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Study of Photochromic Sydnones.
I. Structure of 3-Phenyl-4-(3-methyl-1-buten-2-yl)sydnone

BY J. HAŠEK, J. OBRDA,* K. HUML, S. NEŠPŮREK, H. CHOJNACKI† AND M. ŠORM

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 *Praha* 6, *Czechoslovakia*

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The structure of $C_{13}H_{14}N_2O_2$ has been determined by direct methods and refined to $R = 0.049$ for 1641 counter reflexions. The cell is monoclinic, space group $P2_1/c$, with $a = 9.732$ (6), $b = 11.644$ (4), $c = 12.098$ (6) Å, $\beta = 115.83$ (4)°, $Z = 4$. An angle of 54·9° was found between the planes of the sydnone and phenyl rings; the sydnone ring structure is in agreement with earlier results.

Introduction

The structure determination of 3-phenyl-4-(3-methyl-1-buten-2-yl)sydnone is part of a study of the photochromic properties of 4-alkenylsydnones (Nešpůrek & Šorm, 1975, 1977; Šorm & Nešpůrek, 1975*a*,*b*).

The objective of this work is the evaluation of the effects of molecular conformation and intermolecular contacts on the photochromism of the compound.

Experimental

The title compound forms transparent white crystals. The sample was prepared by cooling a saturated solution in ethanol (Šorm & Nešpůrek, 1975*b*).

Cell parameters were obtained by least-squares calculations from a calibrated powder photograph and also from the positions of 22 reflexions recorded with a Syntex $P2_1$ diffractometer. Results of the two determinations were identical to within one standard deviation.

Crystal data

$C_{13}H_{14}N_2O_2$, FW 230·3, m.p. 105–106 °C, monoclinic, $P2_1/c$, $a = 9.732$ (6), $b = 11.644$ (4), $c = 12.098$ (6) Å, $\beta = 115.83$ (4)°, $V = 1234$ Å^3, $F(000) = 488$, $\lambda(\mathrm{Cu}\ K\alpha) = 1.54178$ Å, $\mu(\mathrm{Cu}\ K\alpha) = 6.95$ cm^{-1}, $Z = 4$, $D_x = 1.239$, $D_m = 1.23$ (1) g cm^{-3}; the density was determined by flotation in aqueous KI solution; systematic absences (ψ scan check): $h0l$ for l odd; $0k0$ for k odd.

A crystal was ground to a sphere with $r = 0.3$ mm. Intensities were measured with the diffractometer (graphite monochromator, θ–2θ scan, Cu $K\alpha$ radiation, scan rate varied according to the intensity of the reflexion from 0·5 to 29·3° min^{-1}). Up to $\sin\theta/\lambda = 0.53$ Å^{-1}, 1691 independent reflexions were measured; 50 of these were classed as unobserved with $I < 1.96\sigma(I)$. 24 reflexions with $I > 80\,000$ c.p.s. were measured with a lower anode current. Three standard reflexions measured after every 30 reflexions showed no intensity decrease (40 kV, 20 mA, 200 h). No corrections for absorption or extinction were made.

Determination and structure refinement

The positions of all non-hydrogen atoms were determined with *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974). The correct solution was

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* On leave from: Geological Institute, Czechoslovak Academy of Sciences, 165 000 Praha 6, Czechoslovakia.

† Institute of Organic and Physical Chemistry, Technical University, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland.

indicated by the highest value of the combined figure of merit. The $\sum_1$ relationship was not used in the solution, but subsequent checks showed that correct signs were obtained in all nine cases.

The structure was refined by block-diagonal least squares with a modified *NRC*-10 program (Ahmed, Hall, Pippy & Huber, 1966). The function minimized was $\sum w(|F_o| - |F_c|)^2$, with $1/w = \sigma_F^2 + (0{\cdot}02F_o)^2$, where σ_F^2 was determined from the counting statistics.

Scattering factors for non-hydrogen atoms were taken from *International Tables for X-ray Crystallography* (1974); for H those from Stewart, Davidson & Simpson (1965) were used.

Anisotropic refinement of the non-hydrogen atoms reduced R to 0·093. At this stage the H atoms were determined from a difference map. In subsequent cycles R fell to its final value of 0·049.*

In the last cycle, nine parameters were refined for each non-hydrogen atom and four for each H atom. Positional shifts of the non-hydrogen atoms were <0·05 of their e.s.d.'s (<0·25 e.s.d. for H atoms). The maximum changes in the temperature parameters were 0·07 e.s.d.. The final atomic parameters are given in Tables 1 and 2.

