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4-[2-(3-Methoxyphenyl)ethenyl]-*N*-methylpyridinium tetraphenylborate[1]

Dan Jin,[a] Zhao-Fu Dai[a] and De-Chun Zhang[b]*

[a]Wannan Medical College, Wuhu 241002, People's Republic of China, and [b]Department of Chemistry, Suzhou University, Suzhou 215006, People's Republic of China
Correspondence e-mail: dczyqz@tom.com

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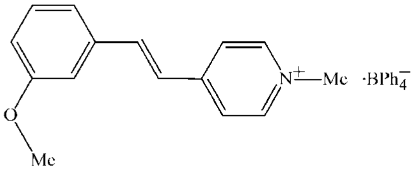
In the title compound, $C_{15}H_{16}NO^+\cdot C_{24}H_{20}B^-$, the pyridinium ring of the cation makes a dihedral angle of 4.3 (2)° with the benzene ring. Each is rotated in the same direction with respect to the central C—CH═CH—C linkage, by 10.0 (2) and 7.8 (2)°, respectively. The anions have a slightly distorted tetrahedral geometry. The most interesting feature of the structure is that the anions form a honeycomb-like hexagonal structure down the *b* axis through C—H···π interactions. The hexagon is constructed from six BPh_4^- anions. The cations interact in a head-to-tail fashion along [010], forming chains, and pack antiparallel inside the above honeycomb-like structure through C—H···π interactions.

Comment

Considerable effort has been made to investigate organic salts with large second-order optical nonlinearities (Chemla & Zyss, 1987). Marder *et al.* (1994) have synthesized a number of stilbazolium salts with large powder second harmonic generation (SHG) efficiencies. During our systematic research for organic nonlinear optical materials, we isolated the title compound, (I), and describe its crystal structure here.

Molecule (I) consists of a 3-methoxy-*N*-methyl-4-stilbazolium cation and a BPh_4^- anion. In the cation, which is nearly planar and in the *trans* form (Fig. 1), the pyridinium ring makes a dihedral angle of 4.3 (2)° with the benzene ring. They are rotated in the same direction with respect to the central C—CH═CH—C linkage, by 10.0 (2) and 7.8 (2)°, respectively. The anion takes a slightly distorted tetrahedral geometry. The B—C bond lengths are in the range 1.640 (3)–1.652 (3) Å, and the C—B—C bond angles are in the range 104.8 (2)–113.7 (2)°. Further geometric parameters are given in Table 1

The most interesting feature in the crystal structure is that the anions form a honeycomb-like hexagonal structure along the *b* axis. Table 2 lists the most important C—H···π interactions (type I; Umezawa *et al.*, 1998). We can see the interactions between the fundamental molecule (FM) and its surrounding molecules (SMs). In particular, the anion–anion and cation–anion interactions are C—H···π type. The cations pack in an antiparallel fashion inside the above honeycomb-like structure (Fig. 2) through C—H···π interactions. In the crystal structure, a hexagon is constructed by the six BPh_4^- anions whose central B atoms are labelled B1–B6 in Fig. 2. The portioning scheme in the program *OPEC* (Gavezzotti, 1983) with largely improved parameters (Gavezzotti & Filippini, 1994) was used to analyse the packing mode. Table 3 lists the corresponding data. According to Table 3, these factors probably contribute to the macroscopic morphology of the crystal structure. Therefore, the crystal might have potential applications in a field other than SHG.



(I)

The organic salt methodology principle (Marder *et al.*, 1989) suggests that the anion–cation interaction in organic salts could override the dipole–dipole interaction, which provides a strong driving force for centrosymmetric packing in dipolar crystals. However, compound (I) is crystallized in the centrosymmetric space group $P2_1/c$ and shows no SHG effect. To analyse the reason for this, a search was carried out of the Cambridge Structural Database (CSD; Version 5.26; Allen, 2002) for stilbazolium tetraphenylborates. The total packing energies for cation–cation, anion–anion and anion–cation interactions were calculated using *OPEC*. The results for the

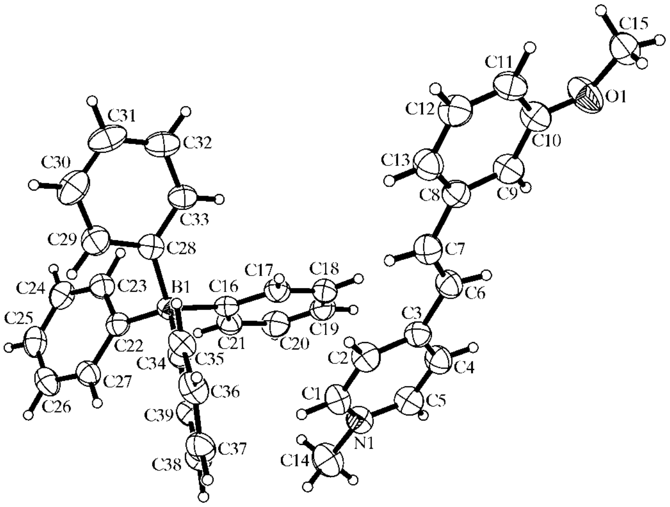


Figure 1
The molecular structure of the title compound, showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms are shown as small spheres of arbitrary radii.

