

4-[2-(4-Cyanophenyl)ethenyl]-*N*-methylpyridinium tetraphenylborate

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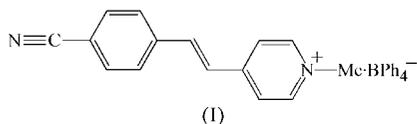
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In the title compound,  $C_{15}H_{13}N_2^+ \cdot C_{24}H_{20}B^-$ , the pyridyl ring of the cation makes a dihedral angle of  $1.6^\circ$  with the benzene ring. Each is rotated in the same direction with respect to the central  $-C-CH=CH-C-$  linkage, by  $3.8$  and  $5.3^\circ$ , respectively. The anions have a slightly distorted tetrahedral geometry. Molecular packing analysis was carried out using the packing energy portioning scheme in the program *OPEC*. Around each anion in the crystal structure there are eight anions, which interact with the central anion through  $C-H \cdots \pi$  interactions. The cations are hydrogen bonded in a head-to-tail fashion, forming chains along  $[10\bar{1}]$ .

## Comment

Considerable effort has been made to investigate organic salts with large second-order optical non-linearities (Chemla & Zyss, 1987). Marder *et al.* (1994) have synthesized a number of stilbazolium salts with large powder second harmonic generation (SHG) efficiencies. According to the organic 'salt methodology' principle (Marder *et al.*, 1989, 1994), Coulombic interactions in organic salts could override dipole-dipole interactions which are favoured for antiparallel centrosymmetric packing. During our systematic search for organic non-linear optical (NLO) materials, we isolated the title compound, (I), and describe its crystal structure here.



Compound (I) consists of a 4'-cyano-4-*N*-methylstilbazolium cation and a  $BPh_4^-$  anion. In the cation, which is nearly planar and in the *trans* form (Fig. 1), the pyridyl ring makes a dihedral angle of  $1.6^\circ$  with the benzene ring. The rings are rotated in the same direction with respect to the central  $-C-CH=CH-C-$  linkage, by  $3.8$  and  $5.3^\circ$ , respectively. The anion adopts a slightly distorted tetrahedral geometry. The  $B-C$  bond lengths are in the range  $1.628$  (6)– $1.660$  (6) Å and

the  $C-B-C$  bond angles are in the range  $102.8$  (4)– $114.0$  (2) $^\circ$  (Table 1).

The portioning scheme in the program *OPEC* (Gavezzotti, 1983) with largely improved parameters (Gavezzotti & Filippini, 1994) was used to analyse the packing mode for the cations and anions in the crystal structure of (I). Table 3 lists the most important  $C-H \cdots \pi$  interactions (type I; Umezawa *et al.*, 1998) in the title crystal. Table 4 lists the calculated packing energy (PE) between the fundamental molecule (FM) and its surrounding molecules (SMs) which most strongly interact with the FM. Although the absolute total PE calculated is not very accurate (about  $2 \text{ kcal mol}^{-1}$ ;  $1 \text{ kcal mol}^{-1} = 4.184 \text{ kJ mol}^{-1}$ ; Gavezzotti & Filippini, 1994), the relative order after portioning into the contributions for individual SMs is believed to be meaningful. According to Table 4, the anion in the FM most strongly interacts with the first eight anions in the SMs, or in this sense, it is surrounded by these eight anions. When comparing the SMs in both Tables 3 and 4, one can see that the interactions between the FM and SMs, particularly the anion-anion and cation-anion interactions, are  $C-H \cdots \pi$  type (type I; Umezawa *et al.*, 1998). On the other hand, the major cation-cation interaction is the hydrogen bond (line 1 in Table 2) between the N atom in CN and the  $C-H$  group on the opposite side of the cation. This is therefore in a head-to-tail mode and forms chains along  $[10\bar{1}]$ .

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. Compound (I) crystallized in the non-centrosymmetric space group *Cc*, belonging to point group *m*, one of the favourable groups for SHG, and is therefore a potential SHG crystal. However, not all similar crystals are non-centrosym-