The highest residual maximum on the final difference map was 0·15 e $Å^{-3}$; the minimum was −0·3 e $Å^{-3}$.

Structure description and discussion

Fig. 1 shows a projection of the molecule along **b**. The temperature ellipsoids of 20% probability were computed with the *ŮMCH* 108 program (Šoler, 1973).

Table 1. *Final positional parameters* (×10⁴) *and their e.s.d.'s for the non-hydrogen atoms*

	x	y	z
O(1)	6133 (1)	6051 (1)	10067 (1)
N(2)	4710 (2)	6473 (1)	9835 (1)
N(3)	3951 (1)	6401 (1)	8633 (1)
C(4)	4740 (2)	5971 (1)	8042 (1)
C(5)	6220 (2)	5752 (1)	8974 (2)
O(6)	7409 (1)	5389 (1)	9004 (1)
C(7)	2405 (2)	6847 (1)	8099 (1)
C(8)	1381 (2)	6420 (1)	8504 (1)
C(9)	−90 (2)	6860 (2)	7990 (2)
C(10)	−490 (2)	7702 (2)	7107 (2)
C(11)	552 (2)	8123 (2)	6716 (2)
C(12)	2026 (2)	7691 (1)	7211 (2)
C(13)	4137 (2)	5746 (1)	6724 (1)
C(14)	4938 (2)	6126 (2)	6141 (2)
C(15)	2726 (2)	4999 (1)	6132 (1)
C(16)	1845 (3)	5188 (2)	4762 (2)
C(17)	3198 (2)	3741 (2)	6419 (2)

Bond lengths and angles are given in Fig. 2 and Table 3.

Fig. 3 shows a projection of the structure along **b**. The shortest intermolecular distances are C(5)···H(81^{i}) 2·97 (2), O(6)···H(81^{i}) 2·49 (2), O(1)···H(101^{ii}) 2·62 (2), and O(6)···H(91^{iii}) 2·68 (2) Å, where the indices denote molecules in the following crystallographically-equivalent positions: (i) $1-x$, $1-y$, $2-z$, (ii) $1+x$, $1{\cdot}5-y$, $0{\cdot}5-z$, (iii) $1+x, y, z$. Only O(6)···H(81^{i}) is shorter than the sum of the van der Waals radii (Nyburg, 1961). According to Kvick, Koetzle & Thomas (1974), it may be assumed that a

Table 2. *Final parameters and their e.s.d.'s for the* H *atoms*

Fractional coordinates are × 10³.

	x	y	z	B ($Å^2$)
H(81)	169 (2)	586 (1)	914 (2)	5·5 (4)
H(91)	−85 (2)	660 (2)	821 (2)	6·5 (5)
H(101)	−152 (2)	795 (2)	682 (5)	6·6 (5)
H(111)	29 (2)	872 (2)	612 (2)	6·6 (5)
H(121)	277 (2)	801 (2)	696 (2)	6·3 (4)
H(141)	464 (2)	595 (2)	526 (2)	6·5 (4)
H(142)	594 (3)	664 (2)	656 (2)	9·1 (6)
H(151)	208 (2)	522 (1)	655 (1)	4·4 (3)
H(161)	248 (2)	492 (2)	432 (2)	8·3 (6)
H(162)	103 (3)	459 (2)	449 (3)	10·0 (7)
H(163)	142 (3)	592 (2)	471 (2)	10·3 (7)
H(171)	376 (3)	356 (2)	723 (3)	10·2 (7)
H(172)	391 (3)	359 (2)	601 (3)	10·3 (7)
H(173)	225 (2)	320 (2)	615 (2)	8·1 (6)

