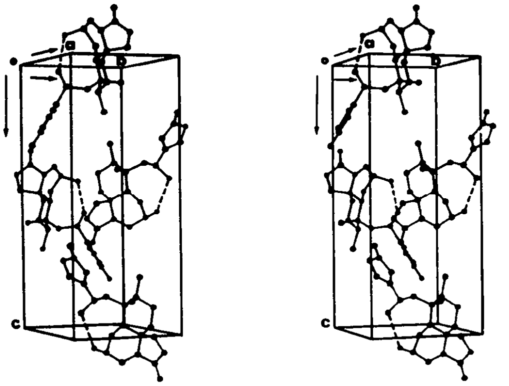

Fig. 2. Stereoview illustrating the intramolecular hydrogen-bonding interaction and crystal packing.

The crystal structure contains both intra- and intermolecular hydrogen bonds which play an important role in the stabilization. Fig. 2 shows the intramolecular hydrogen bonds which play an important role in the stabilization. The O(2)···O(1) and H···O(1) distances are 2·820 (6) and 2·11 (5) Å and the O(2)—H···O(1) angle is 162 (5)°. In addition, the O(1)—H hydroxyl group participates in an intermolecular hydrogen bond involving the O(4) carbonyl group ($1{\cdot}5-x$, $-y$, $-0{\cdot}5+z$). The O(1)···O(4) and H(1)···O(4) distances are 2·767 (6) and 2·11 (5) Å and the O(1)—H···O(4) angle is 150 (5)°. There are two intermolecular approaches <3·3 Å involving non-H atoms: C(2)···O(4)($1{\cdot}5-x$, $-y$, $-0{\cdot}5+z$) 3·08 (1) Å and C(14)···O(6)($0{\cdot}5+x$, $0{\cdot}5-y$, $1-z$) 3·25 (1) Å. The H(14)···O(6) distance is 2·31 Å, indicating a possible C—H···O hydrogen bond.

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The Structures of Epinine-*O*-sulfates

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Abstract. $C_9H_{13}NO_5S$, 2-hydroxy-5-[2-(methylamino)ethyl]phenyl hydrogen sulfate (epinine-3-*O*-sulfate): $M_r = 247{\cdot}27$, triclinic, $P\bar{1}$, $a = 7{\cdot}610\,(1)$, $b = 10{\cdot}387\,(2)$, $c = 7{\cdot}195\,(2)$ Å, $\alpha = 101{\cdot}33\,(2)$, $\beta = 104{\cdot}38\,(2)$, $\gamma = 74{\cdot}50\,(1)$°, $V = 525{\cdot}6\,(4)$ Å³, $Z = 2$, D_m(flotation in $CHCl_3/CCl_4$) = 1·54 (2), $D_x = 1{\cdot}563$ Mg m^{-3}, Mo $K\alpha$ radiation ($\lambda\,K\alpha_{1,2} = 0{\cdot}70926$, $0{\cdot}71354$ Å), $\mu = 0{\cdot}2996$ mm^{-1}, $F(000) = 260$, $T = 293$ K, $R = 0{\cdot}035$ for 2613 observations, $I > 3\sigma(I)$. $C_9H_{13}NO_5S.0{\cdot}33H_2O$, 2-hydroxy-4-[2-(methylamino)ethyl]phenyl hydrogen sulfate 0·33 hydrate (epinine-4-*O*-sulfate): $M_r = 253{\cdot}27$, monoclinic, $P2_1/c$, $a = 7{\cdot}481\,(2)$ $b = 7{\cdot}473\,(1)$, $c = 21{\cdot}023\,(5)$ Å, $\beta = 96{\cdot}23\,(2)$°, $V = 1168{\cdot}4\,(8)$ Å³, $Z = 4$, D_m(flotation in $CHCl_3/C_2H_4Cl_2$) = 1·42 (2), $D_x = 1{\cdot}440$ Mg m^{-3}, Mo $K\alpha$ radiation, $\mu = 0{\cdot}2696$ mm^{-1}, $F(000) = 530{\cdot}67$, $T = 293$ K, $R = 0{\cdot}039$ for 2136 observations, $I \geq 3\sigma(I)$. Both epinine sulfate molecules crystallize as zwitterions with the sulfate group ionized and the amino group protonated.

