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N-(9-Anthrylmethyl)propylaminium diphenylphosphinate monohydrate

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Key indicators

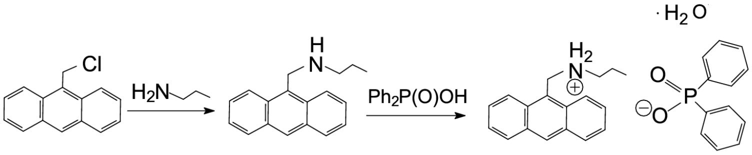
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.011 Å
R factor = 0.103
wR factor = 0.317
Data-to-parameter ratio = 13.8

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

In the title compound, $C_{18}H_{20}N^+\cdot C_{12}H_{10}O_2P^-\cdot H_2O$, the propylaminomethyl side chain lies above the plane of the anthracene moiety. In the crystal structure, the phosphinate O atoms are involved in hydrogen bonds with the water molecule of crystallization and the NH group of the proplyamine side chain of the anthracene moiety.

Comment

Molecular systems that combine binding ability and photochemical properties are of great interest for designing chemosensors. Many of these fluorescent sensors have been designed for protons (Bissell *et al.*, 1992). Detection of the proton concentration in nature is important for protection of the environment (Wang & Morawetz, 1976). We report here the synthesis and crystal structure of the title compound, (III).



(I) (II) (III)

9-Chloromethylanthracene was reacted with *n*-propylamine in a benzene solution to afford an orange–yellow solution of 9-propylaminemethylanthracene, (II). Compound (II) was reacted further with diphenylphosphoric acid to give a yellow powder of (II)·$Ph_2P(O)OH$ as the monohydrated salt, (III).

In the title compound, the propylaminomethyl chain of the anthracene moiety lies above the anthracene ring plane (Fig. 1). The N1—C15 and N1—C16 bond distances [1.575 (9) and 1.512 (10) Å, respectively] are longer than those [C71—N72 = 1.494 (6) Å and N72—C73 = 1.509 (6) Å] observed in 9,10-dibenzylaminemethylanthracene (Chang *et al.*, 2000). The C16—N1—C15 bond angle is 119.2 (6)°, which is larger than that [C71—N72—C73 = 111.2 (4)°] found in 9,10-dibenzylaminemethylanthracene.

In the crystal structure, the phosphoride O atoms are involved in hydrogen bonds with the water molecule of crystallization and the NH group of the proplyamine side chain of the anthracene moiety. The $D\cdots A$ distances range from 2.725 (8) to 2.827 (7) Å, and the $D—H\cdots A$ angles from 145 to 163°. Details are given in Table 1 and Fig. 2.

Experimental

A benzene suspension of 9-chloromethylanthracene, (I) (21.00 g, 0.091 mol), and *n*-propylamine (5.37 g, 0.091 mol), in the presence of K_2CO_3 (125.58 g, 0.910 mmol) and KI (4.55 g, 27.30 mmol), was

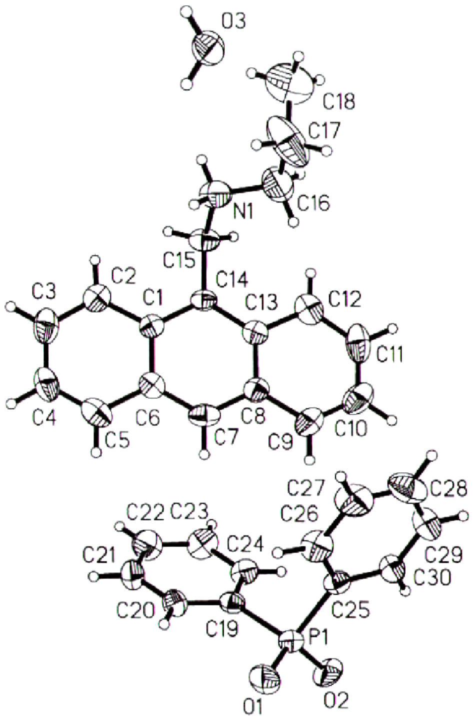


Figure 1
A view of the title compound, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

