

Nitrilotriacetanilide

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Key indicators

Single-crystal X-ray study

$T = 91$ K

Mean $\sigma(\text{C}-\text{C}) = 0.006$ Å

R factor = 0.067

wR factor = 0.239

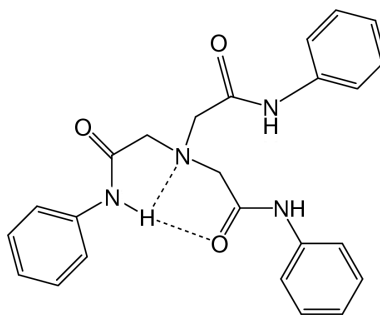
Data-to-parameter ratio = 31.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The crystal structure of the title compound, $\text{C}_{24}\text{H}_{24}\text{N}_4\text{O}_3$, is dominated by one bifurcated intramolecular and two intermolecular hydrogen bonds. This demonstrates the flexible nature of the organic molecule and the strong tendency of carboxamide groups to form hydrogen bonds.

Comment

The synthesis of new tripodal ligands with amidate groups that are based upon the tris(2-aminoethyl)amine unit has received attention in recent years due to their ability to complex M^{n+} ions (Macbeth *et al.*, 2000). Incorporation of amidate linkages within a tripodal ligand has also been utilized to develop tris-catecholate enterobactin analogs (Cohen & Raymond, 2000). In addition, a variety of ligands designed to stabilize anion coordination are based in part on tripodal frames and utilize hydrogen-bond networks from amido groups to stabilize the ligand-anion interaction (Schmidtchen, 1997). The common synthetic route of coupling carboxylic acid groups with primary amines *via* the use of triphenyl phosphite has been utilized here to afford the title compound, (I), in high yield.



(I)

The molecular structure of (I) is presented in Fig. 1. The three tripodal arms of the ligand are extended, in spite of the intramolecular hydrogen bonding involving the amide N1—H1 group and both N4 and O3. Additional hydrogen bonding is depicted in Fig. 2. The amide N3—H3 group forms a centrosymmetrically related pair of hydrogen bonds between H3 and O2'. The amide N2—H2 group hydrogen bonds to O1'' in a molecule translated along a .

It is interesting to note that the similar molecule tris[2-(benzoylamino)ethyl]amine, (II), has recently been reported (Goldcamp *et al.*, 2000). In its structure, the molecule adopts a folded conformation that contrasts with the extended arrangement of (I) (Fig. 3). It also has an intramolecular hydrogen bond between a carboxamido N—H group of one arm of the tripodal ligand and a carbonyl O atom of a second

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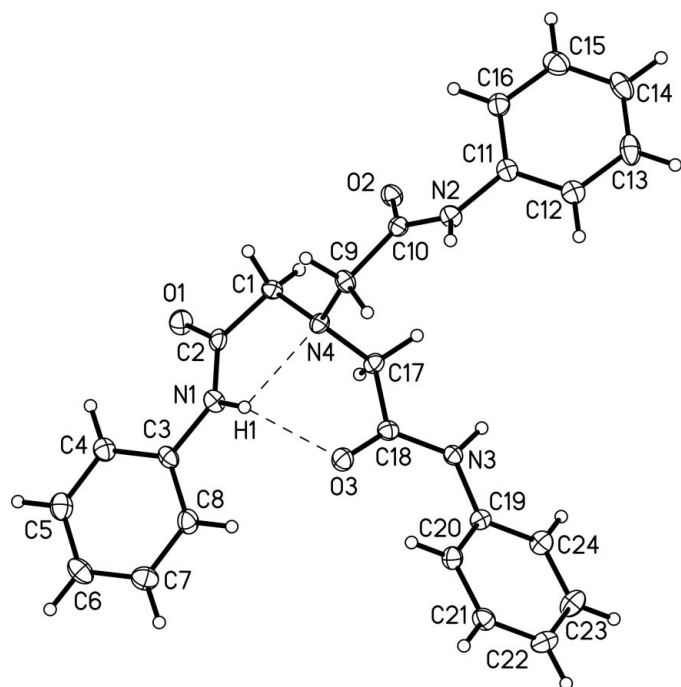


Figure 1
The molecular structure of (I) showing the atom-labeling scheme. Displacement ellipsoids are shown at the 50% probability level.

