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N,N′-Dibenzyl-4,7-phenanthrolinium dibromide methanol solvate

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Key indicators

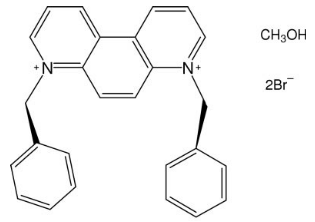
Single-crystal X-ray study
T = 90 K
Mean σ(C–C) = 0.002 Å
R factor = 0.027
wR factor = 0.071
Data-to-parameter ratio = 22.9

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

The structure of the phenanthroline-derived viologen, $C_{26}H_{22}N_2^{2+}\cdot 2Br^-\cdot CH_3OH$, as the methanol solvate, was determined as part of a fluorescence-quenching study. There is intermolecular π–π stacking of the phenanthroline and benzyl arms as well as methanol hydrogen bonding to a bromide.

Comment

N,N′-dibenzyl-4,7-phenanthrolinium dibromide methanol solvate, (I), contains a dication and belongs to a class of compounds called viologens (Monk, 1998), which have received attention for their ability to quench fluorescence and act as redox indicators. In the present case, the compound has been studied as a fluorescence quencher of pyranine (Suri *et al.*, 2003). Although the persistence of π–π stacking in aqueous solution is an unknown factor, it is of interest to examine the propensity of this process to occur in the solid. In addition, the proximity of the bromides to the dication was of interest because of possible charge transfer interactions.



(I)

As shown in Fig. 1, the dication is an *N,N′*-dibenzylated phenanthroline. The two benzyl arms project on opposite sides of the phenanthroline plane. The C14–C19 and C21–C26 phenyl rings subtend dihedral angles of 65.14 (3) and 78.04 (4)°, respectively, with the phenanthroline group. Although the phenanthroline is essentially planar, with an r.m.s. deviation of 0.067 Å, there is a slight twist [7.72 (8)°] between the two end six-membered rings. This twist may arise from repulsion between atoms H3 and H6, which have a short contact distance of 2.07 Å. Both Br^- ions have short intermolecular contacts to an acidic H atom that is *ortho* to the N atoms bearing the positive charges. In addition, atom Br2 is hydrogen bonded to the methanol group. These contacts are listed in Table 1.

A herringbone type of packing leads to π–π interactions for all aromatic rings in the structure, as depicted in Fig. 2. The phenyl ring involving atoms C14—C19 and the phenanthroline ring system form an alternating set of π–π stacks, as shown in more detail in Fig. 3. The distances between the ring centroids (DC), those between the planes through the rings

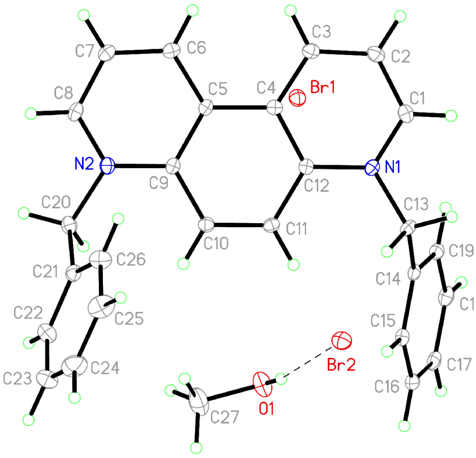


Figure 1
A view of (I), showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level.

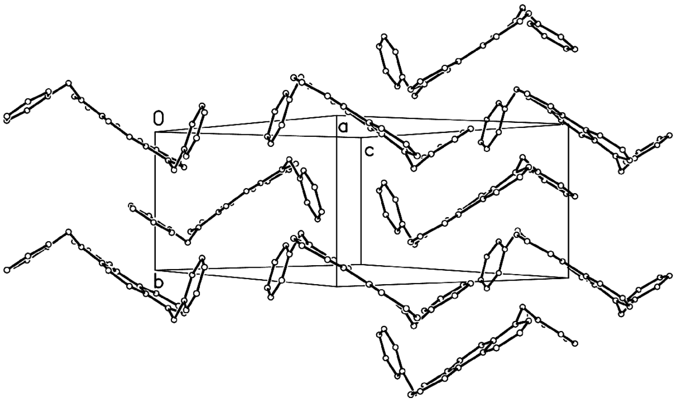


Figure 2
The packing of the cations, emphasizing the π–π stacking.

