$w = 1/[\sigma^2(F_o^2) + (0.0352P)^2 + 0.3251P]$ where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from *International Tables for Crystallography* (Vol. C)

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

N1—S2	1.661 (2)	S1—C1	1.761 (2)
N1—S1	1.664 (2)	S2—O4	1.421 (2)
S1—O1	1.422 (2)	S2—O3	1.424 (2)
S1—O2	1.424 (2)	S2—C2	1.760 (2)
S2—N1—S1	113.26 (11)	O4—S2—C2	112.69 (11)
O1—S1—O2	119.19 (10)	O3—S2—C2	107.71 (11)
O1—S1—N1	109.37 (10)	N1—S2—C2	96.73 (10)
O2—S1—N1	107.07 (10)	C2—C1—S1	113.15 (16)
O1—S1—C1	109.07 (10)	C6—C1—S1	125.62 (15)
O2—S1—C1	112.70 (10)	C1—C2—S2	113.49 (15)
N1—S1—C1	97.10 (10)	C3—C2—S2	125.09 (17)
O4—S2—O3	120.04 (12)	H01—N1—S1	108 (2)
O4—S2—N1	108.06 (11)	H01—N1—S2	114 (2)
O3—S2—N1	109.05 (11)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H01$\cdots$N99	0.86 (3)	1.99 (3)	2.834 (3)	169 (3)
C99—H99C$\cdots$O3^{i}	0.98	2.70	3.488 (4)	138
C99—H99C$\cdots$O4^{ii}	0.98	2.65	3.418 (3)	136

Symmetry codes: (i) $1 + x, y, z$; (ii) $2 - x, 1 - y, -z$.

The methyl group was refined as a rigid group allowed to rotate but not tip, the NH H atom was refined freely, and other H atoms were treated as riding.

Data collection: *DIF*4 (Stoe & Cie, 1991*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1991*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

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Acta Cryst. (1997). C**53**, 1899–1901

A π-Stacked Complex Between 4,4′-Dimethyl-4,4′-bipyridinium Bis(hexafluorophosphate) and 1,5-Bis[(hydroxyethoxy)ethoxy]naphthalene

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Abstract

The title π-electron-rich naphthalene-containing polyether {alternative name: 2,2′-[1,5-naphthylenebis(oxyethoxy)]diethanol} forms a 1:1 crystalline complex with the π-electron acceptor 4,4′-dimethyl-4,4′-bipyridinium bis(hexafluorophosphate), $C_{12}H_{14}N_2^{2+}.2PF_6^{-}.C_{18}H_{24}O_6$. The molecular packing exhibits extensive intermolecular hydrogen bonding and infinite π-stacking of the complex along the direction of the *b* axis.

Comment

The π-electron-rich molecule 1,5-bis[(hydroxyethoxy)ethoxy]naphthalene, (I), is well known for its propensity to enter into aromatic π–π stacking interactions with π-electron-acceptor bipyridinium-containing compounds (Asakawa *et al.*, 1997). However, the 1:1 complex of

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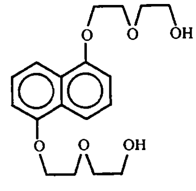
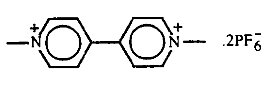
the acyclic naphthalene-containing polyether with 4,4′-dimethyl-4,4′-bipyridinium, (II), has not been examined previously, despite the possibility that this simple case may provide fundamental structural information regarding the nature of the interaction between such π-electron donors and acceptors.



(I)



(II)

Upon mixing of equimolar solutions of the two compounds, a dark red colour is produced almost instantaneously as a result of the formation of a charge-transfer complex (Ballardini *et al.*, 1993) between the two molecular components. An X-ray structural study confirmed that the complex crystallized in a 1:1 ratio, as determined by mass spectrometry.

