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meso-Octacyclopropylcalix[4]pyrrole ethanol solvate

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.027 Å
H-atom completeness 97%
Disorder in solvent or counterion
R factor = 0.088
wR factor = 0.267
Data-to-parameter ratio = 12.9

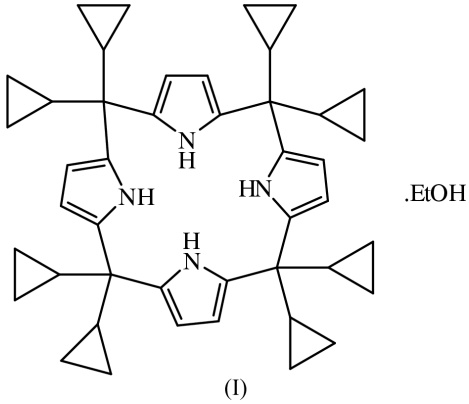
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{44}H_{52}N_4\cdot C_2H_5OH$, is a calix[4]pyrrole-type macrocycle acting as a receptor, by means of hydrogen-bond interactions to an ethanol solvent. The pyrrole groups are arranged in a 1,3-alternate conformation which gives rise to disorder in the ethanol guest, due to its ability to coordinate both above and below the plane of the macrocycle.

Comment

There has been considerable interest over the past decade in the application of calix[4]pyrroles as anion and neutral substrate receptors (Sessler & Gale, 2000). A large number of pyrrolic macrocycles with a wide range of substituents have been shown to coordinate a variety of anions and neutral molecules *via* a combination of hydrogen-bonding and electrostatic interactions.

The structure of the title compound, (I) (Fig. 1), is the *meso*-octacyclopropyl derivative of calix[4]pyrrole, coordinated through hydrogen-bonding interactions (see Table 1) to an ethanol guest molecule. The symmetry of the macrocycle is approximately fourfold; however, due to the orientational flexibility of the cyclopropyl groups, it possesses crystallographic twofold symmetry. The geometry of the macrocyclic ring is in reasonable accordance with expected values and related structures (Sessler & Gale, 2000) in the Cambridge Structural Database (Allen *et al.*, 1983). The macrocycle adopts a 1,3-alternate conformation such that adjacent pyrrole rings are orientated in opposite directions. This orientation is observed in the methyl analogue (Gale *et al.*, 1996) and is presumably due to steric interactions within the macrocycle.



(I)

In these systems, the geometry of the macrocyclic backbone is of particular importance in determining receptor properties. The nitrogen–nitrogen cross-ring distances are 4.61 (3) and 4.57 (3) Å for N1···N1^{i} and N2···N2^{i}, respectively [symmetry code: (i) $-x, y, \frac{1}{2}-z$]. The *meso*-C atoms deviate from

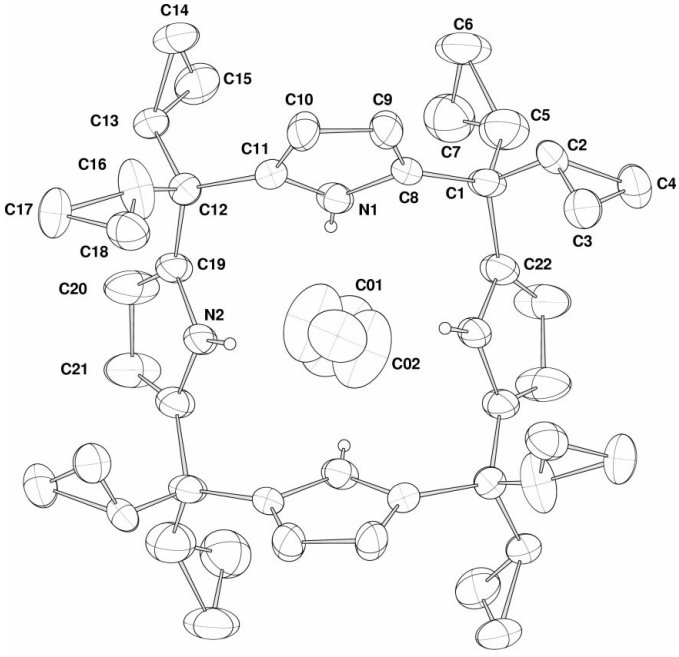


Figure 1
View of (I) (50% probability displacement ellipsoids).

coplanarity, with an average r.m.s. deviation of 0.2541 (5) Å from their plane, with the dihedral angles between this plane and the pyrrole rings being 57.26 (5) and 56.63 (6)° for the N1 and N2 rings, respectively. The average angles about these *meso*-C atoms are 109.41 (2) and 109.45 (2)° for C1 and C12, respectively, indicating a strain-free macrocycle. The cavity formed by the *meso*-C atoms is 5.07 (5) Å in length and has a diagonal distance of 7.15 (4) Å. A comparison with the same geometric parameters of the octamethyl analogue (Gale *et al.*, 1996), which has no guest molecule present, shows (I) to have a similar macrocyclic geometry, thus demonstrating that the interaction with the ethanol solvent has little effect on the backbone geometry. However, the pyrrole rings are significantly more angled into the cavity than in the methyl substituted case [average N···N = 4.83 (4) Å and average dihedral angle between pyrrole and *meso*-C atom plane = 71.5 (2)°], which is presumably due to the interactions with the ethanol guest molecule.

