

## Low-Temperature X-Ray Structural Investigation of $[\text{PhCH}_2\text{Py}]^+[\text{BPh}_4]^-$

TAMARA M. POLYANSKAYA<sup>1</sup>, VLADIMIR V. VOLKOV<sup>1</sup>, CAROLINE PRICE<sup>2</sup>,  
MARK THORNTON-PETT<sup>2</sup> and JOHN D. KENNEDY<sup>2</sup>

<sup>1</sup>*Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, Pr. Akademika Lavrentyeva 3, Novosibirsk 630090 (Russia)*

<sup>2</sup>*School of Chemistry, University of Leeds, LS2 9JT Leeds (UK)*

### Abstract

The crystal structure of  $[\text{PhCH}_2\text{Py}]^+[\text{BPh}_4]^-$  is determined by means of X-ray structural analysis at 190(2) K. Crystals are monoclinic, space group  $P2_1/c$ ,  $a = 18.4968(3)$ ,  $b = 13.4402(2)$ ,  $c = 21.8638(3)$  Å,  $\beta = 97.0610(6)^\circ$ ,  $Z = 8$ ,  $d_{\text{calc}} = 1.205$  g/cm<sup>3</sup>,  $R = 0.0506$  (autodiffractometer Nonius KAPPA CCD,  $\lambda\text{MoK}\alpha$ , 10 551 independent reflections). The crystals are built of two crystallographically independent sorts of cations  $[\text{PhCH}_2\text{Py}]^+$  and two crystallographically independent sorts of anions  $[\text{BPh}_4]^-$ . Both cations are not flat, dihedral angles between the planes of phenyl and pyridine rings are 93.2 and 79.4°. The interactions of the edge-to-face type are recorded between aromatic fragments of the cations and the Ph rings of the anions.

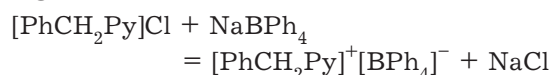
### INTRODUCTION

The interactions between the electron systems of components are important for molecular design of complicated compounds aimed at the creation of new materials. The consequence of these interactions can be the occurrence of valuable functional properties (optical, electro-physical, magnetic, etc.). This is to a substantial extent determined by the types of components and by structural features of the formed crystal phases. It is known that the interactions of electron systems and fields can arise in crystal phases containing cyclic aromatic structural fragments with electron delocalization [1, 2]. Because of this, it seems interesting to study the structure of compounds containing aromatic cyclic fragments. This condition is met by the composition of a salt-like N-benzylpyridinium(+) tetraphenylborate(−) complex,  $[\text{C}_6\text{H}_5\text{-CH}_2\text{-C}_5\text{H}_5\text{N}]^+[\text{B}(\text{C}_6\text{H}_5)_4]^-$ , or  $[\text{PhCH}_2\text{Py}]^+[\text{BPh}_4]^-$  (**1**). Compound **1** incorporates three types of aromatic cycles, two of them are phenyl groups (Ph) of the cation and anion, and the third one is the pyridine cycle in the cation (Py). In the present paper we report

the results of low-temperature X-ray structural analysis of complex **1** at 190 K. The salts of the above-mentioned cation are poorly investigated: the Cambridge crystal structure database contains the data on the structure of relatively simple bromide  $(\text{PhCH}_2\text{Py})\text{Br}$  (**2**) studied at 188, 208 and 218 K.

### EXPERIMENTAL

Salt-like complex **1** was synthesized according to the reaction



conducted by mixing aqueous solutions of the initial salts at 70 °C. The resulting white fine crystalline precipitate of **1** was filtered and dried in vacuum at 75 °C till constant mass. The yield of **1** was 92 %. Crystals suitable for X-ray structural analysis were obtained by recrystallization of **1** from acetone.

