Crystal data

$C_{10}H_8Cl_3NOS$	Mo $K\alpha$ radiation
$M_r = 296.58$	$\lambda = 0.71069$ Å
Monoclinic	Cell parameters from 15 reflections
$C2/c$	$\theta = 11.8–26.4°$
$a = 21.595$ (13) Å	$\mu = 0.899$ mm^{-1}
$b = 12.323$ (7) Å	$T = 293$ (2) K
$c = 9.266$ (6) Å	Block
$\beta = 98.90$ (5)°	0.35 × 0.25 × 0.20 mm
$V = 2436$ (3) Å^3	Colourless
$Z = 8$	
$D_x = 1.617$ Mg m^{-3}	
$D_m = 1.63$ (1) Mg m^{-3}	
D_m measured by flotation in bromoform/hexane	

Data collection

Syntex $P2_1$ diffractometer	$\theta_{max} = 27.60°$
$\theta/2\theta$ scans	$h = 0 \rightarrow 28$
Absorption correction: none	$k = 0 \rightarrow 16$
2822 measured reflections	$l = -12 \rightarrow 11$
2822 independent reflections	2 standard reflections
1352 reflections with $I > 2\sigma(I)$	frequency: 100 min intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.024$
$R(F) = 0.039$	$\Delta\rho_{max} = 0.215$ e Å^{-3}
$wR(F^2) = 0.070$	$\Delta\rho_{min} = -0.221$ e Å^{-3}
$S = 1.149$	Extinction correction: none
2822 reflections	Scattering factors from *International Tables for Crystallography* (Vol. C)
178 parameters	
H atoms refined isotropically	
$w = 1/[\sigma^2(F_o^2) + (0.0332P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. *Selected geometric parameters (Å, °)*

S1—C10	1.713 (3)	C5—C6	1.373 (4)
S1—C4	1.733 (3)	C5—C10	1.400 (4)
O1—C2	1.374 (3)	C6—C7	1.355 (4)
N1—C4	1.272 (3)	C7—C8	1.374 (4)
N1—C5	1.394 (3)	C8—C9	1.383 (4)
C1—C4	1.493 (4)	C9—C10	1.375 (4)
C10—S1—C4	89.40 (14)	N1—C4—S1	116.2 (2)
C4—N1—C5	110.7 (2)	N1—C5—C10	114.4 (2)
O1—C2—C1	109.8 (2)	C5—C10—S1	109.2 (2)
O1—C2—C3	110.8 (2)		

Non-H atoms were refined anisotropically, H atoms were located from a difference Fourier map and all parameters were refined isotropically.

Data collection: Syntex $P2_1$ software. Cell refinement: Syntex $P2_1$ software. Data reduction: *XP*21 (Pavelčík, 1987). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1264). Services for accessing these data are described at the back of the journal.

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2,4,6-Tris(2-pyridyl)-1,3,5-triazine

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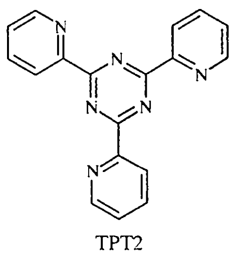
Abstract

Molecules of the title compound, $C_{18}H_{12}N_6$, were significantly distorted from planarity, with the three least-squares mean planes of the pyridine rings twisted from the plane of the central triazine ring by 15.7 (1), 33.8 (1) and 19.8 (1)°.

