

Acta Cryst. (1999). **C55**, 1938–1939**4-[2-(3,4-Dimethoxyphenyl)ethenyl]-1-methylpyridinium tetraphenylborate**DE-CHUN ZHANG,^a LI-QIN GE,^a TIAN-ZHU ZHANG,^b
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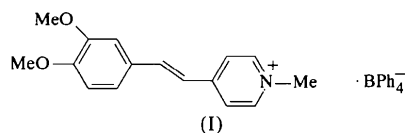
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Abstract

In the title compound, $C_{16}H_{18}NO_2^+ \cdot C_{24}H_{20}B^-$, the pyridyl ring of the cation makes a dihedral angle of $150.4(4)^\circ$ with the phenyl ring. The cations are packed in a parallel fashion along the *c* axis through C—H...O hydrogen bonds. The anions, which take a slightly distorted tetrahedral geometry, are located between the cations.

Comment

During our systematic study of organic salts with non-linear optical properties (Marder *et al.*, 1990; Zhang *et al.*, 1997), we isolated the title compound, (I), and describe here its crystal structure.



In the crystal structure of (I), each cation consists of one phenyl ring (the maximum deviation of phenyl-ring non-H atoms from their mean plane is 0.008 Å) and one pyridyl ring (the corresponding maximum deviation 0.005 Å), which are nearly planar and make a dihedral angle of $150.4(4)^\circ$ with one another (Fig. 1). However, in the cation of $C_{16}H_{18}NO_2^+ \cdot BF_4^-$ (Zhang *et al.*, 1998), the corresponding dihedral angle is $12.4(6)^\circ$ and the C7—C8, C4—C7 and C8—C9 bond lengths are 1.331 (3), 1.447 (3) and 1.452 (3) Å, respectively.

Neighbouring cations, related by the *c* glide, are connected by hydrogen bonds (Taylor & Kennard, 1982; Berkovitch-Yellin & Leiserowitz, 1984; Krishnamohan Sharma & Desiraju, 1994) (Table 3). The BPh_4^- anions, which take a slightly distorted tetrahedral conformation (Table 1), are located in an electrostatically favorable position adjacent to the pyridyl rings (Table 2).

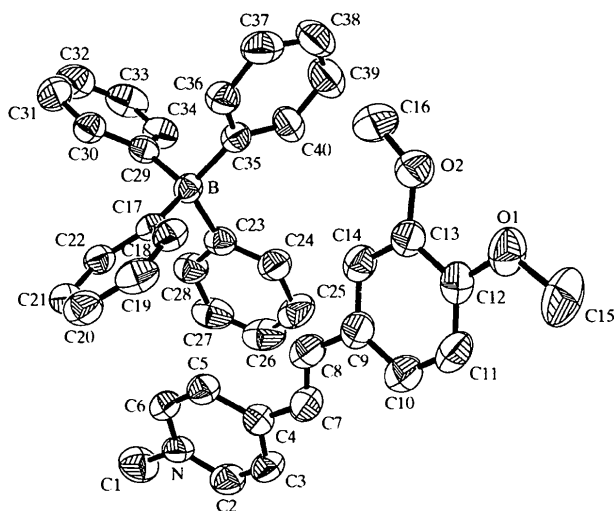


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Compound (I) crystallizes in the non-centrosymmetric space group *Cc*, while the BF_4^- analogue (Zhang *et al.*, 1998) crystallizes in the centrosymmetric space group *Pbca*. The authors believe that in (I), the volume of the anion is large enough to separate the cations and overcome the forces which would lead the compound to crystallize in a centrosymmetric space group. The above idea is supported by the result of our preliminary search on the Cambridge Structural Database (version 5.15; Allen & Kennard, 1993). Our search was based on organic salts which have an organic cation (including at least a benzene ring) with either a BPh_4^- or BF_4^- anion. The ratios of non-centrosymmetric space groups for the 47 BPh_4^- and 147 BF_4^- salts are 25.5 and 20.4%, respectively.

Experimental

1,4-Dimethylpyridinium iodide (7.05 g, 30 mmol, prepared from CH_3I and 1-methylpyridine) and 3,4-dimethoxybenzaldehyde (8.14 g, 49 mmol) in methanol (10 ml) were heated at 353 K for 8 h (Okada *et al.*, 1990). The product was recrystallized twice from ethanol–water (2:1), dissolved in water (0.74 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 *N,N*-dimethylformamide (m.p. 467–468 K). Spectroscopic analysis, IR: 3400, 3051, 2998, 2983, 1620, 1593, 1287, 1138, 1081, 969, 854, 734 cm^{-1} . Elemental analysis, found: C 83.58, H 6.65, N 2.41%; $C_{16}H_{18}NO_2^+ \cdot BPh_4^-$ requires: C 83.74, H 6.66, N 2.43%.

