organic compounds

4-[2-(4-Methoxyphenyl)ethenyl]-N-methylpyridinium tetraphenylborate

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In the cation of the title compound, $C_{15}H_{16}NO^+ \cdot C_{24}H_{20}B^-$, the pyridyl ring makes a dihedral angle of 14.03° with the phenyl ring. The anion has a slightly distorted tetrahedral geometry and forms honeycomb-like sheets which extend along the b axis, forming channels containing the cations. A comparison of packing energies reveals a difference between the title compound and a similar material which has non-linear optical properties.

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 line of thought, we synthesized the title compound, (I).

MeO—⟨phenyl⟩—CH=CH—⟨pyridinium⟩—N⁺—Me ·BPh₄⁻

(I)
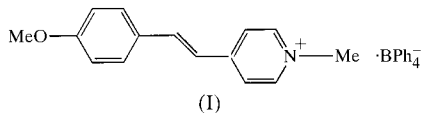
Compound (I) is a salt consisting of a $C_{15}H_{16}NO^+$ cation and a BPh_4^- anion. In the cation, the pyridyl ring makes a dihedral angle of 14.03° with the phenyl ring and both of these rings are essentially planar. The anion has a slightly distorted tetrahedral geometry (Table 1).

The crystals of (I) failed to crystallize in a non-centrosymmetric space group and therefore show no SHG effect. To analyse the reason for this, the molecular packing in the crystal was studied by calculating packing energies using the *OPEC* program (Gavezzotti, 1983); the results are listed in Table 2. The total packing energies for anion–anion, cation–cation and anion–cation interactions are −65.7, −47.0 and −124.6 kJ mol⁻¹, respectively. Crystals of a well known SHG
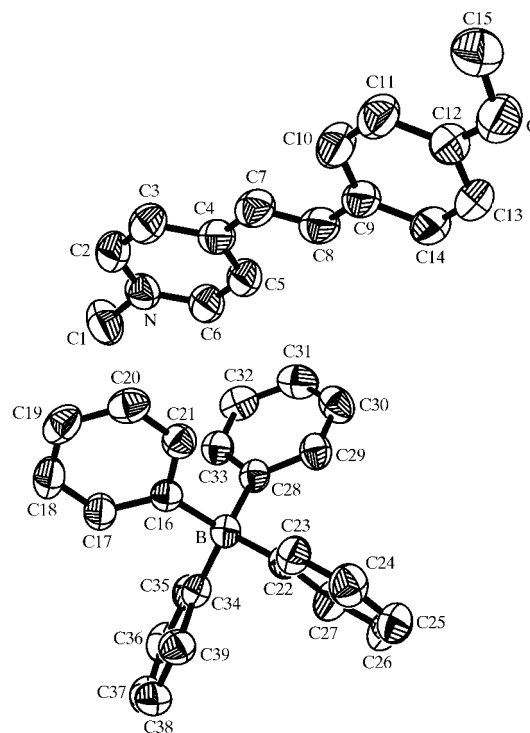

Figure 1
The molecular structure of (I) showing the atom-numbering scheme and 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

system, *i.e.* 4′-methoxy-N-methyl-4-stilbazolium tosylate (Marder *et al.*, 1994), have corresponding packing energies of −20.6, −76.1 and −126.6 kJ mol⁻¹, respectively. The centrosymmetric packing in the crystal of (I) is likely to be due to its
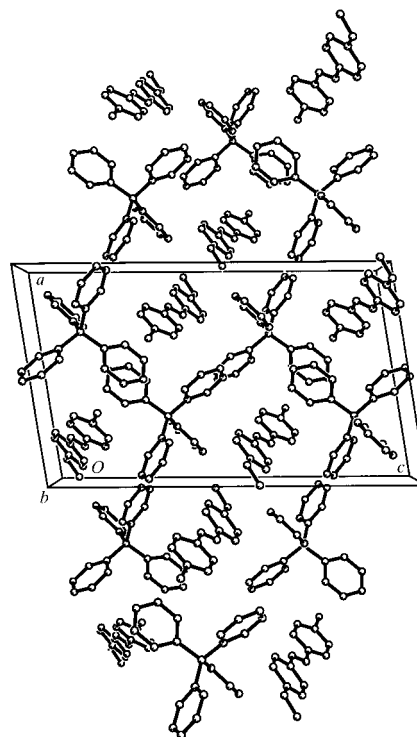

Figure 2
The packing diagram for (I) viewed down the b axis.

much stronger anion–anion interaction.