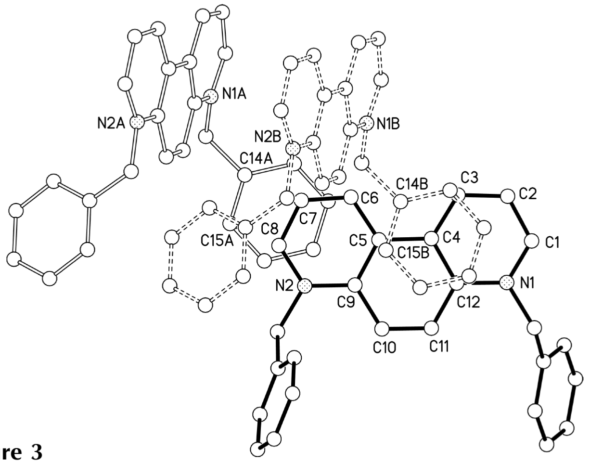


Figure 3
A view of the π–π stacking between phenanthroline and the C14–C19 phenyl ring. The molecules with open bonds and dashed open bonds are below and above, respectively, the molecule with solid bonds. [Symmetry codes: *A* (open bonds) $x, \frac{1}{2} - y, \frac{1}{2} + z$; *B* (dashed-open bonds) $x, \frac{3}{2} - y, \frac{1}{2} + z$.]

(DP) and the lateral shifts (SH) are, for C1–C4/C12/N1 and C14–C19 at $(x, \frac{3}{2} - y, \frac{1}{2} + z)$, DC = 3.524 (2) Å, DP = 3.247 (1) Å and SH = 1.370 (6) Å; for C4/C5/C9–C12 and C14–C19 at $(x, \frac{3}{2} - y, \frac{1}{2} + z)$, DC = 3.644 (2) Å, DP = 3.208 (2) Å and SH = 1.728 (6) Å; and for C5–C8/N2,C9 and C14–C19 at $(x, \frac{1}{2} - y, \frac{1}{2} + z)$, DC = 3.492 (2) Å, DP = 3.049 (5) Å and SH = 1.702 (10) Å. The DP separations are moderately short, and can be explained by the effects of the dipositive charge in the phenanthroline ring system on the van der Waals forces. The C21–C26 phenyl ring is stacked with respect to an inversion-related ring but only overlaps at the edge. The shortest contact is 3.676 (2) Å, between atom C24 and atom C25 at $(1 - x, 1 - y, 1 - z)$.

Experimental

The compound was synthesized as described in the Supporting Information of Suri *et al.* (2003). Crystals were obtained following recrystallization from methanol.

Crystal data

$C_{26}H_{22}N_2^{2+}\cdot 2Br^{-}\cdot CH_4O$
$M_r = 554.32$
Monoclinic, $P2_1/c$
$a = 21.134$ (4) Å
$b = 7.6390$ (15) Å
$c = 14.384$ (3) Å
$\beta = 98.625$ (7)°
$V = 2296.0$ (8) Å^3
$Z = 4$
$D_x = 1.604$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 778 reflections
$\theta = 5.7$–30°
$\mu = 3.55$ mm^{-1}
$T = 90$ (2) K
Plate, yellow
0.43 × 0.31 × 0.06 mm

Data collection

Bruker SMART 1000 diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{\min} = 0.280$, $T_{\max} = 0.815$
29 338 measured reflections
6700 independent reflections
5903 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.041$
$\theta_{\max} = 30.0°$
$h = -29 \rightarrow 29$
$k = -10 \rightarrow 10$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.071$
$S = 1.05$
6700 reflections
293 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0363P)^2 + 0.9274P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.99$ e Å^{-3}
$\Delta\rho_{\min} = -0.36$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···Br2	0.816 (16)	2.544 (16)	3.3514 (14)	170 (2)
C1—H1···Br1$^{\rm i}$	0.95	2.76	3.6067 (18)	149
C20—H20A···Br2$^{\rm ii}$	0.99	2.70	3.6865 (18)	175

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

H atoms bonded to C were refined as riding on their parent C atoms, with C—H distances of 0.95 Å (0.98 Å for methyl H atoms). The methanol H atom was located in a difference Fourier map and its position was freely refined. All $U_{\rm iso}$(H) values were set to $1.2U_{\rm eq}$ of the bonded atoms ($1.5U_{\rm eq}$ for methyl H atoms).

Data collection: *SMART* (Bruker, 2002); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL*97.

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