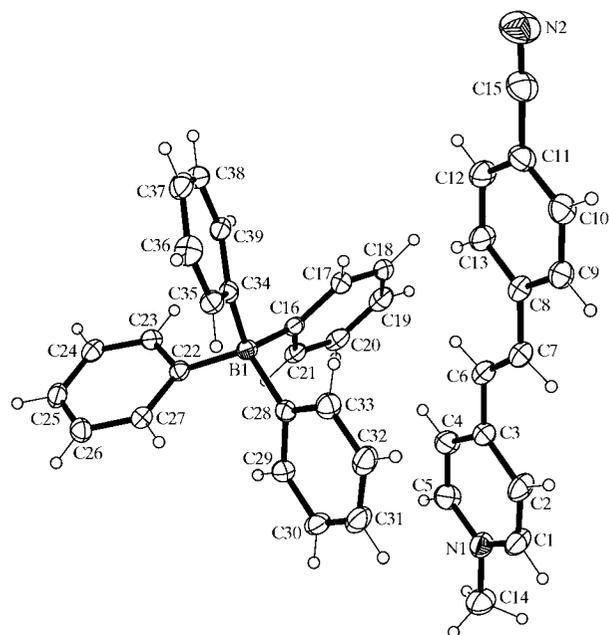
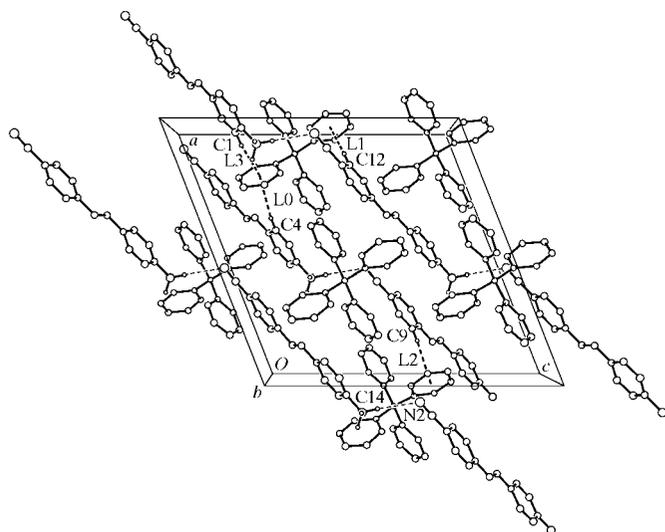


Figure 1

A view of 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.



**Figure 2**

A packing diagram for (I), viewed down the *b* axis. Key: L0 is C4–H4··P4; L1 is C12–H12··P5( $x, 1 - y, z + \frac{1}{2}$ ); L2 is C9–H9··P5( $x + \frac{1}{2}, \frac{1}{2} - y, z + \frac{1}{2}$ ); L3 is C1–H1··P4( $x + \frac{1}{2}, y + \frac{1}{2}, z$ ); for detailed geometric data, see Table 3.

metric. A search was carried out of the Cambridge Structural Database (CSD, Version 5.26; Allen, 2002) for stilbazolium tetraphenylborates and resulted in three structures. In order to estimate the relative contributions of the cation–cation, anion–anion and anion–cation interactions, packing energies were calculated on these three structures and (I) using the program *OPEC*. The results are listed in Table 5. Although the data are very limited and the calculated absolute total PE value is not very accurate, we could tentatively state that the non-centrosymmetric packing of the title crystal is possibly due to the much stronger anion–cation interaction.

### Experimental

1,4-Dimethylpyridinium iodide (7.05 g, 30 mmol) (prepared from CH<sub>3</sub>I and 1-methylpyridine), 4-cyanobenzaldehyde (6.42 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 *v/v*), 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). Yellow crystals of (I) (m.p. 489–490 K) were grown by slow evaporation at ambient temperature from *N,N*-dimethylformamide over a period of 18 d. Elemental analysis (Perkin–Elmer 240C elemental analyser): calculated for C<sub>15</sub>H<sub>13</sub>N<sub>2</sub><sup>+</sup>·BPh<sub>4</sub><sup>−</sup>: C 86.67, H 6.11, N 5.19%; found: C 87.09, H 6.27, N 4.85%. IR (FT–IR spectrometer with KBr pellets,  $\nu$ , cm<sup>−1</sup>): 3050 (Ar–H), 2995 (–C–H), 2227 (cyano), 1644 (–CH=CH–), 1627 (–CH=N–), 1519 (Ph), 1478 (Ph), 1427 (Ph), 1334 (–CH<sub>3</sub>), 1188 (–CH=C–H), 1151 (–CH=C–H), 1031 (Ar–H), 972 (Ar–H), 955 (Ar–H), 848 (Ar–H), 733 (Ar–H), 711 (Ar–H); <sup>1</sup>H NMR (Bruker AV-400 NMR spectrometer, DMSO, 399.97 MHz, ambient temperature):  $\delta$  8.91 (*d*, 2H, pyridyl ring), 8.25 (*d*, 2H, pyridyl ring), 8.03 (*d*, 1H, –CH=CH–), 7.97 (*d*, 2H, Ph), 7.91 (*d*, 2H, Ph), 7.32 (*d*, 1H, –CH=CH–), 7.18 (*s*, 8H, Ph), 6.94–6.90 (*m*, 8H, Ph), 6.80–6.77 (*m*, 4H, Ph), 2.50 (*s*, 3H, –CH<sub>3</sub>).

