

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)
$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Cl(1)	0.2122 (3)	0.2497 (4)	0.0577 (1)	0.043 (1)
O(1)	0.3922 (6)	-0.4067 (9)	0.2281 (2)	0.031 (2)
O(2)	0.0428 (6)	0.0606 (10)	0.2712 (2)	0.037 (2)
N(1)	0.1881 (7)	-0.1111 (10)	0.3580 (2)	0.024 (2)
N(2)	0.2200 (6)	-0.1508 (10)	0.2406 (2)	0.021 (2)
C(1)	0.1974 (9)	-0.2382 (15)	0.3999 (3)	0.025 (2)
C(2)	0.2038 (10)	-0.1125 (14)	0.4431 (3)	0.033 (3)
C(3)	0.3433 (10)	0.0288 (14)	0.4441 (3)	0.033 (3)
C(4)	0.3469 (9)	0.1567 (14)	0.4001 (3)	0.031 (3)
C(5)	0.3275 (9)	0.0162 (14)	0.3577 (3)	0.026 (3)
C(6)	0.3071 (8)	-0.3249 (12)	0.2535 (3)	0.024 (3)
C(7)	0.2746 (10)	-0.3854 (13)	0.3010 (3)	0.029 (3)
C(8)	0.1555 (9)	-0.2278 (15)	0.3166 (3)	0.027 (3)
C(9)	0.1281 (8)	-0.0859 (14)	0.2747 (3)	0.027 (3)
C(10)	0.2162 (9)	-0.0529 (13)	0.1967 (3)	0.024 (3)
C(11)	0.2756 (9)	0.1433 (12)	0.1920 (3)	0.025 (3)
C(12)	0.2724 (8)	0.2387 (15)	0.1511 (3)	0.027 (3)
C(13)	0.2113 (9)	0.1334 (14)	0.1123 (3)	0.031 (3)
C(14)	0.1502 (9)	-0.0647 (13)	0.1148 (3)	0.025 (3)
C(15)	0.1520 (8)	-0.1590 (14)	0.1576 (3)	0.026 (3)
C(16)	0.2134 (12)	-0.2593 (20)	0.4854 (3)	0.046 (3)
C(17)	0.4914 (9)	0.2846 (15)	0.3999 (3)	0.034 (3)

Table 2. Geometric parameters (\AA , $^\circ$)

Cl(1)—C(13)	1.758 (9)	C(3)—C(4)	1.53 (1)
O(1)—C(6)	1.22 (1)	C(4)—C(5)	1.53 (1)
O(2)—C(9)	1.21 (1)	C(4)—C(17)	1.52 (1)
N(1)—C(1)	1.47 (1)	C(6)—C(7)	1.49 (1)
N(1)—C(5)	1.48 (1)	C(7)—C(8)	1.56 (1)
N(1)—C(8)	1.43 (1)	C(8)—C(9)	1.53 (1)
N(2)—C(6)	1.40 (1)	C(10)—C(15)	1.41 (1)
N(2)—C(9)	1.40 (1)	C(11)—C(12)	1.34 (1)
N(2)—C(10)	1.42 (1)	C(12)—C(13)	1.39 (1)
C(1)—C(2)	1.50 (1)	C(13)—C(14)	1.39 (1)
C(2)—C(3)	1.53 (1)	C(14)—C(15)	1.38 (1)
C(2)—C(16)	1.55 (1)		
C(1)—N(1)—C(5)	109.1 (6)	C(6)—C(7)—C(8)	106.5 (7)
C(1)—N(1)—C(8)	113.3 (7)	N(1)—C(8)—C(7)	119.9 (6)
C(5)—N(1)—C(8)	113.5 (6)	N(1)—C(8)—C(9)	111.1 (7)
C(6)—N(2)—C(9)	112.9 (6)	C(7)—C(8)—C(9)	103.2 (6)
C(6)—N(2)—C(10)	124.9 (7)	O(2)—C(9)—N(2)	124.6 (7)
C(9)—N(2)—C(10)	122.1 (6)	O(2)—C(9)—C(8)	126.6 (7)
N(1)—C(1)—C(2)	112.9 (7)	N(2)—C(9)—C(8)	108.8 (7)
C(1)—C(2)—C(3)	108.4 (7)	N(2)—C(10)—C(11)	121.0 (7)
C(1)—C(2)—C(16)	109.3 (8)	N(2)—C(10)—C(15)	119.1 (7)
C(3)—C(2)—C(16)	111.1 (7)	C(11)—C(10)—C(15)	119.9 (7)
C(2)—C(3)—C(4)	112.3 (7)	C(10)—C(11)—C(12)	121.9 (8)
C(3)—C(4)—C(5)	110.1 (7)	C(11)—C(12)—C(13)	118.3 (9)
C(3)—C(4)—C(17)	112.0 (7)	Cl(1)—C(13)—C(12)	119.6 (7)
C(5)—C(4)—C(17)	111.0 (7)	Cl(1)—C(13)—C(14)	118.2 (6)
N(1)—C(5)—C(4)	111.4 (7)	C(12)—C(13)—C(14)	122.2 (8)
O(1)—C(6)—N(2)	122.8 (7)	C(13)—C(14)—C(15)	118.5 (8)
O(1)—C(6)—C(7)	128.7 (7)	C(10)—C(15)—C(14)	119.0 (8)
N(2)—C(6)—C(7)	108.5 (7)		

