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2,2′-Diaminodibenzyl: a rare case of crystallographically non-compliant molecular symmetry

R. S. Narasegowda,[a] S. M. Malathy Sony,[b] S. Mondal,[c] B. Nagaraj,[a] H. S. Yathirajan,[a] T. Narasimhamurthy,[c] P. Charles,[b] M. N. Ponnuswamy,[b] M. Nethaji[d] and R. S. Rathore[e]*

[a]Department of Studies in Chemistry, University of Mysore, Manasagangotri, Mysore 570 006, India, [b]Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Chennai 600 025, India, [c]Bioinformatics Centre, Indian Institute of Science, Bangalore 560 012, India, [d]Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India, and [e]Oriental Organisation of Molecular and Structural Biology, 204 Agarwal Bhavan, Malleshwaram, Bangalore 560 055, India

Correspondence e-mail: ravindranath_rathore@yahoo.com

Key indicators

Single-crystal X-ray study
T = 292 K
Mean σ(C–C) = 0.003 Å
R factor = 0.040
wR factor = 0.103
Data-to-parameter ratio = 9.0

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

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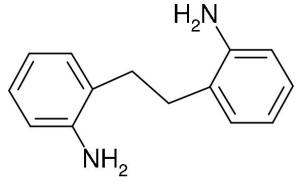
The title compound, $C_{14}H_{16}N_2$, adopts a *trans*-planar conformation. However, the molecule, which possesses C_i point group symmetry, crystallizes in the non-centrosymmetric space group $P2_12_12_1$. In the crystal structure, the molecular symmetry is only approximately retained. The crystal packing is predominantly stabilized by N—H···N hydrogen bonds. Weak C—H···π interactions also contribute to the stability.

Comment

Investigations of the present structure were carried out independently by two groups, MNP (authors MNP, SMMS, PC and MN) and RSR (authors RSR, RSN, SM, BN, HSY and TN). Papers from the two groups were submitted to this journal within days of each other. Since the results of the two studies were very similar, the authors were requested to produce a joint paper. The amalgamated report is presented here.



(I)

Among organic molecules there is a tendency for molecular symmetry to be retained in the crystal symmetry. Non-retention of molecular symmetry (*i.e.* complete lack of symmetry or the presence of non-crystallographic symmetry) is usually regarded as a consequence of dominant strong intermolecular forces. After seminal work by Kitaigorodskii (1961), which proposed that crystal symmetry is the outcome of the aim of achieving close-packed structures, many attempts have been made to correlate molecular and crystal symmetry (Yao *et al.*, 2002, and references cited therein). Recent work (Pidcock *et*

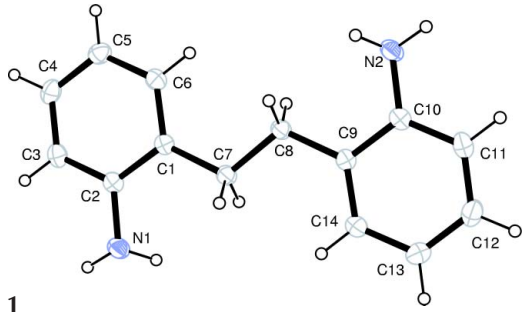


Figure 1
A view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Color key: C black, H white and N blue.