### Crystal data

C<sub>15</sub>H<sub>13</sub>N<sub>2</sub><sup>+</sup>·C<sub>24</sub>H<sub>20</sub>B<sup>−</sup>  
*M<sub>r</sub>* = 540.48  
 Monoclinic, *Cc*  
*a* = 16.930 (3) Å  
*b* = 10.7694 (18) Å  
*c* = 17.665 (3) Å  
 $\beta$  = 111.543 (5)°  
*V* = 2995.8 (9) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.198 Mg m<sup>−3</sup>  
 Mo *K*α radiation  
 Cell parameters from 5327 reflections  
 $\theta$  = 3.0–25.3°  
 $\mu$  = 0.07 mm<sup>−1</sup>  
*T* = 193 (2) K  
 Block, yellow  
 0.50 × 0.19 × 0.11 mm

### Data collection

Rigaku Mercury diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (Jacobson, 1998)  
*T<sub>min</sub>* = 0.966, *T<sub>max</sub>* = 0.993  
 14471 measured reflections  
 2726 independent reflections

2355 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.047  
 $\theta_{max}$  = 25.3°  
*h* = −20 → 20  
*k* = −12 → 12  
*l* = −20 → 21

**Table 1**

Selected geometric parameters (Å, °).

N1–C5	1.339 (6)	C7–C8	1.464 (6)
N1–C1	1.344 (6)	C11–C15	1.443 (6)
N1–C14	1.479 (6)	C16–B1	1.643 (6)
N2–C15	1.148 (6)	C22–B1	1.628 (6)
C3–C6	1.451 (6)	C28–B1	1.660 (6)
C6–C7	1.328 (5)	C34–B1	1.635 (6)
C5–N1–C1	120.0 (4)	C13–C8–C9	118.8 (4)
C5–N1–C14	120.0 (4)	C13–C8–C7	121.5 (4)
C1–N1–C14	120.0 (4)	C9–C8–C7	119.6 (4)
C4–C3–C2	116.8 (4)	C10–C11–C12	120.6 (4)
C4–C3–C6	119.6 (4)	C10–C11–C15	121.1 (4)
C2–C3–C6	123.6 (4)	C12–C11–C15	118.3 (4)
C7–C6–C3	126.3 (3)	N2–C15–C11	177.7 (5)
C6–C7–C8	125.7 (3)		

**Table 2**

Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
C14 <sup>i</sup> –H14A <sup>i</sup> ··N2	0.98	2.54	3.463 (7)	157
C35 <sup>ii</sup> –H35 <sup>ii</sup> ··N2	0.95	2.65	3.359 (8)	131

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

**Table 3**

C–H···π interactions (Å, °) in (I).

C	H	Plane†	<i>d</i> <sub>HP</sub> ‡	τ§	Molecule¶
C4	H4	<i>P</i> <sub>4</sub>	2.88	13.3	FM
C12	H12	<i>P</i> <sub>5</sub>	2.46	20.9	3
C9	H9	<i>P</i> <sub>5</sub>	2.91	12.5	5
C1	H1	<i>P</i> <sub>4</sub>	2.53	16.6	7
C37	H37	<i>P</i> <sub>4</sub>	2.13	23.4	1
C37	H37	<i>P</i> <sub>6</sub>	2.27	30.9	1
C5	H5	<i>P</i> <sub>7</sub>	2.60	23.8	2
C18	H18	<i>P</i> <sub>6</sub>	2.51	30.5	3
C29	H29	<i>P</i> <sub>2</sub>	2.66	17.0	4
C26	H26	<i>P</i> <sub>7</sub>	2.27	20.7	4
C31	H31	<i>P</i> <sub>5</sub>	2.09	24.0	7
C31	H31	<i>P</i> <sub>7</sub>	2.27	29.5	7
C39	H39	<i>P</i> <sub>1</sub>	2.79	15.5	8

† The planes *P*<sub>1</sub> (C1–C5/N1), *P*<sub>2</sub> (C8–C13), *P*<sub>3</sub> (C3/C6–C8), *P*<sub>4</sub> (C16–C21), *P*<sub>5</sub> (C22–C27), *P*<sub>6</sub> (C28–C33) and *P*<sub>7</sub> (C34–C39) in the fundamental molecule (FM). The C–H group is in a particular surrounding molecule (SM), specified by the code in the last column. ‡ *d*<sub>HP</sub> is the distance of the H atom from the plane. § τ is the angle formed by the vectors of C–H and the perpendicular line passing through the H atom to the plane. ¶ The SMs which interact most strongly with the FM, numbered as in Table 4. The first four interactions are indicated in Fig. 2 by bold dashed lines and labelled L0–L3.

