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### (9-Anthrylmethyl)bis(2-pyridylmethyl)-amine

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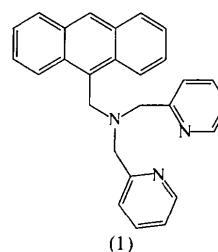
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#### Abstract

The title compound,  $C_{27}H_{23}N_3$ , crystallizes in space group  $P2_1/c$ . The anthryl groups of molecules related by a center of symmetry stack together forming dimers. These units pack in a herring-bone pattern in the (100) plane.

#### Comment

The title compound, (1), was prepared as part of our research on novel photo-induced electron-transfer (PET) sensors for protons and post transition metal ions. It behaves as an off-on-off fluorescent switch for protons, due to two independent PET processes which occur between the anthracene chromophore and the proton receptors (tertiary nitrogen and the pyridyl groups) at different pH values. The sensor (1) responds to zinc(II) ions as an off-on switch by using only one of these PET processes (de Silva *et al.*, 1997). Compound (1) has also been reported as a ligand in a cobalt(II) complex used for DNA cleavage (Bhattacharya & Mandal, 1996).



The numbering scheme and a displacement ellipsoid plot of (1) are shown in Fig. 1. Bond distances and angles are in agreement with related compounds containing a (1-naphthylmethyl)bis(2-pyridylmethyl)amine fragment (Bag *et al.*, 1995). The molecular structure consists of three nearly planar fragments connected to an amine N atom by methylene groups. The largest deviation from the mean plane of the anthryl group (C11–C16, C21–C24, C31–C34) is 0.022 (2) Å for C11, and the largest deviations from the mean planes through the pyridyl groups are 0.007 (3) Å for C45 and –0.007 (3) Å for C44. The dihedral angles between the anthryl group and the two pyridyl rings are 68.97 (9)° for the N40-containing ring and 66.16 (8)° for the N50-containing ring. The angle between the two pyridyl rings is 51.2 (1)°. A view of the packing in the crystal is shown in Fig. 2. The molecules pack as dimers about inversion centers with the anthryl groups stacked together. The separation of the best planes between centrosymmetrically related anthryl groups is 3.45 (1) Å (symmetry code:  $-x, -y, 2-z$ ). These units form a herring-bone pattern in a layer about the (100) plane of the unit cell. The bis(*N*-pyridylmethyl)methyleneamine portions of the molecules jut out from each side of the layer interacting with the pyridyl rings from adjacent layers. The packing of anthryl groups in (1) resembles that of aromatic compounds such as pyrene. This pattern has

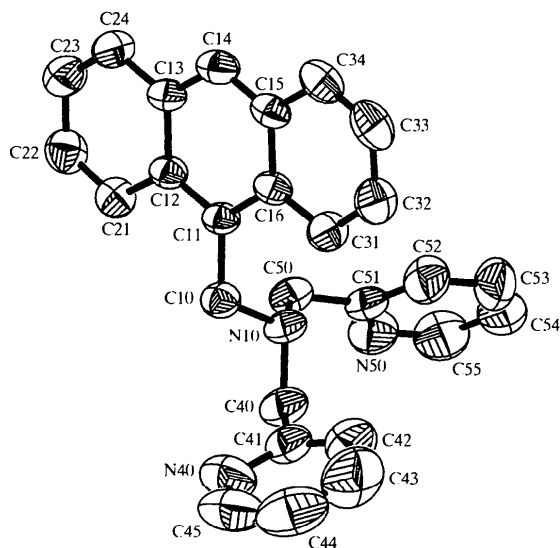


Fig. 1. The structure of (1) showing 50% probability displacement ellipsoids. The H atoms have been omitted for clarity.

been designated the 'sandwich herring-bone' structure (Desiraju, 1997).

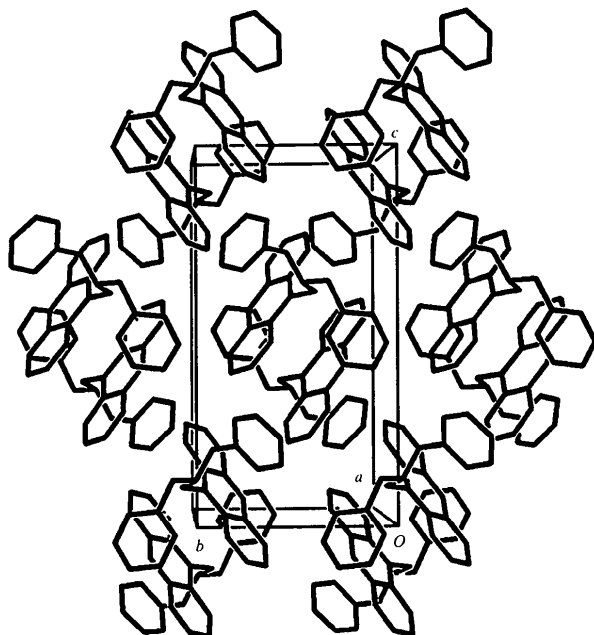


Fig. 2. View of the packing in (1). The H atoms have been omitted for clarity.

