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Tris[2-(benzoylamino)ethyl]amine

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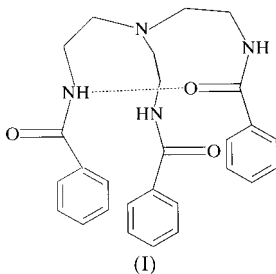
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Tris[2-(benzoylamino)ethyl]amine [alternatively, *N,N',N''*-(nitrioltriethyl)tribenzamide], $C_{27}H_{30}N_4O_3$, adopts a folded structure, forming a symmetrical cavity with an average depth of 7.3 Å and width ranging from 4.1–4.4 Å. The folded structure is a result of one intramolecular N—H···O hydrogen bond. A linear chain motif along the *c* axis best describes the extended intermolecular N—H···O hydrogen bonding.

Comment

Compounds with amidate donor groups are useful for the stabilization of high valent metals. Additionally, tripodal type ligand structures are useful for enforcing trigonal pyramidal (or similar) geometry in metal complexes. Tris[2-(benzoylamino)ethyl]amine, (I), was synthesized as a tris-amidate tripodal amine-type ligand for the stabilization of high valent metal complexes with trigonal–pyramidal geometry.



The molecular structure of (I) is similar to the tripodal amine compounds, tris(3-aza-4-oxo-5-hydroxy-5-phenylpent-1-yl)amine, (II) (Byrne *et al.*, 1998), and tris[(4-diphenylphosphinobenzamido)ethyl]amine, (III) (Lang *et al.*, 1995). Compound (I) exhibits a folded structure due to the presence of an intramolecular N1···O2 hydrogen bond. When (I) is viewed down the molecule towards N4, one observes a symmetrical cavity with an average depth of 7.3 Å (distance from N4 to *p*-phenyl C atoms) with closest N···N contact distances between the three arms of 4.1–4.4 Å. This may lead to a restriction in reactivity or solvent accessibility within the

cavity since upon metallation of the ligand it is presumed that the three donor arms fold down into the expected tripod motif thereby encapsulating the metal within the cavity.

The folded structure is also observed in (II) and (III), exhibiting one or two intramolecular hydrogen bonds. A symmetrical cavity is observed for (III) (N···P distances of approximately 8.8 Å and closest N···N contact distances between the arms ranging 4.2–4.6 Å). On the other hand, an asymmetrical cavity is observed for (II) due to the presence of the two intramolecular hydrogen bonds ‘pulling back’ the arms which would possibly allow for greater accessibility into the cavity.

In contrast, an extended structure is observed for [*N*-(1-propan-2-one oxime)]bis[*N*-2-(*N',N''*-trimethylacetyl)aminoethyl]amine, (IV) (Goldcamp *et al.*, 2000), and tris[*N*-(*S*)-(–)-(α -methylbenzylcarbamoylmethyl)amine, (IV) (Hammes *et al.*, 1998), which is attributed to the lack of intramolecular hydrogen bonding. This extended structure allows for easy access for metal and solvent interactions.

In addition to the intramolecular hydrogen bond, (I) participates in two intermolecular N—H···O hydrogen bonds (N2···O3 and N3···O1) forming linear chains along the *c* axis.

Experimental

The synthesis of (I) and related tripodal amines were first described by Valiyaveetil *et al.* (1993) starting from tris(aminoethyl)amine and reacting it with the appropriate acid chloride in the presence of triethylamine. An alternate route to the preparation of (I) is described here. To a solution of tris(2-aminoethyl)amine (1.00 g, 6.84 mmol) in chloroform (20 ml) at 273 K was added a solution of benzoic anhydride (4.80 g, 21.2 mmol) in chloroform (20 ml). The reaction was stirred for 3 h and the temperature was allowed to gradually increase to room temperature. The solvent was then removed by rotary evaporation, leaving a yellow coloured oil. This oil was washed with four 20 ml portions of diethyl ether until an off-white solid was obtained, which was then filtered to yield (I) (2.97 g, 6.48 mmol, 95% yield). Crystals suitable for diffraction were obtained from DMF–acetone. ^1H NMR (250 MHz, d_6 -DMSO): 2.73 (*t*, 6H), 3.48 (*q*, 6H), 7.36–7.49 (*m*, 9H), 7.81 (*d*, 6H), 8.37 (*t*, 3H) p.p.m. IR (CH_2Cl_2): 3349 (*w*), 3325 (*m*, *br*), 3056 (*w*), 2947 (*w*), 2824 (*m*), 1650 (*s*), 1529 (*s*), 1296 (*m*), 1165 (*w*), 1072 (*w*) cm^{-1} . M.p. 419–421 K.