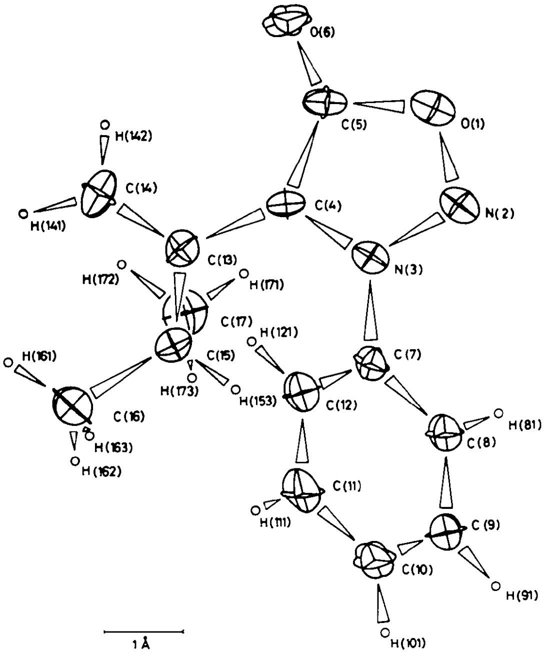

Fig. 1. Thermal-motion ellipsoids of 20% probability; projection along **b**.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33536 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

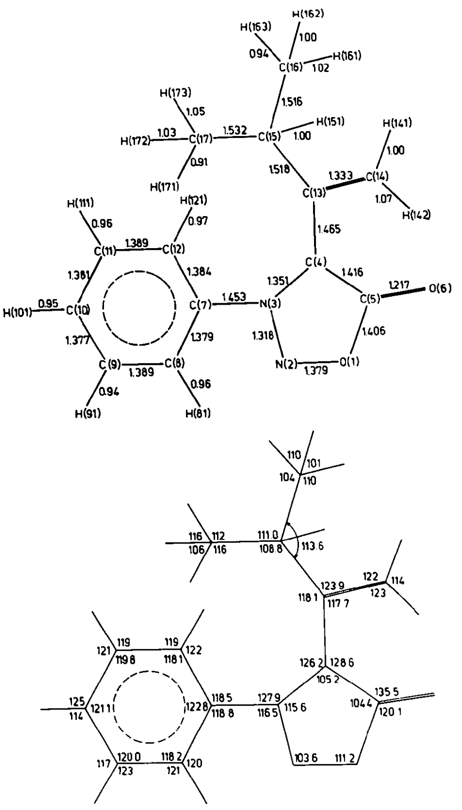

Fig. 2. Bond lengths (Å) and angles (°) with the numbering scheme. The maximal e.s.d. of the bond lengths for the non-hydrogen atoms is 0·003 Å; e.s.d.'s of bond lengths with H are <0·03 Å. E.s.d.'s of angles are 0·2° for non-hydrogen atoms, 1·2° for phenyl H and 2·5° for other H atoms.

Table 3. *Bond angles (°) not given in Fig. 2 and their e.s.d.'s*

C(15)–C(16)–H(162)	104 (2)
H(161)–C(16)–H(163)	126 (2)
C(15)–C(17)–H(172)	104 (2)
H(171)–C(17)–H(173)	103 (2)
C(13)–C(15)–H(151)	105 (1)
C(16)–C(15)–H(151)	110 (1)
C(17)–C(15)–H(151)	109 (1)

hydrogen bond is involved here; this is also suggested by the value of the angle C(8^i)–H(81^i)···O(6), 172 (2)°.

The structure of the sydnone ring (Fig. 2) is in agreement with other structures (Bärnighausen, Jellinek, Munnik & Vos, 1963; Hope & Thiessen, 1969). The bonds in this ring are aromatic, except for O(1)–C(5). This is explained by quantum-mechanical calculations as incomplete conjugation of the π electrons in the sydnone ring (Barber, Broadbent, Connor, Guest, Hillier & Puxley, 1972). The $\chi^2 = 196$ of the weighted mean plane calculated by the *NRC*-22 program (Ahmed *et al.*, 1966) for O(1), N(2), N(3), C(4), C(5) shows a slight non-planarity [maximum deviation 0·016 (2) Å] of the sydnone ring (Table 4).

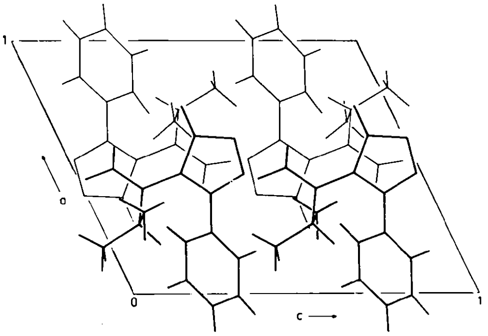

Fig. 3. The structure viewed along **b**. The molecule in the lower right-hand corner drawn in thick lines corresponds to the coordinates given in Tables 1 and 2, that in the lower left-hand corner is at x, $1\cdot5-y$, $z-0\cdot5$, that in the upper left-hand corner at $1-x$, $1-y$, $1-z$, and that in the upper right-hand corner at $1-x, y-0\cdot5, 1\cdot5-z$.