All calculations were performed with *SHELXTL-PC* (Sheldrick, 1990) programs on an IBM PC/AT computer

Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71116 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: VS1003]

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Structure of the Partial Cone Conformer of 25,26,27,28-Tetrakis[(2-pyridylmethyl)-oxy]calix[4]arene

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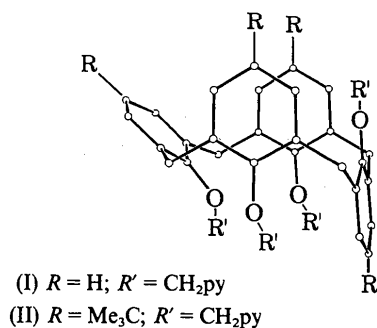
Abstract

The partial cone conformer of tetrakis[(2-pyridylmethyl)-oxy]pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosane-1(25),-3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene, (I), adopts a conformation in which the pendant OCH_2py group of the rotated aryl ring is oriented away from the calixarene cavity produced by the other three aryl rings, with its N atom *exo* to the calixarene cup. The orientation of the four aromatic rings is such that two rings are almost parallel to each other and the other two are at an angle of 42° . This conformation precludes any solvent molecule being enclathrated within the small molecular cavity.

Comment

We have recently shown that the conformer distribution in the exhaustive *o*-alkylation of calix[4]arenes with 2-(chloromethyl)pyridine hydrochloride is strongly affected by the base used: NaH induces only cone conformers, while K_2CO_3 or Cs_2CO_3 lead preferentially to partial cone and/or 1,3 alternate conformers (Pappalardo, Giunta, Foti, Ferguson, Gallagher & Kaitner, 1992). The title

compound (I) displays an ^1H NMR spectrum which has been interpreted in favour of a conformation in which the 'inverted' OCH_2py moiety lies outside the cavity. This contrasts with our solid-state and solution studies of the *tert*-butylated partial cone conformer (II) which showed the 'inverted' pyridine moiety to be tightly accommodated inside the hydrophobic cavity as a self-inclusion complex (Pappalardo *et al.*, 1992). In order to assess a possible influence of the *para*-substituent on the overall conformation of partial cone tetrakis[(2-pyridyl)methyl]oxy]calix[4]arene conformers, the crystal structure of (I) (which is devoid of *tert*-butyl groups) was determined.



The molecular conformation of (I) is defined by the angles which the aromatic rings *A–D* make with the plane through the macrocyclic ring methylene *C* atoms (*C7A*, *C7B*, *C7C*, *C7D*): *A* $-93.5(4)^\circ$, *B* $88.0(4)^\circ$, *C* $135.6(4)^\circ$ and *D* $89.0(4)^\circ$. The aromatic rings *A* and *C* are at an interplanar angle of $42.1(5)^\circ$ to one another but oriented in opposite directions (the inverted ring *A* is almost normal to the methylene *C*-atom plane; ring *C* is tilted away from the cavity). The aromatic rings *B* and *D* are almost parallel [interplanar angle $1.0(4)^\circ$], with the shortest $\text{C}\cdots\text{C}$ cross-cup calix distances in the range $5.28(1)–5.39(1)$ Å [average $5.33(1)$ Å]. The $\text{O}\cdots\text{O}$ separations of ethereal *O* atoms are $\text{OC}\cdots\text{OD}$ $3.341(5)$, $\text{OB}\cdots\text{OC}$ $3.392(5)$, $\text{OA}\cdots\text{OB}$ $4.542(5)$ and $\text{OA}\cdots\text{OD}$ $4.668(5)$ Å [the range is $3.03–3.72$ Å in molecule (II)].

