The conformation of the valine residue is defined by the torsion angles χ^{31}[N—C(1)—C(2)—C(4)] and χ^{32}[N—C(1)—C(2)—C(3)] describing the orientation of the two C^{β}—C^{γ} bonds about C^{α}—C^{β}. The values of χ^{31} and χ^{32} are different from those found in *P*-valine where N—C(1) is *gauche* [$\chi^{31} = -49{\cdot}5$ (10), $\chi^{32} = 76{\cdot}4$ (10)°] to both C^{β}—C^{γ} bonds.

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Structures of 3-(*p*-Benzyloxyphenyl)sydnone (1) and 3-(*p*-Isopropoxyphenyl)sydnone (2)

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Abstract. (1): $C_{15}H_{12}N_2O_3$, $M_r = 268$, monoclinic, $P2_1/c$, $a = 6{\cdot}582$ (3), $b = 6{\cdot}190$ (1), $c = 20{\cdot}848$ (2) Å, $\beta = 96{\cdot}77$ (3)°, $V = 1252{\cdot}26$ Å^3, $Z = 4$, $D_m = 1{\cdot}4$ (3), $D_x = 1{\cdot}42$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7093 Å, μ(Mo $K\alpha$) = 0·094 mm^{-1}, $F(000) = 560$, $T = 298$ K, final $R = 0{\cdot}048$ for 2222 observed reflections. (2): $C_{11}H_{12}N_2O_3$, $M_r = 220$, triclinic, $P\bar{1}$, $a = 6{\cdot}916$ (1), $b = 8{\cdot}089$ (1), $c = 10{\cdot}820$ (2) Å, $\alpha = 108{\cdot}49$ (1), $\beta = 82{\cdot}89$ (1), $\gamma = 108{\cdot}42$ (1)°, $V = 544{\cdot}45$ Å^3, $Z = 2$, $D_m = 1{\cdot}3$ (3), $D_x = 1{\cdot}34$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7093 Å, μ(Mo $K\alpha$) = 0·093 mm^{-1}, $F(000) = 232$, $T = 298$ K, final $R = 0{\cdot}041$ for 1609 observed reflections. The bond distances in the sydnone ring are similar in both structures and also similar to those in 3-(*p*-ethoxyphenyl)sydnone and 3-(*p*-tolyl)sydnone [Wang, Lee & Yeh (1984). *Acta Cryst.* C**40**, 1226–1228]. The N(1)—C(7) and C(7)—C(8) distances of (1), (2) and 3-(*p*-ethoxyphenyl)sydnone are significantly shorter than the corresponding bonds in other 3-phenylsydnone derivatives. The dihedral angles between the sydnone ring and the phenyl ring of (1) and (2) are 39·1 (1) and 24·4 (1)°, respectively. The sydnone ring can be described as having a cyclic azomethine-imide type of bonding.

Introduction. There are a few studies on the unique aromaticity of the sydnone ring (Stewart, 1964; Ohta & Kato, 1969). The dominant delocalized form of the

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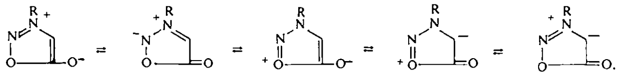
sydnone ring among the possible resonance structures (Stewart, 1964) of the sydnone ring depicted here,



is particularly interesting. The known photochromic properties of such compounds are also interesting. In order to understand the bond pattern of the sydnone ring and the relationship between the variation of color and the structural conformation, the structure determinations of the title compounds and those of the previous work (Wang, Lee & Yeh, 1984) were undertaken as part of a series of studies on such compounds.

