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# Low-Temperature X-Ray Structural Investigation of $[2, 2'\text{-N-Me-Bipy}]^+[BPh_4]^-$

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## Abstract

The crystal structure of [*cis*-2,2′-N-Me-Bipy]$^+$[BPh$_4$]$^-$ is determined by means of X-ray structural analysis at 190(2) K. Crystals are triclinic, space group $P\bar{1}$, $a = 9.3101(2)$, $b = 16.3759(5)$, $c = 19.1774(5)$ Å, $\alpha = 70.786(1)$, $\beta = 83.271(2)$, $\gamma = 89.279(2)^\circ$, $V = 2740.87(12)$ Å$^3$, $Z = 4$, $d_{calc} = 1.188$ g/cm$^3$, $R = 0.0496$ (autodiffractometer Nonius KAPPA CCD, $\lambda \text{Mo}K_\alpha$, 9995 independent reflections). The crystals are built of two crystallographically independent sorts of cations [2,2'-N-Me-Bipy]$^+$ and two crystallographically independent sorts of anions [BPh$_4$]$^-$. *Cis*-conformation of cations corresponds to dihedral angles between the planes of pyridine rings 53.0 and 53.1°. The interactions of the edge-to-face type are recorded between aromatic fragments of the cations containing Me group and the Ph rings of the anions.

### INTRODUCTION

Tetraphenylborate anion $B(C_6H_5)_4^-$, or $(BPh_4)^-$, is known to be a depositer of voluminous cations in aqueous media because it interacts with them forming difficultly soluble salts. Four cyclic aromatic radicals Ph are present in this anion. It is of interest to prepare and investigate salt-like complexes containing $BPh_4^-$ anion and aromatic heterocycles of the tertiary ammonium cations, in particular 2,2′-bipyridyl derivatives. Among numerous publications concerning the structures of tetraphenylborates and bipyridinium salts and derivatives (there are more than 1000 data on the former and more than 50 on the latter in the Cambridge crystal structure database), there is only one communication concerning the structure of *cis*-2,2′-bipyridinium tetraphenylborate (**2**) at 253 K [1]. In the compounds of this type, along with the anion-to-cation electrostatic interaction, the interactions between electron systems of different aromatic fragments are also possible. This can result in interesting functional properties (optical, luminescent, *etc.*). In order to study major structural features of such salts, we synthesized a salt-like complex containing the $[2,2'\text{-N}-CH_3-C_5H_4N-C_5H_4N]^+$ cation, 2,2′-N-methylbipyridinium (1+) and $BPh_4^-$ anion (further designated as [N-Me-Bipy]$^+$[BPh$_4$]$^-$ (**1**)), and investigated it by means of X-ray structural analysis. One formula unit of this complex contains six aromatic cyclic fragments of two types.

### EXPERIMENTAL

Complex **1** was synthesized by mixing aqueous solutions of [N-Me-Bipy]$^+$I$^-$ and Na$^+$BPh$_4^-$ at 70 °C. It is a fine crystalline precipitate. It was isolated by filtering and dried till constant mass in vacuum at 75 °C. The yield was 85 %. Compound **1** is insoluble in ethanol and benzene but soluble in acetone. When illuminated with sunlight it changes its colour from colourless to pink slowly and reversibly. The crystals suitable for X-ray structural investigations were prepared by slow crystallization from ace-

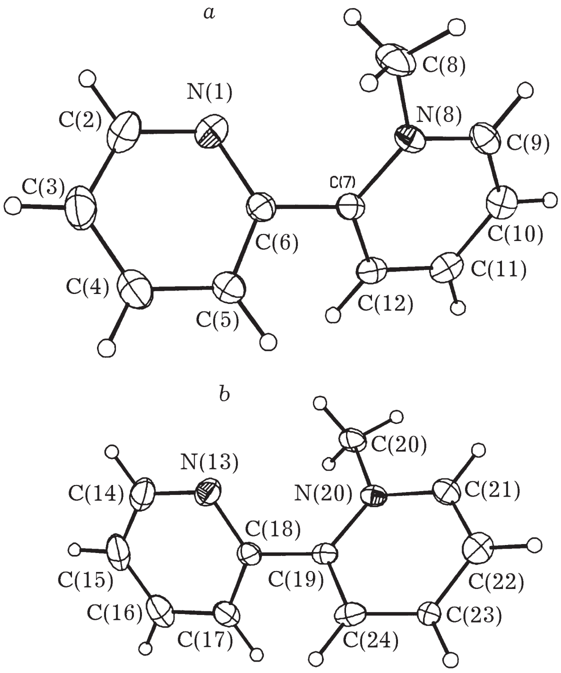

Fig. 1. The structure of two crystallographically independent cations $[2,2'\text{-N-Me-Bipy}]^+$ with numbered atoms and ellipsoids of heat vibrations of the atoms other than hydrogen. H atoms are shown as circles of arbitrary radii.

tone solution under the action of $H_2O$ vapour in a tightly closed container. The structure and chemical formula of compound **1** were established by means of X-ray structural analysis using well-faced single crystals. Elementary cell parameters and the intensities of reflections were obtained using the Nonium Kappa CCD autodiffractometer at 190(2) K using the crystal of the dimensions 0.56 × 0.49 × 0.42 mm with the help of $\mathrm{Mo}K_\alpha$ radiation.