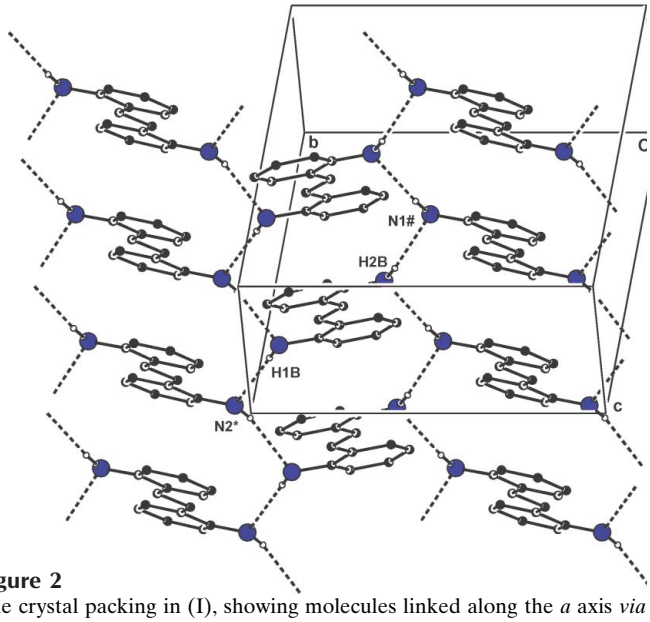


Figure 2
The crystal packing in (I), showing molecules linked along the *a* axis *via* N—H···N hydrogen bonds (dashed lines). Atoms labelled with an asterisk (*) or hash symbol (#) are at the symmetry positions ($-x$, $y+\frac{1}{2}$, $\frac{3}{2}-z$) and ($1-x$, $y-\frac{1}{2}$, $\frac{3}{2}-z$), respectively. Color key: C black, H white and N blue.

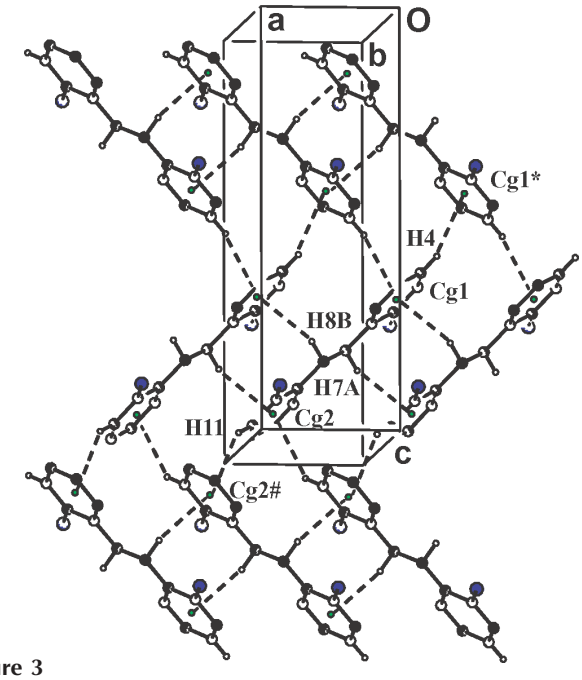


Figure 3
A view of the crystal packing in (I), showing molecules in the (040) plane, interconnected by C—H···π interactions (dashed lines). Atoms labelled with an asterisk (*) or hash symbol (#) are at the symmetry positions ($x-\frac{1}{2}$, $\frac{3}{2}-y$, $1-z$) and ($x+\frac{1}{2}$, $\frac{3}{2}-y$, $2-z$), respectively. *Cg*1 and *Cg*2 (shown in green) are the centroids of rings C1–C6 and C9–C14, respectively.

al., 2003) has led to the conclusion that the inversion centre (C_i point group symmetry) is conserved in over 99% of cases. Higher molecular symmetries are retained in the crystal structure to a lesser extent. The present example of 2,2′-diaminodibenzyl, (I), which possesses an inversion centre at the mid-point of the ethylene bridge, is a case where the molecular symmetry is only approximately conserved as pseudosymmetry in the noncentrosymmetric space group, $P2_12_12_1$.

The title compound is an intermediate in the syntheses of the anticonvulsant and antidepressant drugs carbamazepine, imipramine and desipramine (Yathirajan *et al.*, 2004).

The molecular structure of (I), which is planar, is shown in Fig. 1. Bond lengths and angles are unexceptional. The maximum deviation from the least-squares plane through all C, N and aromatic H atoms is 0.05 (1) Å for atom N1. The N1 amino group is inclined at an angle of 49 (1)° to the C1–C6 ring, and the N2 amino group is inclined at 43 (1)° to the C9–C14 ring. A similar observation was also found in the related structure, 2,2′-dinitrodibenzyl (Yathirajan *et al.*, 2004). The torsion angles describing the molecular conformation are as follows: C2—C1—C7—C8 = 179.1 (2)°, C7—C8—C9—C10 = −179.6 (1)°, C1—C7—C8—C9 = −179.6 (2)°, C9—C10—N2—H2*A* = 39 (2)°, C1—C2—N1—H1*A* = −43 (2)°, C9—C10—N2—H2*B* = 168 (2)° and C1—C2—N1—H1*B* = −168 (2)°.

The r.m.s. deviation between all atoms related by the pseudo-inversion centre is 0.23 Å; if the H atoms attached to N1 and N2 are excluded this value is reduced to 0.02 Å. The maximum difference between corresponding torsion angles is 4° for C9—C10—N2—H2*A* and C1—C2—N1—H1*A*.