Our X-ray analysis of the calix[4]arene (I) shows that it does indeed have a partial cone conformation in which the pendant OCH_2py group of the rotated aryl ring (*A*) is oriented away from the calixarene cavity produced by the other three aryl rings, with its *N* atom *exo* to the calixarene cup (Fig. 1) and with the non-*N* atom 'edge' of the ring nestled against the calix cavity. The overall partial cone conformation for molecule (I), while broadly similar to that observed in the previous structural determination of the *para*-(*tert*-butyl) derivative (II), differs significantly in the orientation of the aromatic rings and in the size of the calixarene cavity. The actual calix conformation adopted by (I) is more closed, *i.e.* the cross calix $\text{C}\cdots\text{C}$ distances are shorter, than was found in (II) [(II) had a more open calix conformation but the inverted pyridinyl

ring filled the cavity]; the resulting calix cavity in (I) is too small to accommodate a solvent molecule, primarily because the parallel rings *B* and *D* are too close (Fig. 2). This structural evidence is entirely in accord with the solution (NMR) work which suggested that the 'inverted' OCH_2py moiety, in the absence of stabilizing interactions with the *tert*-butyl groups, lies outside the cavity.

Molecular dimensions (summarized in Table 2) are unexceptional and serve to establish the structure. The shortest intermolecular contacts are between pyridine *N* atoms and *H* atoms of neighbouring molecules and correspond to normal van der Waals contacts.

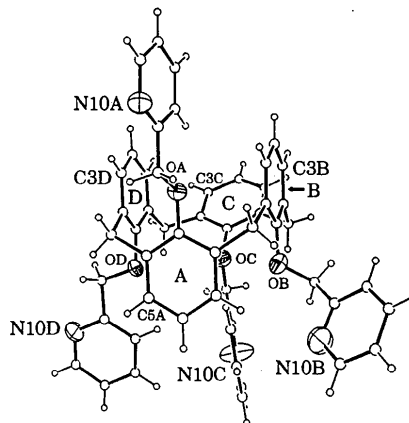


Fig. 1. An ORTEP view of the partial cone conformer of molecule (I) with the crystallographic numbering scheme; the *O* and *N* atoms are shown with thermal ellipsoids drawn at the 50% probability level. For clarity, the *C* and *H* atoms are drawn as small spheres of arbitrary size.

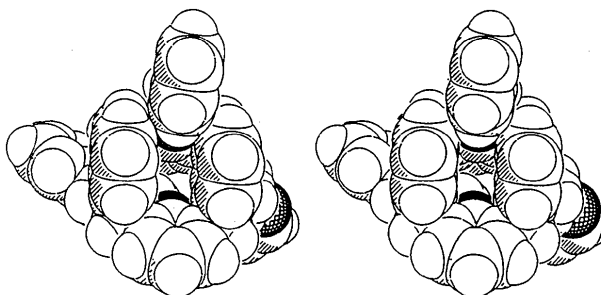


Fig. 2. A stereoview of (I) with the atoms depicted as their van der Waals spheres showing the cavity in the calix cup which is too small to accommodate any solvent molecule.

Experimental

Crystal data

$\text{C}_{52}\text{H}_{44}\text{N}_4\text{O}_4$
 $M_r = 788.93$
 Triclinic
 $P\bar{1}$
 $a = 10.3739(5)$ Å
 $b = 12.0037(6)$ Å
 $c = 17.3827(9)$ Å

Mo $K\alpha$ radiation
 $\lambda = 0.70930$ Å
 Cell parameters from 25 reflections
 $\theta = 9.50–19.30^\circ$
 $\mu = 0.08$ mm^{-1}
 $T = 293$ K

$\alpha = 81.416 (4)^\circ$
 $\beta = 78.567 (4)^\circ$
 $\gamma = 78.379 (4)^\circ$
 $V = 2064.63 (18) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.269 \text{ Mg m}^{-3}$