The bipyridinium dication is found to be essentially planar; nearly 44% of related dications in the Cambridge Structural Database (Allen & Kennard, 1993) are also planar or nearly so. In the crystal, the naphthalene-containing molecules are stacked with the 4,4′-dimethyl-4,4′-bipyridinium cations, with an interplanar spacing of 3.33 (2) Å, as shown in Fig. 1. The plane normals of the naphthalene system and the 4,4′-dimethyl-4,4′-bipyridinium are inclined at 3.6 (2) and 5.0 (2)°, respectively, to the *b* axis. Each component of the complex occupies a special position, with centres of symmetry located in the middle points of the C9—C9^{i} and C13—C13^{ii} bonds [symmetry codes: (i) $-x$, $-y$, $1-z$; (ii) $-x$, $-1-y$, $1-z$]. The angle between the long axis of the naphthalene moiety and that of the dication is approximately 63°. Complexes form infinite stacks along the *b* axis. The stacks are joined by short hydrogen bonds, O1—H1···O2($\frac{1}{2}-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$) [O···O 2.812 (7) Å], directed along the 2_1 axis, into sheets parallel to (101). The disordered anions are located between these hydrogen- and π-bonded cationic layers.

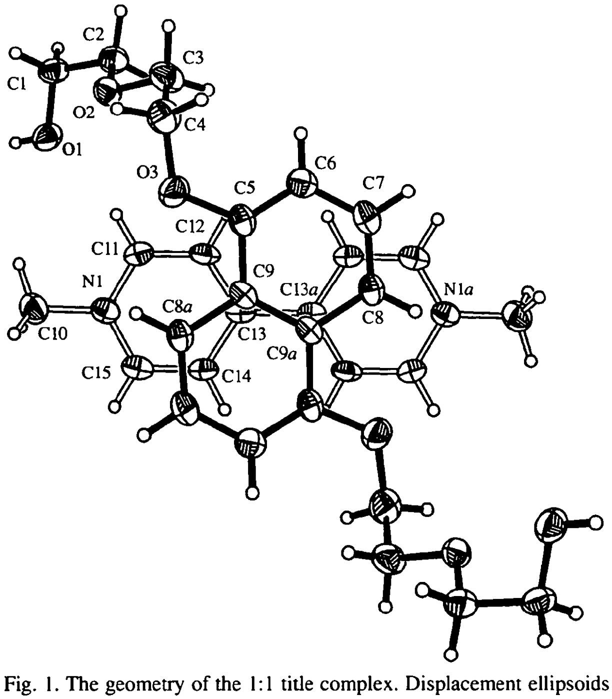


Fig. 1. The geometry of the 1:1 title complex. Displacement ellipsoids are shown at the 25% probability level.

Experimental

1,5-Bis[(hydroxyethoxy)ethoxy]naphthalene was prepared according to the literature method of Brown *et al.* (1992), as was 4,4′-dimethyl-4,4′-bipyridinium bis(hexafluorophosphate). The complex was prepared by mixing equimolar acetonitrile solutions of the two compounds (FAB mass spectrometry: m/z = 667 $[M-PF_6]^+$) and was subsequently crystallized by slow vapour diffusion of diisopropyl ether into the acetonitrile solution.

Crystal data

$C_{12}H_{14}N_2^{2+}.2PF_6^-.C_{18}H_{24}O_6$
M_r = 349.28
Monoclinic
$P2_1/n$
a = 15.005 (5) Å
b = 6.829 (5) Å
c = 17.749 (5) Å
β = 102.250 (5)°
V = 1777.3 (15) Å^3
Z = 4
D_x = 1.305 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 22 reflections
θ = 7.7–18.1°
μ = 0.195 mm^{-1}
T = 293 (2) K
Plate
0.50 × 0.45 × 0.01 mm
Brown–red

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
4009 measured reflections
2941 independent reflections
1344 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.046
$\theta_{\rm max}$ = 24.48°
$h = -17 \rightarrow 2$
$k = -7 \rightarrow 1$
$l = -20 \rightarrow 20$
3 standard reflections
frequency: 120 min
intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.076
$wR(F^2)$ = 0.280
S = 1.032
2939 reflections
229 parameters
H-atom parameters constrained (riding)