Chemical formula of compound **1** was confirmed and its structure was established by means of X-ray structural analysis. Elementary

TABLE 1

Coordinates of atoms ( $\times 10^4$ ) and equivalent isotropic heat parameters of atoms different from hydrogen ( $\times 10^3$ ,  $U_{\text{equiv}} = 1/3(U_{11} + U_{22} + U_{33})$ ) in  $[\text{PhCH}_2\text{Py}]^+[\text{BPh}_4]^-$

Atom	$x$	$y$	$z$	$U_{\text{equiv}}, \text{\AA}^2$
N(1)	4137.8(8)	5181.7(11)	1545.6(6)	44.4(3)
C(2)	3589.5(10)	5809.3(13)	1540.8(8)	49.5(4)
C(3)	2913.9(12)	5539(2)	1295.9(11)	80.5(8)
C(4)	2824.0(13)	4533(3)	1059.0(10)	97.2(12)
C(5)	3439.6(16)	3928.1(19)	1106.3(10)	75.0(7)
C(6)	4080.7(12)	4267.5(14)	1337.9(9)	56.8(5)
C(7)	4881.2(12)	5503(2)	1830.5(10)	77.3(7)
C(8)	5428.5(10)	5528.9(14)	1382.8(8)	48.4(4)
C(9)	6132.0(11)	5244.2(14)	1588.2(10)	58.7(5)
C(10)	6662.6(11)	5334.8(16)	1205.0(14)	72.3(7)
C(11)	6493.4(13)	5684.6(18)	613.8(13)	73.5(7)
C(12)	5793.4(13)	5934.1(15)	404.0(10)	62.7(5)
C(13)	5260.6(10)	5863.0(14)	782.9(8)	50.8(4)
N(14)	991.9(7)	5226.6(10)	3561.1(6)	38.6(3)
C(15)	1385.2(9)	5952.2(12)	3864.0(8)	41.9(4)
C(16)	2100.7(9)	5796.0(13)	4088.9(8)	43.9(4)
C(17)	2417.7(9)	4888.5(13)	3993.0(8)	43.9(4)
C(18)	2007.6(9)	4157.1(12)	3677.4(8)	43.7(4)
C(19)	1293.5(10)	4337.2(12)	3464.8(7)	41.7(4)
C(20)	225.2(9)	5420.7(17)	3311.5(10)	60.6(5)
C(21)	-323.5(8)	4903.6(12)	3659.7(8)	39.7(4)
C(22)	-147.7(9)	4422.1(14)	4218.4(8)	47.5(4)
C(23)	-683.6(11)	3999.4(15)	4524.3(9)	55.7(5)
C(24)	-1402.8(11)	4070.1(16)	4277.4(11)	61.2(5)
C(25)	-1582.2(10)	4552.2(16)	3722.6(11)	61.5(5)
C(26)	-1047.4(9)	4964.5(13)	3411.7(9)	49.4(4)
B(1)	633.3(8)	3677.5(12)	1352.2(7)	26.6(3)
C(111)	841.4(7)	4831.2(11)	1566.8(6)	29.2(3)
C(112)	1390.0(8)	5089.5(12)	2039.5(7)	34.9(3)
C(113)	1557.1(10)	6074.1(13)	2203.9(8)	46.8(4)
C(114)	1184.6(10)	6845.3(13)	1889.1(9)	52.9(5)
C(115)	648.6(10)	6625.2(13)	1414.2(10)	51.7(4)
C(116)	476.1(9)	5640.6(12)	1262.2(8)	40.7(4)
C(121)	983.9(7)	2909.0(10)	1900.6(6)	27.3(3)
C(122)	604.2(8)	2481.2(11)	2351.8(6)	31.7(3)
C(123)	937.3(9)	1880.2(12)	2825.1(7)	40.2(4)
C(124)	1674.8(9)	1685.9(12)	2871.5(7)	40.8(4)
C(125)	2073.8(8)	2085.2(12)	2433.8(7)	37.5(3)
C(126)	1731.7(8)	2674.6(11)	1962.6(7)	33.1(3)
C(131)	968.5(7)	3414.6(10)	705.8(6)	27.3(3)
C(132)	1115.9(8)	2431.0(11)	547.1(7)	32.3(3)
C(133)	1371.5(9)	2181.0(12)	-4.7(7)	39.0(3)
C(134)	1486.0(9)	2913.2(13)	-426.3(7)	43.2(4)
C(135)	1335.4(9)	3890.0(13)	-293.6(7)	41.7(4)
C(136)	1082.3(8)	4128.8(11)	261.6(6)	33.9(3)
C(141)	-263.6(7)	3605.4(10)	1220.8(6)	29.4(3)
C(142)	-643.4(8)	3337.7(11)	648.9(7)	34.0(3)
C(143)	-1403.0(9)	3313.5(12)	543.4(8)	42.9(4)
C(144)	-1813.8(8)	3544.6(12)	1009.8(9)	46.2(4)
C(145)	-1461.7(8)	3827.5(13)	1577.0(9)	45.1(4)
C(146)	-705.3(8)	3865.3(12)	1673.7(7)	38.4(3)
B(2)	4439.2(8)	6432.7(12)	3731.2(7)	25.8(3)

