Discussion. The bond distances and angles follow the same trends observed in similar molecules, notably HMTD (Schaefer *et al.*, 1985) and BTDD (Fourkas & Schaefer, 1986). The average O—O distance is 1·456 (4) Å as compared to 1·465 (8) Å for HMTD and 1·464 (10)Å for BTDD (in which both of the peroxide groups are disordered); the value for H_2O_2 is 1·453 (7) Å (Busing & Levy, 1965). The average N—C(—O) distance is 1·410 (4) Å, compared to 1·424 (3) Å for BTDD and 1·421 (8) Å for HMTD. The N—C bond lengths to the cyclohexane ring are larger, as expected, averaging 1·461 (4) Å.

The N atoms are very nearly coplanar with the C atoms to which they are bonded. N(1) is 0·14 (1) Å from the C(1),C(7),C(8) plane and N(2) is 0·14 (1) Å from the C(2),C(9),C(10) plane. Similar distances for BTDD are 0·16 (1) and 0·10 (1) Å; the N atoms in HMTD are essentially coplanar with the corresponding C atoms. These similarities suggest that the near planarity of the bridgehead N atoms is due primarily to the peroxide groups, since analogous compounds with all-C bridges show nearly normal tetrahedral N atoms (Alder, Orphen & Sessions, 1983).

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Structure of Methyl 4-Hydroxy-2-methyl-2*H*-1,2-benzothiazine-3-carboxylate 1,1-Dioxide

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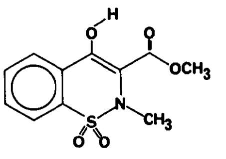
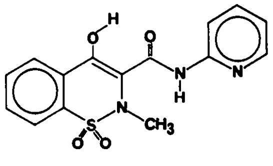
Abstract. $C_{11}H_{11}NO_5S$, $M_r = 269·3$, monoclinic, $P2_1/c$, $a = 8·432$ (3), $b = 6·970$ (2), $c = 19·650$ (7) Å, $\beta = 98·80$ (2)°, $V = 1141·3$ Å^3, $Z = 4$, $D_m = 1·56$ (5), $D_x = 1·567$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 2·83$ cm^{-1}, $F(000) = 560$, $T = 293$ (1) K, final $R = 0·067$ for 1265 observed reflexions. An intramolecular hydrogen bond [O···O = 2·626 (7) Å] is formed between the hydroxy group and the carbonyl O of the methoxycarbonyl group. The benzene ring is planar, the maximum deviation being 0·014 (7) Å. The thiazine ring is in a distorted half-chair conformation. Bond lengths and angles agree with expected values.

Introduction. Recently much attention has been devoted to structural investigations of the non-steroidal anti-inflammatory agent 4-hydroxy-2-methyl-*N*-2-pyridyl-2*H*-1λ^6,2-benzothiazine-3-carboxamide 1,1-dioxide, known as piroxicam. The crystal structures of piroxicam (II) and piroxicam monohydrate have been elucidated (Kojić-Prodić & Ružić-Toroš, 1982; Bordner, Richards, Weeks & Whipple, 1984; Golič & Koželj, 1984). The crystal structure of (I), the precursor in the synthesis of piroxicam, is described in this paper.



(I)



(II)

The crystals of the compound were kindly supplied by Professor F. Kozjek, Department of Pharmacy of this university.

Experimental. Density measured by flotation in chlorobenzene/CCl_4; colourless prisms, 0·42 × 0·38 × 0·26 mm; Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation (graphite monochromator), lattice

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parameters by least-squares fit of 45 reflexions ($7 < \theta < 13°$); $\omega/2\theta$ scans, variable scan rate (min. 1·8, max. 20·1° min^{-1}), max. scan time 45 s, scan width (2θ) ($0{\cdot}8 + 0{\cdot}2\tan\theta$)°, aperture ($2{\cdot}5 + 0{\cdot}9\tan\theta$) mm, background measured for $\frac{1}{4}$ of scan time at each of scan limits, $(\sin\theta/\lambda)_{\max}$ in intensity measurements: 0·64 Å^{-1}. Three reflexions monitored at intervals of 240 reflexions, no intensity decline; data corrected for intensity variation and Lp effects, but absorption ignored. 4911 ($+h$, $\pm k$, $\pm l$) measured reflexions, 2253 unique ($R_{\rm int} = 0{\cdot}037$), 1265 observed ($h$ −10/10, k 0/8, l 0/24) with $I > 3\sigma(I)$, $\sigma(I)$ based on counting statistics. Structure solution by direct methods with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), full-matrix least-squares refinement minimizing $\sum w(\Delta F)^2$ with *SHELX*76 (Sheldrick, 1976); final R and wR values: 0·067 and 0·079 with $w = 2{\cdot}86/[\sigma^2(F_o) + 0{\cdot}00005F_o^2]$; H atoms found from a difference synthesis and included in the refinement at calculated positions [d(C—H) = 1·08 Å], a common isotropic temperature factor U for H atoms refined to 0·094 (9) Å^2, H of OH group refined separately [U = 0·022 (16) Å^2]. $\Delta\rho$ within −0·26 and 0·24 e Å^{-3} in final difference map. At convergence max. and mean values of Δ/σ: 0·44 and 0·04. Scattering factors for S, O, N and C and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974), for H from Stewart, Davidson & Simpson (1965). All calculations performed on the DEC 1091 computer at RCU of this university. *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) was used for data reduction and interpretation.