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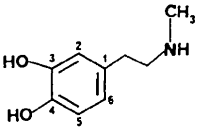
The unusual synclinal conformation of the (methylamino)ethyl side chain in epinine-3-*O*-sulfate ($\tau_1 = -34{\cdot}4^\circ$) is accompanied by significant [up to 0·176 (2) Å] out-of-plane distortions of the primary substituents from the hydroxyphenyl ring and a widening of the tetrahedral bond angle at the nexus for the side chain to 116·5°. In contrast, the side chain in epinine-4-*O*-sulfate is nearly maximally extended with $\tau_1 = -91{\cdot}1$ (3), $\tau_2 = -175{\cdot}1$ (3) and $\tau_3 = -177{\cdot}1$ (4)°. There is extensive hydrogen bonding in both crystal structures with all available donors participating. Of particular note are the intramolecular hydrogen bond in epinine-4-*O*-sulfate, formed between the phenolic hydroxyl group and the adjacent sulfate group, and the absence of such an interaction in the epinine-3-*O*-sulfate structure.

Introduction. The presence of catecholamine sulfoconjugates in brain and other vital peripheral organs (Elchisak & Carlson, 1982) has focused considerable attention on the possible physiological role of the sulfate esters of catecholamines in general. Since one of the possible fates of all ingested phenolic substances is sulfoconjugation, the identity and availability of analytical samples of unambiguous structure are crucial to studies of drug metabolism. We have recently characterized crystalline samples of the dopamine-*O*-sulfates (Eggleston, Chodosh, Jain, Kaiser & Ackerman, 1985) and continue these investigations by crystallographic authentication and characterization of the epinine (1) 3- and 4-*O*-sulfate analogs.



(1)

