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(Anthracen-9-ylmethyl)dimethylamine at 120 K

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.003 Å
R factor = 0.055
wR factor = 0.140
Data-to-parameter ratio = 18.3

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

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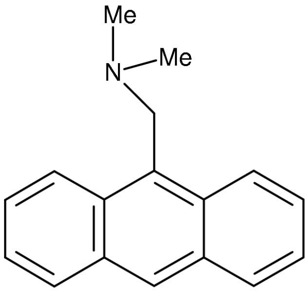
In the structure of the title compound, $C_{17}H_{17}N$, the two molecules in the asymmetric unit are confined to distinct layers, one for each type of molecule. The layers differ in the orientation, relative to the edges of the unit cell, of the molecules within them.

Comment

The determination of the structure of the title compound, (I), reported here, follows on from the recent report of the structure of (anthracen-9-ylmethyl)diethylamine, (II) (Howie *et al.*, 2005). Compound (I) was unexpectedly isolated from a reaction mixture of 9-(chloromethyl)anthracene and 1,4,8,11-tetraazacyclotetradecane (cyclam) in *N*,*N*-dimethylformamide (DMF). Clearly, DMF had acted as a dimethylaminating reagent in the preparation of (I). There are scattered reports in the literature of DMF acting as a dimethylaminating agent in reactions with organic halides, activated for nucleophilic attack. Some examples include reactions with haloheteroarenes, such as chloropyridazines (Lee, Yoon & Kim, 2000) and bromopyridines (Watanabe *et al.*, 1980), acyl chlorides (Lee, Park & Yoon, 2000; Knunyants *et al.*, 1966), and (chloromethyl)arenes (Min'kov & Kravtsov, 1976). Subsequently, (I) was synthesized successfully by the reaction of 9-(chloromethyl)anthracene with excess Me_2NH in CH_2Cl_2 with a procedure similar to that used for (II) (Howie *et al.*, 2005), except that triethylamine was not added to the reaction mixture. The title compound has also been reported as the product of the Leuckart reaction between 9-anthracenecarboxaldehyde and DMF in 90% formic acid (Marcus & Fitzpatrick, 1959).



(I)

The asymmetric unit of (I) contains two molecules, which have been labelled in an identical manner (Fig. 1) and are distinguished by suffixes *A* and *B*. Leaving aside the difference in methyl and ethyl N-substituents, the molecular geometries of the molecules *A* and *B* of (I) and the molecule of (II) are, as would be expected, virtually identical. For the molecules of

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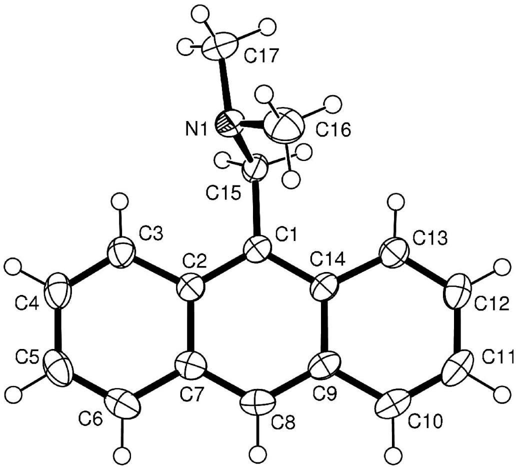

Figure 1
Molecule *A* of (I), showing the labelling scheme used for both molecules. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small circles of arbitrary radii.

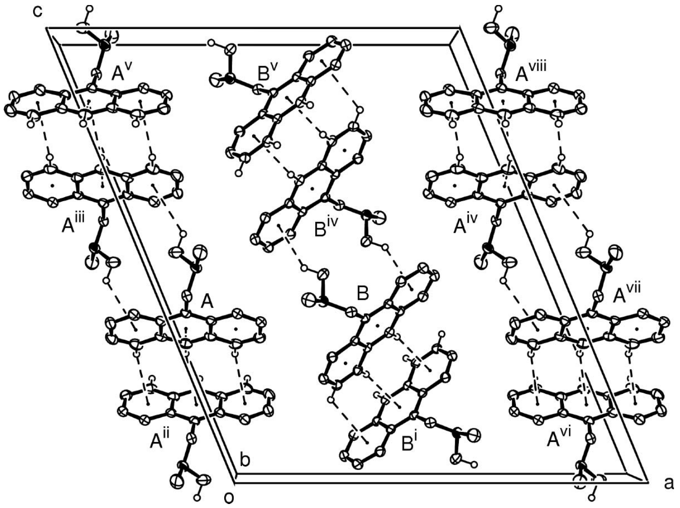

Figure 2
A view of the unit cell contents of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms involved in C—H$\cdots\pi$ interactions (dashed lines) are shown as small circles of arbitrary radii. Labels indicate molecule type. [Symmetry codes: (i) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $-x, 1 - y, 1 - z$; (iv) $1 - x, 1 - y, 1 - z$; (v) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (vi) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (vii) $1 + x, y, z$; (viii) $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$.]

