

## C—H... $\pi$ interactions in 9-(*n*-dodecylaminomethyl)anthracene

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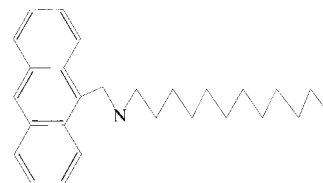
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The title compound, C<sub>27</sub>H<sub>37</sub>N, which is intended to be included in the structure of a sulfonamide porphyrin for the preparation of Langmuir–Blodgett films, consists of a dodecyl chain linked to an anthracene molecule through an aminomethyl group. The angle between the least-squares plane of the anthracene and the dodecyl chain is 11.44 (8)°. The molecules are arranged in zigzag layers head-to-head, with the hydrocarbon chains side-by-side. The structure is stabilized by C—H... $\pi$  interactions, the strongest having an H...centroid distance of 2.63 Å.

### Comment

Langmuir–Blodgett (LB) films, built by transferring monolayers floating on a water surface to a solid substrate, are the focus of many different fields of current scientific research. Their applications range from the study of kinetic reactions in

biological membranes, to molecular electronics and optical data storage (Petty, 1996). The title compound, (I), was prepared within a project of developing highly ordered



(I)

molecular films of new porphyrin-based materials. This compound is intended to be included in the structure of a sulfonamide porphyrin for the preparation of LB films, since porphyrins substituted with long hydrocarbon chains have been shown to form stable films (Hudson *et al.*, 1993). Porphyrin materials are of interest since they can exist readily in different electronic states, easily probed by examining the optical properties of the thin films (Grieve *et al.*, 1994).

The conformation of the chain in (I) is *trans* throughout, the largest deviation being 6.05 (17)° for the C13—C14—C15—C16 torsion angle. The average C—C bond length of the C atoms in the chain is 1.516 (3) Å and the average valency angle is 113.8 (8)°. These values agree well with those observed in other long-chain structures; *e.g.* 1.516 (8) Å and 113 (1)° for dodecyldimethylpropylammonium bromide monohydrate (Taga *et al.*, 1986). The zigzag dodecyl chain is roughly planar with an average deviation of 0.10 (6) Å from the least-squares plane of the carbon backbone. The chain is twisted around the N12 atom, as shown by the C11—N12—C13—C14 torsion angle [68.2 (2)°].

There is an in-plane bending of the substituted anthracene unit, as shown from the somewhat larger valency angles C9—C9a—C1 123.09 (16) and C9—C8a—C8 123.59 (17)° when compared with the corresponding valency angles C10—C4a—C4 121.90 (17) and C10—C10a—C5 121.31 (17)°. The deviations of the C atoms from the 14-membered ring least-squares plane are as big as -0.100 (2) Å for the C9 atom while in the

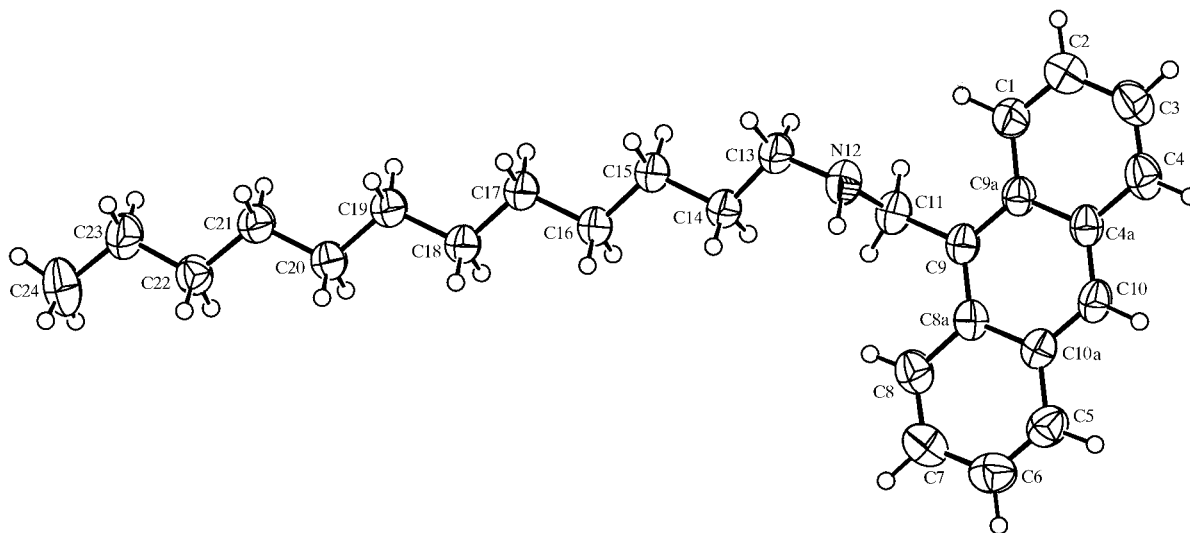
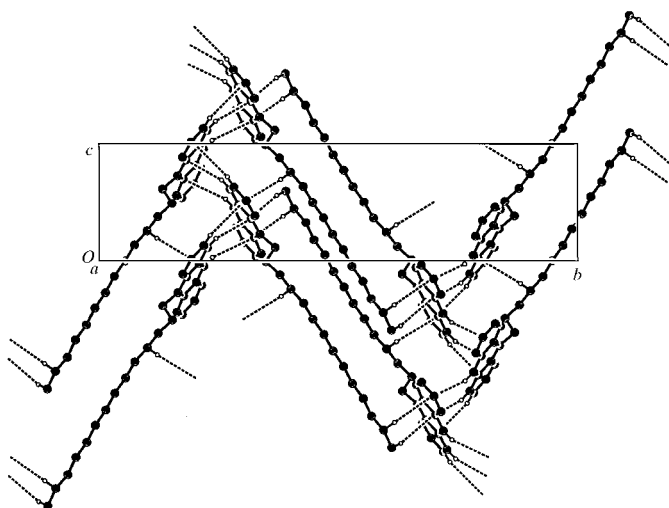