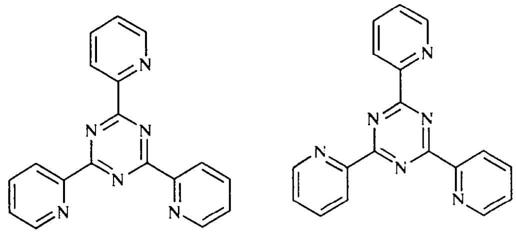
Comment

There is much current interest in the use of triazine ligands such as 2,4,6-tris(2-pyridyl)-1,3,5-triazine (L^1, TPTZ) for the extraction and separation of metal ions (Byers *et al.*, 1994, 1996; Chan *et al.*, 1996). TPTZ and its substituted derivatives such as 2,4,6-tris(4-*tert*-butyl-2-pyridyl)-1,3,5-triazine (L^2) are used in the nuclear industry as solvent-extraction reagents since they are able to separate trivalent actinides (An^{III}) and lanthanides (Ln^{III}) from nitric acid media. The ligands have been found to form metal complexes in which they act as approximately planar tridentate ligands (Chan *et* *al.*, 1996) and this is likely to be the mode by which they effect the separation of the metal ions. TPTZ has also been found to form protonated complexes with a variety of anions and several have been structurally characterized (Chan *et al.*, 1996).



TPT2

There are two possible conformations for TPTZ (*A* and *B*) which are dependent upon the relative positions of the N atoms in the pyridine rings [in conformation *A*, all three cavities contain different numbers (three, two, one) of N atoms, and in conformation *B*, all three cavities contain two N atoms (see scheme below)].



Conformation *A* Conformation *B*

Conformation *B* has a threefold axis. Calculations using the *GAUSSIAN*94 program (Frisch *et al.*, 1995) were carried out on the two conformations in order to obtain their relative energies. The 6-31G** basis set was used and the geometries were optimized. The relative energies were −1015.3607 and −1015.3650 a.u., *i.e.* an energy difference of 0.0043 a.u. or 2.70 kcal mol^{-1}. Thus, conformation *B* has the lower energy and this is the conformation found in the crystal structure of L^1 (Fig. 1). The conformation of the molecule can be described by the interplanar angles between each of the three pyridine rings and the central triazine ring. The angles are 15.7 (1), 33.8 (1) and 19.8 (1)° for the rings containing atoms N22, N42 and N62, respectively.

It is interesting that conformation *B* has not been observed in any of the crystal structures of complexes in which L^1 or L^2 is coordinated either with metals or in protonated complexes. In conformation *B*, each of the three cavities contains two N atoms and one C—H moiety, while in conformation *A*, the first cavity contains three N atoms, the second two and the third only one N atom. This was found in the structure of $[Ce^{IV}(L^2)(NO_3)_4]$ and also in nickel complexes of

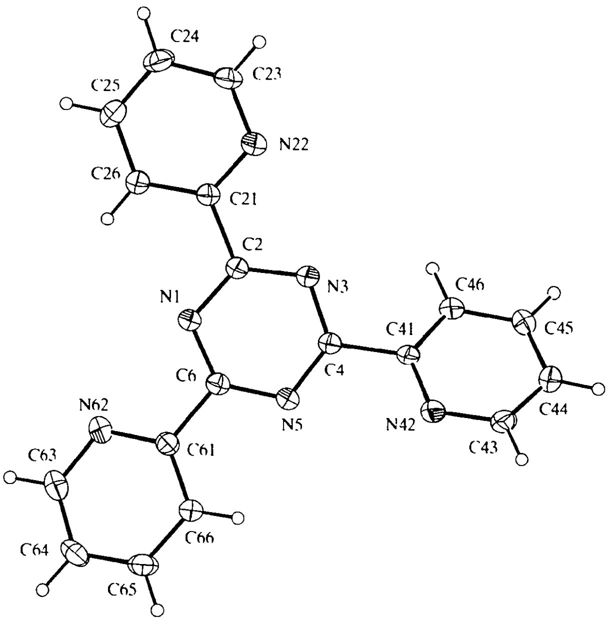


Fig. 1. The structure of the title compound. Ellipsoids are scaled at 25% probability. H atoms are included with small arbitrary radii.

L^2 (Chan *et al.*, 1996) and L^1 (Barclay *et al.*, 1977). Conformation *A* is also observed in the protonated complexes of L^1 and L^2. Crystal structures have been obtained in which the two outer pyridine N atoms in the first cavity are protonated. When this double protonation occurs, the two H atoms are invariably bonded to a hydrogen-bond acceptor and examples are known with L^2 interacting with H_2O, OH^-, PF_6^- and NO_3^- (Chan *et al.*, 1996).

