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A Dibenzotetraaza[14]annulene

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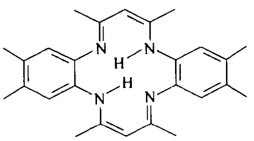
Abstract

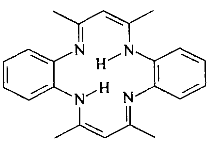
The ligand 2,3,6,8,11,12,15,17-octamethyl-5,14-dihydro-5,9,14,18-tetraazadibenzo[*b*,*i*]cyclotetradecene (H_2omtaa, $C_{26}H_{32}N_4$) has a pronounced saddle shape as a result of interactions between the methyl groups and the phenyl rings [the dihedral angle between the phenyl rings is 139.2 (3)°]. The overall geometry of H_2omtaa is very similar to that of H_2tmtaa (6,8,15,17-tetramethyl-5,14-dihydro-5,9,14,18-tetraazadibenzo[*b*,*i*]cyclotetradecene, $C_{22}H_{24}N_4$) [Goedken, Pluth, Peng & Bursten (1976). *J. Am. Chem. Soc.* **98**, 8014–8021]. The central cavity in H_2omtaa has a radius of 1.915 (3) Å (where the radius is defined as half the mean distance between diagonally opposite N atoms), which is significantly smaller than that in a porphyrin (2.04 Å).

Comment

The aims of this study were to confirm the expected *mm* symmetry of the ligand H_2omtaa, and to compare its structure with those of similar compounds, including H_2tmtaa (Goedken, Pluth, Peng & Bursten, 1976).

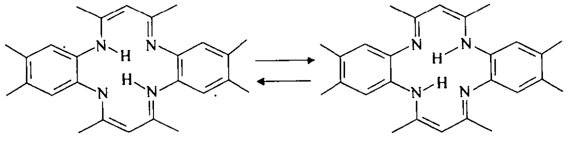


H_2omtaa



H_2tmtaa

Like H_2tmtaa, H_2omtaa has a markedly non-planar geometry, shown in Fig 1, which results from steric interactions. Both free ligands have a conjugated imine–enamine double-bond arrangement in the 2,4-pentanediimine moieties that connect the benzene rings. The N atoms in these moieties are linked by hydrogen bonds.



It is interesting to note that the addition of four methyl groups to the benzene rings does not affect the delocalization around the carbon–nitrogen framework of the ligand, as the average benzenoid C—N bond distance in H_2omtaa [1.412 (3) Å] is similar to that in H_2tmtaa [1.404 (8) Å]. The square-planar array of the four N atoms has a slight rhombic distortion with *trans* N atoms separated by 3.823 (3) and 3.838 (3) Å for N11···N4 and N1···N8, respectively. The average distance from the N atoms to the centre of the cavity is 1.915 (3) Å in H_2omtaa compared with 1.902 (3) Å in H_2tmtaa. The radius of the cavity in H_2omtaa is notably smaller than that in similar systems, such as porphyrins (Hoard, Hamor & Hamor, 1963) and phthalocyanines (Webb & Fleischer, 1965), for which the crystal structures have also been determined (Hoskins, Mason & White, 1969).

Overall, the crystal structure and molecular geometry of H_2omtaa show a close resemblance to those of H_2tmtaa. The additional four methyl groups appear to have very little effect on the geometry of the ligand or the size of the central cavity. This was also observed for the complex formed between monomethylgallium(III) and H_2omtaa (Cannadine, Errington, Moore & Wallbridge, 1994), in which the Ga atom coordinates symmetrically to the four planar N atoms resulting in a saddle-shaped structure. The Ga atom in the complex is located 0.656 (3) Å above the N_4 plane, compared with 0.65 (1) Å in the analogous complex formed by H_2tmtaa (Alcock, Blacker, Errington & Wallbridge, 1993).