Colourless
 $0.25 \times 0.25 \times 0.15 \text{ mm}$
 Block
 Crystal source: synthesized
 as described by Pap-
 palardo *et al.* (1992)

Data collection

Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 6450 measured reflections
 6450 independent reflections
 2605 observed reflections
 $[I_{\text{net}} > 2.0\sigma(I_{\text{net}})]$

$\theta_{\text{max}} = 23.92^\circ$
 $h = -11 \rightarrow 11$
 $k = 0 \rightarrow 13$
 $l = -19 \rightarrow 19$
 3 standard reflections
 frequency: 60 min
 intensity variation: 2.0%

Refinement

Refinement on F
 Final $R = 0.053$
 $wR = 0.054$
 $S = 1.30$
 2605 reflections
 542 parameters
 C—H H atoms riding
 $w = 1/[\sigma^2(F) + 0.0006F^2]$
 $(\Delta/\sigma)_{\text{max}} = 0.000$

$\Delta\rho_{\text{max}} = 0.20 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$
 Extinction correction: Larson (1970)
 Extinction coefficient: 5897 (1131)
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

	x	y	z	U_{eq}
OA	0.8651 (3)	0.3009 (3)	0.14747 (20)	0.0380 (22)
C1A	0.7824 (6)	0.3646 (5)	0.2046 (3)	0.038 (3)
C2A	0.8030 (6)	0.3380 (5)	0.2826 (3)	0.041 (4)
C3A	0.7221 (7)	0.4049 (5)	0.3378 (3)	0.052 (4)
C4A	0.6235 (7)	0.4922 (5)	0.3176 (4)	0.055 (4)
C5A	0.5976 (6)	0.5118 (5)	0.2409 (4)	0.048 (4)
C6A	0.6773 (5)	0.4477 (4)	0.1832 (3)	0.037 (4)
C7A	0.9086 (6)	0.2387 (5)	0.3058 (3)	0.053 (4)
C8A	0.9719 (6)	0.3558 (5)	0.1036 (3)	0.052 (4)
C9A	1.0567 (5)	0.2800 (5)	0.0445 (3)	0.040 (4)
N10A	1.1605 (5)	0.3235 (4)	0.0017 (3)	0.047 (3)
C11A	1.2442 (6)	0.2582 (5)	-0.0502 (3)	0.055 (4)
C12A	1.2281 (6)	0.1512 (5)	-0.0610 (3)	0.053 (4)
C13A	1.1208 (6)	0.1088 (5)	-0.0162 (4)	0.054 (5)
C14A	1.0329 (5)	0.1733 (5)	0.0371 (3)	0.048 (4)
OB	0.6883 (4)	0.1474 (3)	0.39097 (21)	0.052 (3)
C1B	0.7698 (6)	0.0819 (5)	0.3341 (3)	0.045 (4)
C2B	0.7362 (6)	-0.0171 (5)	0.3176 (3)	0.044 (4)
C3B	0.8256 (7)	-0.0791 (5)	0.2626 (4)	0.058 (4)
C4B	0.9416 (7)	-0.0437 (6)	0.2242 (4)	0.064 (5)
C5B	0.9697 (6)	0.0577 (6)	0.2397 (4)	0.057 (4)
C6B	0.8834 (6)	0.1238 (5)	0.2936 (4)	0.046 (4)
C7B	0.6014 (6)	-0.0544 (5)	0.3524 (3)	0.052 (4)
C8B	0.6656 (7)	0.0954 (5)	0.4712 (4)	0.068 (5)
C9B	0.7344 (7)	0.1444 (5)	0.5227 (3)	0.048 (4)
N10B	0.6739 (6)	0.2458 (5)	0.5461 (3)	0.079 (4)
C11B	0.7320 (9)	0.2876 (7)	0.5955 (5)	0.089 (6)
C12B	0.8435 (10)	0.2316 (8)	0.6226 (4)	0.090 (7)
C13B	0.9031 (8)	0.1298 (8)	0.5962 (5)	0.097 (7)
C14B	0.8465 (8)	0.0868 (6)	0.5462 (4)	0.075 (5)
OC	0.4377 (4)	0.1430 (3)	0.29291 (20)	0.0431 (24)