Experimental. (1) Crystal 0·3 × 0·3 × 0·5 mm. CAD-4 diffractometer. Unit cell: 24 reflections, 2θ range 11 to 26°. D_m by flotation (C_6H_6/CCl_4). $2\theta_{max} = 60°$. Ranges of h, k, l: −9 to 9, 0 to 13, 0 to 29, respectively. Three standard reflections monitored every 2 h: variation <2%. 3666 unique reflections, 2222 observed with $I > 2\sigma(I)$. No absorption correction. $R(F) = 0{\cdot}048$, $wR(F) = 0{\cdot}032$, $S = 2{\cdot}50$. Weighting scheme from counting statistics. Structure solved by direct method using *MULTAN*, with 180 highest E's, 60 smallest E's and 1834 $\sum_2$ relationships. H atoms found in difference Fourier map after isotropic refinement, and then refined. $(\Delta/\sigma)_{max} = 0{\cdot}08$. Peaks in final ΔF 0·20 to −0·19 e Å^{-3}. Extinction coefficient 0·266 (length in µm). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Computing programs: NRCC *SDP PDP*-11 package (Gabe & Lee, 1981), *MULTAN* and *ORTEP* from Enraf–Nonius (1979) *Structure Determination Package*. (2) Crystal 0·4 × 0·3 × 0·5 mm. Unit cell: 24 reflections, 2θ range 15 to 33°. D_m by flotation (C_6H_6/CCl_4). $2\theta_{max} = 60°$. Ranges of h, k, l: −9 to 9, −11 to 11, 0 to 15, respectively. Three standard reflections monitored every 2 h: variation <2%. 3176 unique reflections, 1609 observed with $I > 2\sigma(I)$. No absorption correction. $R(F) = 0{\cdot}041$, $wR(F) = 0{\cdot}031$, $S = 2{\cdot}43$. Structure solved by direct method with 264 highest E's, 12 smallest E's and 2124 $\sum_2$ relationships. H atoms found in difference Fourier map after isotropic refinement, and then refined. $(\Delta/\sigma)_{max} = 0{\cdot}11$. Peaks in final ΔF map 0·18 to −0·16 e Å^{-3}. Extinction coefficient 0·258 (length in µm). Other details as for (1).

Discussion. Atomic positional parameters and equivalent isotropic temperature factors are listed in Table 1.* Bond lengths and angles are shown in Fig. 1. Packing diagrams are given in Fig. 2.

Table 1. *Atomic positional parameters and equivalent isotropic temperature factors for* (1) *and* (2)

$$B_{eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	B_{eq}(Å^2)
Compound (1)				
C(4)	0·3445 (3)	0·3401 (2)	0·1437 (1)	3·3 (1)
C(5)	0·3395 (3)	0·2303 (2)	0·0978 (1)	3·6 (1)
C(6)	0·1659 (3)	0·2076 (2)	0·0553 (1)	3·6 (1)
C(1)	−0·0016 (2)	0·2958 (2)	0·0594 (1)	3·1 (1)
C(2)	−0·0014 (3)	0·4049 (2)	0·1043 (1)	3·6 (1)
C(3)	0·1749 (3)	0·4284 (2)	0·1468 (1)	3·8 (1)
C(7)	−0·3097 (3)	0·3759 (2)	−0·0123 (1)	3·9 (1)
C(8)	−0·4674 (3)	0·3038 (2)	−0·0510 (1)	4·1 (1)
C(9)	0·5340 (3)	0·4702 (2)	0·2302 (1)	4·6 (1)
C(10)	0·7383 (3)	0·4656 (2)	0·2705 (1)	3·6 (1)
C(11)	0·8776 (3)	0·5768 (2)	0·2669 (1)	4·2 (1)
C(12)	1·0629 (3)	0·5753 (2)	0·3063 (1)	4·7 (1)
C(13)	1·1094 (3)	0·4624 (2)	0·3483 (1)	4·6 (1)
C(14)	0·9716 (3)	0·3512 (2)	0·3526 (1)	4·7 (1)
C(15)	0·7856 (3)	0·3539 (2)	0·3142 (1)	4·4 (1)
N(1)	−0·1861 (2)	0·2732 (2)	0·0156 (1)	3·3 (1)
N(2)	0·2415 (2)	0·1388 (2)	0·0012 (1)	4·3 (1)
O(1)	0·4183 (2)	0·1553 (1)	−0·0410 (1)	4·5 (1)
O(2)	−0·6172 (2)	0·3386 (2)	−0·0866 (1)	5·6 (1)
O(3)	0·5229 (2)	0·3526 (1)	0·1843 (1)	4·1 (1)
Compound (2)				
C(1)	0·9012 (3)	0·3407 (2)	0·1178 (2)	3·2 (1)
C(6)	0·0011 (3)	0·2292 (3)	0·1397 (2)	3·7 (1)
C(5)	0·1629 (3)	0·3067 (3)	0·2214 (2)	3·8 (1)
C(4)	0·2250 (3)	0·4939 (3)	0·2817 (2)	3·4 (1)
C(3)	0·1186 (3)	0·6024 (3)	0·2624 (2)	3·7 (1)
C(2)	0·9563 (3)	0·5258 (2)	0·1786 (2)	3·5 (1)
C(7)	0·5864 (3)	0·3316 (3)	0·0239 (2)	3·8 (1)
C(8)	0·5323 (3)	0·7861 (3)	0·0830 (2)	4·2 (1)
C(9)	0·4483 (3)	0·7398 (3)	0·4442 (2)	3·9 (1)
C(10)	0·6918 (4)	0·2537 (3)	0·4378 (2)	5·7 (2)
C(11)	0·6681 (4)	0·7825 (3)	0·4746 (2)	5·4 (1)
N(1)	0·7368 (3)	0·2632 (2)	0·0275 (1)	3·4 (1)
N(2)	0·2645 (3)	0·8892 (2)	0·0647 (2)	4·3 (1)
O(1)	0·4346 (2)	0·9248 (2)	0·1351 (1)	4·4 (1)
O(2)	0·6808 (2)	0·7932 (2)	0·1355 (2)	5·5 (1)
O(3)	0·3948 (2)	0·5557 (2)	0·3545 (1)	4·2 (1)