TABLE 1 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>equiv</sub> , Å <sup>2</sup>
C(211)	4151.6(7)	7192.8(10)	3160.4(6)	27.6(3)
C(212)	4596.1(8)	7665.7(11)	2772.7(7)	34.0(3)
C(213)	4320.3(10)	8265.0(12)	2277.5(7)	42.3(4)
C(214)	3578.2(10)	8413.2(11)	2145.4(7)	41.0(4)
C(215)	3116.5(9)	7970.4(11)	2519.2(7)	36.0(3)
C(216)	3399.8(8)	7383.8(11)	3014.3(6)	31.1(3)
C(221)	5331.2(7)	6450.4(10)	3910.9(6)	29.3(3)
C(222)	5679.6(8)	6705.2(12)	4494.3(7)	36.7(3)
C(223)	6435.3(9)	6643.3(14)	4647.7(9)	49.0(4)
C(224)	6871.6(8)	6336.4(13)	4215.1(9)	48.9(4)
C(225)	6549.7(8)	6082.0(12)	3631.1(8)	43.0(4)
C(226)	5798.6(8)	6127.1(12)	3490.1(7)	37.0(3)
C(231)	4218.3(7)	5274.2(10)	3526.8(6)	26.3(3)
C(232)	5439.4(8)	4471.5(11)	3871.6(7)	31.9(3)
C(233)	4343.0(9)	3488.5(11)	3750.2(7)	38.3(3)
C(234)	3825.5(9)	3254.4(12)	3258.2(8)	40.6(4)
C(235)	3507.9(8)	4018.0(12)	2895.5(7)	38.0(3)
C(236)	3698.0(7)	5003.8(11)	3032.9(6)	30.6(3)
C(241)	4047.5(7)	6736.8(10)	4346.0(6)	25.6(3)
C(242)	3841.8(8)	7717.1(11)	4460.6(6)	31.5(3)
C(243)	3516.4(8)	7982.1(12)	4979.8(7)	36.4(3)
C(244)	3389.1(8)	7270.0(12)	5410.2(7)	37.1(3)
C(245)	3604.1(8)	6299.9(12)	5324.4(7)	35.9(3)
C(246)	3925.9(7)	6047.7(11)	4803.7(6)	30.0(3)

cell parameters and reflection intensities were obtained with an Nonius Kappa CCD autodiffractometer at 190(2) K with the crystal shaped as a sphere with the dimensions  $0.59 \times 0.59 \times 0.59$  mm using MoK<sub>α</sub> radiation.

Crystallographic data for **1** are: monoclinic syngony,  $a = 18.4968(3)$ ,  $b = 13.4402(2)$ ,  $c = 21.8638(3)$  Å,  $\beta = 97.0610(6)^\circ$ ,  $V = 5394.13(14)$  Å<sup>3</sup>,  $Z = 8$ , space group  $P2_1/c$ ,  $d_{\text{calc}} = 1.205$  g/m<sup>3</sup>,  $\mu = 0.068$  mm<sup>-1</sup>,  $2\theta_{\text{max}} = 52^\circ$ , 20 571 reflections measured, with  $-22 \leq h \leq 22$ ,  $-16 \leq k \leq 16$ ,  $-26 \leq l \leq 26$ , among which 10 551 were used in calculations. The intensities were corrected for the Lorentz and polarization factors, absorption was not taken into account. The structure was deciphered directly and corrected using a full-matrix least squares method in the anisotropic/isotropic (for H atoms) approximation using the complex of programmes SHELX-97 [3]. The coordinates of H atoms were fixed in the calculated positions (C—H bond length 0.950 Å). 685 parameters of the structure were corrected till the final divergence factors:  $R(F) = 0.0506$ ,  $wR(F^2) = 0.1281$  for the reflections with  $I > 2\sigma(I)$ ,  $R(F) = 0.0599$ ,  $wR(F^2) = 0.1387$  for all the reflections. Residual extremums

(min/max) were 0.678 and  $-0.401 e/\text{Å}^3$ . Coordinates and equivalent isotropic heat parameters of atoms different from hydrogen are shown in Table 1, main bond lengths and valence angles in Tables 2 and 3. Anisotropic heat parameters and the coordinates of hydrogen atoms are available from the authors on request.