C1C	0.4521 (5)	0.0440 (5)	0.2560 (3)	0.037 (4)
C2C	0.3960 (5)	0.0501 (5)	0.1894 (3)	0.039 (4)
C3C	0.3963 (6)	-0.0514 (5)	0.1611 (3)	0.048 (4)
C4C	0.4559 (7)	-0.1547 (5)	0.1952 (4)	0.057 (4)
C5C	0.5221 (6)	-0.1568 (5)	0.2566 (4)	0.055 (4)
C6C	0.5227 (6)	-0.0567 (5)	0.2883 (3)	0.043 (4)
C7C	0.3472 (6)	0.1640 (5)	0.1442 (3)	0.045 (4)
C8C	0.3092 (6)	0.1568 (5)	0.3439 (4)	0.063 (4)
C9C	0.2997 (7)	0.2396 (5)	0.4022 (3)	0.048 (4)
N10C	0.1842 (7)	0.2487 (5)	0.4514 (4)	0.099 (5)
C11C	0.1649 (10)	0.3211 (8)	0.5051 (5)	0.124 (8)
C12C	0.2563 (9)	0.3822 (7)	0.5136 (4)	0.093 (6)
C13C	0.3741 (7)	0.3706 (6)	0.4629 (4)	0.077 (5)
C14C	0.3964 (6)	0.2989 (6)	0.4054 (4)	0.059 (5)
OD	0.4011 (3)	0.3822 (3)	0.16751 (19)	0.0398 (23)
C1D	0.4947 (6)	0.3177 (5)	0.1135 (3)	0.035 (3)
C2D	0.6104 (6)	0.3589 (4)	0.0774 (3)	0.038 (4)
C3D	0.6960 (5)	0.2972 (5)	0.0205 (3)	0.042 (4)
C4D	0.6688 (6)	0.1985 (5)	0.0022 (3)	0.046 (4)
C5D	0.5560 (6)	0.1571 (5)	0.0418 (3)	0.047 (4)
C6D	0.4674 (5)	0.2155 (5)	0.0991 (3)	0.036 (4)
C7D	0.6447 (5)	0.4646 (4)	0.1000 (3)	0.042 (4)
C8D	0.3087 (6)	0.4647 (5)	0.1280 (3)	0.050 (4)
C9D	0.1889 (6)	0.5110 (5)	0.1848 (3)	0.039 (4)
N10D	0.1000 (5)	0.5876 (4)	0.1510 (3)	0.059 (3)
C11D	-0.0128 (7)	0.6279 (6)	0.1971 (4)	0.066 (5)
C12D	-0.0421 (7)	0.5946 (6)	0.2755 (5)	0.071 (5)
C13D	0.0491 (8)	0.5158 (6)	0.3094 (4)	0.080 (5)
C14D	0.1694 (6)	0.4738 (5)	0.2632 (4)	0.058 (4)

Table 2. Selected bond lengths (\AA)

	Range	Mean
C _{ar} —O _{ether}	1.390 (6)–1.406 (6)	1.398 (6)
C _{sp³} —O _{ether}	1.431 (7)–1.441 (7)	1.435 (7)
C _{sp³} —C _{py}	1.491 (8)–1.502 (8)	1.497 (8)
C _{ar} —C _{ar}	1.367 (9)–1.396 (8)	1.382 (9)
C _{ar} —C _{sp³}	1.506 (8)–1.536 (9)	1.518 (8)
C _{py} —N _{py}	1.322 (9)–1.345 (11)	1.332 (9)
C _{py} —C _{py}	1.334 (10)–1.388 (9)	1.360 (11)

Data collection and cell refinement: Enraf–Nonius CAD-4 software. Data reduction, program used to solve and refine structure, software used to prepare material for publication: *NRC-VAX* (Gabe, Le Page, Charland, Lee & White, 1989). Software used for molecular graphics: *ORTEPII* (Johnson, 1976); *PLUTON* (Spek, 1991). Molecule (I) crystallized in the triclinic system; space group $P\bar{1}$ was assumed and confirmed by the analysis. All H atoms attached to the C atoms were clearly visible in difference maps; they were positioned geometrically (C—H 0.95 \AA) and included as riding atoms in the structure-factor calculations. The distinction between N or C in the pyridine rings was easily made after examining difference maps which clearly showed all the pyridine C—H H atoms.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71144 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1052]