Experimental. The epinine-*O*-sulfate molecules were synthesized by a method reported elsewhere (Tickner & Mendelson, 1986). Crystals of epinine-3-*O*-sulfate were grown by slow evaporation from water; epinine-4-*O*-sulfate crystallizes as a hydrate from aqueous acetone. Both crystals were tabular with approximate dimensions of 0·10 × 0·40 × 0·60 mm for the 3-*O*-sulfate and 0·50 × 0·50 × 0·20 mm for the 4-*O*-sulfate. Cell constants were derived from a least-squares fit to the angular settings of 25 reflections with $30 \leq 2\theta(\mathrm{Mo}) \leq 35^\circ$ measured on an Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator. Systematic absences of $0k0$ for k odd, $h0l$ for l odd for 4-*O*-sulfate; no systematic absences for 3-*O*-sulfate. Intensity data were collected with Mo radiation in an ω–θ scan mode. There were no systematic fluctuations in three standard reflections measured every 3 h of exposure time for either data set. (For 3-*O*-sulfate: 12 times; 362, av. $F = 283{\cdot}80$, max. dev. = 0·83%; $62\bar{1}$, av. $F = 270{\cdot}17$, max. dev. = 1·07%; $4\bar{5}\bar{1}$, av. $F = 344{\cdot}77$, max. dev. = 0·64%. For 4-*O*-sulfate: 12 times, $6\bar{1}\bar{1}$, av. $F = 147{\cdot}81$, max. dev. = 3·28%; $4\bar{4}1$, av. $F = 136{\cdot}86$, max. dev. = 1·58%; 351, av. $F = 185{\cdot}03$, max. dev. = 2·76%.) Data corrected for Lorentz–polarization effects but not for absorption. For 3-*O*-sulfate: 3290 measured intensities, $2\theta \leq 60^\circ$, $-10 \leq h \leq 10$, $-14 \leq k \leq 14$, $0 \leq l \leq 10$, symmetry-equivalent reflections were averaged (agreement factors 0·008 on I and 0·011 on F_o), leaving 2613 independent data. For 4-*O*-sulfate: 3237 measured intensities, $2\theta \leq 56^\circ$, $0 \leq h \leq 9$, $0 \leq k \leq 9$, $-27 \leq l \leq 27$, symmetry-equivalent reflections averaged (agreement factors 0·019 on I and 0·029 on F_o), leaving 2136 independent data. Both structures determined using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and difference Fourier syntheses. All least-squares refinements were full matrix on F, weights $4F_o^2/\sigma^2(I)$ with $\sigma(I) = [\sigma(I)^2 + (pF_o)^2]^{1/2}$ as defined by Corfield, Doedens & Ibers (1967), where p, a small percentage value which dampens the weights of large intensities to prevent them from biasing the least-squares refinement, was 0·05 for both structures. The function minimized was $\sum w(|F_o| - |F_c|)^2$. Non-H atoms were refined with anisotropic librational parameters. H-atom positions were located from difference Fourier maps; all H positions and isotropic thermal parameters were refined. For 3-*O*-sulfate, $wR = 0{\cdot}052$, $S = 1{\cdot}58$, 2613 observations with $I > 3\sigma(I)$, 198 variables, extinction coefficient, of the type defined by Zacharisen (1963), included in later stages refined to $7{\cdot}96\,(2) \times 10^{-7}$, $(\Delta/\sigma)_{\max} = 0{\cdot}01$, max. and min. excursions in final difference map 0·416 and $-0{\cdot}257$ e Å^{-3}, respectively. Refinement using 2928 observations with $I \geq 0{\cdot}01\sigma(I)$ gave $R = 0{\cdot}039$, $wR = 0{\cdot}054$. For 4-*O*-sulfate, $wR = 0{\cdot}056$, $S = 1{\cdot}52$, 2136 observations with $I \geq 3\sigma(I)$, 208 variables, extinction coefficient, of the type defined by Zacharisen (1963), included in later stages refined to $6{\cdot}812\,(3) \times 10^{-7}$, occupancy factor of water of hydration refined to 0·33 (1), $(\Delta/\sigma)_{\max} = 0{\cdot}01$, max. and min. excursions in final difference Fourier map were 0·270 and $-0{\cdot}201$ e Å^{-3}, respectively. Refinement using 2509 observations with $I \geq 0{\cdot}01\sigma(I)$ gave $R = 0{\cdot}047$, $wR = 0{\cdot}059$. Values of the neutral-atom scattering factors and effects of anomalous dispersion from *International Tables for X-ray Crystallography* (1974). H-atom scattering factors from Stewart, Davidson & Simpson (1965). Programs in the CAD-4 *SDP* with local modifications.*

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* Lists of structure factors, anisotropic thermal parameters and refined H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43313 (58 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. *Epinine-*3-*O-sulfate:* $^{-}SO_4$-$[C_6H_3(OH)]$-$(CH_2)_2$-$NH_2^{+}CH_3$. The 3-*O*-sulfate crystallizes as a zwitterion and is illustrated in Fig. 1. Atomic parameters are listed in Table 1. Principal bond distances are displayed on the figure while principal bond angles are contained in Table 2. The (methylamino)ethyl side chain is protonated and the sulfate group is ionized. Intramolecular bond distances and angles are comparable to values observed in the epinine-4-*O*-sulfate (see below), the dopamine-*O*-sulfates and epinine hydrobromide (Giesecke, 1976). The ionic nature of the sulfate group is demonstrated by the three S—O bond lengths: S—O(2) 1·430 (1), S—O(3) 1·442 (1) and S—O(4) 1·444 (1) Å.