The anions form inversion-related pairs through $\pi \cdots \pi$ interactions. The planes defined by the phenyl ring made up of atoms C28–C33 and its closest symmetry-related partner $(1 - x, -1 - y, 1 - z)$ are separated by 2.2 Å; the centres of these two rings are 5.91 Å apart. The next closest anion–anion interaction occurs through the operation $(1 - x, \frac{1}{2} - y, \frac{3}{2} - z)$, and these three anions and their inversion-related counterparts form a distorted hexahedron-shaped channel along the b direction, similar in appearance to a honeycomb. Two inversion-related strands of cations run along these channels. This kind of three-dimensional structure probably contributes to the macroscopic morphology of the crystals, which grow as distinct granules, and might contribute to their application in a field other than SHG.

Experimental

1,4-Dimethylpyridinium iodide (7.05 g, 30 mmol, prepared from CH_3I and 1-methylpyridine), 4-methoxybenzaldehyde (6.67 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. Compound (I) was separated and recrystallized twice from ethanol–water (4:1), and yellow–green crystals (m.p. 509–510 K) were grown from a solution in *N,N*-dimethylformamide. IR spectroscopic analysis, cm^{-1}: 706, 976, 1142, 1173, 1304, 1335, 1424, 1516, 1598, 1647, 3052; elemental analysis, found: C 86.28, H 6.57, N 2.49%; $C_{15}H_{16}NO^+ \cdot BPh_4^-$ requires: C 85.86, H 6.65, N 2.57%.

Crystal data

$C_{15}H_{16}NO^+ \cdot C_{24}H_{20}B^-$	$D_x = 1.202$ Mg m^{-3}
$M_r = 545.50$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 26
$a = 13.029$ (2) Å	reflections
$b = 10.819$ (2) Å	$\theta = 3.81$–$17.23°$
$c = 21.660$ (3) Å	$\mu = 0.070$ mm^{-1}
$\beta = 99.160$ (10)°	$T = 296$ (2) K
$V = 3014.3$ (8) Å^3	Granular, yellow–green
$Z = 4$	$0.60 \times 0.56 \times 0.52$ mm

Data collection

Siemens $P4$ diffractometer	$h = 0 \rightarrow 15$
ω scans	$k = -1 \rightarrow 12$
6502 measured reflections	$l = -25 \rightarrow 25$
5318 independent reflections	3 standard reflections
3204 reflections with $I > 2\sigma(I)$	every 97 reflections
$R_{int} = 0.010$	intensity decay: 2.74%
$\theta_{max} = 25.01°$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.047P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.036$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.088$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.868$	$\Delta\rho_{max} = 0.13$ e Å^{-3}
5318 reflections	$\Delta\rho_{min} = -0.11$ e Å^{-3}
382 parameters	Extinction correction: *SHELXL*97
H-atom parameters constrained	Extinction coefficient: 0.0103 (7)

H atoms were placed theoretically according to standard geometries, with all C—H distances being 0.93 Å, except for those involving C1 and C15 which were 0.96 Å.

Table 1
Selected geometric parameters (Å, °).

O—C12	1.3642 (19)	N—C1	1.468 (2)
O—C15	1.4221 (19)	C4—C7	1.449 (2)
N—C2	1.340 (2)	C7—C8	1.325 (2)
N—C6	1.3443 (19)	C8—C9	1.453 (2)
C12—O—C15	118.24 (14)	C28—B—C34	113.07 (12)
C2—N—C6	119.41 (15)	C22—B—C16	113.01 (12)
C2—N—C1	119.98 (15)	C28—B—C16	105.12 (11)
C6—N—C1	120.56 (14)	C34—B—C16	109.94 (11)
C22—B—C28	109.87 (12)	C8—C7—C4	126.42 (16)
C22—B—C34	105.98 (12)	C7—C8—C9	126.94 (15)
C3—C4—C7—C8	168.18 (16)	C7—C8—C9—C14	176.17 (16)
C4—C7—C8—C9	−175.97 (15)	C15—O—C12—C11	−5.8 (2)
C7—C8—C9—C10	−3.9 (3)	C15—O—C12—C13	175.51 (14)

Table 2
Ion-packing energies (PE) (kJ mol^{-1}).

Interaction	PE	Interaction	PE
anion–anion[i]	−12.1	cation–cation[viii]	−12.6
anion–anion[ii]	−10.0	anion–cation[i]	−23.6
anion–anion[iii]	−10.0	anion–cation[ii]	−25.7
anion–anion[iv]	−7.1	anion–cation[ii]	−25.7
anion–anion[v]	−7.1	anion–cation[vii]	−6.9
cation–cation[vi]	−15.3	anion–cation[viii]	−6.9
cation–cation[vii]	−12.6	anion–cation[vi]	−0.2

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

Data collection and cell refinement: *XSCANS* (Siemens, 1994); data reduction: *SHELXTL* (Sheldrick, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics and software used to prepare material for publication: *SHELXTL*.

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