(I), the C—N distances and the C—N—C angles lie in the ranges 1.454 (3)–1.470 (2) Å and 109.43 (14)–111.58 (14)°, respectively; the C—C bond lengths and internal angles of the essentially planar anthracene ring systems (r.m.s. displacements for the atoms C1–C14 defining them of 0.0263 and 0.0376 Å) are in the ranges 1.352 (3)–1.446 (2) Å and 116.91 (15)–123.56 (16)°, respectively, and, finally, the C1—C15 bond length is 1.512 (2) Å in both molecules. It is noticeable that the pairs of values, one from each of the molecules in the bimolecular asymmetric unit from which the limiting values in the ranges given above are selected, always have the same designations, *e.g.* C5—C6 is the shortest bond in the anthracene ring system for both molecules. This fact provides a crude indication of the close similarity of the molecular geometries, as well as confirming the conformity of the labelling scheme as applied to the two molecules. As shown by the torsion angles given in Table 1, the representative molecules *A* and *B* of the asymmetric unit of (I) are enantiomers. This arises purely from the choice of molecules because the centrosymmetric space group requires that the structure be completely racemic. In (I), the displacements of the atoms of the methylamine substituent from the least-squares plane defined by C1–C14, with the values for molecule *B* in square brackets, are 0.033 (2) [0.024 (2)], 2.387 (2) [2.383 (2)], 1.201 (4) [1.067 (3)] and 1.322 (2) Å [1.257 (2) Å], respectively for the atoms in the order C15, C16, C17 and N1, and are very similar to the displacements of the corresponding atoms in the molecule of (II). The anthracene moieties of molecules *A* and *B* of (I), as is the case for the molecule of (II), are in fact very slightly U shaped, as shown by the dihedral angles between the outer and inner rings, which are in the range 1.38 (10)–2.30 (10)°. Molecules *A* and *B* of (I) are found in separate layers parallel to (100), which differ (Fig. 2) in the orientation of the molecules within the unit cell. As a consequence, the type *A* and type *B* molecules differ slightly in the C—H$\cdots\pi$ intermolecular interactions (see later) in which they participate. For the choice of origin used in the refinement of the structure, the layers of type *A* molecules are centred on x = 0 and 1 and alternate with layers of type *B* molecules at $x = \frac{1}{2}$. Contacts between the molecules take the form of the C—H$\cdots\pi$ interactions given in Table 2 and occur entirely within the layers, as shown for type *A* molecules in Fig. 3. The connectivity within the layers in (I) is identical in form to that observed in (II). However, in comparing (I) and (II), the cell edges *b* and *c* are interchanged in length, as is the orientation of the molecules and therefore of the intermolecular connectivity within the layers relative to the symmetry elements of the space group $P2_1/c$, which is common to both structures. Moreover, in (II), neighbouring layers are related by cell translation in the direction of *a*, whereas in (I) they are not, and the cell edge *a* is therefore doubled in (I) compared with (II). Overall, the structures of (I) and (II) are closely related but the compounds are not isostructural.

Experimental

A solution of 9-chloromethylanthracene and cyclam (each 2 mmol) in dry DMF (20 ml) was refluxed for 6 h. Much of the solvent was then removed under high vacuum and the residue was chromatographed on a silica column, using as eluant hexane/ethyl acetate (ethyl acetate increasing from 5 to 100%). The pure title compound was obtained from intermediate fractions and was recrystallized from EtOH (m. p. 348–350 K).

Crystal data

$C_{17}H_{17}N$
M_r = 235.32
Monoclinic, $P2_1/c$
a = 19.6924 (4) Å
b = 6.2383 (1) Å
c = 23.4415 (7) Å
β = 112.4743 (10)°
V = 2661.01 (11) Å^3
Z = 8

D_x = 1.175 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 28 370 reflections
θ = 2.9–27.5°
μ = 0.07 mm^{-1}
T = 120 (2) K
Plate, pale yellow
0.36 × 0.16 × 0.08 mm

Data collection

Enraf–Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{\min} = 0.936$, $T_{\max} = 0.995$
28 370 measured reflections
6034 independent reflections
3938 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.085$
$\theta_{\max} = 27.5°$
$h = -23 \rightarrow 25$
$k = -7 \rightarrow 8$
$l = -30 \rightarrow 30$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.140$
$S = 1.03$
6034 reflections
329 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.062P)^2 + 0.4189P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.18$ e Å^{-3}
$\Delta\rho_{\min} = -0.22$ e Å^{-3}

Table 1
Selected torsion angles (°).