Discussion. The final atomic parameters are in Table 1.* Bond lengths are given in Table 2. Views of the molecule with the atomic numbering and of the molecular packing are presented in Figs. 1 and 2.

The results of previous structure determinations revealed two different conformations of the piroxicam molecule. The amide group forms one intramolecular hydrogen bond to the hydroxy group in the structure of piroxicam, whilst a zwitterionic structure with two intramolecular hydrogen bonds occurs in the structure of piroxicam monohydrate. The zwitterion is formed by the transfer of the enolic H to the pyridine N atom, accompanied by a change of conformation.

The crystal structure of the title compound is similar to that of neutral piroxicam. The enolic H on O(1) is involved in an intramolecular hydrogen bond to O(4) of the methoxycarbonyl group [O(1)—H(1)···O(4)

Table 1. *Fractional atomic coordinates* (×10^4) *and equivalent isotropic temperature factors* (Å^2 ×10^3) (*Hamilton*, 1959)

	x	y	z	$U_{\rm eq}$
S(1)	7313 (2)	2983 (3)	3705 (1)	37 (1)
N(2)	7103 (6)	1589 (8)	3035 (3)	41 (3)
C(3)	8424 (7)	1635 (9)	2651 (3)	35 (4)
C(4)	9945 (8)	1726 (10)	2975 (3)	40 (4)
C(5)	11944 (8)	1513 (9)	4038 (4)	44 (5)
C(6)	12332 (9)	1660 (10)	4748 (4)	54 (5)
C(7)	11189 (10)	2229 (10)	5147 (4)	51 (5)
C(8)	9639 (9)	2576 (9)	4841 (4)	44 (5)
C(9)	9232 (8)	2420 (8)	4132 (3)	34 (4)
C(10)	10389 (8)	1832 (9)	3713 (3)	33 (4)
C(11)	8042 (8)	1608 (9)	1898 (3)	39 (4)
C(12)	6072 (9)	1524 (10)	921 (3)	49 (5)
C(13)	6153 (9)	−191 (11)	3028 (4)	56 (5)
O(1)	11231 (6)	1722 (8)	2640 (3)	50 (3)
O(2)	7357 (5)	4917 (6)	3483 (2)	47 (3)
O(3)	6151 (6)	2418 (7)	4133 (2)	60 (3)
O(4)	9086 (6)	1538 (7)	1522 (2)	55 (3)
O(5)	6486 (5)	1612 (7)	1645 (2)	44 (3)

Table 2. *Bond distances* (Å) *with e.s.d.'s in parentheses*

S(1)—O(2)	1·419 (5)	C(5)—C(6)	1·387 (10)
S(1)—O(3)	1·440 (5)	C(6)—C(7)	1·390 (12)
S(1)—N(2)	1·624 (6)	C(7)—C(8)	1·374 (11)
S(1)—C(9)	1·749 (6)	C(8)—C(9)	1·387 (10)
N(2)—C(3)	1·438 (9)	C(9)—C(10)	1·429 (10)
N(2)—C(13)	1·476 (9)	C(11)—O(4)	1·234 (9)
C(3)—C(4)	1·343 (8)	C(11)—O(5)	1·330 (8)
C(3)—C(11)	1·465 (8)	C(12)—O(5)	1·413 (7)
C(4)—O(1)	1·352 (9)	O(1)—H(1)	0·87 (5)
C(4)—C(10)	1·443 (8)	H(1)···O(4)	1·82 (5)
C(5)—C(10)	1·386 (9)	O(1)···O(4)	2·626 (7)

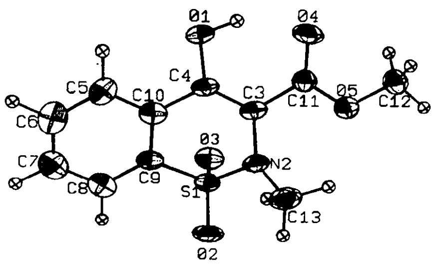

Fig. 1. *ORTEP* (Johnson, 1965) view of the molecule. The atoms are represented by thermal ellipsoids at the 50% probability level.