## RESULTS AND DISCUSSION

The complex has an ionic structure. An asymmetric unit contains two crystallographically independent organic cations (PhCH<sub>2</sub>Py)<sup>+</sup> and two crystallographically independent anions (BPh<sub>4</sub>)<sup>-</sup>. All the atoms of the structure occupy common positions. The geometry of ions with numbered atoms is shown in Figs. 1 and 2.

Both cations are not flat, dihedral angles between the planes of phenyl and pyridine rings are 93.2 and 79.4° for the first and second cation, respectively. The twisting of Py and Ph rings is such that the atoms C(5) and C(12) in the first cation and the atoms C(18) and C(23) of the second cation are located to different sides of the planes passing through the atoms N(1), C(7), C(8) (plane M) and N(14), C(20),

TABLE 2  
Basic interatomic distances in  $[\text{PhCH}_2\text{Py}]^+[\text{BPh}_4]^-$ , Å

Bond	Length	Bond	Length
N(1)–C(6)	1.310(2)	N(1)–C(2)	1.318(2)
N(1)–C(7)	1.501(3)	C(2)–C(3)	1.347(3)
C(3)–C(4)	1.450(4)	C(4)–C(5)	1.392(4)
C(5)–C(6)	1.313(3)	C(7)–C(8)	1.493(3)
C(8)–C(9)	1.377(3)	C(8)–C(13)	1.385(2)
C(9)–C(10)	1.372(3)	C(10)–C(11)	1.375(4)
C(11)–C(12)	1.361(3)	C(12)–C(13)	1.367(3)
N(14)–C(15)	1.342(2)	N(14)–C(19)	1.347(2)
N(14)–C(20)	1.479(2)	C(15)–C(16)	1.370(2)
C(16)–C(17)	1.380(2)	C(17)–C(18)	1.374(2)
C(18)–C(19)	1.367(2)	C(20)–C(21)	1.511(2)
C(21)–C(26)	1.384(2)	C(21)–C(22)	1.385(2)
C(22)–C(23)	1.384(3)	C(23)–C(24)	1.376(3)
C(24)–C(25)	1.379(3)	C(25)–C(26)	1.383(3)
B(1)–C(131)	1.650(2)	B(1)–C(141)	1.651(2)
B(1)–C(111)	1.652(2)	B(1)–C(121)	1.653(2)
C(111)–C(112)	1.401(2)	C(111)–C(116)	1.405(2)
C(112)–C(113)	1.396(2)	C(113)–C(114)	1.381(3)
C(114)–C(115)	1.377(3)	C(115)–C(116)	1.392(2)
C(121)–C(122)	1.403(2)	C(121)–C(126)	1.409(2)
C(122)–C(123)	1.395(2)	C(123)–C(124)	1.380(2)
C(124)–C(125)	1.386(2)	C(125)–C(126)	1.389(2)
C(131)–C(136)	1.400(2)	C(131)–C(132)	1.402(2)
C(132)–C(133)	1.390(2)	C(133)–C(134)	1.382(2)
C(134)–C(135)	1.380(2)	C(135)–C(136)	1.391(2)
C(141)–C(146)	1.403(2)	C(141)–C(142)	1.404(2)
C(142)–C(143)	1.396(2)	C(143)–C(144)	1.380(3)
C(144)–C(145)	1.381(3)	C(145)–C(146)	1.390(2)
B(2)–C(221)	1.649(2)	B(2)–C(211)	1.649(2)
B(2)–C(241)	1.655(2)	B(2)–C(231)	1.657(2)
C(211)–C(212)	1.404(2)	C(211)–C(216)	1.412(2)
C(212)–C(213)	1.395(2)	C(213)–C(214)	1.382(2)
C(214)–C(215)	1.387(2)	C(215)–C(216)	1.389(2)
C(221)–C(222)	1.399(2)	C(221)–C(226)	1.407(2)
C(222)–C(223)	1.399(2)	C(223)–C(224)	1.380(3)
C(224)–C(225)	1.384(3)	C(225)–C(226)	1.387(2)
C(231)–C(236)	1.403(2)	C(231)–C(232)	1.405(2)
C(232)–C(233)	1.387(2)	C(233)–C(234)	1.386(2)
C(234)–C(235)	1.383(2)	C(235)–C(236)	1.394(2)
C(241)–C(246)	1.402(2)	C(241)–C(242)	1.402(2)
C(242)–C(243)	1.395(2)	C(243)–C(244)	1.383(2)
C(244)–C(245)	1.383(2)	C(245)–C(246)	1.390(2)

