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4′-Hydroxy-4-methylstilbazolium tetraphenylborate dimethyl sulfoxide solvate

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In the title salt, $C_{14}H_{14}NO^{+}\cdot C_{24}H_{20}B^{-}\cdot C_2H_6OS$, the cation is nearly planar and is totally disordered, each of the two positions being occupied equally. The crystal structure has an O—H⋯O hydrogen bond between the disordered cation and the dimethyl sulfoxide molecule. A C—H⋯π interaction between the disordered cation and a phenyl ring of the tetraphenylborate anion is also present.

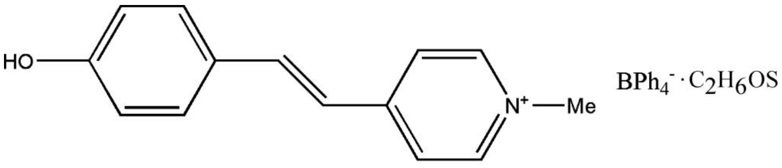
Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.046
wR factor = 0.121
Data-to-parameter ratio = 12.7

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

Comment

Considerable efforts have been made to investigate organic non-linear optical (NLO) materials (Chemla & Zyss, 1987). Marder *et al.* (1994) have successfully synthesized a number of crystals exhibiting second-harmonic generation (SHG) using their 'salt methodology', which suggests that the anion–cation interaction in organic salts can override the dipole–dipole interaction, which favours antiparallel centrosymmetric packing. During our systematic search for organic NLO compounds following this approach, we synthesized the title compound, (I), and we describe here its crystal structure.



(I)

In the title salt, (I) (Fig. 1), the cation is nearly planar, as shown in Table 1. The anion has a distorted tetrahedral geometry, the largest C—B—C angle being 112.99 (17)° and the smallest 104.87 (16)°.

In the crystal structure, the cation is totally disordered, with occupancy 0.5 for both positions. To analyse the reason for this disorder, the molecular packing in the crystal structure was studied by calculating packing energies using the *OPEC* program (Gavezzotti, 1983). The cations with unprimed and primed atoms are referred to as 1 and 2, respectively, and the results are given in Table 2. The data show that 1 and 2 have similar packing energies, and this may be the reason why the cation is disordered in the crystal structure. The cation and solvent molecule of the title compound are connected by an O—H⋯O hydrogen bond, with O⋯O = 2.73 (1) and 2.48 (1) Å and angles of 177 and 157° for the two disorder components. The cation, anion and solvent molecule of the title compound also have C—H⋯π interactions (Suezawa *et al.*, 2001), shown in Table 3 and Fig. 2.

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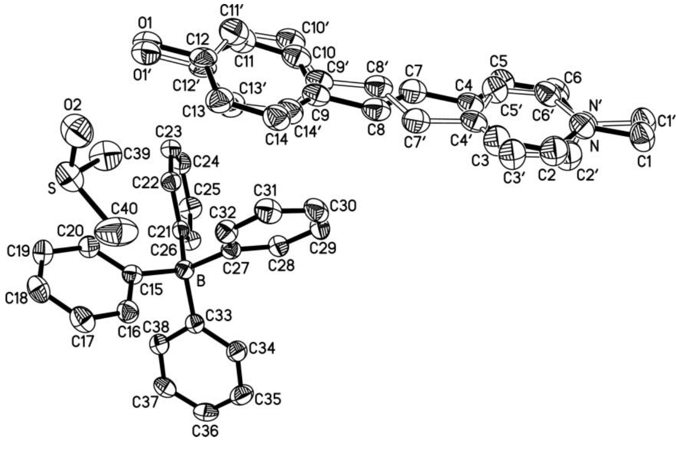

Figure 1

Molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. Both disorder components are shown, and H atoms have been omitted.