Crystal data

$C_{27}H_{30}N_4O_3$	$D_x = 1.250 \text{ Mg m}^{-3}$
$M_r = 458.55$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 40 reflections
$a = 10.004$ (2) Å	
$b = 17.151$ (4) Å	$\theta = 5\text{--}15^\circ$
$c = 14.472$ (3) Å	$\mu = 0.083 \text{ mm}^{-1}$
$\beta = 101.06$ (2)°	$T = 293$ (2) K
$V = 2437.0$ (9) Å ³	Block, colourless
$Z = 4$	$0.40 \times 0.40 \times 0.20 \text{ mm}$

Data collection

Siemens P3 diffractometer	$h = 0 \rightarrow 13$
θ – 2θ scans	$k = 0 \rightarrow 22$
5938 measured reflections	$l = -18 \rightarrow 18$
5625 independent reflections	3 standard reflections
2590 reflections with $I > 2\sigma(I)$	every 300 reflections
$R_{\text{int}} = 0.030$	intensity decay: none
$\theta_{\text{max}} = 27.56^\circ$	

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.059$
 $wR(F^2) = 0.165$
 $S = 1.004$
 4975 reflections
 307 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0605P)^2 + 0.5052P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = -0.001$
 $\Delta\rho_{\max} = 0.16 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

O1—C3	1.231 (3)	N4—C1	1.465 (3)
O2—C12	1.239 (3)	N4—C10	1.467 (3)
O3—C21	1.228 (3)	C1—C2	1.517 (4)
N1—C3	1.331 (3)	C3—C4	1.489 (4)
N1—C2	1.444 (3)	C4—C9	1.377 (4)
N2—C12	1.339 (3)	C10—C11	1.513 (4)
N2—C11	1.443 (3)	C12—C13	1.492 (4)
N3—C21	1.333 (3)	C19—C20	1.510 (4)
N3—C20	1.444 (4)	C21—C22	1.492 (4)
N4—C19	1.458 (3)		
C3—N1—C2	122.9 (2)	N4—C10—C11	114.2 (2)
C12—N2—C11	122.6 (2)	N2—C11—C10	113.9 (2)
C21—N3—C20	123.5 (2)	O2—C12—N2	121.6 (3)
C19—N4—C1	111.0 (2)	O2—C12—C13	120.7 (3)
C19—N4—C10	110.5 (2)	N2—C12—C13	117.6 (2)
C1—N4—C10	110.1 (2)	N4—C19—C20	114.4 (2)
N4—C1—C2	114.0 (2)	N3—C20—C19	113.2 (2)
N1—C2—C1	109.9 (2)	O3—C21—N3	121.5 (3)
O1—C3—N1	122.0 (3)	O3—C21—C22	120.6 (3)
O1—C3—C4	121.7 (2)	N3—C21—C22	117.9 (2)
N1—C3—C4	116.3 (2)		

Table 2

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots O2	0.86	2.16	2.932 (3)	150
N2—H2 \cdots O3 ⁱ	0.86	2.15	2.896 (3)	145
N3—H3 \cdots O1 ⁱⁱ	0.86	2.13	2.950 (3)	160

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

The H-atom positions were either located directly or calculated based on geometric criterion and allowed to ride on their respective atoms. H-atom U values were assigned as $1.2U_{\text{eq}}$ of the parent atom.

Data collection: *P3-P4/PC* (Siemens, 1989); cell refinement: *P3-P4/PC*; data reduction: *XDISK* (Siemens, 1989); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994); program(s) used to refine structure: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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