C(21) (plane  $M'$ ), at a distance of  $-1.148, 0.776, -1.152, 0.243$  Å, respectively. Dihedral angles of the Py and Ph rings with the M and  $M'$  planes are  $115.8, 37.8$  and  $73.4, 8.4^\circ$ , respectively. The cycles Py and Ph of the first cation are more crimped, compared to the second cation. The corresponding mean square deviations are  $0.009, 0.008$  Å in the first cation and  $0.003, 0.003$  Å in the second one. The atoms C(6) and C(13), C(19) and C(22) are separated at a distance of  $3.389$  and  $3.304$  Å due to the twisting of rings.

The presence of voluminous anions  $(\text{BPh}_4)^-$  in structure of **1** introduced substantial changes of the conformation in comparison with that ob-

served in  $(\text{PhCH}_2\text{Py})\text{Br}$  though it is crystallized in the same space group  $P2_1/c$  and its asymmetric unit of elementary cell contains two crystallographically independent cations and two anions [4]. In the structure of **2**, the twisting of Py and Ph rings with respect to each other and with respect to the above-mentioned planes M and  $M'$  at 188 K is  $70.2, 85.9, 68.6$  and  $109.3, 88.2, \text{ and } 65.0^\circ$  for the first and the second cations, respectively.

Each tetraphenylborate anion  $(\text{BPh}_4)^-$  contains practically flat phenyl rings, mean square deviations for eight rings containing C(111) (ring 1), C(121) (ring 2), C(131) (ring 3), C(141) (ring 4), C(211) (ring 5), C(221) (ring 6), C(231)

TABLE 3

Valence angles  $\phi$  in [PhCH<sub>2</sub>Py]<sup>+</sup>[BPh<sub>4</sub>]<sup>-</sup>, deg

