Structure of 4-(1-Cyclohexenyl)-3-phenylsydnone*

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Abstract. $C_{14}H_{14}N_2O_2$, monoclinic, $P2_1/c$, $a = 11\cdot015$ (2), $b = 10\cdot042$ (2), $c = 15\cdot164$ (3) Å, $\beta = 132\cdot0$ (1)°, $V = 1246\cdot7$ (4) Å^3, $Z = 4$, $D_x = 1\cdot29$, $D_m = 1\cdot30$ (3) Mg m^{-3}, $M_r = 242\cdot28$, $\mu(Mo\ K\alpha) = 0\cdot1$ mm^{-1}, m.p. 397–399 K. The structure was solved by direct methods. The final R value was $0\cdot046$ for 1473 observed reflexions. The compound was studied for its photochromic properties. The angle between the planes of the phenyl and sydnone rings is $63\cdot0°$ and the angle between the plane of the sp^2 orbitals of the double bond C(13)=C(14) and the sydnone ring is $28\cdot0°$.

Introduction. The title compound is a member of the alkenyl sydnones, which are studied for their photochromic properties (Hašek, Obrda, Huml, Nešpůrek, Chojnacki & Šorm, 1978; Hašek, Obrda, Huml, Nešpůrek & Šorm, 1979). It exhibits photochromism in the crystalline state with a short half-time of decoloration and weak photochromism in solid solutions at low temperatures (Nešpůrek & Šorm, 1977).

Bright-yellow crystals stable in air in the dark were prepared by freezing from ethanol solution. The crystal used was ground to an approximately spherical shape with a diameter varying between 0·65 and 0·75 mm. The unit-cell dimensions were obtained by refining 15 reflexions measured with a Syntex $P2_1$ four-circle diffractometer. The intensities were collected by the θ–2θ scan with a variable scan speed of 1·5–29·5° min^{-1} and graphite-monochromated Mo $K\alpha$ radiation. 1639 reflexions were measured up to $\sin\theta/\lambda = 0\cdot55$ Å^{-1}; 1473 of these were taken as observed. A reflexion was taken as observed if $I > 1\cdot96\sigma_I$, where σ_I was calculated from counting statistics. The data analysis showed that the measurements were not significantly influenced by extinction or absorption.‡

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* Study of Photochromic Sydnones. III.

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‡ Full experimental details, lists of structure factors, thermal parameters, and refined fractional coordinates of four H atoms and some projections of the structure including the thermal ellipsoids have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34542 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The structure was solved by direct methods with the *MULTAN* program (Main, Woolfson, Lessinger, Germain & Declercq, 1974). The correct solution was indicated by the highest value of the combined figure of merit. The atomic parameters were refined by a least-squares method in the block-diagonal approximation by the modified program *NRC*-10 (Ahmed, Hall, Pippy & Huber, 1966). The function minimized was $\sum w\varDelta^2$, where $\varDelta = ||F_o| - |F_c||$, $w^{-1} = \sigma_F^2 + (0\cdot01F_o)^2$ (σ_F determined from the counting statistics). The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974); for H the scattering factor was taken as a spherical approximation of the H atom in the hydrogen molecule (Stewart, Davidson & Simpson, 1965).

The anisotropic refinement of non-H atoms and the isotropic refinement of the H atoms proceeded until the parameter shifts of all atoms dropped below $\frac{1}{5}$ of their e.s.d.'s. In the last refinement cycle $n = 219$ atomic parameters were refined and all $m = 1473$ observed reflexions were used. This led to $R_1 = \sum \varDelta/\sum |F_o| = 0\cdot046$, $R_2 = (\sum \varDelta^2/\sum |F_o|^2)^{1/2} = 0\cdot045$, $Rw_2 = (\sum w\varDelta^2/\sum w|F_o|^2)^{1/2} = 0\cdot063$, $S = [\sum w\varDelta^2/(m-n)]^{1/2} = 4\cdot1$.