Figure 1

The ORTEP (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 50% probability level.



**Figure 2**  
A view of the unit-cell packing along **a** showing the zigzag layers and with the hydrogen-bonding scheme shown as dashed lines. For clarity, H atoms not involved in the intermolecular interactions have been omitted.

unsubstituted anthracene the deviations do not exceed 0.010 (2) Å (Brock & Dunitz, 1990). The angle between the least-squares plane of the anthracene and the dodecyl chain is 11.44 (8)°. The molecules are arranged in zigzag layers head-to-head, with the hydrocarbon chains side-by-side.

The structure is stabilized by six C—H... $\pi$  intermolecular interactions, thereby saturating the hydrogen-bonding capability of the aromatic  $\pi$  electron clouds (three rings  $\times$  two sides = six bonds). Three of the bonds belong to a geometric type I with a classical T-shape arrangement ( $\alpha$  greater than 150°,  $\theta$  angle  $\simeq$  81–82°), the others to type III ( $\alpha$  less than 150°) according to the classification of Malone *et al.* (1997). The strongest bond is C4—H4...Cg2<sup>i</sup> [(i)  $x, \frac{1}{2} - y, \frac{1}{2} + z$ ] (type I) with an angle of 161.1° and an H...Cg2<sup>i</sup> distance of 2.63 Å, shorter than those found in unsubstituted anthracene (Cg1 is the ring centroid of the six-membered C1—C9a ring, Cg2 of C4a—C10 and Cg3 of C5—C10a). Two other bonds (C10—H10...Cg3<sup>i</sup> and C3—H3...Cg1<sup>i</sup>) link ring C atoms to the  $\pi$ -electron clouds of symmetry-related anthracenes. Three C atoms of the chain (C14, C23, C24) also have one of their H atoms directed towards the  $\pi$  clouds, as shown in Table 2. C—H... $\pi_{\text{arene}}$  interactions have been previously shown to have a profound effect on the molecular-packing patterns of macrocycles (Ferguson *et al.*, 1996). Interestingly, the amine-H atom does not participate in hydrogen bonding although the N—H group is not too far from the  $\pi$  clouds of neighbouring molecules.

## Experimental

9-Anthracenaldehyde (1.11 g, 5.39 mmol) and *n*-dodecylamine (1.00 g, 5.39 mmol) were stirred in toluene (150 ml) under a nitrogen atmosphere in the presence of 3 Å molecular sieves previously activated at 523 K. After 2 h, the molecular sieves were filtered off and the toluene removed by evaporation. Crude 9-(*n*-dodecylimino-

methyl)anthracene (1.5 g) in diethyl ether (100 ml) was added slowly to a refluxing mixture of LiAlH<sub>4</sub> (0.600 g, 0.0192 mol) in dry diethyl ether (50 ml). After 5 h, excess LiAlH<sub>4</sub> was eliminated through gradual additions of water at 273 K, and the resulting lithium salt treated with NaOH (2 M). The required compound was extracted immediately into ether and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The 9-(*n*-dodecylaminomethyl)anthracene was purified by preparative thin-layer chromatography on silica using a mixture of ethyl acetate and dichloromethane (2:8) and crystallized by slow evaporation of the solvent, giving 0.28 g of pure product (14% yield, m.p. 318–320 K). Visible/UV spectra (CH<sub>2</sub>Cl<sub>2</sub>; nm, absorbance in arbitrary units): 320, 0.398; 351, 0.731; 369, 1.073; 390, 0.995. IR (cm<sup>-1</sup>, % transmission, bond): 3438, 75.3 (N—H); 3045, 81.3 (C—H aromatic); 2952, 70.1 (C—H alkane); 1677, 82.3 (C=C aromatic); 1444, 74.8 (C=C aromatic). MS/FAB<sup>+</sup>, *M*<sup>+</sup> *m/z* 374. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , p.p.m.): 8.4 (s, 1H, H10), 8.3 (*d*, 2H, H4, *J* = 8.8 Hz), 7.9 (*d*, 2H, H1, *J* = 8.4 Hz), 7.5 (*m*, 4H, H2, H3), 4.7 (s, 2H, Anth—CH<sub>2</sub>—NH), 2.8 (*t*, 2H, NH—CH<sub>2</sub>—C<sub>11</sub>H<sub>23</sub>, *J* = 7.2 Hz), 1.2 (*m*, 20H, NH—CH<sub>2</sub>—C<sub>10</sub>H<sub>20</sub>), 0.8 (*t*, 3H, NH—C<sub>11</sub>H<sub>22</sub>—CH<sub>3</sub>, *J* = 6.4 Hz). Elemental analysis calculated for C<sub>27</sub>H<sub>37</sub>N: C 86.4, H 9.8, N 3.7%; found: C 86.6, H 9.7, N 3.3%.