$w = 1/[\sigma^2(F_o^2) + (0.1256P)^2 + 3.21P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.002$
$\Delta\rho_{\rm max}$ = 0.570 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.538 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—C1	1.393 (8)	C5—C9	1.411 (9)
O2—C2	1.422 (8)	C6—C7	1.400 (10)
O2—C3	1.439 (8)	C7—C8	1.364 (10)
O3—C5	1.387 (8)	C8—C9^{i}	1.415 (8)
O3—C4	1.438 (9)	C9—C9^{i}	1.426 (12)
N1—C15	1.331 (9)	C11—C12	1.344 (10)
N1—C11	1.353 (8)	C12—C13	1.395 (9)
N1—C10	1.487 (9)	C13—C14	1.387 (9)
C1—C2	1.490 (10)	C13—C13^{ii}	1.472 (13)
C3—C4	1.428 (11)	C14—C15	1.352 (10)
C5—C6	1.350 (9)		
C2—O2—C3	111.7 (6)	C8—C7—C6	121.9 (7)
C5—O3—C4	120.3 (6)	C7—C8—C9^{i}	119.1 (7)
C15—N1—C11	119.5 (6)	C5—C9—C8^{i}	121.9 (6)
C15—N1—C10	121.3 (6)	C5—C9—C9^{i}	118.7 (7)
C11—N1—C10	119.2 (6)	C8^{i}—C9—C9^{i}	119.3 (7)
O1—C1—C2	108.9 (6)	C12—C11—N1	120.6 (6)
O2—C2—C1	109.9 (6)	C11—C12—C13	121.8 (6)
O2—C3—C4	110.6 (6)	C14—C13—C12	115.3 (6)
C3—C4—O3	113.1 (7)	C14—C13—C13^{ii}	122.5 (7)
C6—C5—O3	125.0 (7)	C12—C13—C13^{ii}	122.2 (7)
C6—C5—C9	120.9 (7)	C15—C14—C13	121.6 (7)
O3—C5—C9	114.1 (6)	N1—C15—C14	121.2 (7)
C5—C6—C7	120.1 (7)		

Symmetry codes: (i) $-x, -y, 1 - z$; (ii) $-x, -1 - y, 1 - z$.

Data collection was stopped at 24.8° in θ because the last shell ($>22°$ in θ) contained less than 20% observed reflections. The PF_6^- anion is severely disordered and the largest peaks on the residual electron-density map are located in the vicinity of the disordered F atoms. The anion was refined with constrained P—F bond lengths and equal populations of disordered F atoms. The difficulty in modelling the disorder is presumably the main cause of the rather high residual indices. All H-atoms were placed in calculated positions and refined in riding mode with $U(H) = 1.5U_{iso}(C)$.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1995). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *GX* (Mallinson & Muir, 1985). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1184). Services for accessing these data are described at the back of the journal.

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L-Threonine at 12 K

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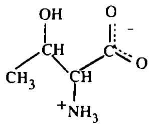
Abstract

The crystal structure of L-threonine, $C_4H_9NO_3$, was redetermined at 12 K. The present X-ray data allowed the determination of more accurate molecular geometry and of all the H-atom positions. The precision of the C—C, C—N and C—O distances is 0.002 Å or better, while that of the H-atom distances is 0.02 Å. The shape of the molecule relative to the C^α—C^β bond corresponds to the staggered (D_{3d}) conformation, with the H atoms at C^α and C^β *trans* to each other, yielding the least-crowded molecular conformation. All H atoms of the NH_3 and OH groups are involved in intermolecular hydrogen bonds, which interconnect the molecules to form a three-dimensional network.

Comment

L-Threonine (*threo*-α-amino-β-hydroxy-*n*-butyric acid) is an especially important amino acid. It is a significant constituent of many common proteins, such as egg albumin, human γ-globulin, β-lactoglobulin, gelatin, human serum albumin, insulin, silk fibroin and hemoglobin. L-Threonine plays a crucial role in many biological processes (Craig & Dekker, 1986; White, Berget & Nall, 1987; Krause, Volz & Lipscomb, 1987; Gouax, Krause & Lipscomb, 1987; Fierke & Benkovic, 1989; Raag *et al.*, 1991; Waldrop *et al.*, 1992; Chen *et al.*, 1993). From the X-ray analysis of L-lacate dehydrogenase, the threonine was identified as an active site residue that plays a major role in the control of catalysis and specificity (Bur *et al.*, 1989; Wigley *et al.*, 1992; Sakowicz *et al.*, 1992, 1993). This specificity is closely related to the conformation of L-threonine and its ability to form hydrogen bonds (Wigley *et al.*, 1992; Sakowicz *et al.*, 1993). We decided to redetermine the crystal structure of L-threonine, (I), at a low temperature (12 K) because



(I)

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