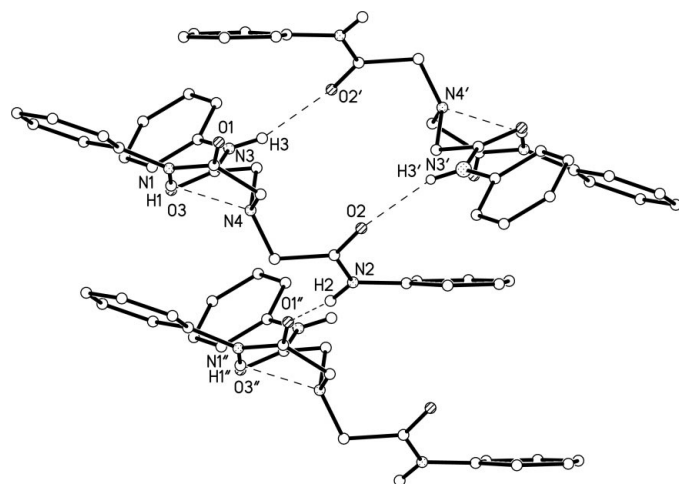


Figure 2
A view of the hydrogen-bonding scheme.

carboxamide group. The difference in the tripodal unit of (II) compared to (I) is a simple rearrangement of the carboxamide units. Compound (II) is obtained from the reaction between tris(2-aminoethyl)amine and benzoic acid, while (I) is synthesized from nitrilotriacetic acid and aniline. The comparable intramolecular N—H...O hydrogen bond is part of an eight-membered ring in (I), while it is a ten-membered ring in (II). This slight change appears to have a profound effect on the structure of the resulting molecule, although other crystal-packing effects probably play a role. However, this may have implications in the development of molecular motifs that are specifically designed to stabilize a pre-formed molecular structure.

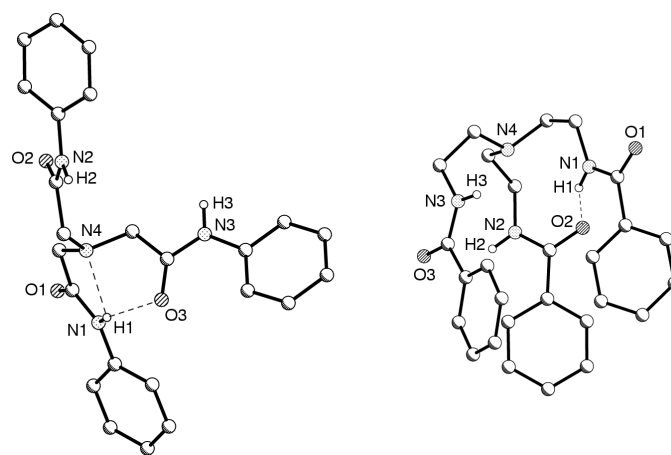


Figure 3
A comparison of the relatively extended structure of (I) on the left with the more folded structure of tris[2-(benzoylamino)ethyl]amine (II) on the right (Goldcamp *et al.*, 2000).

Experimental

The title compound, (I), was synthesized *via* the coupling reaction of nitrilotriacetic acid and aniline in the presence of triphenyl phosphite using pyridine as the solvent. A mixture of 3.04 g of nitrilotriacetic acid (15.9 mmol), 4.44 g of aniline (47.7 mmol) and 14.81 g of triphenyl phosphite (47.7 mmol) in 25 ml of pyridine was heated to reflux for 4 h. The solvent was then removed and a viscous brown oil remained. The resulting oil was dissolved in chloroform and the solution was washed with small batches (3 × 10 ml) of water. Pure (I) was obtained as a white powder following removal of the chloroform solvent. Crystals of (I) were produced by diffusion of methanol into the DMSO solution (yield 70%).