Angle	$\phi$	Angle	$\phi$
C(6)–N(1)–C(2)	124.6(2)	C(6)–N(1)–C(7)	116.4(2)
C(2)–N(1)–C(7)	118.9(2)	N(1)–C(2)–C(3)	120.4(2)
C(2)–C(3)–C(4)	117.0(2)	C(5)–C(4)–C(3)	117.4(2)
C(6)–C(5)–C(4)	121.2(2)	N(1)–C(6)–C(5)	119.4(2)
C(8)–C(7)–N(1)	113.3(2)	C(9)–C(8)–C(13)	119.4(2)
C(9)–C(8)–C(7)	118.0(2)	C(13)–C(8)–C(7)	122.5(2)
C(10)–C(9)–C(8)	119.6(2)	C(9)–C(10)–C(11)	120.5(2)
C(12)–C(11)–C(10)	119.9(2)	C(11)–C(12)–C(13)	120.4(2)
C(12)–C(13)–C(8)	120.2(2)		
C(15)–N(14)–C(19)	120.83(14)	C(15)–N(14)–C(20)	119.4(2)
C(19)–N(14)–C(20)	119.7(2)	N(14)–C(15)–C(16)	120.5(2)
C(15)–C(16)–C(17)	119.4(2)	C(18)–C(17)–C(16)	119.3(2)
C(19)–C(18)–C(17)	119.7(2)	N(14)–C(19)–C(18)	120.4(2)
N(14)–C(20)–C(21)	113.95(14)	C(26)–C(21)–C(22)	119.0(2)
C(26)–C(21)–C(20)	116.9(2)	C(22)–C(21)–C(20)	124.0(2)
C(23)–C(22)–C(21)	120.9(2)	C(24)–C(23)–C(22)	119.8(2)
C(23)–C(24)–C(25)	119.6(2)	C(24)–C(25)–C(26)	120.7(2)
C(21)–C(26)–C(25)	120.0(2)		
C(131)–B(1)–C(141)	108.29(11)	C(131)–B(1)–C(111)	110.21(11)
C(141)–B(1)–C(111)	107.38(11)	C(131)–B(1)–C(121)	109.40(11)
C(141)–B(1)–C(121)	112.67(11)	C(111)–B(1)–C(121)	108.87(11)
C(112)–C(111)–C(116)	114.89(14)	C(112)–C(111)–B(1)	124.38(13)
C(116)–C(111)–B(1)	120.70(13)	C(113)–C(112)–C(111)	122.8(2)
C(114)–C(113)–C(112)	120.2(2)	C(115)–C(114)–C(113)	118.9(2)
C(114)–C(115)–C(116)	120.5(2)	C(115)–C(116)–C(111)	122.7(2)
C(122)–C(121)–C(126)	114.27(13)	C(122)–C(121)–B(1)	125.49(12)
C(126)–C(121)–B(1)	120.16(12)	C(123)–C(122)–C(121)	123.06(14)
C(124)–C(123)–C(122)	120.43(14)	C(123)–C(124)–C(125)	118.76(14)
C(124)–C(125)–C(126)	120.01(14)	C(125)–C(126)–C(121)	123.46(14)
C(136)–C(131)–B(1)	123.50(13)	C(136)–C(131)–C(132)	115.13(13)
C(132)–C(131)–B(1)	121.25(12)	C(133)–C(132)–C(131)	122.67(14)
C(134)–C(133)–C(132)	120.2(2)	C(135)–C(134)–C(133)	119.05(14)
C(134)–C(135)–C(136)	120.1(2)	C(135)–C(136)–C(131)	122.87(14)
C(146)–C(141)–C(142)	114.92(13)	C(146)–C(141)–B(1)	121.49(12)
C(142)–C(141)–B(1)	123.51(12)	C(143)–C(142)–C(141)	122.5(2)
C(144)–C(143)–C(142)	120.5(2)	C(143)–C(144)–C(145)	118.92(14)
C(144)–C(145)–C(146)	120.1(2)	C(145)–C(146)–C(141)	123.1(2)
C(221)–B(2)–C(211)	113.06(11)	C(221)–B(2)–C(241)	109.16(11)
C(211)–B(2)–C(241)	109.20(11)	C(221)–B(2)–C(231)	106.51(11)
C(211)–B(2)–C(231)	109.39(11)	C(241)–B(2)–C(231)	109.45(10)
C(212)–C(211)–C(216)	114.51(13)	C(212)–C(211)–B(2)	125.38(12)
C(216)–C(211)–B(2)	120.07(11)	C(213)–C(212)–C(211)	123.02(14)
C(214)–C(213)–C(212)	120.30(14)	C(213)–C(214)–C(215)	118.87(14)
C(214)–C(215)–C(216)	120.15(14)	C(215)–C(216)–C(211)	123.13(13)
C(222)–C(221)–C(226)	114.88(13)	C(222)–C(221)–B(2)	123.79(12)
C(226)–C(221)–B(2)	121.15(12)	C(223)–C(222)–C(221)	122.6(2)
C(224)–C(223)–C(222)	120.3(2)	C(223)–C(224)–C(225)	118.99(14)
C(224)–C(225)–C(226)	120.0(2)	C(225)–C(226)–C(221)	123.2(2)
C(236)–C(231)–C(232)	114.75(13)	C(236)–C(231)–B(2)	125.02(12)
C(232)–C(231)–B(2)	120.18(12)	C(233)–C(232)–C(231)	123.03(14)
C(234)–C(233)–C(232)	120.3(2)	C(235)–C(234)–C(233)	118.75(14)
C(234)–C(235)–C(236)	120.24(14)	C(235)–C(236)–C(231)	122.89(14)
C(246)–C(241)–C(242)	114.98(12)	C(246)–C(241)–B(2)	122.77(12)
C(242)–C(241)–B(2)	122.18(12)	C(243)–C(242)–C(241)	122.61(13)
C(244)–C(243)–C(242)	120.25(14)	C(245)–C(244)–C(243)	118.99(13)
C(244)–C(245)–C(246)	120.02(14)	C(245)–C(246)–C(241)	123.10(14)

