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N,*N*′-Dimethyl-*N*,*N*′-diphenylethylenediamine

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The centrosymmetric title compound, $C_{16}H_{20}N_2$, was synthesized by deprotonation of *N*,*N*′-diphenylethylenediamine with *n*-BuLi in tetrahydrofuran. The coordination geometry around the N atoms is trigonal planar and the conformation about the ethane bond is staggered. The crystal structure displays intermolecular C—H$\cdots\pi$ interactions which give rise to infinite pleated layers extended in the *bc* plane. The possibility of obtaining an amine that can undergo crystallization-induced asymmetric transformation is discussed. This would enable the preparation of the pure enantiomers by absolute asymmetric synthesis.

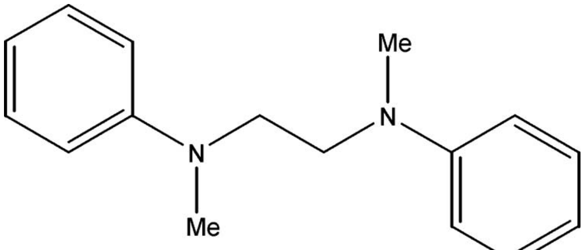
Key indicators

Single-crystal X-ray study
T = 291 K
Mean σ(C–C) = 0.003 Å
R factor = 0.055
wR factor = 0.155
Data-to-parameter ratio = 10.7

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

Comment

We recently reported the crystal structure of *N*,*N*′-diphenylethylenediamine (DPHEDA), which was found to crystallize in space group $P2_1/c$ (Lennartson, Kokoli & Håkansson, 2005). Furthermore, the compound was found to form a C—H$\cdots\pi$- and N—H$\cdots\pi$-bonded network in the solid state. In order to find an amine crystallizing in a Sohncke space group, we prepared the *N*,*N*′-dimethylated derivative *N*,*N*′-dimethyl-*N*,*N*′-diphenylethylenediamine, (I). This derivative was prepared by deprotonation of DPHEDA with *n*-BuLi in tetrahydrofuran (THF) solution at 195 K, followed by treatment with methyl iodide, yielding (I) as monoclinic crystals.



(I)

N atoms in amines having three different substituents are chirogenic, a fact that early gained considerable interest (van Ryn, 1897, and references therein), and the amine (I) displays two chirogenic N atoms in solution. Separation into pure enantiomers by common methods, such as enantioselective chromatography, is nevertheless virtually impossible due to the low inversion barrier of trivalent N atoms, resulting in a very high rate of enantiomerization in solution (Lambert, 1971). In principle, however, there will be one pair of enantiomers, and one *meso* form. If (I) were chiral in the solid state and crystallized in one of the Sohncke space groups (Flack, 2003), it would theoretically be possible to separate the pure enantiomers by means of crystallization-induced asymmetric

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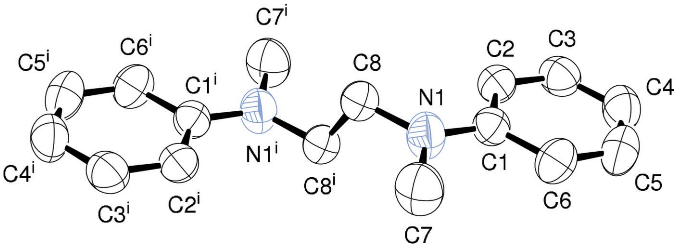

Figure 1
ORTEP3 plot (Farrugia, 1997) of (I), with the atom-numbering scheme. Displacement ellipsoids have been drawn at the 50% probability level. All H atoms have been omitted. [Symmetry code: (i) $-x, -y, -z$.]

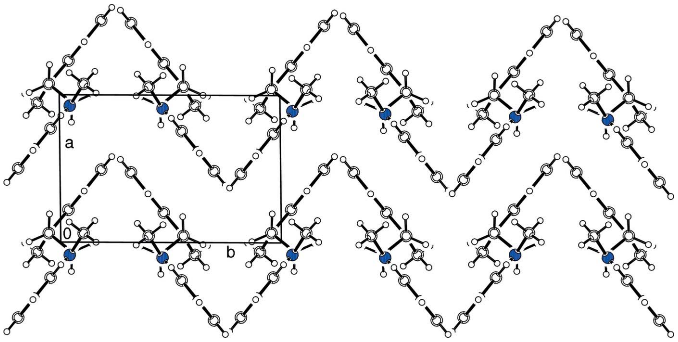

Figure 2
The pleated form of the layers, viewed in the direction of propagation of the pleats.