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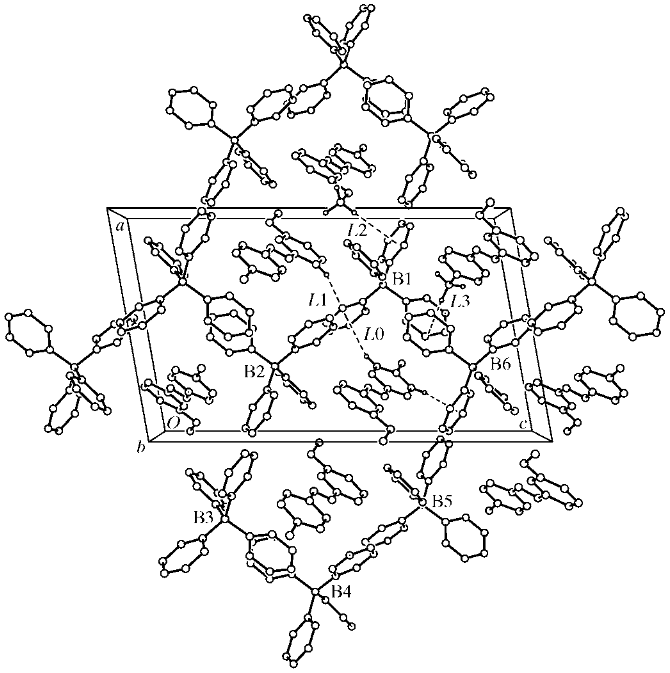

Figure 2
The packing for (I), viewed down the b axis. Key: $L0$ = C1—H1$\cdots$$P7$; $L1$=C13—H13$\cdots$$P7(1-x,1-y,1-z)$; $L2$=C15—H15$B$$\cdots$$P5(x+1,y-1,$ $y-1,z)$; $L3$ = C14—H14$A$$\cdots$$P4(-x+1, y+\frac{1}{2}, -z+\frac{3}{2})$. Table 2 lists the detailed geometric data.

related structures found in the search are listed in Table 4. As shown by Table 4, the data are very limited and the calculated absolute total PE value is not very accurate, but we could tentatively state that the centrosymmetric packing of the title crystal is likely to be due to the much stronger anion–anion interaction.

Experimental

1,4-Dimethylpyridinium iodide (7.05 g, 30 mmol), prepared from CH_3I (4.5 ml, 89 mmol) and 1-methylpyridine (7.0 ml, 72 mmol), 3-methoxybenzaldehyde (6.67 g, 49 mmol) and piperidine (0.2 ml) in methanol (40 ml) were heated at 353 K with stirring for 8 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, recrystallized twice from ethanol–water (4:1), and finally crystallized from ethanol–acetone (2:1). Brown–yellow crystals of (I) (m.p. 462–463 K) were grown by slow evaporation at ambient temperature for two weeks. Elemental analysis calculated for $C_{15}H_{16}NO^+\cdot BPh_4^-$: C 85.87, H 6.61, N 2.57%; found: C 85.97, H 6.84, N 2.47%. IR (KBr pellets, cm^{-1}): 3053 (Ar—H), 3001 (C—H), 1620 (–CH=CH–), 1579 (–CH=N–), 1515 (Ph), 1467 (Ph), 1427 (Ph), 1250 (–CH_3), 1186 (–C—O–), 1032 (–CH=C—H), 953(–CH=C—H), 842 (Ar—H), 735 (Ar—H), 708 (Ar—H), 681 (Ar—H). ^1H NMR (DMSO, 399.97 MHz, ambient temperature): δ 8.85 (*d*, 2H, pyridyl ring), 8.20 (*d*, 2H, pyridyl ring), 7.94 (*s*, 1H, Ph), 7.53 (*d*, 1H, Ph), 7.40 (*m*, 1H, Ph), 7.32 (*s*, 2H, –CH=CH–), 7.17 (*s*, 8H, Ph), 7.04 (*d*, 1H, Ph), 6.94–6.90 (*m*, 8H, Ph), 6.80–6.77 (*m*, 4H, Ph), 4.25 (*s*, 3H, –CH_3), 3.83 (*s*, 3H, –CH_3).