**Table 4**The packing energy (PE) portioning in (I) (kcal mol<sup>-1</sup>).

Molecule†	PE‡	c-c§	a-a¶	c-a††	d <sub>B...B‡‡</sub>	Symmetry code
1	-12.1	-5.9	-2.6	-3.6	10.03	(x - 1/2, y + 1/2, z)
2	-12.1	-5.9	-2.6	-3.6	10.03	(x + 1/2, y - 1/2, z)
3	-10.2	-0.4	-4.4	-5.4	8.84	(x, -y + 1, z + 1/2)
4	-10.2	-0.4	-4.4	-5.4	8.84	(x, -y + 1, z - 1/2)
5	-10.0	-0.9	-0.7	-8.4	11.00	(x + 1/2, -y + 1/2, z + 1/2)
6	-10.0	-0.9	-0.7	-8.4	11.00	(x - 1/2, -y + 1/2, z - 1/2)
7	-7.2	-0.3	-2.6	-4.3	10.03	(x + 1/2, y + 1/2, z)
8	-7.2	-0.3	-2.6	-4.3	10.03	(x - 1/2, y - 1/2, z)
9	-4.1	-0.4		-3.7		(x, -y, z + 1/2)
10	-4.1	-0.4		-3.7		(x, -y, z - 1/2)
11	-3.5		-1.6	-1.9		(x - 1/2, -y + 3/2, z - 1/2)
12	-3.5		-1.6	-1.9		(x + 1/2, -y + 3/2, z + 1/2)
13	-2.6		-0.7	-1.9		(x, y - 1, z)
14	-2.6		-0.7	-1.9		(x, y + 1, z)
Total	-123.7	-16.7	-25.9	-81.1		

† Taking one molecule in the crystal as the fundamental molecule (FM), then all surrounding molecules (SMs) interact with the FM, each of which may correspond to a certain symmetry operator when the asymmetric unit consists of one or less than one molecule. ‡ The packing energies, calculated using the program *OPEC* (Gavezzotti, 1983) with the improved set of parameters (Gavezzotti & Filippini, 1994). Value omitted if it is less than 1% of the total PE in the column. § The PE between the cation in the FM and that in the SM indicated by the symmetry code in the last column. ¶ The PE between the anion in the FM and that in the SM indicated by the symmetry code in the last column. †† The PE between the cation in the FM and the anion in the SM indicated by the symmetry code in the last column. ‡‡ The distance between the central B atoms. Value omitted if it is greater than 11 Å.

**Refinement**

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.051$   
 $wR(F^2) = 0.121$   
 $S = 1.11$   
 2726 reflections  
 381 parameters  
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0568P)^2 + 0.9638P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.15 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.18 \text{ e } \text{Å}^{-3}$

All H atoms were treated as riding using the riding model. C—H distances for C<sub>ar</sub> and Csp<sup>2</sup> were set at 0.95 Å, and for Csp<sup>3</sup> were set at 0.98 Å;  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for C<sub>ar</sub> and Csp<sup>2</sup>, and  $1.5U_{\text{eq}}(\text{C})$  for Csp<sup>3</sup>.

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

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**Table 5**Packing energies† of some stilbazolium tetraphenylborates (kcal mol<sup>-1</sup>).

CSD refcode	Total PE	Space group	(a-a)%‡	(c-a)%§	μ¶	Substituent group
QOBDEQ <sup>a</sup>	-235.73	<i>P2<sub>1</sub>/c</i>	22.63	53.16	15.61	4-N(OCH <sub>3</sub> ) <sub>2</sub>
WOCRAH <sup>b</sup>	-257.22	<i>P2<sub>1</sub>/c</i>	23.29	58.42	14.63	4-OCH <sub>3</sub>
BOOKEX <sup>c</sup>	-264.73	<i>Cc</i>	16.35	68.51	18.34	3,4-OCH <sub>3</sub>
(I) <sup>d</sup>	-258.74	<i>Cc</i>	20.97	65.51	18.85	4-CN

† Packing energies calculated using the program *OPEC* (Gavezzotti, 1983). ‡ (a-a)% is the percentage for the anion–anion interaction in the total PE. § (c-a)% is the percentage for the cation–anion interaction in the total PE. ¶ The dipole moment of the cation (Debye), calculated by the program *MOPAC* (Dewar *et al.*, 1985) using the dipole moment summation method (Kurtz *et al.*, 1990). References: (a) Li *et al.* (2000a); (b) Li *et al.* (2000b); (c) Zhang *et al.* (1999); (d) this study.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF1010). Services for accessing these data are described at the back of the journal.

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