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9,10-Bis(propylammoniomethyl)anthracene dichloride

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.008 Å
R factor = 0.060
wR factor = 0.175
Data-to-parameter ratio = 16.4

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

In the title compound, $C_{22}H_{30}N_2^{2+}\cdot 2Cl^-$, one of the side chains lies above the anthracene plane and the other lies beneath it. In the crystal structure, N—H···Cl hydrogen bonds result in a two-dimensional network structure.

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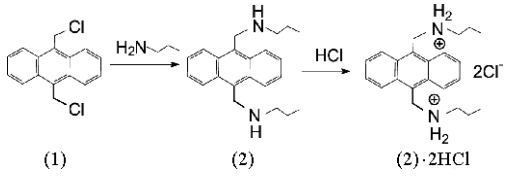
Comment

Fluorescent chemosensors form an important aspect of supramolecular chemistry (de Silver *et al.*, 1997) and many with anthracene rings have been designed and investigated (Gunnlaugsson *et al.*, 2002). The fluorescent intensity of amine compounds with anthracene chromophores can be effectively modulated by protonation (Luigi & Antonio, 1995). As a result, such amine compounds can be used to monitor acidic changes of water in rivers or lakes; this is very important in the protection of the environment (Wang & Morawetz, 1976). We report here the synthesis and crystal structure of 9,10-bis-(propylammoniomethyl)anthracene dichloride, (2)·2HCl.



(1) (2) (2)·2HCl

In the title compound, the two side chains lie above and below the plane of the anthracene ring (Fig. 1). The C—N distances range from 1.483 (5) to 1.495 (6) Å, and the C—N—C angles are 111.4 (4) and 115.3 (4)°. These are very similar to the values in a structure where the side chains of (2)·2HCl are each replaced by benzylammoniomethyl (Chang *et al.*, 2000). Other bond lengths and angles in the title molecule are unexceptional.

The crystal structure involves N—H···Cl hydrogen bonds (Table 1), resulting in a two-dimensional network structure.

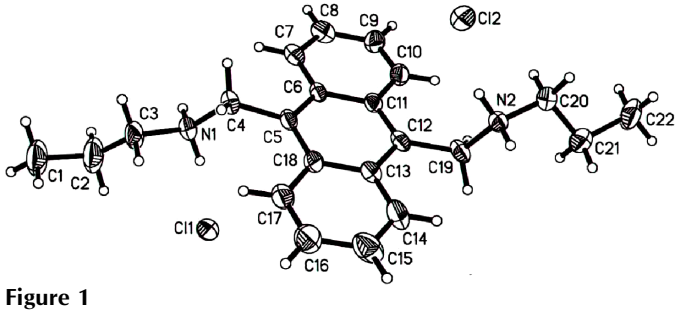


Figure 1
A view of the title compound, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

Experimental

To a benzene (100 ml) solution of 9,10-bis(chloromethyl)anthracene, (1) (11.080 g, 0.040 mol), was added *n*-propylamine (18.880 g, 0.32 mol), and the solution was stirred for 6 h at 303 K. The benzene solution was washed with water (50 ml) and dried with anhydrous $MgSO_4$. It was then concentrated to 50 ml and hexane (5 ml) was added to give an orange–yellow solid, (2) (yield: 9.100 g, 78.5%; m.p. 385–387 K). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.93 (*t, J* = 7.2 Hz, 6H, CH_3), 1.59 (*m*, *J* = 7.2 Hz, 4H, CH_2), 2.15 (*s*, 2H, NH), 2.83 (*t, J* = 7.2 Hz, 4H, CH_2), 4.70 (*s*, 4H, CH_2), 7.50–7.55 (*m*, 4H, AnH), 8.34–8.39 (*m*, 4H, AnH). Compound (2) was reacted with 2 equivalents of hydrochloric acid in benzene solution to give a yellow salt, (2)·2HCl [m.p. 553–555 K (decomposition)]. ^{1}H NMR (300 MHz, DMSO, δ): 0.93 (*t, J* = 7.2 Hz, 6H, CH_3), 1.76 (*m*, *J* = 7.2 Hz, 4H, CH_2), 3.19 (*t, J* = 7.2 Hz, 4H, CH_2), 5.27 (*s*, 4H, CH_2), 7.74–7.79 (*m*, 4H, AnH), 8.60–8.64 (*m*, 4H, AnH). 9.35 (*s*, 2H, NH). ^{13}C NMR (300 MHz, $CDCl_3$, δ): 10.92 (CH_3), 19.79 (CH_3CH_2), 41.81 (CH_2CH_2N), 49.73 (NCH_2N), 123.6, 125.3, 125.7, 127.3, 128.0, 128.5, 129.4, 129.7, 130.5, 131.3, 132.1, 133.7 and 134.2 (AnC). Analysis calculated for $C_{22}H_{30}Cl_2N_2$: C 67.17, H 7.69, N 7.12%; found: C 66.89, H 7.37, N 7.12%. Crystals of (2)·2HCl suitable for X-ray diffraction were obtained by slow evaporation of a methanol solution at room temperature.