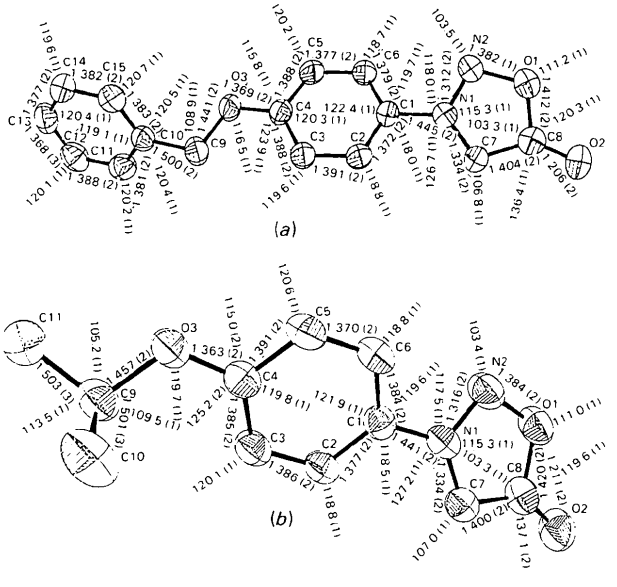


Fig. 1. Bond lengths (Å) and angles (°) for (*a*) compound (1) and (*b*) compound (2).

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42391 (50 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The dihedral angles between the sydnone ring and the phenyl ring of alkoxyphenylsydnone derivatives are given in Table 2; they vary from 2 to 39°. According to the known conformational structures of sydnone derivatives, there is no obvious correlation between the color and the conformation.

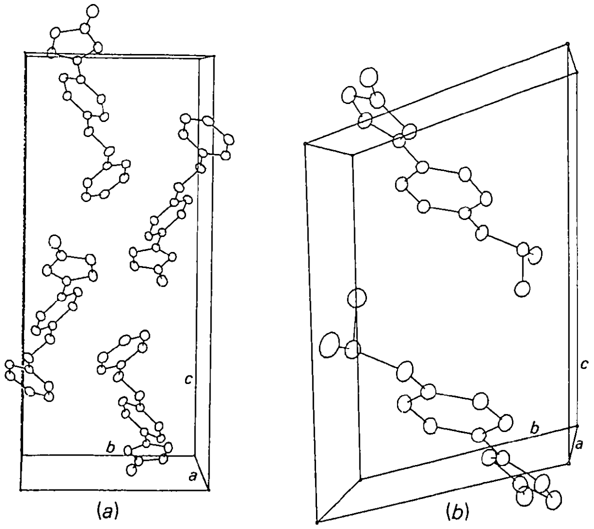


Fig. 2. Packing diagrams for (*a*) compound (1) and (*b*) compound (2).