Table 1. *Final coordinates* ($\times 10^4$) *of the non-hydrogen atoms and their e.s.d.'s, and* B_{eq} (Å^2)

	x	y	z	B_{eq}
O(1)	702 (2)	7789 (2)	−320 (1)	6·5
N(2)	2145 (2)	8269 (2)	35 (2)	6·1
N(3)	2747 (2)	8997 (2)	980 (1)	4·5
C(4)	1854 (2)	9027 (2)	1294 (2)	4·2
C(5)	472 (3)	8224 (2)	437 (2)	5·3
O(6)	−723 (2)	7878 (2)	260 (1)	7·1
C(7)	4317 (2)	9600 (2)	1560 (2)	4·3
C(8)	5661 (3)	9195 (2)	2694 (2)	5·3
C(9)	7171 (3)	9749 (3)	3229 (2)	6·0
C(10)	7301 (3)	668 (2)	2619 (2)	6·0
C(11)	5941 (3)	1043 (2)	1487 (2)	6·1
C(12)	4432 (3)	512 (2)	937 (2)	5·3
C(13)	2188 (2)	9778 (2)	2264 (2)	4·5
C(14)	1555 (4)	9319 (3)	2731 (3)	7·0
C(15)	1730 (5)	51 (3)	3671 (3)	9·7
C(16)	2912 (4)	1166 (3)	4232 (2)	7·2
C(17)	2885 (3)	1900 (2)	3380 (2)	6·7
C(18)	3120 (3)	1035 (2)	2691 (2)	5·4

Table 2. *Fractional coordinates of the hydrogen atoms*
$(\times 10^3)$ *and* B_{iso} $(Å^2)$

The atoms marked by an asterisk are calculated to their ideal
positions; refined positions have been deposited.

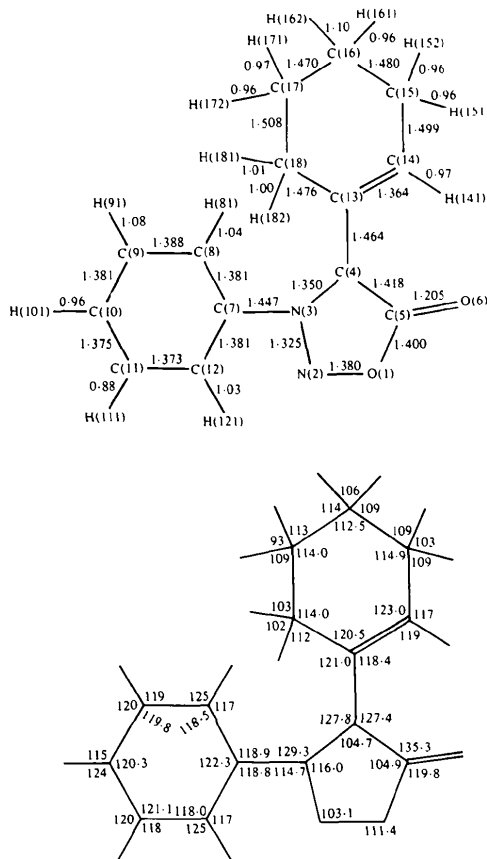|	x	y	z	B_{iso}
H(81)	545 (2)	852 (2)	310 (2)	6·2 (5)
H(91)	825 (3)	935 (2)	406 (2)	7·5 (6)
H(101)	839 (3)	97 (2)	302 (2)	7·6 (6)
H(111)	604 (2)	157 (2)	107 (2)	5·8 (5)
H(121)	335 (3)	80 (3)	12 (2)	8·3 (6)
H(141)	79 (3)	858 (3)	234 (2)	8·8 (7)
H(151)*	202 (–)	944 (–)	427 (–)	15·5 (12)
H(152)*	68 (–)	37 (–)	335 (–)	13·6 (10)
H(161)*	399 (–)	83 (–)	486 (–)	14·8 (11)
H(162)	261 (3)	177 (2)	467 (2)	7·5 (6)
H(171)	354 (3)	270 (3)	371 (2)	8·2 (6)
H(172)*	187 (–)	238 (–)	284 (–)	15·5 (11)
H(181)	434 (3)	89 (3)	327 (2)	8·4 (6)
H(182)	293 (2)	154 (2)	204 (2)	5·5 (4)