Crystal data $C_{16}H_{18}NO_2^+ \cdot C_{24}H_{20}B^-$
 $M_r = 575.52$ Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å

Monoclinic
Cc
a = 11.325 (2) Å
b = 16.996 (2) Å
c = 17.193 (2) Å
 β = 99.780 (10)°
V = 3261.2 (8) Å³
Z = 4
D_x = 1.172 Mg m⁻³
D_m not measured

Cell parameters from 28 reflections
 θ = 2.68–17.07°
 μ = 0.071 mm⁻¹
T = 290 (2) K
 Chunk
 0.5 × 0.4 × 0.4 mm
 Brown–yellow

Data collection: XSCANS (Siemens, 1994a). Cell refinement: XSCANS. Data reduction: SHELXTL (Siemens, 1994b). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL. Software used to prepare material for publication: SHELXTL.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1469). Services for accessing these data are described at the back of the journal.

Data collection

Siemens P4 diffractometer
 ω scans
 Absorption correction: none
 4700 measured reflections
 4147 independent reflections
 2362 reflections with
 $I > 2\sigma(I)$
R_{int} = 0.014

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.034
wR(*F*²) = 0.063
S = 0.82
 4147 reflections
 398 parameters
 H atoms constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0334P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.01$

$\theta_{\max} = 28^\circ$
 $h = 0 \rightarrow 14$
 $k = -1 \rightarrow 22$
 $l = -22 \rightarrow 22$
 3 standard reflections
 every 97 reflections
 intensity decay: 3.6%

$\Delta\rho_{\max} = 0.12 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.09 \text{ e \AA}^{-3}$
 Extinction correction:
 SHELXL93 (Sheldrick,
 1993)
 Extinction coefficient:
 0.0083 (3)
 Scattering factors from
 International Tables for
 Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

O1—C12	1.365 (3)	B—C29	1.634 (4)
O1—C15	1.432 (3)	B—C35	1.638 (3)
O2—C13	1.379 (3)	B—C23	1.647 (3)
O2—C16	1.424 (3)	B—C17	1.651 (4)
N—C2	1.334 (3)	C4—C7	1.457 (3)
N—C6	1.335 (3)	C7—C8	1.312 (3)
N—C1	1.464 (3)	C8—C9	1.471 (4)
C12—O1—C15	117.5 (2)	C35—B—C23	112.5 (2)
C13—O2—C16	117.2 (2)	C29—B—C17	111.6 (2)
C2—N—C6	119.7 (2)	C35—B—C17	113.7 (2)
C2—N—C1	119.6 (2)	C23—B—C17	103.3 (2)
C6—N—C1	120.7 (2)	C8—C7—C4	125.0 (2)
C29—B—C35	104.8 (2)	C7—C8—C9	127.6 (2)
C29—B—C23	111.2 (2)		
C3—C4—C7—C8	166.7 (3)	C7—C8—C9—C14	163.7 (3)
C5—C4—C7—C8	-13.1 (4)	C15—O1—C12—C11	0.1 (4)
C4—C7—C8—C9	179.8 (2)	C16—O2—C13—C14	-11.8 (3)
C7—C8—C9—C10	-16.4 (4)		

Table 2. Contact distances (Å)

N...C37 ⁱ	3.418 (4)	N...C36 ⁱ	3.677 (3)
C2...C36 ⁱ	3.326 (4)	C2...C37 ⁱ	3.381 (5)
C27...C15 ⁱⁱ	3.351 (4)		

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

Table 3. Hydrogen-bonding geometry (Å, °)

<i>D</i> — <i>H</i> ... <i>A</i>	<i>H</i> ... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> — <i>H</i> ... <i>A</i>
C3—H3...O1 ⁱ	2.56	3.388 (4)	149
C3—H3...O2 ⁱ	2.52	3.346 (4)	148
C21—H21...O1 ⁱⁱ	2.65	3.512 (3)	155

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

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6-Benzylidene-2-(2-chlorophenyl)thiazolo[3,2-*b*]-1,2,4-triazol-5(6*H*)-one

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Abstract

In the title compound, C₁₇H₁₀ClN₃OS, the fused thiazolo[3,2-*b*]-1,2,4-triazole system is almost planar. The phenyl substituents are planar within experimental error and make dihedral angles of 16.5 (1) and 10.9 (1)° with the thiazolo-triazole system. There are three intramolec-