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Structure of 3,7-Bis(dimethylamino)-10-(*N*-methylcarbamoyl)phenothiazine (MCDP)-Ethanol (1/1)

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Abstract

In the title structure, 3,7-bis(dimethylamino)-*N*-methylphenothiazine-10-carboxamide, the phenothiazine ring adopts a boat conformation with the S and N atoms occupying the bow and stern positions, respectively. The dihedral angle between the two phenyl rings is 138.4(1)°. The conjugate system in the molecule is remarkably different from those in methylene blue molecules.

Comment

The title compound is one of the functional dyes which are used clinically as diagnostics. MCDP is used to measure the activity of monoamine oxidase in blood. In the presence of peroxidase and hydrogen peroxide, MCDP converts into methylene blue and the blue color is developed. The effective conversion is essential for the sensitivity and accuracy of diagnosis. To understand the relationship between the efficiency of conversion and the molecular structure, structure analysis of the title compound was undertaken.

The molecule as a whole takes a butterfly form. The angles at the N atom in the phenothiazine ring sum to 357(1)° indicating a nearly planar conformation at the atom. The N—C(=O) bond distance of

1.390(4) Å, however, reveals that electron delocalization between the N atom and the carbonyl group of the methylcarbamoyl group is not so significant. Therefore, breaking this N—C bond is relatively easy and results in blue coloration. The amino moiety of the methylcarbamoyl group is almost parallel to the phenothiazine ring. The torsion angles N12—C11—N10—C1a and O11—C11—N10—C5a are -5.0(4) and 15.0(4)°, respectively. The sums of the bond angles around N3 and N7 atoms are 356(1) and 360(1)°, respectively, but the terminal dimethylamino groups are not coplanar with the attached phenyl plane. Bond distances and angles in the molecule are within the expected range, but those in the conjugate system are quite different from those observed in methylene blue pentahydrate (Marr & Stewart, 1973) and methylene blue thiocyanate (Khan-Harari, Ballard & Norris, 1973).

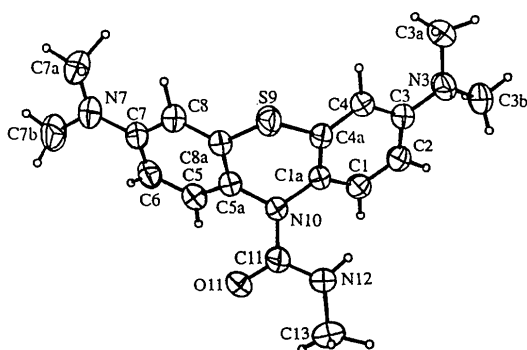


Fig. 1. ORTEP drawing (Johnson, 1976) of the molecule, representing heavy atoms as 30% probability ellipsoids and H atoms as spheres of arbitrary radii.

Experimental

Crystal data

$C_{18}H_{22}N_4OS \cdot C_2H_6O$

$M_r = 388.53$

Monoclinic

$P2_1/n$

$a = 8.6406(8) \text{ \AA}$

$b = 17.151(1) \text{ \AA}$

$c = 14.542(1) \text{ \AA}$

$\beta = 106.106(8)^\circ$

$V = 2070.5(3) \text{ \AA}^3$

$Z = 4$

$D_x = 1.25 \text{ Mg m}^{-3}$

Cu $K\alpha$ radiation

$\lambda = 1.54184 \text{ \AA}$

Cell parameters from 23 reflections

$\theta = 30-35^\circ$

$\mu = 1.522 \text{ mm}^{-1}$

$T = 298(2) \text{ K}$

Rod

$0.5 \times 0.4 \times 0.3 \text{ mm}$

Ice blue

Data collection

Enraf-Nonius CAD-4 Turbo diffractometer

$\omega/2\theta$ scans

Absorption correction:

ψ -scan

$T_{\min} = 0.871$, $T_{\max} = 0.998$

2910 observed reflections

$[F > 3\sigma(F)]$

$R_{\text{int}} = 0.036$

$\theta_{\text{max}} = 75.1^\circ$

$h = -9 \rightarrow 10$

$k = -20 \rightarrow 0$

$l = 0 \rightarrow 17$