(ring 7), and C(241) (ring 8) are 0.006, 0.008, and 0.009 Å, respectively. The deviations of boron atoms from mean square planes of phenyl rings of each anion are more substantial and are –0.030, 0.099, –0.061, 0.029; –0.088, –0.099,

–0.092, 0.003 Å, respectively. Dihedral angles between the planes of phenyl rings fall within the ranges 52.7–113.6 and 54.7–114.1° for the anions with B(1) and B(2), respectively. B–C bond lengths fall within a narrow range

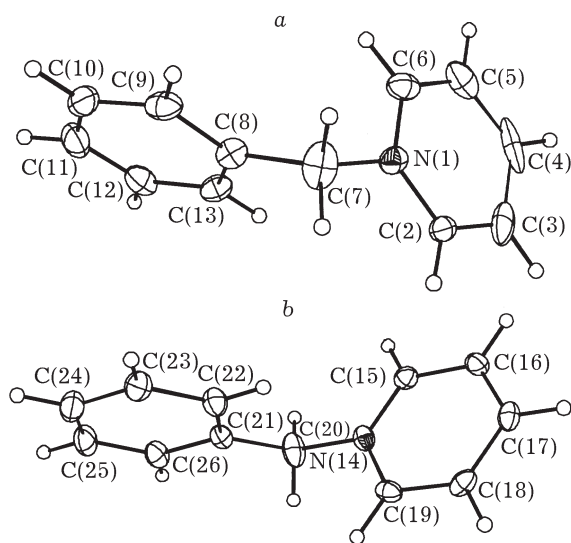


Fig. 1. The structure of two crystallographically independent cations  $[\text{PhCH}_2\text{Py}]^+$  with numbered atoms and the ellipsoids of heat vibrations of the atoms different from hydrogen. H atoms are marked with the circles of arbitrary radii.

1.649(2)–1.657(2) Å, with a mean of 1.652(2) Å, and tetrahedral angles C—B—C are within the range 106.51(11)–113.06(11)°.

The fragment of ion pairs packing in the crystal  $(\text{BPh}_4)^-$  lattice is shown in Fig. 3. The edge-to-face type interactions between aromatic fragments of cations and phenyl rings of anions are recorded in the system [5–8]. The

contacts C—H... $\pi$  corresponding to these interactions are shown with dashed line. The distances from H atoms to the centroids of Ph rings of the anions and the angles at H fall within the ranges 2.67–2.93 Å and 125–163°, respectively. These geometric parameters of hydrogen bonds for the C—H... $\pi$  interaction were reported earlier [9]. The participants are mainly H atoms of pyridine rings and only one H atom of the Ph ring of the second cation. These interactions can be responsible for charge transfer processes and photochromic behaviour of compound **1** which is exhibited by an increase of the intensity of pink colour in the crystals when they are kept in light.

## CONCLUSIONS

The crystal structure of complex **1** was studied by means of low-temperature X-ray phase analysis. Edge-to-face interactions between aromatic fragments of the cations and aromatic fragments of anions were observed. From the viewpoint of the interaction of cyclic aromatic components, the prevailing contribution is made by the interaction of H atoms of Py rings