Table 2. *Comparison of selected bond distances* (Å) *in the sydnone ring*

The bond distances of the sydnone ring in the other related sydnone derivatives are listed in Wang, Lee & Yeh (1984).

	3-Phenyl-sydnone[a]	3-(*p*-Ethoxy-phenyl)syd-none[b]	3-(*p*-Benzyl-oxyphenyl)-sydnone[c]	3-(*p*-Isoprop-oxyphenyl)-sydnone[c]
O(1)–C(8)	1·411 (1)	1·407 (3)	1·412 (2)	1·420 (3)
O(1)–N(2)	1·373 (1)	1·384 (3)	1·382 (1)	1·384 (2)
N(2)–N(1)	1·313 (1)	1·307 (2)	1·312 (2)	1·316 (2)
N(1)–C(7)	1·347 (1)	1·329 (3)	1·334 (2)	1·334 (2)
C(7)–C(8)	1·413 (1)	1·400 (3)	1·404 (3)	1·400 (2)
C(8)–O(2)	1·221 (1)	1·212 (3)	1·206 (2)	1·211 (2)
$\Delta\|O(2)\|$*		0·030	0·0052	0·038
ω (°)	30·0	2	39·1 (1)	24·4 (1)
χ^2		4·1	4·9	22·6
Color		Brown	Brown	Light brown

References: (*a*) Hope (1978); (*b*) Wang, Lee & Yeh (1984); (*c*) this work.

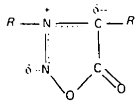
* Deviation (Å) of O(2) from the mean plane of the sydnone ring.

Table 3. *Comparison of selected bond distances* (Å) *in the* 3-*phenyl ring*

	3-(*p*-Ethoxy-phenyl)sydnone	(1)	(2)
C(1)–C(2)	1·371 (3)	1·372 (2)	1·377 (2)
C(2)–C(3)	1·392 (3)	1·391 (2)	1·386 (2)
C(3)–C(4)	1·385 (3)	1·388 (2)	1·385 (2)
C(4)–C(5)	1·381 (3)	1·388 (2)	1·391 (2)
C(5)–C(6)	1·376 (3)	1·377 (2)	1·370 (2)
C(6)–C(1)	1·380 (3)	1·379 (2)	1·384 (2)
C(1)–N(1)	1·477 (3)	1·445 (2)	1·441 (2)
O(3)–C(4)	1·362 (3)	1·369 (2)	1·363 (2)

The planarity of the sydnone ring is also given in Table 2 as χ^2 which is defined as $\sum_{i=1}^{N}\Delta d_i^2/(\sigma_{x_i}^2 + \sigma_{y_i}^2 + \sigma_{z_i}^2)$, where Δd_i is the distance of the atom i from the least-squares plane; σ_{x_i}, σ_{y_i} and σ_{z_i} are the standard deviations of coordinates x, y and z for atom i, respectively. It is obvious that compound (1) has better planarity than compound (2).

The bond lengths of the sydnone ring are compared with those from other 3-phenylsydnone derivatives in Table 2 (Wang, Lee & Yeh, 1984; Hope, 1978). N(1)–C(7) and C(7)–C(8) of the last three compounds in Table 2 are significantly shorter than the corresponding bonds in other 3-phenylsydnone derivatives. From Table 2, C(8)–O(2) is within a typical C=O double-bond range; thus C(8)–O(2) has localized double-bond character. The N(1)–N(2) length is between a single (1·44 Å) and a double bond (1·24 Å). The N(1)–C(7) length is similar to the N–C distance in pyridine [1·352 (5) Å]. From these bond lengths, the sydnone ring can be most satisfactorily described as having a cyclic, resonance-stabilized azomethine-imine type of bonding,



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which is a combination of the second and the last resonance forms mentioned in the *Introduction*. This conclusion is also consistent with that from the previous work (Ohta & Kato, 1969) based on characteristic addition–elimination reactions of the sydnone ring. This description may be further confirmed if the effects of the substituent *R'* on the bond lengths of the sydnone ring are also known. Studies on this effect are under way.