Experimental

The title compound was prepared by the trimerization of 2-cyanopyridine in methanol at ambient temperature and pressure. A methanol solution of 2-cyanopyridine was left to stand for several months whereupon suitable crystals were obtained.

Crystal data

$C_{18}H_{12}N_6$
$M_r = 312.33$
Triclinic
$P\bar{1}$
$a = 7.638\ (8)$ Å
$b = 10.885\ (12)$ Å
$c = 10.845\ (12)$ Å
$\alpha = 60.832\ (10)°$
$\beta = 69.164\ (10)°$
$\gamma = 79.240\ (10)°$
$V = 735.7\ (14)$ Å^3
$Z = 2$
$D_x = 1.410$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 1250 reflections
$\theta = 3.54$–$25.92°$
$\mu = 0.090$ mm^{-1}
$T = 293\ (2)$ K
Parallelepiped
0.25 × 0.25 × 0.18 mm
Colourless

Data collection

Marresearch Image Plate	2211 reflections with $I > 2\sigma(I)$
95 frames at 2° intervals, counting time 2 min	$\theta_{max} = 25.92°$
Absorption correction: none	$h = 0 \rightarrow 9$
2544 measured reflections	$k = -12 \rightarrow 13$
2544 independent reflections	$l = -11 \rightarrow 13$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.050$	$\Delta\rho_{max} = 0.20$ e Å^{-3}
$wR(F^2) = 0.159$	$\Delta\rho_{min} = -0.20$ e Å^{-3}
$S = 1.092$	Extinction correction: *SHELXL*93
2544 reflections	Extinction coefficient: 0.23 (2)
218 parameters	Scattering factors from *International Tables for Crystallography* (Vol. C)
H atoms: see below	
$w = 1/[\sigma^2(F_o^2) + (0.0795P)^2 + 0.3806P]$ where $P = (F_o^2 + 2F_c^2)/3$	

H atoms were fixed at ideal positions with $U_{iso} = 1.2U_{eq}$ of the C atom to which they were bonded. Data analysis used the *XDS* program (Kabsch, 1988). The N atoms in each pyridine ring were unequivocally identified by having the lowest displacement parameters and not having an attached H atom in the difference Fourier map. Uncertainties on C—C bonds do not exceed 0.004 Å.

Data collection: *XDS*. Cell refinement: *XDS*. Data reduction: *XDS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLATON* (Spek, 1994).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1223). Services for accessing these data are described at the back of the journal.

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Tetraundecylpentacyclooctacosadodecaen-octol Tetraethanol Solvate, (I), and Tetra-undecylpentacyclooctacosadodecaenedo-decol Hydrate 2.5-Ethanol Solvate, (II)†

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Abstract

The X-ray crystal structures for the title compounds, (I) ($C_{72}H_{112}O_8.4C_2H_6O$) and (II) ($C_{72}H_{112}O_{12}.2.5C_2H_6O.H_2O$) (also called alkyl calix[4]resorcinarene and calix[4]pyrogallene, respectively), have been determined. The 'legs' of the long alkyl chains on both compounds are deeply interdigitated and this observation accounts for the spontaneous formation of multilayers of such molecules. Both compounds are in a cone conformation in the crystal with very similar geometry parameters. The arrangement of the molecules in the crystal is also similar, with the long alkyl chains lying nearly parallel to the *c* axis and with 'bowl'-to-'bowl' interactions being effected through van der Waals forces and hydrogen bonds involving solvate molecules [ethanol in the case of (I), and ethanol and water in the case of (II)].

Comment

The structures and behaviour of calix[4]resorcinarenes, (I), have attracted widespread attention in recent years

† Systematic names: 2,8,14,20-tetraundecylpentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaen-4,6,10,12,16,18,22,24-octol tetraethanol solvate and 2,8,14,20-tetraundecylpentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-4,5,6,10,11,12,16,17,18,22,23,24-dodecol hydrate 2.5-ethanol solvate.

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