Table 4. *Weighted mean planes*

The equations of the planes are related to the orthonormal system of coordinates where x lies in a, y in b and z is parallel to c^*. Deviations and their e.s.d.'s (in parentheses) are in Å.

Plane 1: sydnone ring, defined by O(1), N(2), N(3), C(4), C(5)
$0\cdot3680x + 0\cdot9257y - 0\cdot087z = 5\cdot8366;\ \chi^2 = 196$

Plane 2: phenyl ring, defined by C(7) to C(12)
$0\cdot0306x - 0\cdot7012y - 0\cdot7123z = 11\cdot9473;\ \chi^2 = 5\cdot88$

	Deviation from plane 1	Deviation from plane 2
O(1)	−0·008 (1)	−0·798 (1)
N(2)	0·005 (1)	−1·001 (1)
N(3)	0·002 (1)	−0·012 (1)
C(4)	−0·009 (1)	0·831 (2)
C(5)	0·016 (2)	0·3164 (2)
O(6)	0·041 (2)	0·6244 (2)
C(7)	0·084 (2)	−0·000 (1)
C(8)	−0·860 (2)	−0·002 (2)
C(9)	−0·746 (2)	0·002 (2)
C(10)	0·256 (2)	0·002 (2)
C(11)	1·197 (2)	−0·003 (2)
C(12)	1·115 (2)	0·002 (2)
C(13)	−0·089 (2)	2·042 (2)
C(14)	0·777 (2)	2·217 (2)
C(15)	−1·230 (2)	3·080 (2)
C(16)	−0·947 (3)	3·985 (2)
C(17)	−2·501 (2)	3·896 (2)

The length N(3)–C(7), 1·453 (2) Å, and the angle between the planes of the phenyl and sydnone rings, 54·9°, suggest no conjugation between the two rings. The primary cause of this rotation can be seen in the steric effect of the methyl groups of the substituent bonded to C(4). The structure of the molecule is illustrated in Fig. 4, which shows projections in the direction of the bonds to both substituents of the

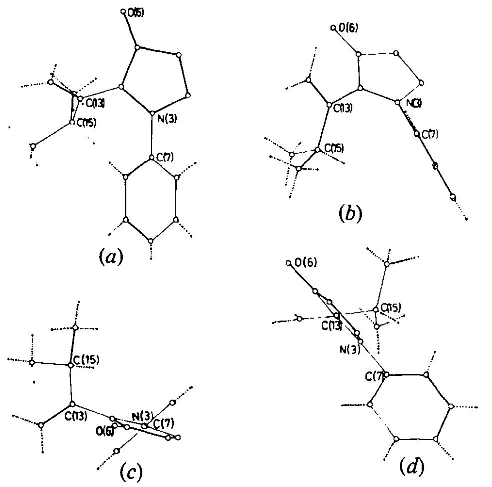

Fig. 4. Projection of molecule (*a*) along the normal to the sydnone ring, (*b*) parallel to the phenyl ring, (*c*) along N(3)–C(7), (*d*) along C(4)–C(13).

sydnone ring, and also perpendicular to the sydnone ring and parallel to the phenyl ring. This structure may be compared with that of bromophenylsydnone (Bärnighausen, Jellinek, Munnik & Vos, 1963), where N(3)–C(7) is 1·41 Å and the angle between the sydnone and phenyl rings is 27·6°. N(3)–C(7) in 3,3′-ethylenebisydnone is 1·472 Å (Hope & Thiessen, 1969).

The C(4)–C(13) (sp^2–sp^2) distance [1·465 (3) Å] is short. The angle (49·8°) between the C(4)–C(13)–C(14) plane and the sydnone ring is an argument against the possibility of overlap of the π orbitals.

The C(13)–C(14) distance corresponds to a double bond; the bond lengths between C(13), C(15), C(16) and C(17) correspond to single bonds.

In 3-*N*-pyridylsydnone, which has been extensively investigated, Mitsui & Ebara (1973) suggested that its photochromism was due to the mutual planarity of the sydnone ring and the aromatic substituent on N(3), which in the planar arrangement of molecules in the solid state makes possible the charge-transfer process. The structure studied by us in the crystalline state shows neither this planarity nor photochromism. On the other hand, the same compound in solid glasses does show photochromism.

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