Crystal data

$C_{24}H_{24}N_4O_3$
 $M_r = 416.47$
 Triclinic, $P\bar{1}$
 $a = 8.411$ (2) Å
 $b = 8.819$ (2) Å
 $c = 14.886$ (4) Å
 $\alpha = 84.684$ (6)°
 $\beta = 82.425$ (6)°
 $\gamma = 68.439$ (6)°
 $V = 1016.7$ (4) Å³

$Z = 2$
 $D_x = 1.360$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 999 reflections
 $\theta = 2.5$ – 31.1 °
 $\mu = 0.09$ mm⁻¹
 $T = 91$ (2) K
 Plate, colorless
 $0.48 \times 0.28 \times 0.04$ mm

Data collection

Bruker SMART 1000 diffractometer
 ω scans
 7955, 7827 measured reflections (two components)
 8879 independent reflections

6786 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.060$
 $\theta_{max} = 30.5$ °
 $h = -11 \rightarrow 11$
 $k = -12 \rightarrow 12$
 $l = -20 \rightarrow 21$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.067$
 $wR(F^2) = 0.239$
 $S = 1.23$
 8879 reflections
 281 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0619P)^2 + 3.3081P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.59$ e Å⁻³
 $\Delta\rho_{min} = -0.47$ e Å⁻³

Table 1
Selected bond lengths (Å).

O1—C2	1.233 (4)	N2—C11	1.422 (5)
O2—C10	1.234 (4)	N3—C18	1.357 (5)
O3—C18	1.225 (4)	N3—C19	1.419 (5)
N1—C2	1.345 (5)	N4—C9	1.451 (5)
N1—C3	1.421 (5)	N4—C1	1.457 (4)
N2—C10	1.351 (5)	N4—C17	1.462 (4)

Table 2
Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N3—H3...O2 ⁱ	0.88	2.17	3.012 (4)	161
N2—H2...O1 ⁱⁱ	0.88	2.00	2.830 (4)	158
N1—H1...O3	0.88	2.35	3.153 (4)	153
N1—H1...N4	0.88	2.18	2.665 (5)	114

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

The compound crystallizes as well formed plates which all appear to suffer from twinning no matter what solvent is used. A full sphere of data was collected in the normal way. The structure could be solved from the data that were culled from a good orientation matrix; however it was clear that many of the data were being discarded. The initial model yielded a value of $R1 = 0.174$ with 4156 reflections [$F_o > 4\sigma(F_o)$]. Subsequently, the existence of rotationally related twin components (a 180° rotation about [001]) was confirmed using the program *GEMINI* (Bruker, 1999). Integration was performed separately on the two components. Several methods of combining the two sets of reflection data were tried. For example, 6476 observed data, including partially overlapped reflections, yielded a $R1$ value of 0.103. With partials omitted, a value of $R1 = 0.056$ was obtained, but this resulted in only 1452 observed data and a rather low data-to-parameter ratio; nevertheless the refinement was quite stable. Finally, the data were integrated at Bruker AXS Inc. using a beta test version of *SAINTE* (Bruker, 2001), modified to handle multi-component integration. *SAINTE* processes the data simultaneously, determining

profile shapes, updating matrices independently. If spots start to overlap *SAINTE* will combine the overlapping integration boxes and do a simple summation. *SAINTE* will not use overlapping reflections for matrix refinement or statistics. The results of this integration are the results being reported because the number of data (8879 unique, 6786 observed) obtained is superior. The minor twin component is 0.357 (2). Cell parameters are based on the reflections of the major component. Although the completeness is only 82% at the θ_{\max} of 30.5° , it is 97% complete at θ of 30.0° .

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2001); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL97*.

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