## Crystal data

C<sub>27</sub>H<sub>37</sub>N  
*M*<sub>r</sub> = 375.58  
Orthorhombic, *Pccn*  
*a* = 17.760 (9) Å  
*b* = 32.336 (11) Å  
*c* = 7.9664 (6) Å  
*V* = 4575 (3) Å<sup>3</sup>  
*Z* = 8  
*D*<sub>x</sub> = 1.091 Mg m<sup>-3</sup>

Cu *K* $\alpha$  radiation  
Cell parameters from 25 reflections  
 $\theta$  = 11.52–21.87°  
 $\mu$  = 0.459 mm<sup>-1</sup>  
*T* = 293 (2) K  
Block, translucent pale yellow  
0.51  $\times$  0.34  $\times$  0.25 mm

## Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega$ – $\theta$  scans  
4111 measured reflections  
4103 independent reflections  
3069 reflections with *I* > 2 $\sigma$ (*I*)  
*R*<sub>int</sub> = 0.049

$\theta_{\text{max}}$  = 67.26°  
*h* = –2  $\rightarrow$  21  
*k* = –4  $\rightarrow$  38  
*l* = 0  $\rightarrow$  9  
2 standard reflections  
frequency: 180 min  
intensity decay: 2%

## Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.056  
*wR*(*F*<sup>2</sup>) = 0.187  
*S* = 1.087  
4108 reflections  
258 parameters  
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1039P)^2 + 1.0675P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
( $\Delta/\sigma$ )<sub>max</sub> < 0.001  
 $\Delta\rho_{\text{max}}$  = 0.32 e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}}$  = –0.19 e Å<sup>-3</sup>  
Extinction correction: *SHELXL97* (Sheldrick, 1997)  
Extinction coefficient: 0.00053 (14)

**Table 1**  
Selected geometric parameters (Å, °).

C8a—C9	1.409 (3)	C9—C11	1.521 (2)
C9—C9a	1.408 (2)		
C11—N12—C13	112.59 (16)	C9a—C9—C11	119.25 (16)
C9a—C9—C8a	120.10 (15)		
C8—C8a—C9—C11	–5.7 (3)	C9a—C9—C11—N12	–79.3 (2)
C11—C9—C9a—C1	7.3 (3)	C8a—C9—C11—N12	101.5 (2)
C13—N12—C11—C9	–178.79 (16)		

**Table 2**

Hydrogen-bonding geometry (Å, °).

Cg1, Cg2 and Cg3 are the centroids of the C1–C9a, C4a–C10 and C5–C10a six-membered rings, respectively.

<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>
C3–H3···Cg1 <sup>i</sup>	0.93	3.35	3.984 (3)	127
C4–H4···Cg2 <sup>ii</sup>	0.93	2.63	3.518 (3)	161
C10–H10···Cg3 <sup>i</sup>	0.93	2.93	3.806 (2)	158
C14–H14B···Cg1 <sup>ii</sup>	0.97	3.12	3.860 (2)	135
C23–H23A···Cg3 <sup>iii</sup>	0.97	3.03	3.798 (3)	137
C24–H24A···Cg2 <sup>iii</sup>	0.96	2.99	3.877 (3)	155

Symmetry codes: (i)  $x, \frac{1}{2} - y, \frac{1}{2} + z$ ; (ii)  $x, y, z - 1$ ; (iii)  $-x, -y, -z$ .

The H atoms were placed at calculated idealized positions and refined as riding atoms, with C–H = 0.93–0.97 Å, with the exception of the amine-H atom whose coordinates were refined in order to better describe the observed pyramidal geometry around the N12 atom. Examination of the crystal structure with *PLATON* (Spek, 1995) showed that there are no solvent-accessible voids in the crystal lattice.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1095). Services for accessing these data are described at the back of the journal.

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