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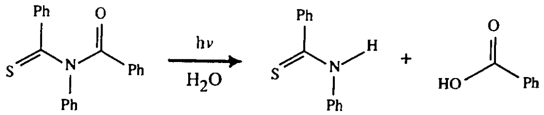
Abstract

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$\cdots$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$^{\bullet}$(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 solvolytic agents (*e.g.* water, methanol), the photoreaction simply does not proceed.

The crystal structure analysis of (1) shows that the molecule adopts the (E_S,Z_O) conformation in the solid state (Fig. 1), with an intramolecular O···C(S) contact of 2.821 (5) Å. Thus, the mechanism proposed for the photocleavage of other monothioimides (Fu *et al.*, 1997) is probably operative in the photolysis of (1), with nucleophilic attack of oxygen on the C=S double bond and hydrolysis of the resulting 1,3-oxazetidinium intermediate. As in the case of the related monothioimides, the conformation of the thioimide group deviates from exact planarity, with torsion angles S=C—N—CO −154.6 (3) and SC—N—C=O 31.4 (5)°. Other molecular dimensions are normal (details in the supplementary material); C=S 1.641 (4) and C=O 1.204 (5) Å.

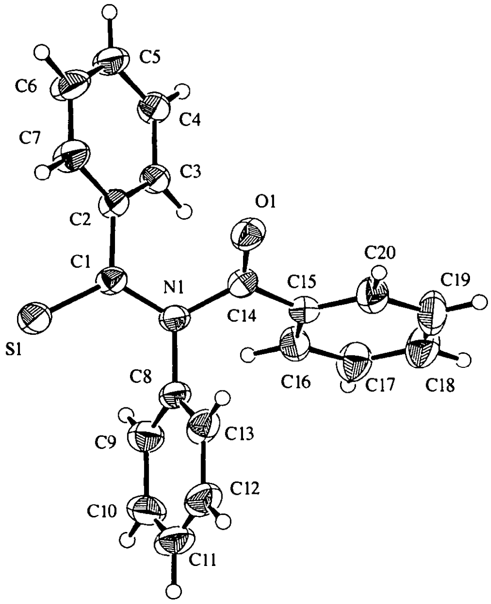


Fig. 1. View of the title molecule (33% probability ellipsoids).

Experimental

The title compound was synthesized from *N*-phenylbenzenecarbothioamide and benzoyl chloride (details in the supplementary material).

Crystal data

$C_{20}H_{15}NOS$
$M_r = 317.40$
Orthorhombic
$P2_12_12_1$
$a = 10.338$ (3) Å
$b = 18.947$ (1) Å
$c = 8.548$ (1) Å
$V = 1674.3$ (6) Å^3
$Z = 4$
$D_x = 1.259$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 23 reflections
$\theta = 37.7–44.3°$
$\mu = 1.691$ mm^{-1}
$T = 294$ K
Prism
0.40 × 0.20 × 0.10 mm
Orange

Data collection

Rigaku AFC-6*S* diffractometer
ω–2θ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.741$, $T_{\max} = 0.844$
1930 measured reflections
1930 independent reflections

1624 reflections with $I > 3\sigma(I)$
$\theta_{\max} = 77.57°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 24$
$l = 0 \rightarrow 10$
3 standard reflections every 200 reflections intensity decay: 1.7%

Refinement

Refinement on F^2
$R(F) = 0.042$
$wR(F^2) = 0.140$ (0.155 for enantiomeric structure)
$S = 2.73$
1930 reflections
208 parameters
H atoms not refined

$w = 1/[\sigma^2(F_o^2) + 0.00022(F_o^2)^2]$
$(\Delta/\sigma)_{\max} = 0.0008$
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

S1—C1	1.641 (4)	N1—C1	1.377 (4)
O1—C14	1.204 (5)	N1—C14	1.451 (5)
C1—N1—C8	120.5 (3)	C8—N1—C14	116.4 (3)
C1—N1—C14	119.7 (3)		

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993). Program(s) used to refine structure: *TEXSAN*. 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: FG1356). Services for accessing these data are described at the back of the journal. Details of the synthesis and photochemistry of the title compound have also been deposited.

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