The geometric parameters for the intermolecular interactions in (I) are listed in Table 1. The crystal structure is stabilized primarily by N—H···N hydrogen bonds and weak C—H···π interactions. The hydrogen bonds N1—H1*B*···N2 and N2—H2*B*···N1 interlink molecules along the *a* axis, as shown in Fig. 2. Atoms C7 and C8 of the ethylene bridge form C—H···π interactions with rings C9–C14 and C1–C6, on either side of the molecular plane. Significant C—H···π interactions are also observed for C4—H4···*Cg*1 (*Cg*1 is the centroid of the C1–C6 ring) and C11—H11···*Cg*2 (*Cg*2 is the centroid of the C9–C14 ring) (Table 1). The aromatic interactions in the crystal structure are illustrated in Fig. 3.

We have examined the structures of similar compounds reported in the Cambridge Structural Database (CSD, Version 5.26; Allen, 2002). All 15 compounds containing the dibenzyl moiety and possessing C_i point group symmetry have been reported in centrosymmetric space groups. For molecules possessing C_i symmetry, crystallization in non-centrosymmetric space groups is very uncommon. In an examination of the CSDSymmetry database, a derived database of the CSD for molecular and crystallographic symmetry (Pidcock *et al.*, 2003), out of 17 893 available compounds possessing C_i point group symmetry, 22 were found in the noncentrosymmetric space group $P2_12_12_1$, which is generally favoured for molecules possessing C_2 point group symmetry (Yao *et al.*, 2002). Inspection of these structures reveals that an overwhelming majority of them are metal-coordination compounds and involve a large number of strong intermolecular hydrogen bonds. They include, however, the case of *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (Ikemoto *et al.*, 1979), where the crystal packing is governed purely by van der Waals forces.

Experimental

The title compound was obtained from Max India Ltd. Crystals were grown by the slow-evaporation method, using both toluene and ethanol solvents. The data presented here correspond to a crystal obtained from toluene.

Crystal data

$C_{14}H_{16}N_2$
M_r = 212.29
Orthorhombic, $P2_12_12_1$
a = 5.4716 (4) Å
b = 12.480 (1) Å
c = 16.695 (1) Å
V = 1140.0 (2) Å^3
Z = 4
D_x = 1.237 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5764 reflections
θ = 5–54°
μ = 0.07 mm^{-1}
T = 292 (2) K
Block, colourless
0.51 × 0.24 × 0.15 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.97, T_{max} = 0.98
9109 measured reflections
1456 independent reflections
1344 reflections with $I > 2\sigma(I)$
R_{int} = 0.021
θ_{max} = 27.4°
$h = -7 \rightarrow 6$
$k = -16 \rightarrow 14$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.103
S = 1.11
1456 reflections
161 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0596P)^2 + 0.1255P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}
Extinction correction: none

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1B···N2^{i}	0.90 (2)	2.46 (2)	3.334 (2)	162 (2)
N2—H2B···N1^{ii}	0.88 (2)	2.45 (2)	3.255 (2)	153 (2)
C7—H7A···$Cg2^{iii}$	0.97	2.81	3.654 (2)	145
C8—H8B···$Cg1^{iv}$	0.97	2.78	3.624 (2)	147
C4—H4···$Cg1^{v}$	0.93	2.85	3.657 (2)	139
C11—H11···$Cg2^{vi}$	0.93	2.92	3.678 (2)	139

Symmetry codes: (i) $-x, y+\frac{1}{2}, \frac{3}{2}-z$; (ii) $1-x, y-\frac{1}{2}, \frac{3}{2}-z$; (iii) $x-1, y, z$; (iv) $x+1, y, z$; (v) $x-\frac{1}{2}, \frac{3}{2}-y, 1-z$; (vi) $x+\frac{1}{2}, \frac{3}{2}-y, 2-z$. $Cg1$ is the centroid of the C1–C6 ring and $Cg2$ is the centroid of the C9–C14 ring.

The aromatic and methylene H atoms were positioned geometrically and refined as riding on their carrier atoms, with C_{ar}—H = 0.93 Å, methylene C—H = 0.97 Å and U_{iso}(H) = 1.2U_{eq}(C). The H atoms attached to N were located in a difference electron-density map, and were refined isotropically; N—H distances are in the range 0.88 (2)–0.91 (2) Å. In the absence of significant anomalous dispersion effects, Friedel pairs were averaged.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PARST* (Nardelli, 1995).

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