C2*A*—C1*A*—C15*A*—N1*A*	71.54 (19)
C2*B*—C1*B*—C15*B*—N1*B*	−68.23 (19)
C14*A*—C1*A*—C15*A*—N1*A*	−109.24 (17)
C14*B*—C1*B*—C15*B*—N1*B*	114.10 (16)
C1*A*—C15*A*—N1*A*—C16*A*	65.22 (19)
C1*B*—C15*B*—N1*B*—C16*B*	−66.82 (18)
C1*A*—C15*A*—N1*A*—C17*A*	−172.65 (15)
C1*B*—C15*B*—N1*B*—C17*B*	170.50 (14)

Table 2
Geometry (Å, °) of the C—H···π contacts in (I).

C—H···*Cg*^{a}	H···*Cg*	H^b_{perp}	γ^c	C—H···*Cg*	C···*Cg*
C5*B*—H5*B*···*Cg*6$^{\text{i}}$	3.114	3.087	8	125	3.745
C6*A*—H6*A*···*Cg*5$^{\text{ii}}$	2.726	2.645	14	139	3.501
C6*B*—H6*B*···*Cg*2$^{\text{i}}$	2.537	2.480	12	138	3.306
C8*A*—H8*A*···*Cg*1$^{\text{ii}}$	2.879	2.819	12	144	3.688
C8*B*—H8*B*···*Cg*4$^{\text{i}}$	2.858	2.858	1	148	3.701
C10*A*—H10*A*···*Cg*3$^{\text{ii}}$	2.933	2.884	10	147	3.763
C16*A*—H16*A*···*Cg*5$^{\text{iii}}$	3.176	2.850	26	128	3.861
C16*B*—H16*D*···*Cg*6$^{\text{iv}}$	2.734	2.687	11	137	3.516

Notes: (*a*) *Cgn*, *n* = 1–6, are the centroids of the rings C1*A*/C2*A*/C7*A*–C9*A*/C14*A*, C1*B*/C2*B*/C7*B*–C9*B*/C14*B*, C2*A*–C7*A*, C2*B*–C7*B*, C9*A*–C14*A* and C9*B*–C14*B*, respectively; (*b*) H_{perp} is the perpendicular distance of the H atom from the mean plane of the ring; (*c*) γ is the angle at the H atom between H···*Cg* and H_{perp}. Symmetry codes: (i) $1-x, 1/2+y, 1/2-z$; (ii) $-x, 1/2+y, 1/2-z$; (iii) $-x, 1-y, 1-z$; (iv) $1-x, 1-y, 1-z$.

In the final stages of refinement, H atoms were placed in calculated positions, with C—H = 0.95, 0.98 and 0.99 Å for aryl, methyl and methylene H atoms, respectively, and refined with a riding model with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ otherwise. The rotational orientation of the methyl groups was also refined.

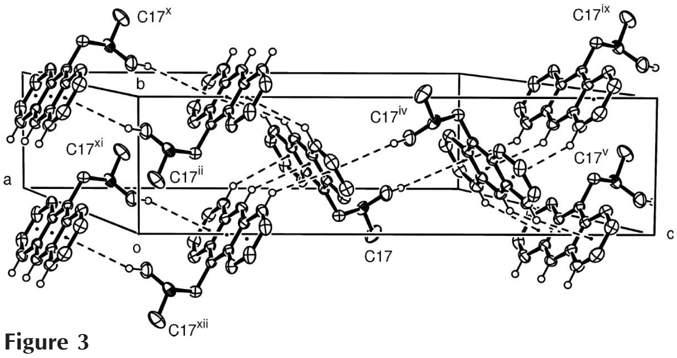

Figure 3
A layer of type *A* molecules of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms involved in C—H···π interactions (dashed lines) are shown as small circles of arbitrary radii. Selected atoms are labelled. [Symmetry codes: (ii) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $1-x, 1-y, 1-z$; (v) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (ix) $x, \frac{3}{2}-y, \frac{1}{2}+z$; (x) $x, \frac{3}{2}-y, z-\frac{1}{2}$; (xi) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (xii) $-x, y-\frac{1}{2}, \frac{1}{2}-z$.]

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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