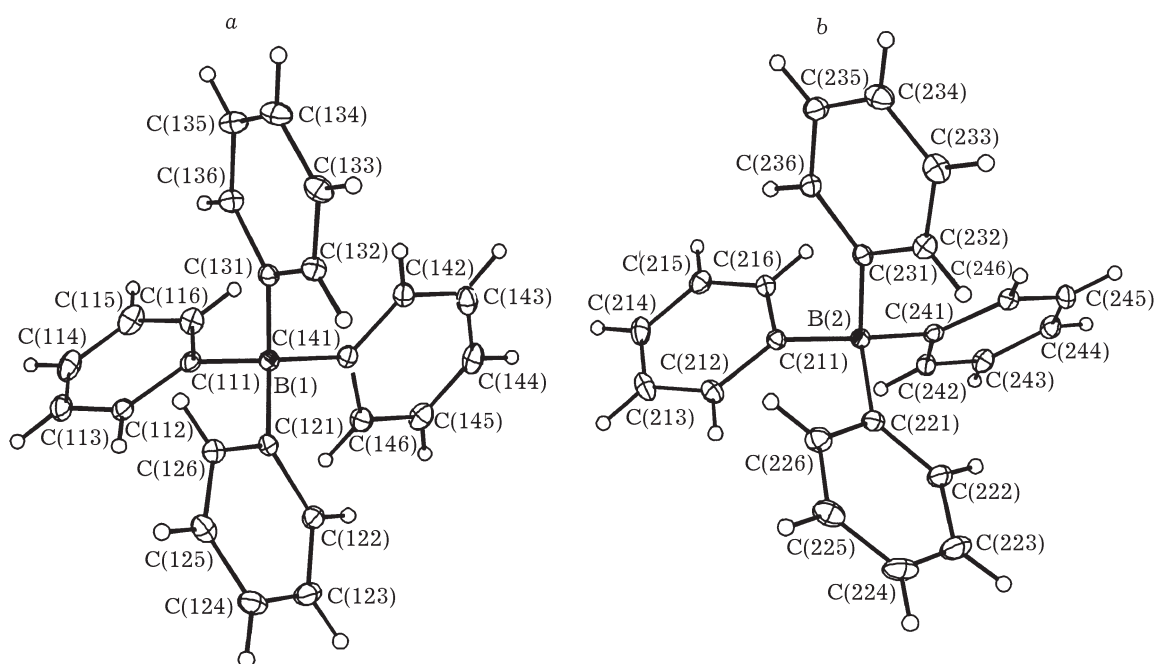


Fig. 2. The structure of two crystallographically independent anions  $\text{Ph}_4\text{B}(1)^-$  (a) and  $\text{Ph}_4\text{B}(2)^-$  (b) with numbered atoms and the ellipsoids of heat vibrations of atoms different from hydrogen. H atoms are marked with the circles of arbitrary radii.

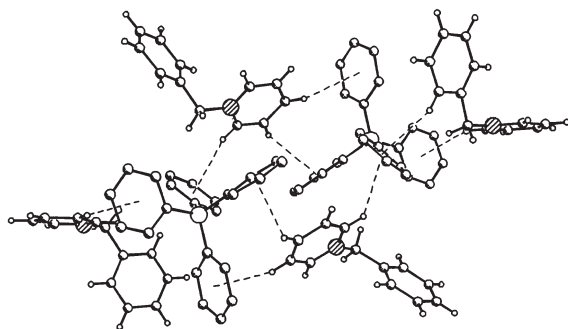


Fig. 3. A fragment of ion pairs packing in the lattice of compound **1**. The contacts C—H... $\pi$  are marked with dashed lines.

with the  $\pi$ -systems of the phenyl rings of anions  $(\text{BPh}_4)^-$ . The interactions between Ph (cation) and Ph (anion) are less typical. The observed interactions can be responsible for electron transfer processes, photochromic behaviour, and possibly some other functional properties of compound **1**.

#### ACKNOWLEDGEMENT

The study has been supported by the Royal Society of the United Kingdom.

#### REFERENCES

- 1 T. M. Polyanskaya, Ninth Intern. Meeting on Boron Chemistry: Program and Abstracts, Heidelberg, Germany, 1996, p. 210.
- 2 V. V. Murakhtanov, T. M. Polyanskaya and V. V. Volkov, *Zhurn. struktur. khimii*, 37 (1996) 652.
- 3 G. M. Sheldrick, SHELX-97, release 97-1, University of Göttingen, 1997.
- 4 E. Anders, J. G. Tropsch, E. Irmner and G. M. Sheldrick, *Chem. Ber.*, 123 (1990) 321.
- 5 S. K. Burley and G. A. Petsko, *Science*, 229 (1985) 23.
- 6 W. L. Jorgensen and D. L. Severance, *J. Am. Chem. Soc.*, 112 (1990) 4768.
- 7 D. R. Boyd, T. A. Evans, W. B. Jennings *et al.*, *Chem. Commun.*, (1996) 2269.
- 8 M. C. Grossel, A. K. Cheetham, D. A. O. Hope and S. C. Weston, *J. Org. Chem.*, 58 (1993) 6654.
- 9 T. Steiner, E. B. Starikov and M. Tamm, *J. Chem. Soc., Perkin Trans. 2*, (1996) 67.