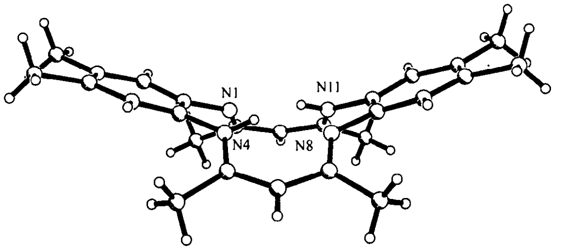


Fig. 1. A side view of H_2omtaa showing the saddle conformation adopted by the ligand.

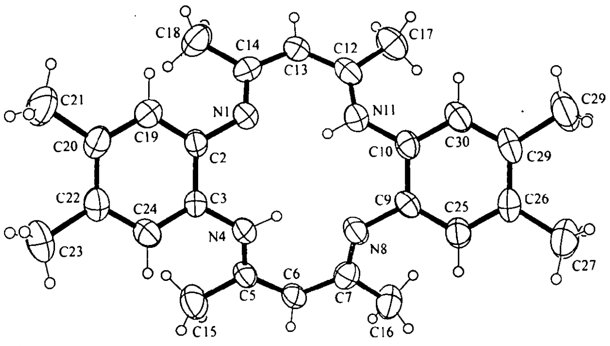


Fig. 2. A face view of H_2omtaa showing the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

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Experimental

A sample of the neutral ligand H_2omtaa was prepared by a method based on the template synthesis of the related macrocycle H_2tmtaa (Goedken & Weiss, 1980) and was recrystallized from a pyridine/water mixture.

Crystal data

$C_{26}H_{32}N_4$
$M_r = 400.56$
Monoclinic
$C2/c$
$a = 20.787$ (3) Å
$b = 11.3823$ (8) Å
$c = 19.443$ (3) Å
$\beta = 97.10$ (2)°
$V = 4565.0$ (10) Å^3
$Z = 8$
$D_x = 1.166$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 500 reflections
$\theta = 4$–25°
$\mu = 0.070$ mm^{-1}
$T = 293$ (2) K
Block
0.15 × 0.05 × 0.05 mm
Orange

Data collection

Enraf–Nonius diffractometer with FAST TV area detector
Absorption correction: none
7578 measured reflections
2732 independent reflections

1352 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0920$
$\theta_{\rm max} = 22.84°$
$h = -22 \rightarrow 20$
$k = -11 \rightarrow 11$
$l = -19 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0404$
$wR(F^2) = 0.0749$
$S = 1.012$
2730 reflections
279 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0187P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.191$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.159$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	$U_{\rm eq}$
N1	0.11257 (11)	−0.0758 (2)	0.30752 (12)	0.0439 (7)
C2	0.13732 (14)	−0.0872 (3)	0.37849 (15)	0.0399 (8)
C3	0.17444 (14)	0.0065 (3)	0.40913 (15)	0.0399 (8)
N4	0.18395 (12)	0.1055 (2)	0.36761 (11)	0.0434 (7)
C5	0.2372 (2)	0.1705 (3)	0.37024 (14)	0.0424 (8)
C6	0.24000 (14)	0.2671 (3)	0.32641 (14)	0.0451 (8)
C7	0.1929 (2)	0.3046 (3)	0.27304 (14)	0.0432 (8)
N8	0.13652 (12)	0.2478 (2)	0.26130 (11)	0.0442 (7)
C9	0.08338 (14)	0.2755 (3)	0.21110 (13)	0.0396 (8)
C10	0.04591 (14)	0.1804 (3)	0.18141 (13)	0.0413 (8)
N11	0.06494 (11)	0.0670 (2)	0.20287 (11)	0.0442 (7)
C12	0.06171 (14)	−0.0287 (3)	0.16328 (15)	0.0468 (9)
C13	0.08141 (14)	−0.1377 (3)	0.19167 (15)	0.0480 (9)
C14	0.10687 (14)	−0.1615 (3)	0.2599 (2)	0.0443 (8)
C15	0.29825 (14)	0.1430 (3)	0.41803 (14)	0.0667 (11)
C16	0.21090 (14)	0.4042 (3)	0.22833 (14)	0.0617 (10)
C17	0.0414 (2)	−0.0260 (3)	0.08561 (14)	0.0660 (10)
C18	0.1306 (2)	−0.2849 (3)	0.27577 (14)	0.0643 (10)
C19	0.12441 (14)	−0.1818 (3)	0.4194 (2)	0.0473 (9)
C20	0.1489 (2)	−0.1909 (3)	0.4888 (2)	0.0488 (9)
C21	0.1357 (2)	−0.2997 (3)	0.52883 (14)	0.0740 (11)
C22	0.18509 (15)	−0.0983 (3)	0.5197 (2)	0.0492 (9)
C23	0.2139 (2)	−0.1012 (3)	0.59576 (13)	0.0762 (12)
C24	0.19550 (14)	0.0002 (3)	0.47983 (15)	0.0486 (9)
C25	0.06343 (14)	0.3892 (3)	0.19361 (14)	0.0487 (9)
C26	0.0102 (2)	0.4120 (3)	0.14547 (14)	0.0499 (9)
C27	−0.0065 (2)	0.5376 (3)	0.1259 (2)	0.0870 (13)
C28	−0.02754 (15)	0.3196 (3)	0.11673 (14)	0.0511 (9)
C29	−0.0877 (2)	0.3387 (3)	0.0660 (2)	0.0798 (12)
C30	−0.00954 (14)	0.2061 (3)	0.13653 (13)	0.0475 (9)