Crystallographic data for **1** are as follows: triclinic syngony, $a = 9.3101(2)$, $b = 16.3759(5)$, $c = 19.1774(5)$ Å, $\alpha = 70.786(1)$, $\beta = 83.271(2)$, $\gamma = 89.279(2)^{\circ}$, $V = 2740.87(12)$ Å$^3$, $Z = 4$, space group $P\bar{1}$, $d_{\text{calc}} = 1.188$ g/cm$^3$, $\mu = 0.068$ mm$^{-1}$, $2\theta_{\max} = 52^{\circ}$, total number of measured reflections is 38 900, with $-11 \le h \le 11$, $-20 \le k \le 20$, $-23 \le l \le 23$, among which 9995 reflections are used in calculations. The intensities are corrected for the Lorentz factor and polarization, absorption is taken into account by means of the semi-empirical method using the SORTAV programme [2]. The structure was deciphered directly and corrected by the 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 being 0.950 Å). 688 parameters of the structure were corrected till the final divergence factors: $R(F) = 0.0496$, $wR(F^2) = 0.1282$ for the reflections with $I > 2\sigma(I)$, $R(F) = 0.0611$, $wR(F^2) = 0.1413$ for all the reflections. Residual extremums (min/max) were 0.257 and −0.225 $e$/Å$^3$. The coordinates and equivalent isotropic heat parameters of the

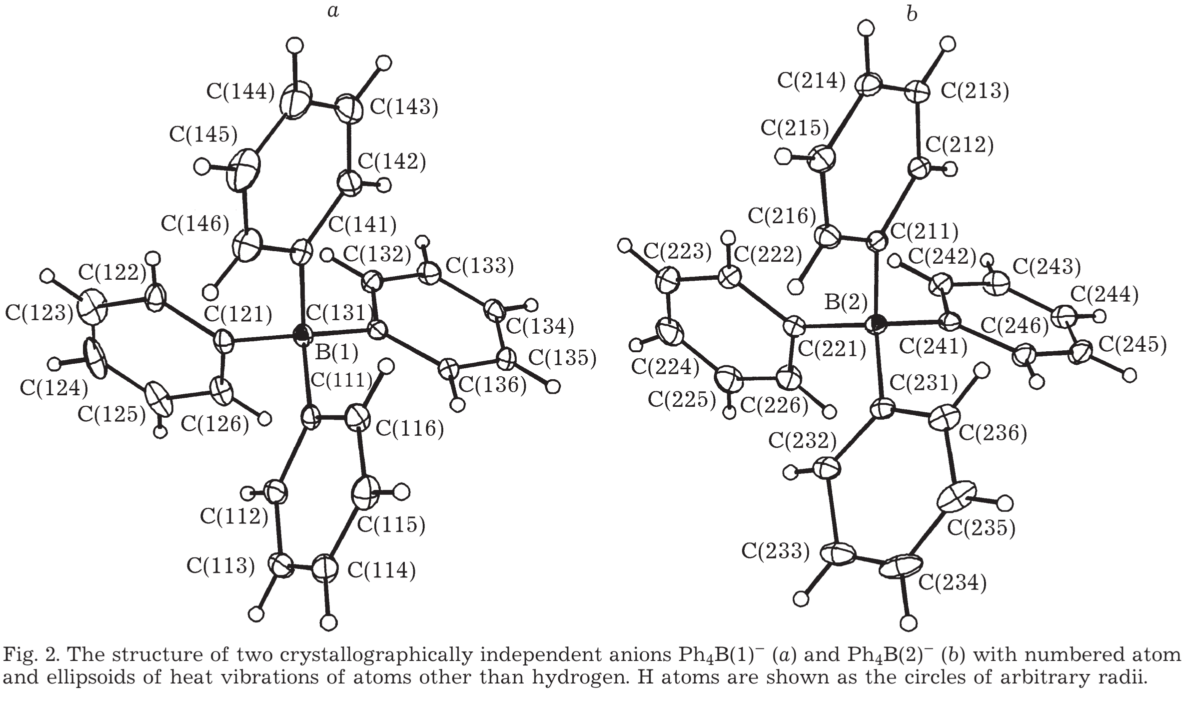

Fig. 2. The structure of two crystallographically independent anions $\mathrm{Ph_4B(1)^-}$ (*a*) and $\mathrm{Ph_4B(2)^-}$ (*b*) with numbered atoms and ellipsoids of heat vibrations of atoms other than hydrogen. H atoms are shown as the circles of arbitrary radii.

