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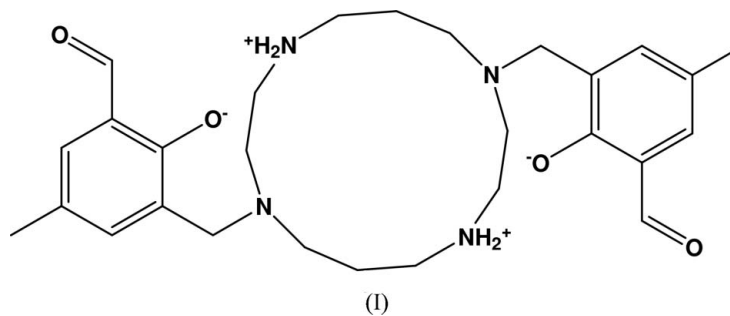
Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.054
 wR factor = 0.161
Data-to-parameter ratio = 18.7For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.1,8-Bis(3-formyl-5-methyl-2-oxidobenzyl)-
1,8-diaza-4,11-diazoniacyclotetradecane
chloroform solvateThe title compound, $\text{C}_{28}\text{H}_{40}\text{N}_4\text{O}_4 \cdot \text{CHCl}_3$, crystallizes with two half-molecules of the macrocycle and one molecule of chloroform solvent in the asymmetric unit. Each macrocycle lies on a centre of inversion. The molecular structure is stabilized by $\text{N}-\text{H} \cdots \text{O}$ and $\text{C}-\text{H} \cdots \text{O}$ intramolecular interactions, and the crystal packing is stabilized by $\text{C}-\text{H} \cdots \text{O}$ and $\text{C}-\text{H} \cdots \pi$ intermolecular interactions.

Received 10 July 2006

Accepted 31 July 2006

Comment

The special feature of the title ligand, (I), is the presence of a formyl group which can be further condensed with polymers. These macrocycle-appended polymers can be used in metal extraction processes (Bianchi *et al.*, 1991) and catalytic applications. The aldehyde group can also be condensed with a fluorescent unit (Kawakami *et al.*, 2001) or redox-active molecules which can be used as sensors (Yamamoto *et al.*, 1996). As the title compound, (I), is of high industrial value, we have undertaken the crystal structure determination by X-ray diffraction.The asymmetric unit of (I) contains two independent half-macrocycles and one solvent (chloroform) molecule. One-half of each macrocycle is inversion-related to the other half (Fig. 1). The $\text{C}-\text{C}$ and $\text{N}-\text{C}$ bond lengths agree well with the reported literature values (Allen *et al.*, 1987). The sums of the bond angles around N1 [334.1°] and N3 [335.3°] indicate sp^3 -hybridization. The exocyclic angles around C6 and C20 show considerable asymmetry, with the $\text{C}9-\text{C}6-\text{C}7$ [122.09 (17°)] and $\text{C}23-\text{C}20-\text{C}21$ [121.16 (16°)] angles larger than the $\text{C}9-\text{C}6-\text{C}5$ [117.97 (15°)] and $\text{C}23-\text{C}20-\text{C}19$ [118.33 (15°)] angles.The conformation of the macrocycle is stabilized by $\text{N}-\text{H} \cdots \text{O}$ and $\text{C}-\text{H} \cdots \text{O}$ intramolecular interactions (Table 1). The molecular structure is also stabilized by intramolecular $\text{C}-\text{H} \cdots \text{O}$ interactions, and the crystal packing is stabilized by $\text{C}-\text{H} \cdots \text{O}$ and $\text{C}-\text{H} \cdots \pi$ intermolecular interactions.

Experimental

5-Methylsalicylaldehyde, 3-chloromethyl-5-methylsalicylaldehyde and 1,4,8,11-tetraazatricyclo[9.3.1.1]hexadecane were prepared according to the methods of Duff (1941), Royal *et al.* (1998) and Gane *et al.* (1991), respectively. 1,4,8,11-Tetraazatricyclo[9.3.1.1]tetradecane (1 g, 0.004 mol) was dissolved in acetonitrile (30 ml) and two equivalents of 3-chloromethyl-5-methylsalicylaldehyde (1.64 g, 0.0089 mol) in acetonitrile (30 ml) were rapidly added; the solution was stirred at 298 K for 24 h. The precipitate formed was filtered off, washed with acetonitrile and dried under vacuum. The resulting crude compound, 1,8-*N,N'*-bis[(3-formyl-2-hydroxy-5-methyl)-benzyl]-4,11-diazatricyclo[9.3.1.1]tetradecane dichloride, was recrystallized from water to give white crystals (yield 85%, m.p. 558 K). This compound (0.5 g) was dissolved in an aqueous NaOH solution (100 ml, 3×10^{-1} M) with stirring. After stirring for 4 h, the solution was extracted with CHCl_3 (5×50 ml). The combined CHCl_3 extracts were dried with anhydrous MgSO_4 and concentrated under vacuum to obtain a light-yellow compound, (I). Light-yellow crystals of the title compound were obtained upon recrystallization from chloroform (yield 70%, m.p. 573 K).