Bond distances in the phenyl ring show a normal distribution with no significant asymmetry. The aromatic ring is planar; no atom deviates from the six-atom least-squares plane by more than 0·012 (1) Å. All three primary substituent atoms sit out of the plane significantly. Atoms O(1) and O(5) are disposed on the same side of the phenyl ring by 0·066 (1) and 0·047 (1) Å, respectively, while atom C(7) sits 0·176 (2) Å out of the plane on the opposite side of the ring from the O atoms.

The considerable out-of-plane distortion for C(7) is accompanied by a remarkable widening of the C(3)—C(7)—C(8) bond angle to 116·5 (1)°. Both of these observations are consistent with observations made in the structure of dopamine-4-*O*-sulfate (Eggleston, Chodosh, Jain, Kaiser & Ackerman, 1985) and can be attributed to the adoption of a somewhat strained synclinal conformation for the (methylamino)ethyl side chain. Thus $\tau_1[C(2)—C(3)—C(7)—C(8)] = -34{\cdot}4°$ in the epinine-3-*O*-sulfate structure and is similar to a value of −47·4° observed for one of the dopamine-4-*O*-sulfate molecules. The remainder of the side chain adopts a typical *trans–trans* conformation with $\tau_2 = 173{\cdot}0$ (4) and $\tau_3 = -176{\cdot}7$ (4)°.

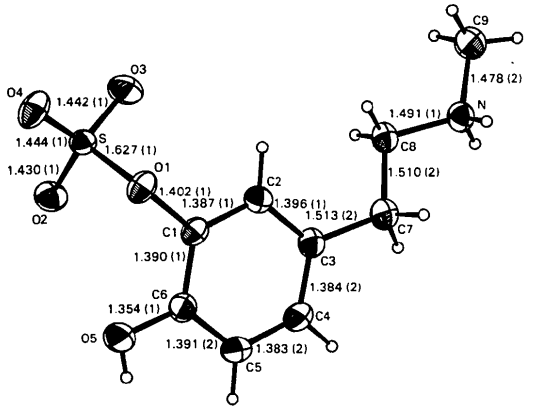

Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the epinine-3-*O*-sulfate molecule. Non-H atoms are displayed as principal ellipses at the 50% probability level; H atoms as small spheres of arbitrary size. Bond distances in Å; numbers in parentheses are e.s.d.'s.

Table 1. *Positional parameters, equivalent isotropic thermal parameters and their e.s.d.'s for epinine-*3-*O-sulfate*

	x	y	z	B_{eq}(Å^2)*
S	0·72776 (4)	0·35606 (3)	0·58845 (4)	1·884 (5)
O(1)	0·8786 (1)	0·25159 (9)	0·7246 (1)	2·25 (2)
O(2)	0·5761 (1)	0·4130 (1)	0·6858 (1)	2·68 (2)
O(3)	0·6764 (2)	0·2763 (1)	0·4043 (2)	3·34 (2)
O(4)	0·8398 (1)	0·4475 (1)	0·5844 (2)	2·98 (2)
O(5)	0·7939 (2)	0·2879 (1)	1·0794 (2)	3·12 (2)
N	0·7586 (2)	−0·3609 (1)	0·2846 (2)	2·27 (2)
C(1)	0·8160 (2)	0·1514 (1)	0·7775 (2)	1·89 (2)
C(2)	0·8075 (2)	0·0322 (1)	0·6526 (2)	2·09 (2)
C(3)	0·7572 (2)	−0·0720 (1)	0·7087 (2)	2·16 (2)
C(4)	0·7132 (2)	−0·0502 (1)	0·8894 (2)	2·57 (2)
C(5)	0·7237 (2)	0·0681 (1)	1·0151 (2)	2·66 (3)
C(6)	0·7774 (2)	0·1711 (1)	0·9614 (2)	2·16 (2)
C(7)	0·7651 (2)	−0·2106 (1)	0·5913 (2)	2·84 (3)
C(8)	0·7206 (2)	−0·2166 (1)	0·3736 (2)	2·18 (2)
C(9)	0·7318 (2)	−0·3836 (2)	0·0711 (2)	3·23 (3)