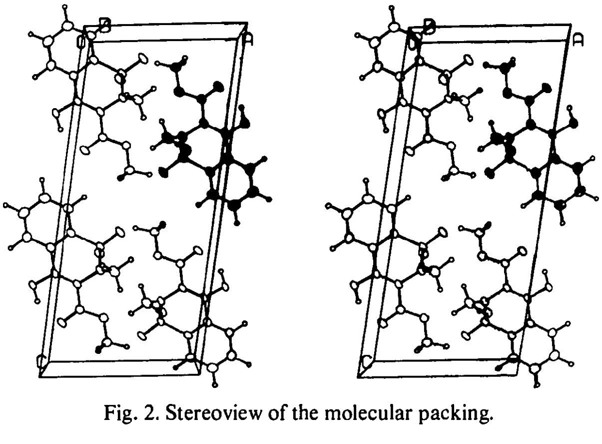

Fig. 2. Stereoview of the molecular packing.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, bond and torsion angles and the results of mean-plane calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43355 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

2·626 (7) Å with the corresponding angle 153 (5)°]. Furthermore, the C(3)—C(4) bond of 1·343 (8) Å has double-bond character and therefore the possible tautomeric keto form of this compound can be ruled out. The benzene ring is planar with the largest deviation from the mean plane 0·014 (7) Å for C(5). The atomic group O(1),C(4),C(3),C(11),O(4) is planar to within 0·023 (7) Å due to the formation of the intramolecular hydrogen bond. The methyl group $C(12)H_3$ is in the expected *trans* orientation with respect to C(3), the corresponding torsion angle C(3)—C(11)—O(5)—C(12) being −178·0 (5)°. The thiazine ring is in a distorted half-chair conformation with endocyclic torsion angles −49·5 (5) about S(1)—N(2), 39·5 (8) N(2)—C(3), −1·6 (10) C(3)—C(4), −18·8 (10) C(4)—C(10), −0·0 (8) C(9)—C(10), 31·0 (6)° S(1)—C(9).

There are no noticeably short intermolecular contacts in the structure.

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Structure of 4-*tert*-Butyl-1-phenoxy-1-λ^5-phosphorinane 1-Oxide

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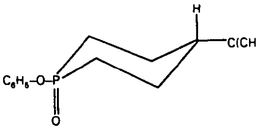
Abstract. $C_{15}H_{23}O_2P$, $M_r = 266·32$, monoclinic, $P2_1/a$, $a = 12·511$ (2), $b = 8·695$ (1), $c = 15·035$ (5) Å, $\beta = 111·63$ (2)°, $V = 1520·4$ Å^3, $Z = 4$, $D_x = 1·16$ g cm^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 15·24$ cm^{-1}, $F(000) = 576$, $T = 298$ K, $R = 0·0578$ for 2261 observed reflections. A chair conformation for the heterocyclic ring with slight flattening at the phosphorus end to relieve steric strain was found in this compound. The phenoxy and *tert*-butyl groups are *trans* to each other and in equatorial positions.

Introduction. The stereochemistry of two phosphorinane oxides has been reported by Macdonell, Berlin, Baker, Ealick, van der Helm and Marsi (1978), and by Mazhar-ul-Haque, Ahmed & Horne (1986). The structure of a phosphorinane sulfide has been reported by Quin, McPhail, Lee & Onan (1974). In each case the phosphorinane ring assumes a chair conformation, slightly flattened at the phosphorus end relative to that of the carbocyclic analogue cyclohexane. It is observed that the positioning of the larger substituent on P is important in determining the extent of flattening. We now report the X-ray crystallographic results for a third phosphorinane oxide (I) which supports the above findings.



(I)

Experimental. A crystal *ca* 0·43 × 0·50 × 0·75 mm grown from chloroform, mounted on an Enraf–Nonius CAD-4 diffractometer, take-off angle 5°, graphite-crystal-monochromatized Cu $K\alpha$ radiation used for the determination of unit-cell parameters from 25 accurately centered reflections ($27 < \theta < 33°$) by least-squares refinement. Intensities of 2981 reflections

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