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

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Key indicators

Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.005 Å
R factor = 0.058
wR factor = 0.140
Data-to-parameter ratio = 15.0

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

The cation of the title compound, $C_{14}H_{13}NCl^{+}\cdot B(C_6H_5)_4^{-}$, has a *cis* configuration at the C=C double bond. The pyridyl ring makes a dihedral angle of 53.8 (4)° with the benzene ring. Each cation is paired with another related by a twofold rotation through a π–π interaction and the cations also interact through a weak C—H$\cdots$Cl interaction. The crystal structure is further stabilized by C—H$\cdots\pi$ interactions.

Comment

Studies have been made on 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. According to the organic 'salt methodology' principle (Marder *et al.*, 1989), Coulombic interactions in organic salts can override dipole–dipole interactions which are favoured for antiparallel centrosymmetric packing. During our systematic research for organic nonlinear optical (NLO) materials, we isolated the title compound, (I), and describe its crystal structure here.

(I)
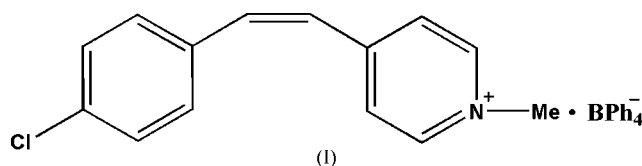
In the cation of the title compound, (I) (Fig. 1 and Table 1), which has a *cis* configuration, the pyridyl ring makes a dihedral angle of 53.8 (4)° with the benzene ring. The anion geometry is unexceptional.

Molecular packing energy calculations were done using the program *OPEC* (Gavezzotti, 1983; Gavezzotti & Filippini, 1994); Table 2 lists the most important interactions. Cations related by twofold rotation are paired through a π–π interaction (the distances between the parallel planes and between their centroids are 3.78 and 4.09 Å, respectively). The cations interact further through a weak C—H$\cdots$Cl interaction in a head-to-tail fashion, forming a chain along [011]. Between the ions, namely cation–cation, anion–anion and particularly anion–cation, there are numerous C—H$\cdots\pi$ interactions (Table 2; Laxmi Madhavi *et al.*, 1997; Umezawa *et al.*, 1998). In Table 2, centroids of atom groups are defined as follows: Cg1 (C1–C5/N1), Cg2 (C8–C13), Cg3 (C3/C6–C8), Cg4 (C15–C20), Cg5 (C21–C26), Cg6 (C27–C32) and Cg7 (C33–C38). These C—H$\cdots\pi$ interactions may be considered as major interactions stabilizing the crystal structure, in addition to Coulombic forces.
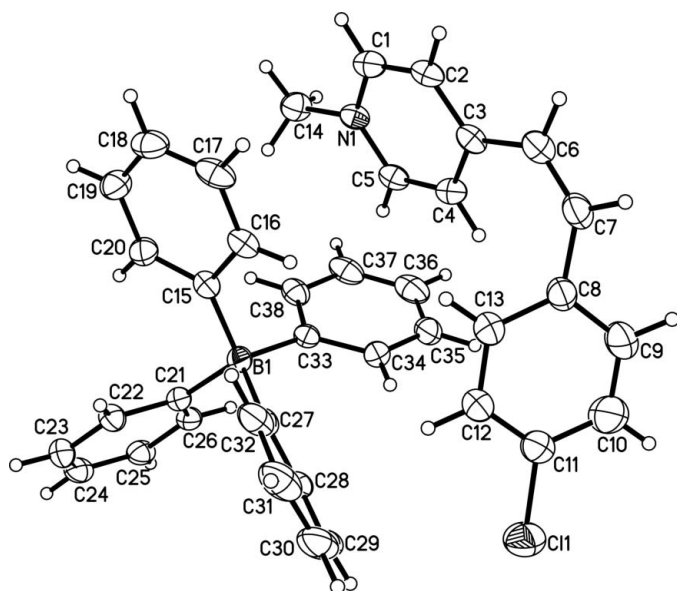
Figure 1
The molecular structure of the title compound, showing 30% probability displacement ellipsoids.

The organic 'salt methodology' principle suggests that the anion–cation interactions in organic salts can override the dipole-dipole interaction which provides a strong driving force for centrosymmetric crystallization in dipolar crystals. Compound (I) was crystallized in the non-centrosymmetric space group $Fdd2$, belonging to point group $mm2$, one of the most favoured groups for SHG, and is therefore a potential SHG crystal. However, not all similar compounds are non-centrosymmetric. A search in the Cambridge Structural Database (CSD; Version 5.26; Allen, 2002) identified three similar structures. The results of packing energy calculations are given in Table 3. Although the data in Table 3 are very limited, by comparing the data for the first pair and the last pair, there seems to be a trend indicating that the non-centrosymmetric packing is possibly due to the much stronger cation-anion interaction.

