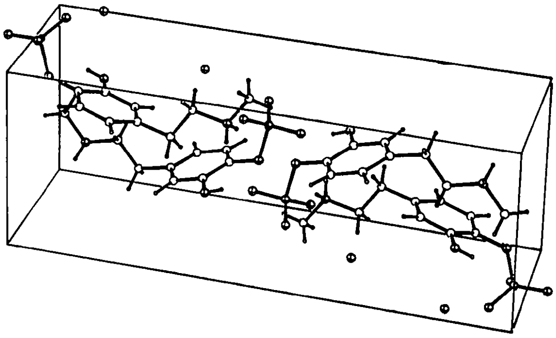

Fig. 4. Projection of the unit-cell contents for epinine-4-*O*-sulfate. The *c* axis is nearly horizontal and the *b* axis is vertical. All atoms are drawn as spheres of arbitrary size.

The (methylamino)ethyl side chain is nearly maximally extended and in a conformation similar to those reported in the crystal structures of the majority of sympathomimetic amines. The five atoms C(4), C(2), C(8), N and C(9) are virtually coplanar and this five-atom plane forms a dihedral angle of 90·7 (2)° with the plane of the phenyl ring. The torsion angles describing the side-chain conformation are $\tau_1$[C(3)—C(4)—C(7)—C(8)] = −91·1 (3), $\tau_2 = -175{\cdot}1$ (3) and $\tau_3 = -177{\cdot}1$ (4)°. These angles are essentially identical to values observed in the epinine hydrobromide structure.

All available donors participate in the hydrogen-bonding network observed in the epinine 4-*O*-sulfate crystal structure. As in the dopamine-*O*-sulfate structures there appears to be an intramolecular hydrogen bond in epinine-4-*O*-sulfate formed between the catechol proton attached to O(5) and the sulfate O(1) atom. In addition, this proton also may participate in an intermolecular interaction with O(3) as detailed in Table 3. Since the H atoms attached to the partial-occupancy water O atom were not located, only limited details of the interactions between this molecule and the epinine-4-*O*-sulfate species can be given. The close contacts are O(1*W*)···O(2) = 3·001 (8) and O(1*W*)···O(4) = 2·930 (9) Å. A diagram of the unit cell is presented as Fig. 4.

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# Structure of Cyclohexane Tetramethylene Diperoxide Diamine*

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**Abstract.** 10,11,14,15-Tetraoxa-1,8-diazatricyclo[6.4.4.0$^{2,7}$]hexadecane (CTDD), $C_{10}H_{18}N_2O_4$, $M_r = 230{\cdot}26$, triclinic, $P\bar{1}$, $a = 6{\cdot}948$ (1), $b = 8{\cdot}153$ (2), $c = 11{\cdot}124$ (2) Å, $\alpha = 73{\cdot}88$ (2), $\beta = 76{\cdot}28$ (1), $\gamma = 68{\cdot}97$ (2)°, $V = 558{\cdot}4$ (4) Å$^3$, $Z = 2$, $D_m = 1{\cdot}33$ (4), $D_x = 1{\cdot}37$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71073 Å, $\mu = 1{\cdot}13$ cm$^{-1}$, $F(000) = 248$, $T = 294$ K, $R = 0{\cdot}0669$ for 1963 independent reflections. The bridgehead N atoms adopt a nearly planar configuration [each is 0·14 (1) Å out of the respective C plane], as expected from similar compounds. N—C bonds to the peroxide bridges [average length 1·410 (4) Å] are shorter than those to the cyclohexane ring [average length 1·461 (4) Å].

**Introduction.** Schaefer, Fourkas & Tiemann (1985) and Fourkas & Schaefer (1986) have reported structures of two medium-ring bicyclic compounds with peroxide

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bridges, hexamethylene triperoxide diamine (HMTD, 3,4,8,9,12,13-hexaoxa-1,6-diazabicyclo[4.4.4]tetradecane) and benzene tetramethylene diperoxide diamine {BTDD, 10,11,14,15-tetraoxa-1,8-diazatricyclo-[6.4.4.0$^{2,7}$]hexadeca-2(7),3,5-triene}, which have planar or nearly planar bridgehead N atoms. We have now synthesized additional analogous compounds, including CTDD, in order to study further this unusual N geometry.