stirred for 5 h at 303 K. After filtration, the solvent was removed with a rotary evaporator, and water (500 ml) was added. The mixture was extracted with CH_2Cl_2 (150 ml). The extracted solution was dried with anhydrous $MgSO_4$. After the solvent had been removed, an orange–yellow viscous liquid was obtained. The crude product was purified by column chromatography (SiO_2, acetone/petroleum ether 1:1) to give an orange–yellow low-melting-point solid, (II) (10.388 g, 45%; m.p. 299 K). ^{1}H NMR (300 MHz, $CDCl_3$, p.p.m.): 0.95 (*t*, J = 7.2 Hz, 3H, CH_3), 1.26 (*s*, NH), 1.62 (*m*, J = 7.2 Hz, 2H, CH_2), 2.84 (*t*, J = 7.2 Hz, 2H, CH_2), 4.72 (*s*, 2H, CH_2), 7.49 (*t*, J = 7.5 Hz, 2H, AnH) (An is anthracene), 7.54 (*t*, J = 7.5 Hz, 2H, AnH), 7.99 (*d*, J = 7.5 Hz, 2H, AnH), 8.34 (*d*, J = 7.5 Hz, 2H, AnH), 8.39 (*s*, 1H, AnH). Compound (II) was reacted with two equivalents of diphenylphosphoric acid in a benzene solution to give (II)·$Ph_2P(O)OH$ quantitatively as a yellow crystalline solid. M.p. 516–518 K. ^{1}H NMR (300 MHz, DMSO-d_6, p.p.m.): 0.82 (*t*, J = 7.2 Hz, 3H, CH_3), 1.68 (*m*, J = 7.2 Hz, 2H, CH_2), 3.02 (*t*, J = 7.2 Hz, 2H, CH_2), 5.09 (*s*, 2H, CH_2), 7.27–8.73 (*m*, 19H, AnH), 8.73 (*s*, NH), 5.81 (*s*, OH). ^{31}P NMR (300 MHZ, DMSO-d_6, p.p.m.): 36.56. Crystals of (III), suitable for X-ray diffraction, were obtained by slow evaporation of a methanol solution at room temperature; water present in the solvent led to the formation of the monohydrate. Analysis calculated for $C_{30}H_{32}NO_3P$: C 77.07, H 6.47, N 3.00%; found: C 76.84, H 6.29, N 3.21%.

Crystal data

$C_{18}H_{20}N^+ \cdot C_{12}H_{10}O_2P^- \cdot H_2O$
M_r = 485.54
Monoclinic, $P2_1/n$
a = 13.572 (4) Å
b = 10.370 (3) Å
c = 19.435 (6) Å
β = 108.899 (5)°
V = 2587.9 (13) Å^3
Z = 4

D_x = 1.246 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 620 reflections
θ = 2.2–25.0°
μ = 0.14 mm^{-1}
T = 293 (2) K
Prism, yellow
0.25 × 0.15 × 0.08 mm

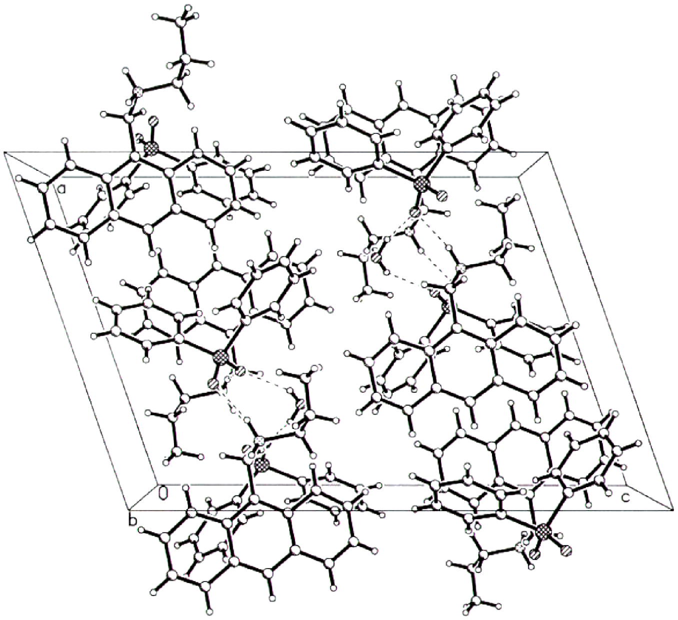


Figure 2
A view down the *b* axis of the packing arrangement in the crystal structure of (III). Hydrogen bonds are indicated by dashed lines.

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.966, T_{max} = 0.989
10 002 measured reflections

4369 independent reflections
2163 reflections with $I > 2\sigma(I)$
R_{int} = 0.078
θ_{max} = 25.0°
$h = -15 \rightarrow 16$
$k = -6 \rightarrow 12$
$l = -23 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.103
$wR(F^2)$ = 0.317
S = 1.02
4369 reflections
317 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1614P)^2 + 1.9131P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.11 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.008 (3)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3—H3$C\cdots$O2^{i}	0.85	2.09	2.827 (7)	145
O3—H3$B\cdots$O1^{ii}	0.85	2.06	2.802 (7)	146
N1—H1$B\cdots$O2^{ii}	0.90	1.96	2.826 (8)	160
N1—H1$A\cdots$O1^{iii}	0.90	1.85	2.725 (8)	163

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

All H atoms were initially located in difference Fourier maps. 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. The other H atoms were placed in idealized positions and constrained to ride on their parent atoms, with N—H distances of 0.90 Å, C—H distances in the range 0.93–0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The water H atoms were constrained to ride on the parent O atom, with O—H distances of

0.85 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(O). The highest peak is located at (0.3417, 0.0695, 0.3005).

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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