Experimental

1,4-Dimethylpyridinium iodide (7.05 g, 30 mmol, prepared from CH_3I and 1-methylpyridine), 4-chlorobenzaldehyde (6.89 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 three times 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 (10 ml). The title compound was separated and recrystallized twice from ethanol–water (4:1 v/v). Yellow crystals (m.p. 490–491 K) were grown from N,N-dimethylformamide by slow evaporation at ambient temperature over a period of 16 d. Elemental analysis (Perkin–Elmer 240 C elemental analyser) calculated for $C_{14}H_{13}ClN^+ \cdot BPh_4^-$ (%): C 82.98, H 6.01, N 2.55%; found: C 82.67, H 6.07, N 2.48%. IR (FT–IR spectrometer with KBr pellets, cm^{-1}): 3052 (Ar—H), 2998 (–C—H), 1620 (–CH═CH–), 1590 (–CH═N–), 1516 (Ph), 1478 (Ph), 1427 (Ph), 1385 (Ph), 1335 (–CH_3), 1184 (–CH═C—H), 1084 (–CH═C—H), 972 (Ar—H), 837 (Ar—H), 745 (Ar—H), 710 (Ar—H). ^{1}H NMR (Bruker AV-400 NMR Spectrometer, DMSO

solvent, ambient temperature): 8.87 (*d*, 1H, pyridyl ring), 8.77 (*d*, 1H, pyridyl ring), 8.20 (*d*, 1H, pyridyl ring), 7.98 (*d*, 1H, pyridyl ring), 7.82 (*d*, 1H, Ph), 7.77 (*d*, 1H, Ph), 7.58–7.51 (*m*, 2H, Ph), 7.41 (*d*, 1H, –CH═CH–), 7.30 (*d*, 1H, –CH═CH–), 7.18 (*s*, 8H, Ph), 6.93–6.78 (*m*, 12H, Ph), 4.32 (*s*, 3H, –CH_3).

Table 1
Selected geometric parameters (Å, °).

Cl1—C11	1.736 (4)	C3—C6	1.453 (4)
N1—C1	1.337 (4)	C6—C7	1.325 (5)
N1—C5	1.340 (4)	C7—C8	1.482 (5)
N1—C14	1.478 (4)		
C1—N1—C5	120.4 (3)	C6—C7—C8	130.5 (3)
C1—N1—C14	119.9 (3)	C12—C11—C10	119.6 (3)
C5—N1—C14	119.6 (2)	C12—C11—Cl1	120.8 (3)
C7—C6—C3	130.6 (3)	C10—C11—Cl1	119.6 (3)
C2—C3—C6—C7	159.8 (4)	C6—C7—C8—C9	134.5 (5)
C4—C3—C6—C7	−23.4 (6)	C6—C7—C8—C13	−50.7 (6)
C3—C6—C7—C8	−2.9 (7)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C14—H14B$\cdots$Cl1^i	0.98	3.07	3.577 (3)	113
C4—H4$\cdots$Cg2	0.95	3.20	3.956 (2)	138
C36—H36$\cdots$Cg3^{ii}	0.95	3.15	3.997 (3)	150
C14—H14C$\cdots$Cg4	0.98	2.86	3.529 (2)	126
C6—H6$\cdots$Cg5^{iii}	0.95	2.82	3.663 (4)	148
C1—H1$\cdots$Cg5^{iv}	0.95	2.65	3.505 (2)	150
C12—H12$\cdots$Cg6	0.95	2.67	3.592 (3)	164
C34—H34$\cdots$Cg6	0.95	3.19	3.887 (4)	132
C14—H14A$\cdots$Cg6^{iv}	0.98	2.62	3.470 (2)	146
C5—H5$\cdots$Cg7	0.95	2.32	3.237 (3)	162

Symmetry codes: (i) $-x + \frac{5}{4}, y + \frac{1}{4}, z - \frac{3}{4}$; (ii) $x + \frac{1}{4}, -y + \frac{1}{4}, z + \frac{1}{4}$; (iii) $x - \frac{1}{4}, -y + \frac{1}{4}, z + \frac{3}{4}$; (iv) $-x + \frac{5}{4}, y + \frac{1}{4}, z + \frac{1}{4}$.

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Table 3
Packing energies (PE) of some stilbazolium tetraphenylborates (kcal mol^{-1}).

CSD refcode	Total PE	Space group	(a–a)%[a]	(c–a)%[a]	Substituent
QOBDEQ[b]	−112.68	$P2_1/c$	22.63	53.16	4-N(CH$_3$)$_2$
WOCRAH[c]	−122.95	$P2_1/c$	23.29	58.42	4-OCH$_3$
BOQKEX[d]	−126.54	Cc	16.35	68.51	3,4-OCH$_3$
This study	−112.00	Fdd2	20.97	68.84	4-Cl

Notes: (a) (a–a)% is the percentage in the total PE for the anion–anion interaction and (c–a)% for the cation–anion interaction. References: (b) Li *et al.* (2000*a*); (c) Li *et al.* (2000*d*); (d) Zhang *et al.* (1999).

H atoms were treated as riding, with C—H = 0.95–0.98 Å, and U_{iso}(H) values of $1.5U_{eq}$(C) for methyl H atoms and $1.2U_{eq}$(C) for other H atoms.

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: *SHELXL97*.

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