$* \; B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

Table 2. *Principal bond angles* (°) *for epinine-*3-*O-sulfate*

O(1)—S—O(2)	106·12 (5)	C(1)—C(2)—C(3)	120·2 (1)
O(1)—S—O(3)	105·78 (5)	C(2)—C(3)—C(4)	117·7 (1)
O(1)—S—O(4)	100·42 (5)	C(2)—C(3)—C(7)	123·7 (1)
O(2)—S—O(3)	113·35 (6)	C(4)—C(3)—C(7)	118·4 (1)
O(2)—S—O(4)	115·36 (6)	C(3)—C(4)—C(5)	122·1 (1)
O(3)—S—O(4)	114·07 (6)	C(4)—C(5)—C(6)	120·4 (1)
S—O(1)—C(1)	117·78 (6)	O(5)—C(6)—C(1)	119·2 (1)
C(8)—N—C(9)	115·2 (1)	O(5)—C(6)—C(5)	123·1 (1)
O(1)—C(1)—C(2)	119·66 (9)	C(1)—C(6)—C(5)	117·7 (1)
O(1)—C(1)—C(6)	118·36 (9)	C(3)—C(7)—C(8)	116·5 (1)
C(2)—C(1)—C(6)	121·8 (1)	N—C(8)—C(7)	108·6 (1)

The crystal structure of epinine-3-*O*-sulfate is stabilized by an extensive hydrogen-bonding network involving all available donors. A list of the metrical parameters for all proposed hydrogen bonds is presented in Table 3 and a drawing of the unit-cell contents is included as Fig. 2. In contrast to other structurally characterized catecholamine sulfates, there does not appear to be an intramolecular hydrogen bond between the catechol proton attached to O(5) and the sulfate O(1) in the epinine-3-*O*-sulfate crystal structure. The disposition of H(O5) is *transoid* to C(1) precluding intramolecular interactions.

*Epinine-*4-*O-sulfate:* The 4-*O*-sulfate crystallizes as a partially hydrated zwitterion with the amino group protonated and the sulfate group ionized. The occupancy factor of the randomly distributed water molecule refined to a value of 0·33 (1). No attempt was made to assign H-atom positions for this water molecule. Atomic parameters are listed in Table 4. Principal bond distances are shown in Fig. 3 and principal bond angles in Table 5. The epinine-4-*O*-sulfate molecule is displayed as Fig. 3. Again, ionization of the sulfate group is demonstrated by the three S—O bond lengths: S—O(2) 1·429 (1), S—O(3) 1·440 (1) and S—O(4) 1·430 (1) Å. These S—O bond lengths are similar to values found in the 3-*O*-sulfate structure.

Bond distances and angles within the phenyl ring display a normal distribution with no apparent asymmetry. The aromatic ring is planar; no atom deviates from the six-atom least-squares plane by more than 0·018 (2) Å. Substituent atom O(1) is nearly coplanar with the ring; however, atoms O(5) and C(7) sit 0·056 (2) and 0·098 (2) Å, respectively, out of the plane on opposite sides of the phenyl ring. Atom H(O5) is also nearly coplanar with the ring and, as may be seen in Fig. 3, points in the direction of the sulfate group. The orientation of H(O5) and the coplanar disposition of atom O(1) are both in stark contrast to observations in the epinine 3-*O*-sulfate structure and coincide with formation of an intramolecular hydrogen bond in the 4-*O*-sulfate structure (see below).