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

N1—C14	1.341 (3)	C7—N8	1.333 (3)
N1—C2	1.418 (3)	N8—C9	1.416 (3)
C2—C19	1.385 (3)	C9—C10	1.414 (4)
C2—C3	1.406 (4)	C10—N11	1.399 (3)
C3—C24	1.392 (3)	N11—C12	1.331 (3)
C3—N4	1.414 (3)	C12—C13	1.398 (4)
N4—C5	1.327 (3)	C13—C14	1.392 (4)
C5—C6	1.397 (3)	C14—C18	1.508 (4)
C6—C7	1.403 (3)		
C14—N1—C2	126.6 (3)	N8—C7—C16	122.9 (3)
C19—C2—C3	118.8 (3)	C7—N8—C9	127.2 (3)
C19—C2—N1	123.9 (3)	C25—C9—C10	118.7 (3)
C3—C2—N1	117.2 (3)	C25—C9—N8	124.1 (3)
C24—C3—C2	117.9 (3)	C10—C9—N8	117.0 (3)
C24—C3—N4	123.8 (3)	C30—C10—N11	124.3 (3)
C2—C3—N4	118.1 (3)	N11—C10—C9	117.6 (3)
C5—N4—C3	126.6 (3)	C12—N11—C10	126.2 (3)
N4—C5—C6	120.8 (3)	N11—C12—C13	120.4 (3)
N4—C5—C15	122.8 (3)	N11—C12—C17	123.2 (3)
C6—C5—C15	116.3 (3)	N1—C14—C13	120.4 (3)
C5—C6—C7	127.8 (3)	N1—C14—C18	122.5 (3)
N8—C7—C6	119.8 (3)		

The structure was solved by direct methods using the *TREF* routine in *SHELXTL-Plus* (Sheldrick, 1986) and refined using *SHELXL*93 (Sheldrick, 1994). H atoms were placed at calculated positions and refined using a riding model with isotropic U's equal to 1.2 (or 1.5 for methyl H atoms) times $U_{\rm eq}$ for the atom to which they are attached. The site occupancy factors for H atoms attached to N1, N4, N8 and N11 were allowed to refine, resulting in values of about 0.5, and were subsequently fixed at 0.5.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving non-H atoms have been deposited with the IUCr (Reference: AB1194). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,2′-Dithiodisalicyclic Acid Tetrahydrofuran Solvate

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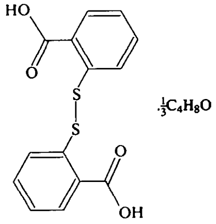
Abstract