## Experimental

The synthesis of (1) was achieved by the alkylation of bis(2-pyridylmethyl)amine with 9-(chloromethyl)anthracene using the general procedure of Hazell *et al.* (1993). A solution of 9-chloromethylanthracene (3.0 g, 13 mmol), bis(2-pyridylmethyl)amine (2.6 g, 13 mmol) and triethylamine (2.0 g, 20 mmol) in ethanol (100 ml) was refluxed for 72 h. Dichloromethane (150 ml) was added after cooling to room temperature and the mixture was extracted with dilute hydrochloric acid (40 ml × 2). The aqueous layer was washed with dichloromethane (50 ml) and neutralized by adding small amounts of solid sodium carbonate with stirring. The product began to precipitate around pH 3 and was completely precipitated around pH 7. The precipitate was filtered and dried on a Büchner funnel to give 4.0 g of crude product in 80% yield. Diffraction quality crystals were obtained by recrystallization from ethanol: m.p. 419–421 K. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 293 K, TMS): δ 8.48–7.04 (*m*, 17H), 4.66 (*s*, 2H), 3.88 (*s*, 4H); <sup>13</sup>C NMR (75 MHz): δ 159.65, 148.66, 136.00, 131.43, 131.30, 129.82, 128.81, 127.52, 125.46, 125.02, 124.70, 123.45, 121.82, 60.51, 50.81; MS (70 eV): *m/z* 389.1896 (*M*<sup>+</sup>); analysis calculated for C<sub>27</sub>H<sub>23</sub>N<sub>3</sub>: C 83.26, H 5.95, N 10.79%; found: C 83.01, H 6.07, N 10.71%.

### Crystal data

C<sub>27</sub>H<sub>23</sub>N<sub>3</sub>  
M<sub>r</sub> = 389.48

Mo Kα radiation  
λ = 0.71073 Å

Monoclinic  
P2<sub>1</sub>/c  
a = 14.590 (1) Å  
b = 8.857 (1) Å  
c = 16.674 (1) Å  
β = 90.22 (1)°  
V = 2154.7 (3) Å<sup>3</sup>  
Z = 4  
D<sub>x</sub> = 1.201 Mg m<sup>-3</sup>  
D<sub>m</sub> not measured

### Data collection

Siemens P4 four-circle diffractometer  
θ/2θ scans  
Absorption correction: ψ scans (XEMP in SHELXTL; Sheldrick 1994)  
T<sub>min</sub> = 0.938, T<sub>max</sub> = 0.965  
4886 measured reflections  
3806 independent reflections

### Refinement

Refinement on F<sup>2</sup>  
R[F<sup>2</sup> > 2σ(F<sup>2</sup>)] = 0.055  
wR(F<sup>2</sup>) = 0.156  
S = 1.009  
3805 reflections  
271 parameters  
H atoms not refined  
w = 1/[σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) + (0.0633P)<sup>2</sup> + 0.5266P]  
where P = (F<sub>o</sub><sup>2</sup> + 2F<sub>c</sub><sup>2</sup>)/3

Cell parameters from 34 reflections  
θ = 4.94–12.33°  
μ = 0.071 mm<sup>-1</sup>  
T = 299 (2) K  
Prism  
0.4 × 0.4 × 0.3 mm  
Pale yellow

2192 reflections with I > 2σ(I)  
R<sub>int</sub> = 0.022  
θ<sub>max</sub> = 25°  
h = -1 → 17  
k = -1 → 10  
l = -19 → 19  
3 standard reflections every 99 reflections  
intensity decay: none

(Δ/σ)<sub>max</sub> < 0.001  
Δρ<sub>max</sub> = 0.306 e Å<sup>-3</sup>  
Δρ<sub>min</sub> = -0.145 e Å<sup>-3</sup>  
Extinction correction: none  
Scattering factors from International Tables for Crystallography (Vol. C)

All non-H atoms were refined with anisotropic displacement parameters. The H atoms were located in a difference map, positioned with idealized geometry and refined with displacement parameters 1.2U<sub>eq</sub> of the parent atom using a riding model.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: XS in SHELXTL (Sheldrick, 1994). Program(s) used to refine structure: XL in SHELXTL. Molecular graphics: XP in SHELXTL.