Crystal data

$C_{15}H_{16}NO^+\cdot C_{24}H_{20}B^-$
M_r = 545.50
Monoclinic, $P2_1/c$
a = 12.8417 (18) Å
b = 10.8158 (16) Å
c = 21.790 (4) Å
β = 100.106 (5)°
V = 2979.5 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.07 mm^{-1}
T = 193 (2) K
0.35 × 0.30 × 0.11 mm

Data collection

Rigaku Mercury diffractometer
Absorption correction: multi-scan (Rigaku, 1999; Jacobson, 1998)
$T_{\min}$ = 0.98, $T_{\max}$ = 0.99
28897 measured reflections
5440 independent reflections
4141 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.062

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.069
$wR(F^2)$ = 0.144
S = 1.18
5440 reflections
383 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.15 e Å^{-3}
$\Delta\rho_{\min}$ = −0.17 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C10	1.367 (3)	N1—C14	1.480 (3)
O1—C15	1.424 (3)	C3—C6	1.461 (3)
N1—C5	1.342 (3)	C6—C7	1.325 (3)
N1—C1	1.344 (3)	C7—C8	1.465 (3)
C10—O1—C15	117.6 (2)	C7—C6—C3	123.8 (2)
C5—N1—C1	119.6 (2)	C6—C7—C8	127.8 (2)
C5—N1—C14	120.3 (2)	O1—C10—C11	123.6 (2)
C1—N1—C14	120.0 (2)	O1—C10—C9	115.9 (2)
C2—C3—C6—C7	−7.3 (4)	C6—C7—C8—C9	5.8 (4)
C4—C3—C6—C7	170.1 (2)	C6—C7—C8—C13	−172.7 (3)
C3—C6—C7—C8	−178.0 (2)		

Table 2
C—H$\cdots\pi$ interactions (Å, °) in (I).

C—H$\cdots$Plane^a	$d_{\rm HP}$^{b}	τ^c	Symmetry code
C1—H1$\cdots$$P7$	2.48	16	x, y, z
C13—H13$\cdots$$P7$	2.62	16	$-x+1, -y+1, -z+1$
C15—H15$B$$\cdots$$P5$	2.71	43	$x-1, y+1, z$
C14—H14$A$$\cdots$$P4$	2.82	56	$-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$

Notes: (*a*) the planes are defined as follows: $P4$ = C16–C21, $P5$ = C22–C27 and $P7$ = C34–C39 in the FM. The CH group is in a certain SM. (*b*) The distance of the H atom from the plane. (*c*) The angle formed by the C—H vectors and the perpendicular line passing from the H atom to the plane. The first five interactions are, respectively, indicated in Fig. 2 with dashed lines $L0$–$L4$.

Table 3
Data related to the honeycomb-like hexagonal structure.

Interacting anions^a	PE^b
B1$\cdots$B2	−5.5
B2$\cdots$B3	−3.3
B3$\cdots$B4	−4.8
B4$\cdots$B5	−5.5
B5$\cdots$B6	−3.3
B6$\cdots$B1	−4.8

Notes: (*a*) symmetry codes: B1 (x, y, z), B2 $(-x+1, -y+1, -z+1)$, B3 $(x-1, -y+\frac{1}{2}, z-\frac{1}{2})$, B4 $(-x, -y+1, -z+1)$, B5 $(x-1, y+1, z)$, B6 $(-x+1, y+\frac{1}{2}, -z+\frac{3}{2})$. (*b*) Packing energies (kcal mol^{-1}) calculated using *OPEC* (Gavezzotti, 1983) with the set of parameters defined by Gavezzotti & Filippini (1994).

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Table 4
Packing energies (PE) of some stilbazolium tetraphenylborates (kcal mol^1).

Refcode	Substituent	Space group	Total PE[a]	(a–a)%[a]	(c–a)%[a]	μ[b]
BOQKEX[c]	3,4-OCH_3	*Cc*	−264.73	16.35	68.51	18.34
A[d]	4-Cl	*Fdd*2	−223.99	20.97	68.84	13.97
B[e]	4-CN	*Cc*	−258.74	20.97	65.51	18.85
QOBDEQ[f]	4-$N(OCH_3)_2$	$P2_1/c$	−235.73	22.63	53.16	15.61
WOCRAH[g]	4-OCH_3	$P2_1/c$	−257.22	23.29	58.42	14.63
I[h]	3-OCH_3	$P2_1/c$	−253.75	24.42	58.23	14.24

Notes: (*a*) packing energies were calculated using *OPEC* (Gavezzotti, 1983). (*a*–*a*)%: the percentage for the anion–anion interaction in the total PE. (*c*–*a*)%: the percentage for the cation–anion interaction in the total PE. (*b*) Dipole moment of the cation (Debye) calculated by *MOPAC* (Dewar *et al.*, 1985) with the dipole moment summation method (Kurtz *et al.*, 1990). References: (*c*) Zhang *et al.* (1999); (*d*) Jin *et al.* (2005); (*e*) Jin & Zhang (2005); (*f*) Li *et al.* (2000*a*); (*g*) Li *et al.* (2000*b*); (*h*) this study.

H atoms were positioned geometrically and treated as riding [C—H = 0.95–0.98 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C aromatic) or $U_{\rm eq}$(H) = 1.5$U_{\rm eq}$(C methyl)].

Data collection: *CrystalClear* (Rigaku, 1999); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3171). Services for accessing these data are described at the back of the journal.

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