**Experimental.** 45 g $H_2O_2$ and 60 ml formaldehyde solution (37%) were mixed and cooled to 273 K; 2 ml *trans*-1,2-diaminocyclohexane added, stirred for one hour; crystals collected, washed with ethanol; recrystallization from pentyl acetate; elemental analysis satisfactory for C,N,H; two irregular crystals used because of crystal decay, 0·41 × 0·26 × 0·30 mm and 0·33 × 0·26 × 0·26 mm; crystals coated with epoxy to lessen decay; $D_m$ by flotation in an aqueous ZnBr solution; Nonius CAD-4 diffractometer: triclinic; intensity measurements with graphite-monochromated Mo $K\alpha$ radiation, $\theta$–$2\theta$ scans, 2° min$^{-1}$ in $2\theta$, backgrounds measured for each reflection at each end of scan, average background as function of $2\theta$ calculated and used to correct measured scan counts; unit cell: 25 reflections each crystal, $19 < 2\theta < 21°$, least-squares refinement, averaged; max. $(\sin\theta/\lambda)$ 0·59 Å$^{-1}$; 2110 and 2113 reflections in $\pm h$, $\pm k$, $l$ and $\pm h$, $\pm k$, $-l$ hemispheres ($h$ −8 to 8, $k$ −9 to 9, $l$ 0 to 13 and −13 to 0), $4 < 2\theta < 50°$; Wilson statistics indicated centrosymmetric space group; solution confirmed $P\bar{1}$; 1963 independent reflections used in structure solution and refinement; $S_{\rm int} = 1{\cdot}26$ {$S_{\rm int}$ is the r.m.s. value of $[\sum w(F_o^2 - \bar{F}_o^2)^2/(n-1)]^{1/2}$ for the 1272 multiple measurements}; $R_{\rm int} = \sum|F_1 - F_2|/\sum\bar{F} = 0{\cdot}045$ for 998 reflections measured just twice; three check reflections monitored every 10 000 s ($\bar{4}\bar{3}\bar{1}$, $0\bar{2}5$ and $1\bar{2}3$; $43\bar{1}$, $02\bar{5}$ and $\bar{1}23$), linear decay of 0·32% h$^{-1}$ (9·4% total) and 0·40% h$^{-1}$ (12·0% total) in $F$ magnitudes; the second crystal showed anisotropic decay which was especially large at high angles, leading to a poor agreement index for the first attempt to merge the two data sets; the data collected from the second quadrant of this crystal (those with $h > 0$) were thus excluded from further calculations; no absorption correction applied as $\mu r_{\rm max} = 0{\cdot}032$; structure solved with *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); H atoms placed at calculated positions, not refined (C—H = 0·95 Å); 145 parameters refined minimizing $\sum w(F_o^2 - F_c^2)^2$ with the programs of the *CRYM* system (Duchamp, 1964), form factors from *International Tables for X-ray Crystallography* (1974); $R = 0{\cdot}0669$ for all $F_o^2 > 0$, $S = 3{\cdot}06$; individual reflections assigned a variance $w^{-1}$ based on counting statistics plus a term $(0{\cdot}014I)^2$ to account for errors proportional to intensity (0·014 chosen by considering duplicate measurements); weights of merged reflections obtained by standard propagation of error plus an additional term, $(0{\cdot}014\bar{I})^2$, to account for other errors; $(\Delta/\sigma)_{\rm max}$ 0·3; $\Delta\rho_{\rm max}$ 0·54, $\Delta\rho_{\rm min}$ −0·28 e Å$^{-3}$. Atomic coordinates are given in Table 1,* atom numbering is shown in Fig. 1, and selected bond distances and angles are given in Table 2; the drawing was made using *ORTEP* (Johnson, 1965).

