for data reduction. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985) and refined by full-matrix least-squares methods using *SHELXL*93 (Sheldrick, 1993).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DU1112). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Dicyclohexylammonium 2-Carboxybenzenesulfonate Dihydrate

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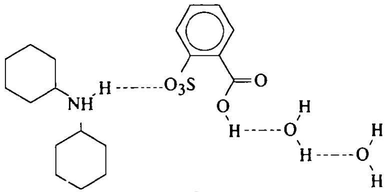
Abstract

In the title compound, $C_{12}H_{24}N^+.C_7H_5O_5S^-.2H_2O$, one of the two water molecules [$OW\cdots OW$ 2.732 (6) Å] forms hydrogen bonds to the adjacent carboxylic acid residues [$OW\cdots O_{\rm carboxyl}$ 2.600 (5), $OW\cdots O_{\rm carbonyl}$ 2.810 (6) Å], whereas the other water molecule forms hydrogen bonds to adjacent sulfonate groups [$OW\cdots O$ 2.791 (5) and 2.855 (5) Å]. The chains are held together by ammonium–sulfonate hydrogen bonds [$N\cdots O$ 2.791 (5) and 2.855 (5) Å].

Comment

Dicyclohexylammonium 2-carboxybenzenesulfonate dihydrate, (I), has been condensed with a triorganotin hemioxide/hydroxide to give dicyclohexylammonium 2-sulfobenzoatotriorganostannate (Ng, Kumar Das & Tiekink, 1991; Ng & Kumar Das, 1992), which displays a covalent carboxyl O—Sn bond. The synthesis implies the presence of a free carboxylic acid entity in the reagent. A free carboxylic group is also present in the ammonium (Okaya, 1967), potassium (Teplova, Turskaya, Shibanova, Nekrasov & Belikova, 1986), rubidium (Teplova, Turskaya, Tovbis, Zavodnik, Shibanova & Belikova, 1984) and caesium (Sorokina, Molchanov, Turskaya, Furmanova & Belikova, 1989) 2-carboxybenzenesulfonates, as well as in the parent acid trihydrate (Attig & Mootz, 1976).



(I)

The dicyclohexylammonium cation forms hydrogen bonds to adjacent negatively charged sulfonate groups. The neutral carboxylic acid group is hydrogen bonded to a water molecule and additional hydrogen bonds give rise to a three-dimensional network.

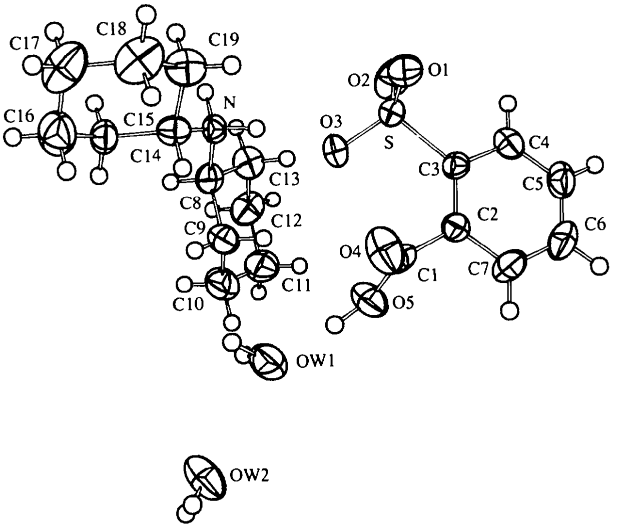


Fig. 1. Atomic labeling scheme for the title salt. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

Dicyclohexylamine was reacted with 2-sulfobenzoic acid in 1:1 molar amounts in hot ethanol. Slow evaporation of the solvent afforded large crystals of the title salt.

Crystal data

$C_{12}H_{24}N^+.C_7H_5O_5S^-.2H_2O$
$M_r = 419.52$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Monoclinic
$P2_1/n$
$a = 14.140\,(6)$ Å
$b = 9.586\,(3)$ Å
$c = 16.118\,(7)$ Å
$\beta = 94.48\,(2)°$
$V = 2178.0\,(15)$ Å^3
$Z = 4$
$D_x = 1.279$ Mg m^{-3}

Cell parameters from 25 reflections
$\theta = 8–11°$
$\mu = 0.178$ mm^{-1}
$T = 298$ K
Parallelepiped
0.29 × 0.25 × 0.23 mm
Transparent