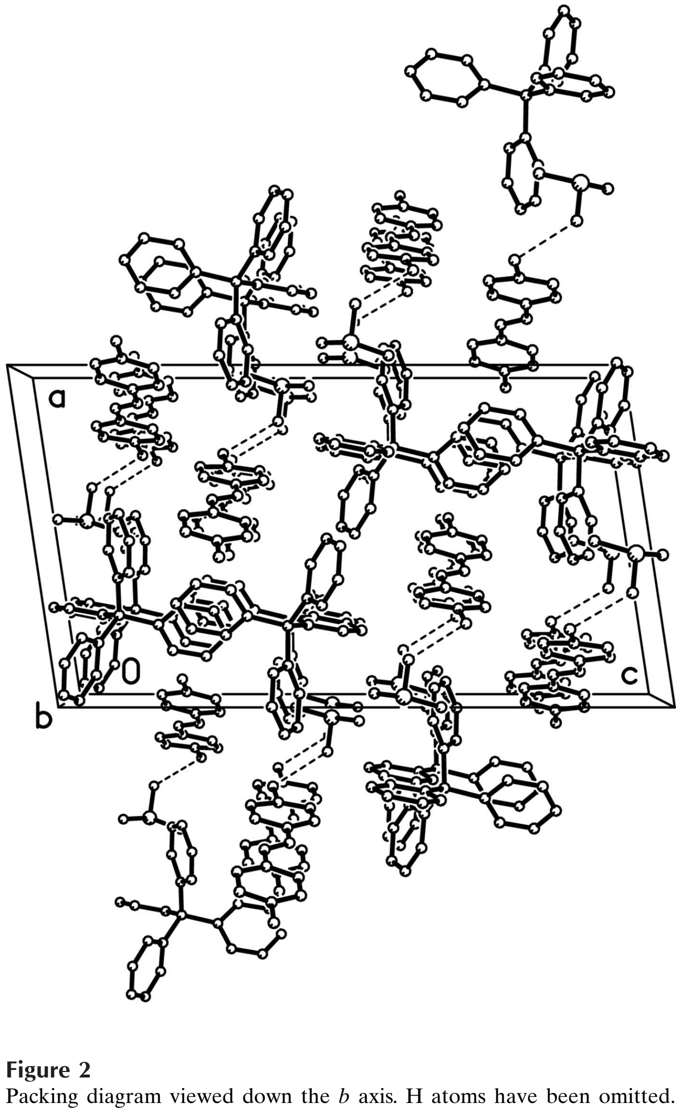

Figure 2

Packing diagram viewed down the *b* axis. H atoms have been omitted. Hydrogen bonds are shown as dashed lines. Only one disorder component is shown.

Experimental

1,4-Dimethylpyridinium iodide (7.05 g, 30 mmol, prepared from iodomethane and 1-methylpyridine), 4-hydroxybenzaldehyde (4.80 g, 49 mmol) and piperidine (0.2 ml) in methanol (40 ml) were heated at 353 K with stirring for 11 h (Okada *et al.*, 1990). The product was recrystallized twice from ethanol–water (2:1), dissolved in water (0.70 g in 100 ml) and treated with a saturated solution of sodium tetraphenylborate. The title compound was separated and recrystallized twice from ethanol–water (4:1), and crystals were grown from a solution in dimethyl sulfoxide.

Crystal data

$C_{14}H_{14}NO^+ \cdot C_{24}H_{20}B^- \cdot C_2H_6OS$
$M_r = 609.61$
Monoclinic, $P2_1/n$
$a = 13.624$ (2) Å
$b = 10.188$ (1) Å
$c = 24.248$ (3) Å
$\beta = 98.53$ (1)°
$V = 3328.4$ (7) Å^3
$Z = 4$
$D_x = 1.217$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 22 reflections
$\theta = 3.1$–13.6°
$\mu = 0.13$ mm^{-1}
$T = 298$ (2) K
Chunk, yellow
0.56 × 0.56 × 0.34 mm

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
6117 measured reflections
5852 independent reflections
3411 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.022$
$\theta_{\max} = 25.0°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 12$
$l = -28 \rightarrow 28$
3 standard reflections every 97 reflections intensity decay: 2.8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.121$
$S = 0.94$
5852 reflections
461 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0631P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.28$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0055 (6)

Table 1

Dihedral angles of the cation (°).

Name	A_{12}	A_{13}	A_{23}	B
Unprimed 1	7.5 (2)	3.9 (3)	3.7 (8)	177.2 (9)
Primed 2	7.7 (3)	9.1 (6)	1.4 (4)	−168.6 (11)

Notes: N—C6 (N′—C6′) pyridine ring is plane 1, C9—C14 (C9′—C14′) phenyl ring is plane 2 and the central C4—C7═C8—C9 unit is plane 3. A_{12}: the dihedral angle between plane 1 and plane 2. A_{13}: the dihedral angle between plane 1 and plane 3. A_{23}: the dihedral angle between plane 2 and plane 3. B: the torsion angle C4—C7═C8–C9.

Table 2

Packing energies calculated by *OPEC* (kJ mol^{-1}).

Interaction	Form 1	Form 2
Total	−290.826	−295.800
Cation–cation	−39.855	−41.409
Anion–anion	−54.143	−54.143
Cation–solvent	−12.933	−13.447
Anion–solvent	−37.652	−37.652
Anion–cation	−123.403	−127.880

Table 3
C—H···π interactions (Å, °).

C	H	P	$d_{\rm HP}$	d_{CP}	$A_{{\rm CH}P}$	Symmetry code
C40	H40*C*	*P*7	2.89	3.556 (4)	127	$-x + 1, -y + 1, -z$
C37	H37	*P*5	2.98	3.774 (4)	144	$-x, y - 1, z$
C6	H6	*P*7	2.49	3.374 (3)	159	$-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$
C6′	H6′	*P*7	2.63	3.527 (3)	162	$-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$
C1	H1*B*	*P*2	2.83	3.487 (4)	127	$x, y - 1, z$

Notes: *P*: the centres of planes; *P*2: the centre of the plane C9–C14; *P*5: the centre of the plane C15–C20; *P*7: the centre of the plane C27–C32; $d_{\rm HP}$: the distance of the H atom from the centre of the plane; d_{CP}: the distance of the C atom from the centre of the plane; $A_{{\rm CH}P}$: the angle between C—H and C···*P*.

H atoms were treated as riding, with C—H = 0.93 and 0.96 Å, and with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

Data collection: *XSCANS* (Siemens 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Sheldrick 1997); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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