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An Octamethyldibenzotetraaza[14]annulene

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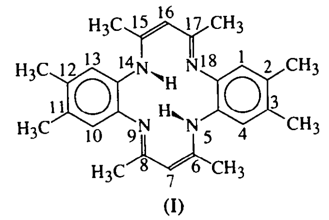
Abstract

The structure of 2,3,6,8,11,12,15,17-octamethyl-5,14-dihydro-5,9,14,18-tetraazadibenzo[*a*,*h*]cyclotetradecene, $C_{26}H_{32}N_4$, a dibenzotetraaza[14]annulene of interest as a ligand for metal complexation, has been determined by single-crystal X-ray diffraction methods. The molecule adopts a pronounced saddle conformation due to steric interactions between methyl groups on the central ring and the phenylene rings. Angles between the least-squares plane of the four N atoms and the two phenylene ring planes are 21.4 (2) and 18.4 (2)°.

Comment

Metal complexes of dibenzotetraaza[14]anulenes are of interest as models for metal sites in proteins (Bailey, Bereman, Rillema & Nowak, 1984) and the B_{12} coenzyme (Cutler, Alleyne & Dolphin, 1985), and as potential catalysts (Uhrhammer, Black, Gardner, Olsen & Jordan, 1993). The chemistry and structural features of metal complexes of the tetramethyl derivative, 6,8,15,17-tetramethyl-5,14-dihydro-5,9,14,18-tetraazadibenzo[*a*,*h*]cyclotetradecene, have been reviewed recently (Cotton & Czuchajowska, 1990). The octamethyl derivative, (I), was synthesized in the hope of generating metal complexes with catalytic activity and increased solubility compared to the complexes of the tetramethyl derivative.



(I)

Steric interactions between the methyl groups at the 6, 8, 15 and 17 positions and the phenylene rings produce the saddle shape of the molecule, similar to that observed for the tetramethyl derivative (Goedken, Pluth, Peng & Bursten, 1976) and metal complexes of the tetramethyl derivative. Interestingly, the angles between the least-squares plane through the four N atoms and the least-squares planes through the phenylene rings are somewhat smaller [21.4 (2) and 18.2 (2)°] than in the tetramethyl derivative (24.1 and 25.1°; Goedken *et al.*, 1976). As in the tetramethyl derivative, the two H atoms are disordered over four possible sites.

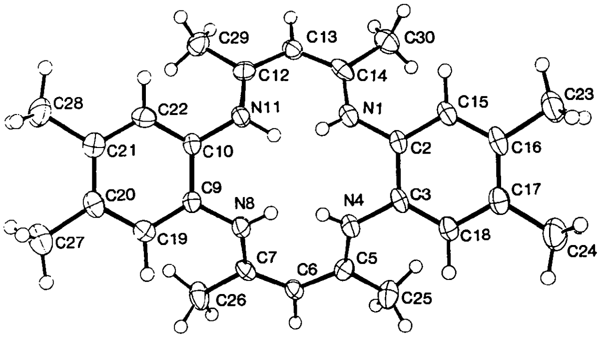


Fig. 1. *ORTEP*II (Johnson, 1976) projection of the molecule perpendicular to the plane of the N atoms showing the atomic numbering scheme used in the structure determination. Displacement ellipsoids are plotted at the 50% probability level. H atoms ate plotted with arbitrary radii.

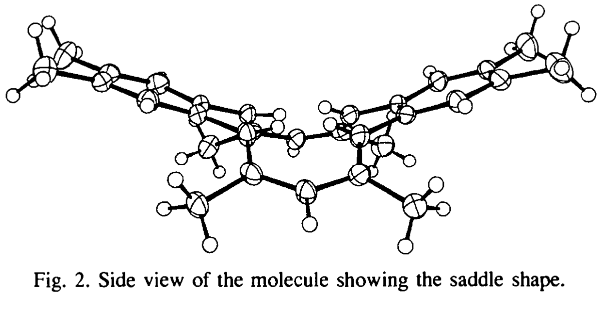


Fig. 2. Side view of the molecule showing the saddle shape.