Fig. 1. Numbering scheme of 4-(1-cyclohexenyl)-3-phenylsydnone
showing bond lengths (Å) and some valence angles (°). E.s.d.'s of
bond lengths are 0·003–0·006 Å for non-H atoms and 0·02–
0·05 Å for bonds involving H atoms. E.s.d.'s of C–C–C angles
are 0·2–0·3°, of C–C–H angles 1·4–2·6° and of H–C–H
angles 2·1–4·8°.

The six highest maxima (0·2–0·3 e $Å^{-3}$) on the final
difference map were located around C(14), C(15),
C(16), C(17). Four H atoms, H(151), H(152), H(161),
H(172), were refined to improbable positions with high
B_{iso} values. Neither their recalculation to theoretical
positions, nor their positioning at maxima on the dif-
ference map improved their refined parameters. There-
fore, the calculated positions for these H atoms are
used in this paper and the refined coordinates have been
deposited.* The final fractional coordinates, B_{eq}
(Hamilton, 1959) and B_{iso} for the H atoms are listed in
Tables 1 and 2.

Discussion. The bond lengths and angles are given in
Fig. 1.

By comparing this structure with that of 3-phenyl-4-
(3-methyl-1-buten-2-yl)sydnone (Hašek *et al.*, 1978),
statistically significant differences were found in the
angles about N(3) and C(4) (see Table 3). Charac-
teristics of the important mean planes are shown in
Table 4. According to χ^2 of the phenyl ring, it seems
that the e.s.d.'s are somewhat underestimated. Never-
theless, the sydnone ring shows significant deviations
from planarity. The angle of 63·0° between planes of
the phenyl and sydnone rings excludes their conjuga-
tion. However, the angle of 28·0° between the plane of
the sp^2 orbitals of the double bond C(13)=C(14) and
the sydnone ring does not reject the possibility of a
slight overlapping of π orbitals. In connexion with this
angle, short intramolecular contacts are observed be-
tween C(14)···O(6) [3·138 (3) Å] and H(141)···O(6)
[2·49 (2) Å]; $\angle$O(6)···H(141)–C(14) is 124 (2)° and
$\angle$C(5)–O(6)···H(141) is 86·0 (9)°.

A figure showing the molecule viewed along the
C(4)–C(13) bond has been deposited.* Six torsion
angles formed by bonds in the cyclohexenyl ring,
starting with C(13)–C(14)–C(15)–C(16), C(14)–
C(15)–C(16)–C(17), *etc.*, are 11·7, –37·5, 54·0,
–43·0, 16·4, and –1·1°.

The thermal motion of molecule was studied by the
TLS method of Schomaker & Trueblood (1968). Part
of the molecule consisting of the sydnone ring and

* See deposition footnote.

Table 3. *Comparison of the valence angles* (°) *around*
N(3) *and* C(4) *in the title compound* (I) *and* 3-phenyl-4-
(3-methyl-1-buten-2-yl)sydnone (II)

	(I)	(II)
N(2)–N(3)–C(4)	116·0 (2)	115·6 (1)
N(2)–N(3)–C(7)	114·7 (2)	116·5 (1)
C(4)–N(3)–C(7)	129·3 (2)	127·9 (1)
N(3)–C(4)–C(5)	104·7 (2)	105·2 (1)
N(3)–C(4)–C(13)	127·8 (2)	126·2 (1)
C(5)–C(4)–C(13)	127·4 (2)	128·6 (2)

Table 4. *Deviations* (Å ×10³) *from weighted mean planes*

Asterisks denote atoms defining the planes.