The title structure (2,2′-disulfanediyldibenzoic acid tetrahydrofuran solvate, $C_{14}H_{10}O_4S_2.\frac{1}{3}C_4H_8O$) contains two crystallographically distinct $[C_6H_4(2\text{-}COOH)S]_2$ molecules, one of which consists of symmetry-related halves. The molecules form extended chains in the crystal by means of hydrogen bonding, but each $[C_6H_4(2\text{-}COOH)S]_2$ unit bonds only to units equivalent to itself resulting in two crystallographically inequivalent chains aligned along the *c* axis. There is also a tetrahydrofuran molecule present, disordered over two sites.

Comment

In the title compound (I), the geometrical parameters of the three $[C_6H_4(2\text{-}COOH)S]$ sub-units are similar. The angle between the best plane through the phenyl ring containing C(1) and that related by $(-x, y, \frac{1}{2}-z)$ is 80.4 (6)°, while the corresponding angle between the rings containing atoms C(8) and C(15) is 73.8 (4)°. The hydrogen bonds, likewise, are all of a similar length, the O(2)···O(1^{i}) distance being 2.641 (12), O(4)···O(5^{ii}) being 2.651 (11) and O(6)···O(3^{iii}) being 2.658 (12) Å [symmetry codes: (i) $-x, -y, 1-z$; (ii) $x, -y, z+\frac{1}{2}$; (iii) $x, -y, z-\frac{1}{2}$]. There appears to be a slight torsional strain in the latter two bonds, since the angle between the planes defined by O(5)—C(21)—O(6) and O(3^{iii})—C(14^{iii})—O(4^{iii}) is 9.3 (6)°. The O(1)—C(7)—O(2) and O(1^{i})—C(7^{i})—O(2^{i}) groups are essentially coplanar.



(I)

The tetrahydrofuran molecule, which refined poorly as an unconstrained group, was known to be present from the observation of characteristic signals in the NMR spectrum of (I). Also, it should be mentioned that there is some ambiguity as to the correct space group for this structure. A possible alternative is *Cc*, although attempts at refinement in this space group were severely hampered by a low data-to-parameter ratio and poor convergence.

A large number of other dithiodiaryl compounds have been structurally characterized and by comparison of the structure of (I) with these, its features can be seen to be broadly typical of the class. Comparable structures are those of $[C_6H_4(4\text{-}Cl)S]_2$ (Spirlet, van den Bossche, Dideberg & Dupont, 1979) and especially $[C_6H_4(2\text{-}COCl)S]_2$, for which the attributed space group is also *C*2/*c* ($Z = 12$) (Parkanyi, Kálmán, Kucsman & Kapovits, 1989).

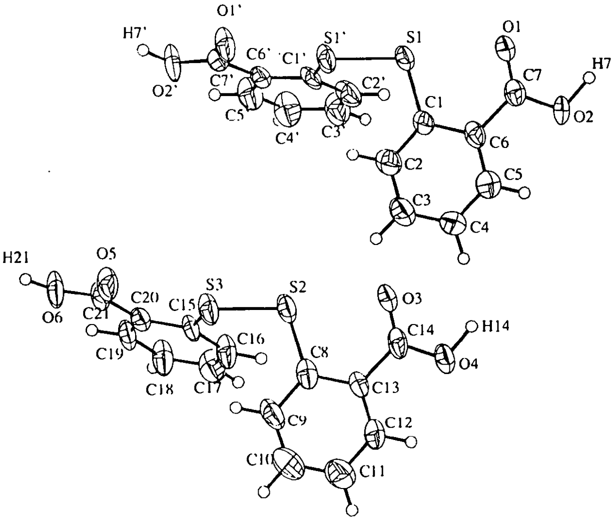


Fig. 1. Molecular diagram (*SNOOPI*; Davies, 1982) of the title compound with displacement ellipsoids depicted at the 50% probability level. Unlabelled H atoms possess the same numerical label as do their parent C atoms. [Symmetry code: (′) $-x, y, \frac{1}{2}-z$.]

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