The bond lengths of the 3-phenyl ring of 3-alkoxy(or aryloxy)sydnone derivatives are listed in Table 3. The bond pattern of the 3-phenyl ring is different from that of 3-(*p*-tolyl)sydnone which does not have an alkoxy group as a substituent. C(1)–C(2) and C(5)–C(6) are significantly shorter than C(2)–C(3) and C(3)–C(4) for these three compounds. C(5)–C(6) is significantly shorter than C(4)–C(5) for (1) and (2). This may be attributed to the fact that the lone-pair electrons of the O atom in the alkoxy group take part in the resonance of the phenyl ring. As a result, C(1)–C(2) and C(5)–C(6) have more double-bond character than C(2)–C(3) and C(3)–C(4).

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Structure of α-Santonin

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Abstract. $C_{15}H_{18}O_3$, $M_r = 246\cdot1$, orthorhombic, $P2_12_12_1$, $a = 34\cdot575\ (7)$, $b = 10\cdot705\ (1)$, $c = 6\cdot991\ (1)$ Å, $V = 2587\cdot5\ (7)$ Å^3, $Z = 8$, $D_x = 1\cdot264$ g cm^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0\cdot7107$ Å, $\mu = 0\cdot94$ cm^{-1}, $F(000) = 1056$, $T = 294$ K, $R = 0\cdot051$ for 3129 observed reflections. The unit cell contains two crystallographically independent molecules of similar conformations. In the packing structure, the dienone rings are nearly stacked parallel along the *b* axis with an interplanar angle of 28°, and their carbonyl O atoms are surrounded by short intermolecular contacts.

Introduction. The stereochemistry of α-santonin has been established both by chemical methods (Nakazaki & Arakawa, 1962; Cocker & McMurry, 1960) and by the X-ray structure analyses of its derivatives (Inayama, Shimizu, Hori, Ohsaka, Hirose, Shibata & Iitaka, 1982; White & Sim, 1975; Asher & Sim, 1965). However, the crystal structure of α-santonin itself has not yet been determined. Santonin undergoes photo-induced rearrangement in solution to give lumisantonin (Kropp, 1967), while in the solid state a cyclopentadienone derivative is obtained (Matsuura, Sata, Ogura & Mori, 1968). The photochemical rearrangement of α-santonin in solution accompanies a large movement of atoms, while in the solid state it results in the migration of an H atom from C(1) to the neighboring C(10). These facts agree with the general rule that the photochemical reaction in the solid state proceeds with a minimum amount of atomic movements from the starting material (Cohen & Schmidt, 1964). The crystal-structure analysis of α-santonin has been undertaken to give a structural basis to the understanding of its photochemical reaction in the solid state.

Experimental. Crystals of α-santonin by slow evaporation from ethanol solution. Crystal dimensions $0\cdot5 \times 0\cdot5 \times 0\cdot5$ mm. Intensity data from Rigaku C–5 automated four-circle diffractometer equipped with graphite-monochromated Mo $K\alpha$ radiation from a rotating anode. Lattice parameters refined using 31 reflections measured in 2θ range 20–40°. 3399 unique reflections measured to the limit $2\theta < 55°$ using ω–2θ scans; range of *hkl*: $0 \le h \le 44$, $0 \le k \le 13$, $0 \le l \le 9$; 3129 significant with $I > 2\sigma(I)$; three standard reflections monitored periodically showed no systematic variation in intensity during course of data collection; Lorentz–polarization corrections, no absorption corrections applied. Structure solved using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Difference electron density maps used to locate all 36 H atoms; anisotropic block-diagonal least-squares refinement for 36 non-H atoms, isotropic for 36 H atoms; final $R = 0\cdot051$ and $wR = 0\cdot064$ for 3129 significant reflections, $\sum w(F_o - F_c)^2$ minimized where $w = 1/[\sigma^2(F) + 0\cdot002F^2]$, $(\Delta/\sigma)_{\max} = 0\cdot6$, largest features in $\Delta\rho$ map $0\cdot2$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Computations performed on an ACOS S-850 computer.

Discussion. The final parameters for the non-H atoms are given in Table 1.* The cornformation of the molecules and the numbering of the atoms are shown in

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and selected torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42403 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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