Plane a/phenyl ring: $\chi^2 = 10$
Plane b/sydnone ring: $\chi^2 = 21$
Plane c/double bond: $\chi^2 = 204$

	Plane a	Plane b	Plane c
O(1)	962 (2)	3 (2)*	412 (2)
N(2)	1147 (2)	−6 (2)*	−242 (2)
N(3)	44 (2)	4 (2)*	−433 (2)
C(4)	−840 (2)	−2 (2)*	12 (2)*
C(5)	−252 (3)	−2 (2)*	586 (3)
O(6)	−558 (2)	−13 (2)	1125 (2)
C(7)	−5 (2)*	−42 (2)	−1150 (2)
C(8)	5 (3)*	−1154 (2)	−2401 (3)
C(9)	−2 (3)*	−1207 (3)	−3098 (3)
C(10)	−1 (3)*	−169 (3)	−2542 (3)
C(11)	−1 (3)*	920 (3)	−1297 (3)
C(12)	4 (3)*	999 (2)	−585 (3)
C(13)	−2150 (3)	52 (2)	−21 (2)*
C(14)	−2662 (4)	−466 (3)	−17 (4)*
C(15)	−4027 (5)	−387 (4)	38 (5)*
C(16)	−4678 (4)	48 (3)	−186 (4)
C(17)	−4398 (3)	1085 (3)	422 (3)
C(18)	−2930 (3)	709 (2)	5 (3)*

Angles between planes: $a \wedge b$ 63·0, $b \wedge c$ 28·0, $a \wedge c$ 65·1°.

O(6), C(7) and C(13) can be approximated by a rigid-body model {r.m.s. $= [\sum_{ik}(U_{ik}^{exp} - U_{ik}^{calc})^2/n]^{1/2} = 0\cdot0018$; e.s.d. $= [\sum_{ik}(U_{ik}^{exp} - U_{ik}^{calc})^2/(n - s)]^{1/2} = 0\cdot0008$; (r.m.s.)$' = [\sum_{ik}\sigma^2(U_{ik}^{exp})/n]^{1/2} = 0\cdot0024$, where $n = 48$ is the number of vibration tensor components and $s = 20$ is the number of derived quantities}. Bond-length corrections (Cruickshank, 1956) lie within two e.s.d.'s.

Fig. 2 shows a projection of the crystal structure along **b**. Some short intermolecular distances are O(6)—H(162^i) 2·43 (3), O(6)—H(91^{ii}) 2·61 (2) O(6)—H(182^{iii}) 2·66 (2), C(5)—H(101^{iv}) 2·87 (2), and C(5)—C(10^{iv}) 3·409 (3) Å, where the superscripts denote atoms in the following crystallographically equivalent positions: (i) −x, 2 − y, 0·5 − z; (ii) x − 1, 1·5 − y, 0·5 − z; (iii) −x, 2 − y, −z; (iv) 1 − x, y − 0·5, 0·5 − z. The distance O(6)$\cdots$H(162^i) is shorter than the sum of the van der Waals radii (Nyburg, 1961). According to Kvick, Koetzle & Thomas (1974), and as in the structure of 3-phenyl-4-(3-methyl-1-buten-2-yl)-sydnone, this may be classified as a very weak hydro-
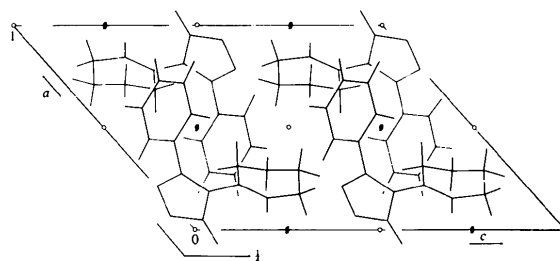
Fig. 2. The crystal structure viewed down **b**. The molecule in the lower left-hand corner drawn in thick lines corresponds to the co-ordinates in Tables 1 and 2.

gen bond: $\angle$C(16^i)—H(162^i)$\cdots$O(6) 153 (2)°, C(16^i)$\cdots$O(6) 3·443 (5) Å.

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