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Supplementary data for this paper are available from the IUCR electronic archives (Reference: SX1063). Services for accessing these data are described at the back of the journal.

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### 3-[(2-Aminoethyl)iminomethyl]-4-hydroxybenzoic Acid 0.28-Hydrate†

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#### Abstract

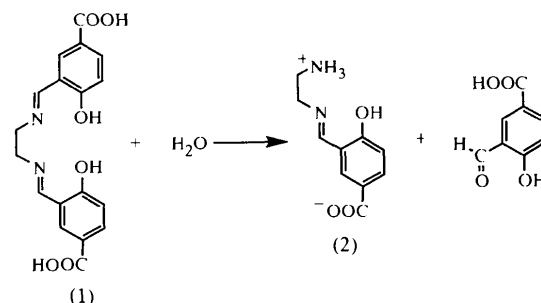
The title compound crystallizes as a hydrated zwitterion with the site for the water molecule only partially occupied [site-occupancy factor 0.28 (1)] and a formula of  $C_{10}H_{12}N_2O_3 \cdot 0.28H_2O$ . The hydroxyl H atom forms an intramolecular hydrogen bond to the imine N atom. The  $NH_3^+$  and  $COO^-$  groups of the zwitterion form a two-dimensional hydrogen-bond network that runs parallel to the *ac* plane. The water molecule forms hydrogen bonds to a hydroxyl O atom and a carboxylate O atom of adjacent molecules.

#### Comment

In our work to develop ligands to form hydrogen-bonded coordination compounds, we attempted to purify compound (1) (Matsushita & Shono, 1986) by recrystallization from a mixture of dimethyl sulfoxide (DMSO) and water. Under these conditions, one of the imine groups of (1) hydrolyzes and crystals of 3-[(2-aminoethyl)iminomethyl]-4-hydroxybenzoic acid, (2), can be isolated with 0.28 molecules of water per formula unit. Compound (2) has also been prepared by Matsushita & Shono (1986) by reaction of equimolar amounts of 3-formyl-4-hydroxybenzoic acid and 1,2-ethylenediamine in ethanol. These workers correctly formulated

† Zwitterionic name: 3-[(2-ammonioethyl)iminomethyl]-4-hydroxybenzoate 0.28-hydrate.

this compound as a zwitterion. The molecular structure and hydrogen-bond patterns of (2) are described here.



A displacement ellipsoid plot and the atom-numbering scheme for (2) are shown in Fig. 1. The crystal structure consists of the zwitterionic form of (2) and hydrate water molecules. Schiff bases like (2) can exist in either the enolimine or ketamine tautomeric forms. The C11—O11 and C18—N18 bond distances of 1.347 (4) and 1.272 (4) Å are indicative of a single and double bond, respectively, which clearly shows that the enolimine form is favored in this compound (Corden *et al.*, 1997, and references therein). Most of the non-H atoms of (2) lie nearly in a plane. The exceptions are the carboxylate O17 and O18 atoms, and the two terminal atoms of the side chain, C22 and N23. The largest deviations from the mean plane formed by all the atoms except the four just mentioned are: C21 0.110 (3), C16 –0.089 (3), C15 –0.083 (3) and C17 0.082 (2) Å. The plane formed by the three atoms at the end of the side chain (C21, C22 and N22) is approximately perpendicular to the rest of the molecule, with a dihedral angle between these three atoms and the C18, N18, C21 plane of 87.7 (4)°. The carboxylate group is tilted by 15.1 (5)° from the best plane through the six atoms of the aromatic ring. The overall shape of the molecule resembles the letter 'L' with the shorter side terminating in the ammonium group and the longer side terminating in the

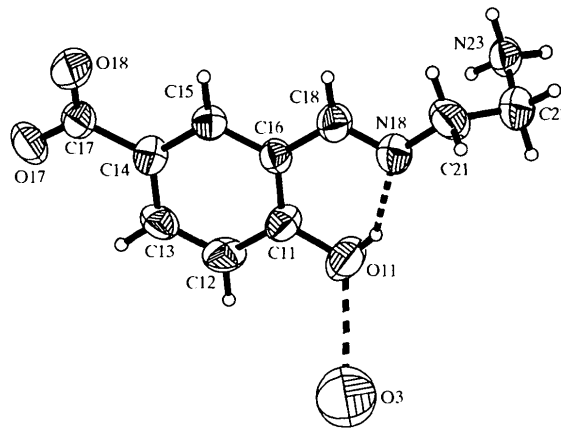


Fig. 1. The structure of (2) showing 50% probability displacement ellipsoids. H atoms have been drawn as spheres of artificially small radii.