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Experimental

The compound was synthesized by nickel-template condensation of 4,5-dimethyl-*o*-phenylenediamine and 2,4-pentanedione. The crystal density D_m was measured by flotation in aqueous zinc chloride solution.

Crystal data

$C_{26}H_{32}N_4$
$M_r = 400.57$
Monoclinic
$C2/c$
$a = 20.569\ (8)$ Å
$b = 11.300\ (6)$ Å
$c = 19.179\ (7)$ Å
$\beta = 96.21\ (2)°$
$V = 4431\ (6)$ Å^3
$Z = 8$
$D_x = 1.20$ Mg m^{-3}
$D_m = 1.20\ (2)$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 15\text{–}22°$
$\mu = 0.067$ mm^{-1}
$T = 100$ K
Plate
$0.75 \times 0.45 \times 0.05$ mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.890$, $T_{\max} = 0.991$
2308 measured reflections
2164 independent reflections

1436 observed reflections $[I > 3.0\sigma(I)]$
$\theta_{\max} = 23°$
$h = -22 \rightarrow 22$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 18$
3 standard reflections frequency: 120 min intensity decay: −3.5%

Refinement

Refinement on F
$R = 0.037$
$wR = 0.044$
$S = 1.911$
1436 reflections
408 parameters
H atoms refined isotropically
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o{}^4]$
$(\Delta/\sigma)_{\max} = 0.044$

$\Delta\rho_{\max} = 0.1664$ e Å^{-3}
$\Delta\rho_{\min} = -0.1972$ e Å^{-3}
Extinction correction: isotropic (Zachariasen, 1963)
Extinction coefficient: $0.55\ (6) \times 10^{-6}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
N1	0.0649 (1)	0.0685 (2)	0.7017 (1)	0.029 (1)
N4	0.1360 (1)	0.2513 (2)	0.7614 (1)	0.029 (1)
N8	0.1835 (1)	0.1070 (2)	0.8686 (1)	0.028 (1)
N11	0.1126 (1)	−0.0745 (2)	0.8072 (1)	0.026 (1)
C2	0.0460 (1)	0.1832 (2)	0.6811 (1)	0.025 (2)
C3	0.0831 (1)	0.2788 (3)	0.7114 (1)	0.025 (2)
C5	0.1927 (1)	0.3086 (2)	0.7732 (1)	0.027 (2)
C6	0.2396 (1)	0.2717 (2)	0.8271 (1)	0.027 (2)
C7	0.2367 (1)	0.1755 (3)	0.8712 (1)	0.027 (2)
C9	0.1744 (1)	0.0071 (2)	0.9100 (1)	0.023 (2)
C10	0.1375 (1)	−0.0864 (2)	0.8781 (1)	0.024 (2)
C12	0.1064 (1)	−0.1601 (3)	0.7592 (1)	0.028 (2)
C13	0.0816 (1)	−0.1366 (3)	0.6906 (1)	0.028 (2)
C14	0.0614 (1)	−0.0278 (3)	0.6617 (1)	0.030 (2)
C15	−0.0095 (1)	0.2080 (3)	0.6353 (1)	0.029 (2)
C16	−0.0275 (1)	0.3216 (3)	0.6157 (1)	0.031 (2)
C17	0.0099 (1)	0.4159 (3)	0.6453 (1)	0.031 (2)
C18	0.0634 (1)	0.3919 (3)	0.6939 (1)	0.029 (2)
C19	0.1953 (1)	−0.0006 (3)	0.9807 (1)	0.028 (2)
C20	0.1859 (1)	−0.1003 (3)	1.0204 (1)	0.029 (2)
C21	0.1494 (1)	−0.1936 (3)	0.9889 (1)	0.030 (2)
C22	0.1248 (1)	−0.1825 (3)	0.9192 (1)	0.031 (2)
C23	−0.0875 (2)	0.3414 (3)	0.5651 (2)	0.046 (2)
C24	−0.0069 (2)	0.5403 (3)	0.6250 (2)	0.050 (2)
C25	0.2107 (1)	0.4086 (3)	0.7282 (2)	0.040 (2)
C26	0.2974 (1)	0.1474 (3)	0.9197 (2)	0.040 (2)
C27	0.2139 (2)	−0.1061 (3)	1.0961 (2)	0.045 (2)
C28	0.1378 (2)	−0.3041 (3)	1.0291 (2)	0.044 (2)
C29	0.1300 (2)	−0.2835 (3)	0.7747 (2)	0.037 (2)
C30	0.0408 (2)	−0.0235 (3)	0.5844 (2)	0.040 (2)