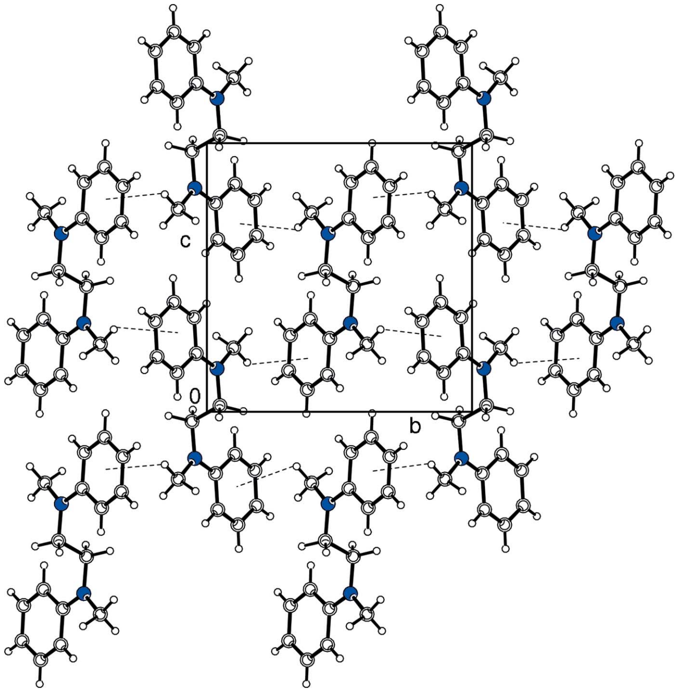

Figure 3
A layer, viewed along the *a* axis, with C—H$\cdots\pi$ interactions indicated by dashed lines.

transformation (Eliel *et al.*, 1994). Although this possibility was realised early (Behrend, 1890), such a resolution of an amine has, to the best of our knowledge, never been achieved, and would also be an example of absolute asymmetric synthesis (Bredig *et al.*, 1923; Feringa *et al.*, 1999; Lennartson, Vestergren & Håkansson, 2005; Vestergren *et al.*, 2003). Resolution of amines which have no other element of chirality than a chirogenic N atom is only known for some bulky tertiary ammonium salts, where the steric crowding around the N centre increases the inversion barrier dramatically (Pope *et al.*, 1899). Quaternary ammonium salts have also been subjected to total spontaneous resolution (Havinga, 1954; Kostyanovsky *et al.*, 2001). However, as in the case of DPHEDA, the coordination geometry around the N atoms in (I) was found to be approximately trigonal planar rather than pyramidal, atom N1 lying only 0.051 (2) Å out of the least-squares plane formed by atoms C1, C7 and C8, and thus the molecule is virtually achiral in the solid state, and the conformation about the ethane bond is perfectly staggered (Fig. 1). There is a crystallographic centre of symmetry at the mid-point of the ethane bond, C8—C8^{i} symmetry code as in Table 1). In contrast to DPHEDA, which forms a three-dimensional network, (I) displays infinite pleated layers extended in the *bc* plane (Fig. 2). The layers are formed by C—H$\cdots\pi$ interactions, which are known to often play a vital role in the formation of crystal structures (Nishio, 2004; Cantrill *et al.*, 2000; Braga *et al.*, 1998; Viswamitra *et al.*, 1993). These interactions involve the phenyl ring and H7A^{ii} [symmetry code: (ii) $-x, \frac{1}{2} + y, \frac{3}{2} - z$], which is directed approximately towards the centre of the ring system, the shortest distance being C4$\cdots$H7A^{ii}, which is 2.85 (2) Å. This means that each molecule interacts with four adjacent molecules in a layer (Fig. 3). There are no interactions within the sum of the van der Waals radii between adjacent layers.

Even though (I) was found to be achiral in the solid state, this does not necessarily mean that resolution is impossible. We are currently working on the preparation of complexes, using (I) as a chelating ligand, which may lead to a successful absolute asymmetric synthesis.