Crystal data

$C_{22}H_{30}N_2^{2+}\cdot 2Cl^-$
M_r = 393.38
Monoclinic, $P2_1/c$
a = 8.340 (3) Å
b = 14.467 (5) Å
c = 17.675 (6) Å
β = 94.200 (8)°
V = 2126.9 (14) Å^3
Z = 4
D_x = 1.228 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 637 reflections
θ = 1.8–25.0°
μ = 0.31 mm^{-1}
T = 293 (2) K
Block, yellow
0.30 × 0.25 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.912, T_{max} = 0.940
8704 measured reflections
3751 independent reflections
1308 reflections with $I > 2\sigma(I)$
R_{int} = 0.105
θ_{max} = 25.0°
$h = -9 \rightarrow 9$
$k = -17 \rightarrow 16$
$l = -15 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.175
S = 0.86
3751 reflections
229 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0684P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2D···Cl2	0.90	2.25	3.098 (4)	157
N2—H2C···Cl1^{i}	0.90	2.19	3.081 (4)	171
N1—H1E···Cl2^{ii}	0.90	2.28	3.090 (4)	150
N1—H1D···Cl1	0.90	2.27	3.120 (4)	158

Symmetry codes: (i) $x, \frac{3}{2}-y, \frac{1}{2}+z$; (ii) $-x, 2-y, 1-z$.

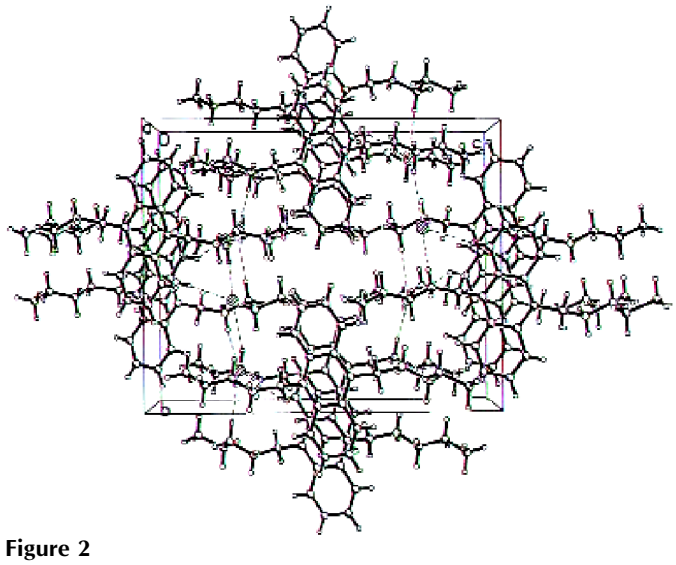


Figure 2
A view, down the *a* axis, of the packing arrangement in the crystal structure. Hydrogen bonds are indicated by dashed lines.

All H atoms were initially located in a difference Fourier map. The methyl H atoms were then constrained to an ideal geometry, with C—H distances of 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C), but each group was allowed to rotate freely about its C—C bond. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with N—H distances of 0.90 Å and C—H distances in the range 0.93–0.97 Å, and U_{iso}(H) = 1.2U_{eq}(C,N).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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