Table 2. *Selected geometric parameters* (Å, °)

N1—C2	1.399 (3)	C9—C19	1.380 (3)
N1—C14	1.330 (3)	C10—C22	1.383 (3)
N4—C3	1.405 (3)	C12—C13	1.386 (3)
N4—C5	1.331 (3)	C12—C29	1.496 (4)
N8—C7	1.338 (3)	C13—C14	1.393 (3)
N8—C9	1.406 (3)	C14—C30	1.497 (4)
N11—C10	1.408 (3)	C15—C16	1.377 (3)
N11—C12	1.332 (3)	C16—C17	1.398 (3)
C2—C3	1.410 (3)	C16—C23	1.501 (4)
C2—C15	1.392 (3)	C17—C18	1.389 (4)
C3—C18	1.371 (3)	C17—C24	1.490 (4)
C5—C6	1.398 (3)	C19—C20	1.385 (3)
C5—C25	1.492 (4)	C20—C21	1.394 (3)
C6—C7	1.382 (3)	C20—C27	1.502 (4)
C7—C26	1.506 (3)	C21—C22	1.385 (3)
C9—C10	1.401 (3)	C21—C28	1.500 (4)
C2—N1—C14	126.8 (3)	N11—C12—C13	121.0 (2)
C3—N4—C5	127.6 (3)	N11—C12—C29	122.5 (2)
C7—N8—C9	127.1 (3)	C13—C12—C29	116.4 (2)
C10—N11—C12	126.5 (2)	C12—C13—C14	127.6 (3)
N1—C2—C3	118.2 (2)	N1—C14—C13	119.8 (2)
N1—C2—C15	123.3 (2)	N1—C14—C30	122.5 (3)
C3—C2—C15	118.4 (2)	C13—C14—C30	117.5 (3)
N4—C3—C2	117.1 (2)	C2—C15—C16	122.5 (3)
N4—C3—C18	124.0 (2)	C15—C16—C17	118.6 (2)
C2—C3—C18	118.7 (2)	C15—C16—C23	119.5 (3)
N4—C5—C6	120.2 (2)	C17—C16—C23	121.8 (3)
N4—C5—C25	122.4 (3)	C16—C17—C18	119.0 (2)
C6—C5—C25	117.4 (2)	C16—C17—C24	120.7 (2)
C5—C6—C7	128.0 (2)	C18—C17—C24	120.3 (3)
N8—C7—C6	121.4 (2)	C3—C18—C17	122.5 (2)
N8—C7—C26	121.4 (3)	C9—C19—C20	123.0 (2)
C6—C7—C26	117.2 (2)	C19—C20—C21	118.5 (2)
N8—C9—C10	117.3 (2)	C19—C20—C27	120.3 (2)
N8—C9—C19	124.0 (2)	C21—C20—C27	121.3 (2)
C10—C9—C19	118.6 (2)	C20—C21—C22	118.3 (2)
N11—C10—C9	118.2 (2)	C20—C21—C28	121.1 (2)
N11—C10—C22	123.7 (2)	C22—C21—C28	120.7 (3)
C9—C10—C22	118.1 (2)	C10—C22—C21	123.2 (3)

The H atoms attached to the four N atoms were assigned occupancies of 50%.