Experimental

The reaction was carried out under a nitrogen atmosphere using dry glassware. Commercial *N*,*N*′-diphenylethylenediamine (Merck), methyl iodide (Merck) and *n*-BuLi in hexane (Acros Organics) were used as received. THF was distilled from sodium/benzophenone shortly prior to use. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian Unity 400 MHz NMR spectrometer. *N*,*N*′-Diphenylethylenediamine (2.0 g, 9.4 mmol) was dissolved in THF (30 ml) and cooled to 195 K. *n*-BuLi (1.6 *M* in hexane, 6.0 ml, 9.6 mmol) was added dropwise at 195 K, followed by dropwise addition of methyl iodide (0.58 ml, 9.3 mmol). The solution was stirred at 195 K for 30 min, and at ambient temperature for 1 h. This procedure was repeated by cooling to 195 K, adding a second equivalent of n-BuLi and subsequently a second equivalent of methyl iodide. After stirring (30 min at 195 K and 1 h at ambient temperature), the reaction was quenched with saturated aqueous NH_4Cl (3 ml). The reaction mixture was extracted with diethyl ether (3 × 10 ml), and the combined ethereal solutions were dried over Na_2SO_4 and evaporated to give an oil. Ethanol (10 ml) was added and the solution was cooled to 253 K overnight, whereupon needles were formed. The mother liquor was filtered off and the crystals washed with cold ethanol to give brown–white needles, which were recrystallized from hot hexane (yield: 1.2 g, 55%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.96 (*s*, 6H, CH$_3$), 3.56 (*s*, 4H, CH$_2$), 6.74 (*m*, 3H, Ph), 7.27 (*m*, 2H, Ph). ^{13}C NMR (100 MHz, CDCl$_3$): δ 30.4 (CH$_3$), 39.0 (CH$_2$), 112 (Ph), 116.6 (Ph), 129.6 (Ph). Single crystals suitable for X-ray analysis were obtained by dissolving the amine (0.2 g) in *n*-hexane (3 ml). Toluene (5 drops) was added and the solution was heated to reflux for a few s. Slow evaporation of the solvent over several days afforded crystals suitable for single-crystal X-ray diffraction analysis.

Crystal data

$C_{16}H_{20}N_2$
$M_r = 240.34$
Monoclinic, $P2_1/c$
$a = 6.374\ (2)$ Å
$b = 10.302\ (4)$ Å
$c = 10.447\ (4)$ Å
$\beta = 91.428\ (14)^\circ$
$V = 685.8\ (4)$ Å^3
$Z = 2$
$D_m = ?$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4655 reflections
$\theta = 2.8\text{–}26^\circ$
$\mu = 0.07$ mm^{-1}
$T = 291\ (2)$ K
Block, light yellow
$0.4 \times 0.4 \times 0.4$ mm

Data collection

Rigaku R-AXIS IIC image-plate system diffractometer
φ scans
Absorption correction: none
4655 measured reflections
1307 independent reflections
987 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.073$
$\theta_{\rm max} = 26.0^\circ$
$h = -7 \rightarrow 7$
$k = -12 \rightarrow 12$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.155$
$S = 1.05$
1307 reflections
122 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.088P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.13$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.12$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—N1	1.3746 (19)	C4—C5	1.359 (3)
C1—C2	1.391 (2)	C5—C6	1.373 (3)
C1—C6	1.397 (2)	C7—N1	1.438 (2)
C2—C3	1.374 (2)	C8—N1	1.441 (2)
C3—C4	1.369 (3)	C8—C8$^{\rm i}$	1.514 (3)
C1—N1—C7	120.25 (14)	C7—N1—C8	117.47 (15)
C1—N1—C8	121.89 (14)		

Symmetry code: (i) $-x, -y+2, -z+2$.

Coordinates and $U_{\rm iso}$ values were refined for all H atoms without constraints in order to avoid a biased hydrogen-bonding scheme.

Data collection: *CRYSTALCLEAR* (Rigaku, 2000); cell refinement: *CRYSTALCLEAR*; data reduction: *CRYSTALCLEAR*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* (Farrugia, 1997) and *PLUTON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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