Table 3. *Proposed hydrogen-bonding interactions*

		Distances (Å)	Angle (°)
Epinine-3-*O*-sulfate			
O(5)–H(O5)···O(3)	O(5)···O(3)	2·736 (1)	167 (3)
	H(O5)···O(3)	2·02 (2)	
N–H(1N)···O(2)	N···O(2)	2·807 (1)	147 (2)
	H(1N)···O(2)	2·14 (2)	
N–H(1N)···O(4)	N···O(4)	3·060 (1)	122 (2)
	H(1N)···O(4)	2·59 (2)	
N–H(2N)···O(4)	N···O(4)	2·910 (1)	166 (1)
	H(2N)···O(4)	2·08 (2)	
Epinine-4-*O*-sulfate			
O(5)–H(O5)···O(1)	O(5)···O(1)	2·783 (2)	112 (2)
	H(O5)···O(1)	2·41 (2)	
O(5)–H(O5)···O(3)	O(5)···O(3)	2·721 (2)	152 (2)
	H(O5)···O(3)	2·03 (2)	
N–H(1N)···O(4)	N···O(4)	2·768 (2)	150 (2)
	H(1N)···O(4)	1·87 (2)	
N–H(2N)···O(2)	N···O(2)	2·799 (2)	171 (2)
	H(2N)···O(2)	2·00 (2)	

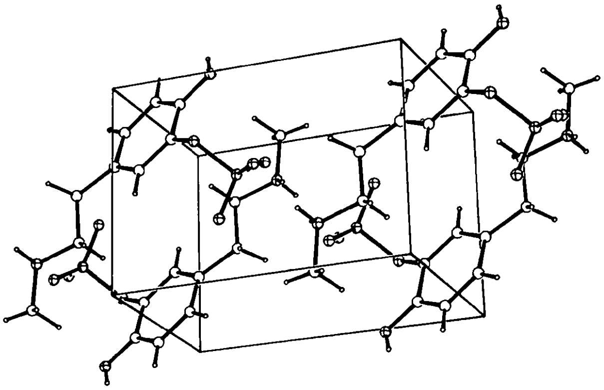

Fig. 2. Projection of the unit-cell contents for epinine-3-*O*-sulfate. The *b* axis is nearly horizontal and the *c* axis is vertical. All atoms are drawn as spheres of arbitrary size.

Table 4. *Positional parameters, equivalent isotropic thermal parameters and their e.s.d.'s for epinine-4-O-sulfate*

	x	y	z	B_{eq}(Å^2)*
S	0·27260 (6)	0·09962 (6)	0·03706 (2)	2·488 (8)
O(1)	0·2788 (2)	−0·1120 (2)	0·05454 (6)	2·84 (3)
O(1*W*)	0·209 (1)	0·341 (1)	0·1745 (5)	11·1 (3)
O(2)	0·4206 (2)	0·1791 (2)	0·07561 (8)	3·88 (3)
O(3)	0·2915 (2)	0·0906 (2)	−0·03029 (7)	3·64 (3)
O(4)	0·1022 (2)	0·1652 (2)	0·05166 (8)	4·13 (3)
O(5)	0·5766 (2)	−0·2115 (2)	0·13800 (7)	3·84 (3)
N	0·2250 (2)	−0·1983 (2)	0·42116 (8)	2·67 (3)
C(1)	0·2571 (3)	−0·1612 (3)	0·11761 (9)	2·66 (3)
C(2)	0·0882 (3)	−0·1714 (3)	0·1381 (1)	3·09 (4)
C(3)	0·0708 (3)	−0·2241 (3)	0·2005 (1)	3·41 (4)
C(4)	0·2214 (3)	−0·2680 (3)	0·2414 (1)	3·20 (4)
C(5)	0·3900 (3)	−0·2627 (3)	0·2198 (1)	3·39 (4)
C(6)	0·4095 (3)	−0·2106 (3)	0·1574 (1)	2·86 (4)
C(7)	0·2046 (3)	−0·3153 (3)	0·3107 (1)	3·66 (4)
C(8)	0·2254 (3)	−0·1517 (3)	0·3521 (1)	3·30 (4)
C(9)	0·2361 (4)	−0·0393 (4)	0·4633 (1)	4·25 (5)