Data collection: CAD-4 diffractometer software (Enraf–Nonius, 1977). Cell refinement: CAD-4 diffractometer software. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MULTAN*80; Main *et al.*, 1980). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1112). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A 2:1 Molecular Complex of Theophylline and 5-Fluorouracil as the Monohydrate

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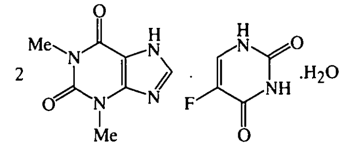
Abstract

Theophylline, 5-fluorouracil and water molecules are packed in parallel sheets in the crystal structure of the title compound, 3,7-dihydro-1,3-dimethyl-1*H*-purine-2,6-dione–5-fluoro-2,4(1*H*,3*H*)-pyrimidinedione–water (2/1/1), $2C_7H_8N_4O_2.C_4H_3FN_2O_2.H_2O$. The planar molecules are held together within the sheets by hydrogen bonds which include C—H···O interactions. Short linear N—CH_3···F and N—CH_3···O contacts are also found between molecules within the sheets.

Comment

Theophylline has the ability to form molecular complexes with various aromatic compounds, and several crystal structures of these complexes have been studied (*e.g.* Shefter, 1969; Shefter & Sackman, 1971; Nakao, Fujii, Sakaki & Tomita, 1977; Aoki, Ichikawa, Koinuma & Iitaka, 1978). The complexing properties of 5-fluorouracil and its derivatives have also been studied extensively through the determination of the structures of purine–pyrimidine hydrogen-bonded complexes (*e.g.* Kim & Rich, 1967; Tomita, Katz & Rich, 1967; Mazza, Sobell & Kartha, 1969). We report here the crystal structure of the title 2:1 complex of theophylline and 5-fluorouracil as the monohydrate, (I), obtained from aqueous solution.



(I)

The bond distances and angles in the two crystallographically independent theophylline molecules in the asymmetric unit are in good agreement, and are similar to those reported previously for theophylline (Sutor, 1958; Koo, Shin & Oh, 1978). The bond distances and angles in the 5-fluorouracil molecule are also similar to those in 5-fluorouracil itself (Fallon, 1973). The 5-fluorouracil molecule is bonded to the one theophylline molecule by two N—H···O hydrogen bonds [N(20)···O(33) 2.772 (4), N(29)···O(26) 2.785 (4) Å], and the two independent theophylline molecules are linked together by an N—H···N hydrogen bond [N(7)···N(22) 2.903 (5) Å] (Fig. 1). The three molecules are approximately coplanar: the largest deviation from the least-squares plane through the 35 non-H atoms is 0.37 Å for F(35). The water O atom also lies on this plane with a deviation of 0.66 Å. The crystal structure consists of these molecules packed in parallel sheets perpendicular to the *ac* plane (Fig. 2).

The water molecule is hydrogen bonded to two 5-fluorouracil molecules within the same sheet [N(27)···O(36) 2.702 (5), O(36)···O(34)(x, $-1+y$, z) 2.829 (4) Å] and is also hydrogen bonded to a theophylline molecule in an adjacent sheet [O(36)···N(9)($-x$, $-1-y$, $-z$) 2.980 (5) Å]. Short C_{sp^2}—H···O_{sp^2} contacts are also found for C(8)—H···O(24)(x, $-1+y$, z) [C···O 3.226 (5), H···O 2.25 (3) Å, C—H···O 159 (3)°] and C(21)—H···O(24)(x, $-1+y$, z) [C···O 3.298 (5), H···O 2.35 (4) Å, C—H···O 171 (3)°]. These C—H···O hydrogen bonds stabilize the sheet structure.

There are also close intermolecular contacts within the sheets between the methyl groups of the theophylline molecules and F and O atoms. The short N—CH_3···F contacts are C(10)···F(35)($1+x$, $\frac{1}{2}-y$, $-\frac{1}{2}+z$) 3.107 (6) Å [N—C···F 170.0 (3)°] and C(12)···F(35)($1+x$, $-\frac{1}{2}-y$, $-\frac{1}{2}+z$) 3.246 (7) Å [N—C···F