Table 1. *Atomic parameters* ($x$, $y$, $z \times 10^4$; $U_{eq}$ *in* Å$^2 \times 10^4$)

| | $x$ | $y$ | $z$ | $U_{\rm eq}$* |
|---|---|---|---|---|
| C(1) | 7888 (4) | 4111 (3) | 2113 (2) | 344 (6) |
| C(2) | 5568 (4) | 4650 (3) | 2695 (2) | 323 (6) |
| C(3) | 4302 (4) | 6094 (4) | 1736 (3) | 443 (7) |
| C(4) | 5072 (5) | 7721 (4) | 1342 (3) | 508 (8) |
| C(5) | 7380 (5) | 7241 (4) | 863 (3) | 508 (8) |
| C(6) | 8629 (4) | 5745 (4) | 1798 (3) | 442 (7) |
| C(7) | 9732 (5) | 839 (4) | 2538 (3) | 549 (9) |
| C(8) | 9420 (5) | 2557 (4) | 4085 (3) | 531 (8) |
| C(9) | 4764 (5) | 2001 (4) | 2529 (3) | 522 (8) |
| C(10) | 4612 (4) | 2545 (4) | 4604 (3) | 462 (7) |
| N(1) | 9209 (3) | 2520 (3) | 2872 (2) | 422 (6) |
| N(2) | 4757 (3) | 3143 (3) | 3268 (2) | 357 (5) |
| O(1) | 8089 (4) | 33 (3) | 2809 (2) | 648 (6) |
| O(2) | 6732 (3) | 1124 (3) | 1869 (2) | 694 (6) |
| O(3) | 7565 (3) | 2898 (3) | 4989 (2) | 588 (6) |
| O(4) | 6573 (3) | 1555 (3) | 5102 (2) | 535 (5) |

* $U_{\rm eq} = \frac{1}{3}\sum_i\sum_j[U_{ij}(a_i^*a_j^*)\mathbf{a}_i.\mathbf{a}_j]$. $\sigma U_{\rm eq} = (1/\sqrt{6})\langle\sigma U_{ii}/U_{ii}\rangle\, U_{\rm eq}$.

Table 2. *Selected distances* (Å) *and angles* (°)

| | | | |
|---|---|---|---|
| N(1)—C(1) | 1·464 (4) | N(2)—C(9) | 1·403 (4) |
| N(1)—C(7) | 1·417 (4) | N(2)—C(10) | 1·420 (4) |
| N(1)—C(8) | 1·401 (4) | O(1)—O(2) | 1·457 (3) |
| N(2)—C(2) | 1·457 (3) | O(3)—O(4) | 1·454 (3) |
| C(1)—N(1)—C(7) | 118·3 (2) | C(2)—N(2)—C(9) | 120·2 (2) |
| C(1)—N(1)—C(8) | 119·9 (2) | C(2)—N(2)—C(10) | 117·0 (2) |
| C(7)—N(1)—C(8) | 119·2 (3) | C(9)—N(2)—C(10) | 119·7 (2) |

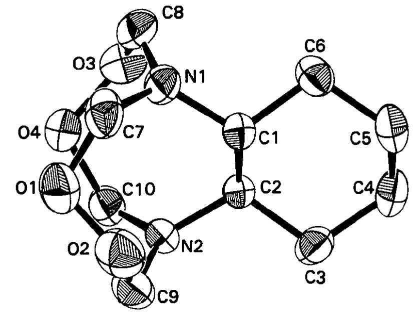

Fig. 1. Atom labeling for CTDD. Thermal ellipsoids are shown at the 50% probability level.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and all bond lengths and angles not involving H have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43202 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

**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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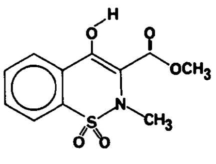
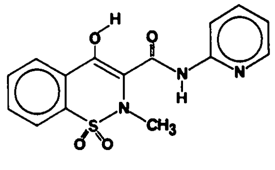
**Abstract.** $C_{11}H_{11}NO_5S$, $M_r = 269{\cdot}3$, monoclinic, $P2_1/c$, $a = 8{\cdot}432\ (3)$, $b = 6{\cdot}970\ (2)$, $c = 19{\cdot}650\ (7)$ Å, $\beta = 98{\cdot}80\ (2)°$, $V = 1141{\cdot}3$ Å$^3$, $Z = 4$, $D_m = 1{\cdot}56\ (5)$, $D_x = 1{\cdot}567$ g cm$^{-3}$, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71069$ Å, $\mu = 2{\cdot}83$ cm$^{-1}$, $F(000) = 560$, $T = 293\ (1)$ K, final $R = 0{\cdot}067$ 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*-1$\lambda^6$,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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