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega–2\theta$ scans
Absorption correction: none
2966 measured reflections
2831 independent reflections
1648 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0266$
$\theta_{\rm max} = 22.47°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 10$
$l = -17 \rightarrow 17$
3 standard reflections
frequency: 60 min
intensity decay: 1.9%

Refinement

Refinement on F^2
$R(F) = 0.0575$
$wR(F^2) = 0.1509$
$S = 1.009$
2831 reflections
260 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0649P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$

$\Delta\rho_{\rm max} = 0.219$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.225$ 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	$U_{\rm eq}$
S	0.59719 (9)	0.48665 (14)	0.21607 (8)	0.0395 (4)
O*W*1	0.3811 (3)	0.6129 (6)	0.5031 (2)	0.0746 (13)
O*W*2	0.2728 (3)	0.7465 (5)	0.6116 (2)	0.0796 (14)
O1	0.6563 (2)	0.3649 (4)	0.2324 (2)	0.0521 (10)
O2	0.6271 (3)	0.5661 (5)	0.1469 (2)	0.0745 (13)
O3	0.5862 (2)	0.5654 (4)	0.2905 (2)	0.0619 (12)
O4	0.4629 (3)	0.3647 (4)	0.3785 (2)	0.0662 (12)
O5	0.3737 (3)	0.5485 (4)	0.3460 (2)	0.0559 (11)
N	0.6900 (3)	0.7877 (4)	0.3629 (2)	0.0349 (10)
C1	0.4210 (4)	0.4368 (6)	0.3273 (3)	0.0392 (13)
C2	0.4117 (3)	0.4040 (5)	0.2359 (3)	0.0340 (12)
C3	0.4828 (3)	0.4221 (5)	0.1822 (3)	0.0315 (12)
C4	0.4676 (4)	0.3843 (5)	0.0994 (3)	0.0430 (13)
C5	0.3827 (4)	0.3268 (6)	0.0699 (3)	0.053 (2)
C6	0.3115 (4)	0.3068 (6)	0.1226 (4)	0.056 (2)
C7	0.3257 (4)	0.3470 (6)	0.2051 (3)	0.0489 (14)
C8	0.6151 (4)	0.8996 (5)	0.3598 (3)	0.0406 (13)
C9	0.5286 (3)	0.8499 (5)	0.3986 (3)	0.0461 (14)
C10	0.4509 (4)	0.9602 (6)	0.3895 (4)	0.065 (2)
C11	0.4270 (4)	0.9973 (7)	0.2989 (4)	0.067 (2)
C12	0.5144 (4)	1.0493 (6)	0.2597 (4)	0.058 (2)
C13	0.5935 (4)	0.9410 (6)	0.2696 (3)	0.0509 (15)
C14	0.7272 (3)	0.7305 (5)	0.4464 (3)	0.0403 (13)
C15	0.7638 (4)	0.8455 (6)	0.5047 (3)	0.0468 (14)
C16	0.8079 (5)	0.7827 (7)	0.5860 (3)	0.074 (2)
C17	0.8869 (5)	0.6814 (7)	0.5701 (4)	0.078 (2)
C18	0.8498 (5)	0.5658 (7)	0.5114 (4)	0.073 (2)
C19	0.8042 (4)	0.6264 (6)	0.4303 (3)	0.057 (2)