Crystal data

| | |
|--|-----------------------------------|
| $\text{C}_{28}\text{H}_{40}\text{N}_4\text{O}_4 \cdot \text{CHCl}_3$ | $V = 1539.74$ (12) \AA^3 |
| $M_r = 616.01$ | $Z = 2$ |
| Triclinic, $P\bar{1}$ | $D_x = 1.329$ Mg m^{-3} |
| $a = 11.1366$ (5) \AA | Mo $K\alpha$ radiation |
| $b = 11.2816$ (5) \AA | $\mu = 0.34$ mm^{-1} |
| $c = 14.2124$ (7) \AA | $T = 293$ (2) K |
| $\alpha = 69.564$ (1) $^\circ$ | Block, yellow |
| $\beta = 84.559$ (1) $^\circ$ | $0.29 \times 0.26 \times 0.25$ mm |
| $\gamma = 67.110$ (1) $^\circ$ | |

Data collection

| | |
|--|--|
| Bruker SMART APEX CCD area-detector diffractometer | 7069 independent reflections |
| ω scans | 5878 reflections with $I > 2\sigma(I)$ |
| Absorption correction: none | $R_{\text{int}} = 0.018$ |
| 17829 measured reflections | $\theta_{\text{max}} = 28.0^\circ$ |

Refinement

| | |
|--|---|
| Refinement on F^2 | $w = 1/[\sigma^2(F_o^2) + (0.0823P)^2 + 0.5118P]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.054$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.161$ | $(\Delta/\sigma)_{\text{max}} = 0.001$ |
| $S = 1.07$ | $\Delta\rho_{\text{max}} = 0.69$ e \AA^{-3} |
| 7069 reflections | $\Delta\rho_{\text{min}} = -0.43$ e \AA^{-3} |
| 379 parameters | |
| H atoms treated by a mixture of independent and constrained refinement | |

Table 1

Hydrogen-bond geometry (\AA , $^\circ$).

Cg1 is the centroid of the C16–C21 ring.

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|---|----------|--------------|--------------|----------------|
| $\text{N2}-\text{H2A} \cdots \text{O2}$ | 0.90 (2) | 1.71 (2) | 2.605 (2) | 169 (2) |
| $\text{N2}-\text{H2B} \cdots \text{N1}^i$ | 0.90 (2) | 2.26 (2) | 2.909 (2) | 128 (2) |
| $\text{N4}-\text{H4A} \cdots \text{O4}$ | 0.90 (2) | 1.85 (2) | 2.741 (2) | 171 (2) |
| $\text{N4}-\text{H4B} \cdots \text{O4}^{ii}$ | 0.90 (2) | 2.01 (2) | 2.883 (2) | 163 (2) |
| $\text{N4}-\text{H4B} \cdots \text{N3}^{ii}$ | 0.90 (2) | 2.47 (2) | 2.984 (2) | 117 (2) |
| $\text{C8}-\text{H8} \cdots \text{O2}$ | 0.93 | 2.46 | 2.808 (3) | 102 |
| $\text{C11}-\text{H11A} \cdots \text{O2}^i$ | 0.97 | 2.50 | 3.231 (3) | 133 |
| $\text{C14}-\text{H14B} \cdots \text{O4}^{iii}$ | 0.97 | 2.59 | 3.557 (3) | 172 |
| $\text{C22}-\text{H22} \cdots \text{O4}$ | 0.93 | 2.49 | 2.828 (3) | 104 |
| $\text{C26}-\text{H26A} \cdots \text{O4}^{ii}$ | 0.97 | 2.56 | 3.213 (2) | 125 |

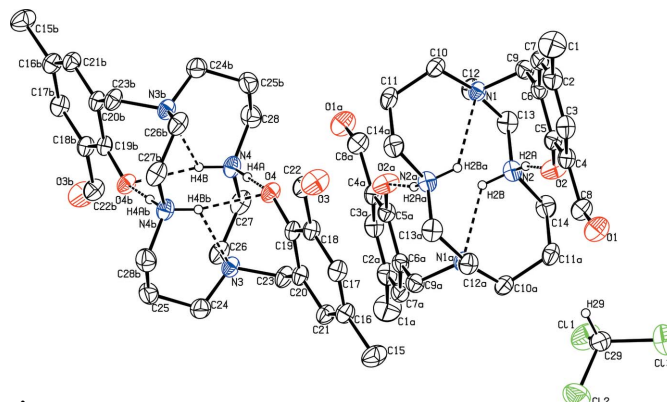


Figure 1

The structure of (I), showing 30% probability displacement ellipsoids. Atoms labelled with the suffixes *a* and *b* are generated by the symmetry operations $(1-x, 1-y, 1-z)$ and $(1-x, 2-y, 2-z)$, respectively. Hydrogen bonds are shown as dashed lines and H atoms not involved in hydrogen bonding have been omitted.

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|--|-------|--------------|--------------|----------------|
| $\text{C27}-\text{H27B} \cdots \text{O1}^{ii}$ | 0.97 | 2.39 | 3.317 (3) | 161 |
| $\text{C29}-\text{H29} \cdots \text{O1}^i$ | 0.98 | 2.46 | 3.326 (3) | 148 |
| $\text{C13}-\text{H13A} \cdots \text{Cg1}^{iii}$ | 0.97 | 2.58 | 3.483 (2) | 154 |

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, -y+2, -z+2$; (iii) $x, y-1, z$.

The amine H atoms were located in a difference map and refined with an N–H distance restraint of 0.90 (1) \AA . The C-bound H atoms were positioned geometrically and allowed to ride on their parent C atoms, with $C-H = 0.93-0.97$ \AA and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1995).

DG and DV acknowledge financial support from the University Grants Commission (UGC-SAP) and the Department of Science and Technology (DST-FIST), Government of India.

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