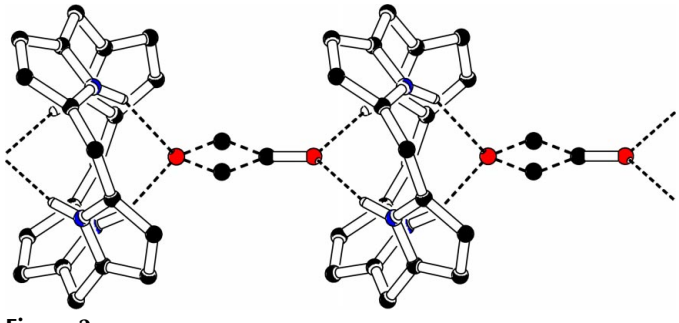


Figure 2
The hydrogen-bonded host–guest assembly, with the cyclopropyl substituents omitted for clarity.

The ethanol guest molecule exhibits disorder, whereby a 50% occupied molecule hydrogen bonds through the alcohol group to a macrocycle above it with the remaining 50% associating *via* the same mechanism to a macrocycle below it (see Fig. 2). This disorder is assumed to be induced by the alternating orientation of the pyrrole rings in the macrocycle, whereby hydrogen bonding is possible both above and below the calix[4]pyrrole plane. This mode of interaction between guest and host produces a supramolecular assembly of one dimensional 'columns'.

Experimental

Dicyclopropyl ketone and pyrrole (1:1) were stirred in ethanol in the presence of methanesulfonic acid (catalytic quantity) for 24 h. The products were column chromatographed on silica-gel 60 with a chloroform eluent and (I) was then crystallized from ethanol.

Crystal data

$C_{44}H_{52}N_4{\cdot}C_2H_6O$
M_r = 682.96
Monoclinic, $C2/c$
a = 23.908 (5) Å
b = 7.6861 (15) Å
c = 22.947 (5) Å
β = 114.31 (3)°
V = 3843.0 (13) Å^3
Z = 4
D_x = 1.180 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 26741 reflections
θ = 3.1–26.4°
μ = 0.07 mm^{-1}
T = 150 (2) K
Plate, colourless
0.22 × 0.15 × 0.05 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)
T_{min} = 0.984, T_{max} = 0.997
25 105 measured reflections
3463 independent reflections
1983 reflections with $I > 2\sigma(I)$
R_{int} = 0.084
θ_{max} = 25.3°
$h = -28 \rightarrow 28$
$k = -9 \rightarrow 9$
$l = -27 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.088
$wR(F^2)$ = 0.267
S = 1.58
3463 reflections
269 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.189
$\Delta\rho_{max}$ = 0.57 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O02	0.88	2.25	3.08 (3)	157
N2—H2···O01	0.88	2.2	3.03 (2)	158
O01—H01···N1^{i}	0.84	2.5	3.23 (2)	145

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

The ethanol guest molecule exhibits disorder (see above), which produces unusual geometric parameters. The anisotropic displacement parameters were restrained to their isotropic equivalent through the use of the *ISOR* command. Attempts to restrain bond lengths resulted in an unstable refinement. Therefore, the geometry of the ethanol molecule was freely refined, which caused difficulty in convergence resulting in a high parameter shift to standard uncertainty ratio. The methyl H atoms of the ethanol molecule were not included as they refined very poorly, due to the nature of the disorder. An attempt was made to solve and refine the structure in the non-centrosymmetric equivalent space group *Cc* in order to resolve the

disordered solvent problem. However, the ethanol molecule occupied two discrete positions and the refinement was problematic with respect to correlation effects. Checks with the *ADDSYM* and *NEWSYM* modules of the *PLATON* package (Spek, 1990), in addition to intensity statistics, confirmed the centrosymmetric nature of the structure.

Cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *CAMERON* (Watkin *et al.*, 1993) and *PLATON* (Spek, 1990).

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References

Allen, F. H., Kennard, O. & Taylor, R. (1983). *Acc. Chem. Res.* **16**, 146–153.
Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–429.
Gale, P. A., Sessler, J. L., Král, V. & Lynch, V. (1996). *J. Am. Chem. Soc.* **118**, 5140–5141.
Hooft, R. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.
Sessler, J. L. & Gale, P. A. (2000). *The Porphyrin Handbook*, Vol. 6, edited by K. M. Kadish, K. M. Smith & R. Guilard, pp.257–278. New York: Academic Press.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.
Watkin, D. M., Pearce, L. & Prout, C. K. (1993). *CAMERON*. Chemical Crystallography Laboratory, University of Oxford, England.