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

S—O1	1.447 (4)	C9—C10	1.523 (7)
S—O2	1.441 (4)	C10—C11	1.515 (8)
S—O3	1.436 (3)	C11—C12	1.515 (8)
S—C3	1.778 (5)	C12—C13	1.525 (7)
O4—C1	1.198 (6)	C14—C15	1.514 (6)
O5—C1	1.310 (6)	C14—C19	1.514 (7)
N—C8	1.506 (6)	C15—C16	1.529 (7)
N—C14	1.509 (6)	C16—C17	1.517 (8)
C1—C2	1.502 (7)	C17—C18	1.523 (8)
C2—C3	1.388 (6)	C18—C19	1.526 (7)
C2—C7	1.389 (7)	O*W*1···O*W*2	2.732 (6)
C3—C4	1.382 (6)	O*W*1···O4$^{\rm i}$	2.810 (6)
C4—C5	1.372 (7)	O*W*1···O5	2.600 (5)
C5—C6	1.380 (7)	O*W*2···O1$^{\rm i}$	2.841 (6)
C6—C7	1.384 (7)	O*W*2···O2$^{\rm ii}$	2.825 (6)
C8—C9	1.495 (6)	O1···N$^{\rm iii}$	2.855 (5)
C8—C13	1.515 (7)	O3···N	2.791 (5)
O1—S—O3	111.7 (2)	C2—C7—C6	120.7 (5)
O1—S—O2	111.5 (2)	N—C8—C9	110.8 (4)
O1—S—C3	105.9 (2)	N—C8—C13	107.9 (4)
O2—S—O3	115.2 (3)	C9—C8—C13	112.0 (4)
O2—S—C3	105.1 (2)	N—C8—C13	107.9 (4)
O3—S—C3	106.5 (2)	C8—C9—C10	110.2 (4)
C8—N—C14	119.0 (4)	C9—C10—C11	111.1 (5)
O4—C1—O5	123.1 (5)	C10—C11—C12	110.6 (5)
O4—C1—C2	123.8 (5)	C11—C12—C13	110.3 (5)
O5—C1—C2	113.0 (5)	C8—C13—C12	111.7 (5)
C1—C2—C3	125.0 (4)	N—C14—C15	111.6 (4)
C1—C2—C7	116.1 (4)	N—C14—C19	107.0 (4)
C3—C2—C7	118.9 (4)	C15—C14—C19	111.7 (4)
S—C3—C2	122.5 (3)	C14—C15—C16	110.0 (5)
S—C3—C4	117.2 (4)	C15—C16—C17	111.3 (5)
C2—C3—C4	120.2 (4)	C16—C17—C18	110.4 (5)
C3—C4—C5	120.4 (5)	C17—C18—C19	110.9 (5)
C4—C5—C6	120.2 (5)	C14—C19—C18	111.5 (5)
C5—C6—C7	119.6 (5)		

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $x - \frac{1}{2}, \frac{3}{2} - y, \frac{1}{2} + z$; (iii) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

The H atoms bonded to C atoms were generated and allowed to ride with displacement factors 1.5 times those of the parent C atoms. The ammonium and water H atoms were located and refined.

Data collection: *CAD*-4 *VAX/PC Fortran System* (Enraf–Nonius, 1988). Cell refinement: *CAD*-4 *VAX/PC Fortran System*. Data reduction: *Xtal*3.0 (Hall & Stewart, 1990). Program(s) used to solve structure: *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). 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.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1017). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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An Octamethyldibenzotetraaza[14]annulene

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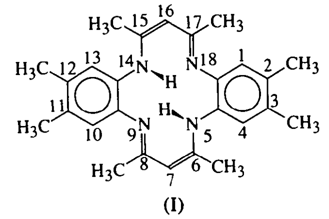
Abstract

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.

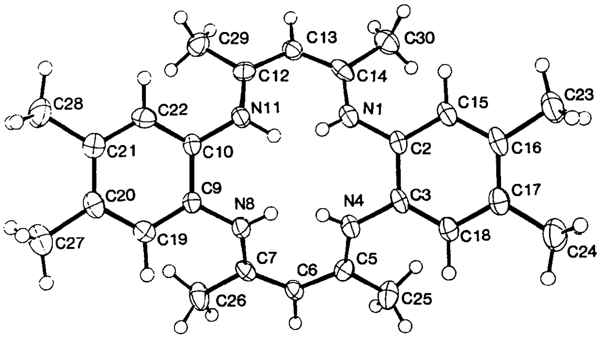


Fig. 1. *ORTEP*II (Johnson, 1976) projection of the molecule perpendicular to the plane of the N atoms showing the atomic numbering scheme used in the structure determination. Displacement ellipsoids are plotted at the 50% probability level. H atoms ate plotted with arbitrary radii.

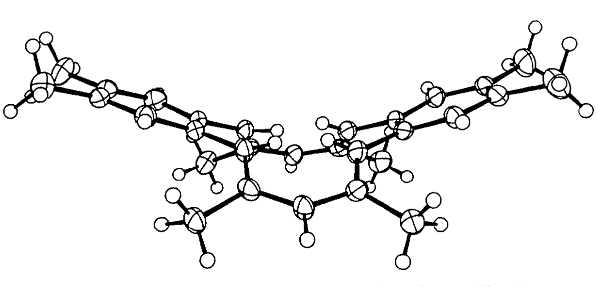


Fig. 2. Side view of the molecule showing the saddle shape.