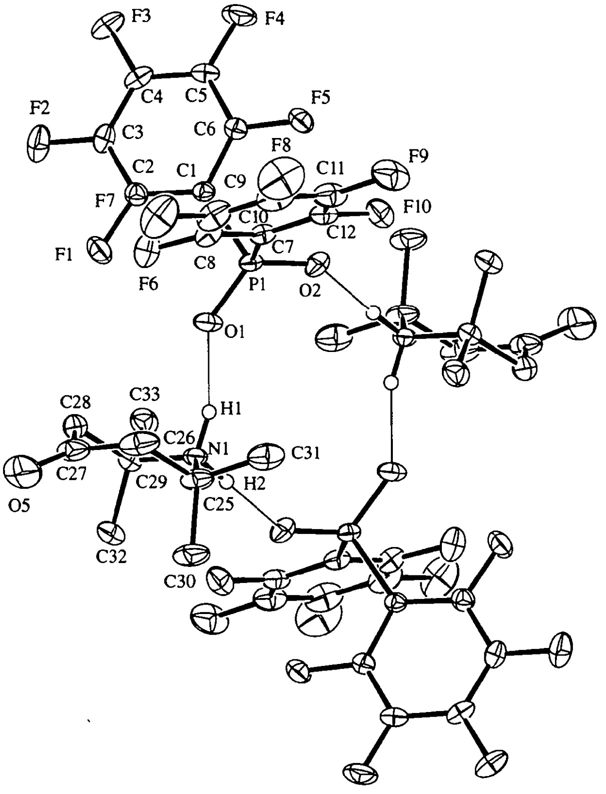


Fig. 1. Perspective view of one of the two crystallographically independent $\{(C_9H_{18}NO)^+[(C_6F_5)_2PO_2]^-\}_2$ units (33% probability ellipsoids are shown for the non-H atoms; fine lines represent hydrogen bonds).

Experimental

On addition of formamide to a clear blue acetone solution containing cobalt(II) acetate and bis(pentafluorophenyl)phosphinic acid monohydrate (Oliver *et al.*, 1997), a red precipitate formed. On standing for several days, the red filtrate deposited pale brown crystals of the title compound.

Crystal data

$C_9H_{18}NO^+.C_{12}F_{10}O_2P^-$
$M_r = 553.34$
Triclinic
$P\bar{1}$
$a = 11.845 (1)$ Å
$b = 14.149 (1)$ Å
$c = 14.766 (1)$ Å
$\alpha = 90.206 (7)°$
$\beta = 108.131 (5)°$
$\gamma = 91.112 (5)°$
$V = 2351.4 (4)$ Å^3
$Z = 4$
$D_x = 1.563$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 8192 reflections
$\theta = 1.5–32.5°$
$\mu = 0.220$ mm^{-1}
$T = 193.2$ K
Prism
0.60 × 0.50 × 0.20 mm
Pale brown

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: semi-empirical ellipsoidal (Siemens, 1995)
$T_{min} = 0.871$, $T_{max} = 0.957$
31 589 measured reflections
22 127 independent reflections

15 913 reflections with $I > 3\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 38.6°$
$h = 0 \rightarrow 15$
$k = -20 \rightarrow 20$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R(F) = 0.060$
$wR(F^2) = 0.112$
$S = 2.016$
22 127 reflections
793 parameters
All H atoms refined
$w = 1/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.68$ e Å^{-3}
$\Delta\rho_{min} = -0.59$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

P1—O1	1.481 (1)	N1—C29	1.521 (2)
P1—O2	1.479 (1)	C25—C26	1.535 (3)
P1—C1	1.825 (2)	C25—C30	1.525 (3)
P1—C7	1.847 (2)	C25—C31	1.533 (3)
P2—O3	1.479 (1)	C26—C27	1.495 (4)