$* \; B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

Table 5. *Principal bond angles (°) for epinine-4-O-sulfate*

O(1)–S–O(2)	106·00 (8)	C(1)–C(2)–C(3)	119·5 (2)
O(1)–S–O(3)	100·00 (7)	C(2)–C(3)–C(4)	120·1 (2)
O(1)–S–O(4)	106·83 (7)	C(3)–C(4)–C(5)	119·9 (2)
O(2)–S–O(3)	115·11 (8)	C(3)–C(4)–C(7)	120·4 (2)
O(2)–S–O(4)	112·95 (9)	C(5)–C(4)–C(7)	119·6 (2)
O(3)–S–O(4)	114·35 (9)	C(4)–C(5)–C(6)	120·6 (2)
S–O(1)–C(1)	117·8 (1)	O(5)–C(6)–C(1)	122·8 (2)
C(8)–N–C(9)	113·0 (2)	O(5)–C(6)–C(5)	118·5 (2)
O(1)–C(1)–C(2)	120·9 (2)	C(1)–C(6)–C(5)	118·7 (2)
O(1)–C(1)–C(6)	117·9 (1)	C(4)–C(7)–C(8)	110·7 (2)
C(2)–C(1)–C(6)	121·1 (2)	N–C(8)–C(7)	111·3 (2)

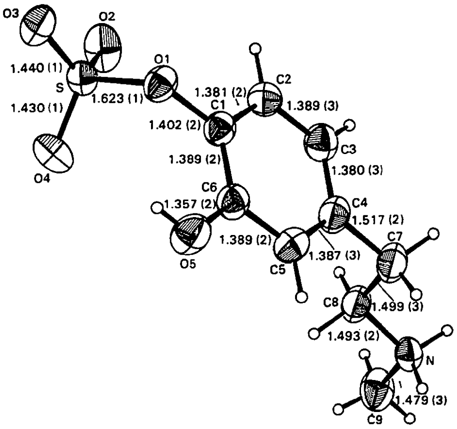

Fig. 3. *ORTEP*II drawing of the epinine-4-*O*-sulfate molecule. Non-H atoms are displayed as principal ellipses at the 50% probability level; H atoms as small spheres of arbitrary size. Bond distances in Å; the S—O(2) distance = 1·429 (1) Å. Numbers in parentheses are e.s.d.'s.

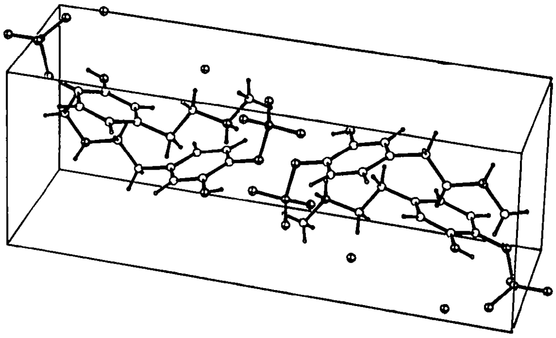

Fig. 4. Projection of the unit-cell contents for epinine-4-*O*-sulfate. The *c* axis is nearly horizontal and the *b* axis is vertical. All atoms are drawn as spheres of arbitrary size.

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 τ_1[C(3)—C(4)—C(7)—C(8)] = −91·1 (3), τ_2 = −175·1 (3) and τ_3 = −177·1 (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 = 230·26, triclinic, $P\bar{1}$, a = 6·948 (1), b = 8·153 (2), c = 11·124 (2) Å, α = 73·88 (2), β = 76·28 (1), γ = 68·97 (2)°, V = 558·4 (4) Å^3, Z = 2, D_m = 1·33 (4), D_x = 1·37 g cm^{-3}, λ(Mo *K*α) = 0·71073 Å, μ = 1·13 cm^{-1}, F(000) = 248, T = 294 K, R = 0·0669 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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