P2—O4	1.479 (1)	C27—C28	1.496 (3)
P2—C13	1.845 (2)	C28—C29	1.532 (3)
P2—C19	1.834 (2)	C29—C32	1.532 (3)
O5—C27	1.214 (3)	C29—C33	1.522 (3)
N1—C25	1.518 (2)		
O1—P1—O2	120.31 (7)	N1—C25—C31	105.6 (2)
O1—P1—C1	109.49 (7)	C26—C25—C30	111.6 (2)
O1—P1—C7	107.03 (8)	C26—C25—C31	111.6 (2)
O2—P1—C1	108.43 (7)	C30—C25—C31	108.9 (2)
O2—P1—C7	108.69 (8)	C25—C26—C27	112.9 (2)
C1—P1—C7	101.20 (7)	O5—C27—C26	123.1 (3)
O3—P2—O4	120.95 (7)	O5—C27—C28	122.5 (3)
O3—P2—C13	107.90 (7)	C26—C27—C28	114.3 (2)
O3—P2—C19	108.16 (8)	C27—C28—C29	112.9 (2)
O4—P2—C13	107.54 (7)	N1—C29—C28	107.6 (2)
O4—P2—C19	109.16 (7)	N1—C29—C32	111.3 (2)
C13—P2—C19	101.37 (7)	N1—C29—C33	105.3 (1)
C25—N1—C29	120.8 (1)	C28—C29—C32	111.3 (2)
N1—C25—C26	106.9 (2)	C28—C29—C33	110.9 (2)
N1—C25—C30	112.1 (2)	C32—C29—C33	110.2 (2)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.94 (2)	1.80 (2)	2.704 (2)	161 (2)
N1—H2···O2^{i}	0.92 (2)	1.78 (2)	2.704 (2)	176 (2)
N2—H3···O3	0.88 (2)	1.82 (2)	2.694 (2)	172 (2)
N2—H4···O4^{ii}	0.89 (2)	1.89 (2)	2.765 (2)	167 (2)
C35—H21···F20^{ii}	0.96 (2)	2.41 (2)	3.364 (2)	173 (2)
C40—H29···F13^{iii}	1.05 (2)	2.43 (2)	3.347 (3)	144 (2)
C42—H36···F13^{iv}	1.03 (2)	2.49 (2)	3.139 (2)	121 (2)

Symmetry codes: (i) $-x, -y, 1-z$; (ii) $1-x, 1-y, -z$; (iii) $-x, 1-y, -z$; (iv) $1+x, y, z$.

One data image per sweep was used to monitor crystal decay. The final refinement was based only on those data collected to $\theta_{\max} = 32.5°$.

Data collection: *ASTRO* (Siemens, 1995). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1990). Program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1995). Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1014). Services for accessing these data are described at the back of the journal.

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N-Phenyl-*N*-(phenylthioxomethyl)benzamide

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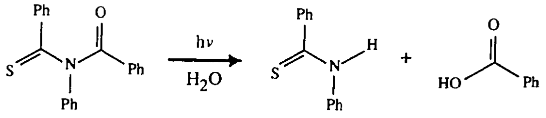
Abstract

The title molecule, $C_{20}H_{15}NOS$, adopts an (E_S,Z_O) conformation, similar to that of other monothioimides, with an intramolecular O···C(S) contact of 2.821 (5) Å; a photochemical cleavage reaction probably proceeds *via* intramolecular nucleophilic attack of oxygen on the C═S double bond in the presence of solvolytic agents.

Comment

Structural studies of the molecular conformations of monothioimides have shown that photocleavage reactions proceed, not *via* the previously proposed γ-hydrogen abstraction mechanism, but probably *via* intramolecular nucleophilic attack of the carbonyl O atom on the C═S double bond, with the presence of water also essential to the reaction (Fu, Scheffer & Trotter, 1997). *N*-Phenyl-*N*-(phenylthioxomethyl)benzamide (*N*-benzoylthiobenzanilide), (1), is a typical example of a monothioimide that undergoes a photocleavage reaction, but possesses no γ-hydrogens. Two previous studies have reported basically identical results (Oda & Machida, 1988; Sakamoto *et al.*, 1988), with isolation of thiobenzanilide, (2). Both studies attributed the formation of (2) to direct homolysis of the N—CO bond, but neither study reported the fate of the liberated PhC•(O) radical.



(1) (2)

In order to understand the reaction more fully, the photolysis of (1) has now been repeated. In anhydrous benzene, photolysis leads to no reaction, even after prolonged irradiation; a solid-state photolysis under anhydrous conditions also gives no reaction. In benzene that has been allowed to equilibrate with the moisture in the atmosphere, however, photolysis gives benzoic acid and thiobenzanilide, (2) (10% yield); a solid-state photolysis without special attempts to exclude moisture gives the same two photoproducts, and in 10% methanol in benzene (*v*/*v*), photolysis gives methyl benzoate and thiobenzanilide (76% yield). These findings indicate that the reaction is a photosolvolysis. In the absence of