TABLE 1

The coordinates of atoms (×$10^4$) and equivalent isotropic heat parameters of atoms other than hydrogen ($U_{\text{equiv}}$ = 1/3($U_{11}$ + $U_{22}$ + $U_{33}$)) in [2,2'-N-Me-Bipy]$^+$[BPh$_4$]$^-$)

| Atom | *x* | *y* | *z* | $U_{\text{equiv}}$, Å$^2$ |
|---|---|---|---|---|
| N(1) | 2001.8(19) | 9145.4(10) | 4954.8(9) | 67.5(4) |
| C(2) | 2063(3) | 9952.1(14) | 4983.8(14) | 81.2(7) |
| C(3) | 2870(3) | 10 203.2(13) | 5441.6(12) | 73.8(6) |
| C(4) | 3661(2) | 9594.9(13) | 5899.4(11) | 67.4(5) |
| C(5) | 3629(2) | 8755.1(11) | 5886.3(9) | 53.7(4) |
| C(6) | 2789.7(18) | 8563.3(10) | 5407.8(8) | 45.2(4) |
| C(7) | 2668.9(16) | 7658.2(10) | 5407.1(8) | 40.6(3) |
| N(8) | 2917.2(14) | 7482.1(8) | 4757.5(7) | 44.7(3) |
| C(8) | 3407(2) | 8161.6(13) | 4042.2(9) | 68.8(5) |
| C(9) | 2783.5(19) | 6666.9(11) | 4747.2(10) | 53.4(4) |
| C(10) | 2413.0(19) | 5991.4(12) | 5379.6(11) | 56.2(4) |
| C(11) | 2167.5(18) | 6143.3(11) | 6049.2(10) | 53.7(4) |
| C(12) | 2292.2(16) | 6980.1(10) | 6057.0(8) | 45.7(4) |
| N(13) | 3108.6(17) | 1006.1(10) | 138.4(8) | 60.8(4) |
| C(14) | 3103(3) | 182.3(14) | 160.8(13) | 76.7(6) |
| C(15) | 2368(3) | −129.2(15) | −288.0(14) | 86.5(7) |
| C(16) | 1587(3) | 438.3(15) | −791.7(13) | 82.7(7) |
| C(17) | 1564(2) | 1295.7(13) | −831.3(10) | 61.0(5) |
| C(18) | 2335.5(17) | 1545.6(10) | −356.9(8) | 45.9(4) |
| C(19) | 2397.4(15) | 2464.4(10) | −399.5(7) | 39.8(3) |
| N(20) | 2071.0(13) | 2681.3(8) | 226.4(6) | 40.8(3) |
| C(20) | 1538(2) | 2025.3(11) | 951.3(8) | 54.8(4) |
| C(21) | 2165.3(18) | 3509.8(11) | 206.8(9) | 49.8(4) |
| C(22) | 2570.4(19) | 4162.5(12) | −438.3(10) | 56.6(4) |
| C(23) | 2888.6(18) | 3973.8(11) | −1086.7(10) | 56.3(4) |
| C(24) | 2804.0(16) | 3121.9(11) | −1065.3(8) | 48.8(4) |
| B(1) | 8282.2(16) | 8282.2(16) | 3467.6(8) | 29.4(3) |
| C(111) | 7888.6(14) | 7888.6(14) | 4335.8(7) | 32.1(3) |
| C(112) | 6626.3(16) | 6626.3(16) | 4787.0(8) | 44.8(4) |
| C(113) | 6302.1(18) | 6302.1(18) | 5516.3(9) | 56.8(5) |
| C(114) | 7232.2(19) | 7232.2(19) | 5827.0(8) | 54.7(4) |
| C(115) | 8515.7(19) | 8515.7(19) | 5408.3(9) | 50.7(4) |
| C(116) | 8830.8(16) | 8830.8(16) | 4680.3(8) | 40.9(3) |
| C(121) | 6779.8(14) | 6779.8(14) | 3106.2(7) | 33.2(3) |
| C(122) | 6187.0(17) | 6187.0(17) | 2599.7(8) | 44.8(4) |
| C(123) | 4884(2) | 4884(2) | 2328.6(10) | 67.5(6) |
| C(124) | 4118(2) | 4118(2) | 2552.6(12) | 75.0(7) |
| C(125) | 4666.8(19) | 4666.8(19) | 3044.1(12) | 62.8(5) |
| C(126) | 5982.3(16) | 5982.3(16) | 3305.7(9) | 45.1(4) |
| C(131) | 9270.9(13) | 9270.9(13) | 3424.8(7) | 28.6(3) |
| C(132) | 9446.3(15) | 9446.3(15) | 2770.4(7) | 35.8(3) |
| C(133) | 10 324.6(16) | 10 324.6(16) | 2684.0(8) | 40.4(3) |
| C(134) | 11 062.8(16) | 11 062.8(16) | 3258.9(8) | 40.5(3) |
| C(135) | 10 921.9(15) | 10 921.9(15) | 3914.4(8) | 39.8(3) |
| C(136) | 10 045.7(14) | 10 045.7(14) | 3991.4(7) | 33.5(3) |
| C(141) | 9191.7(15) | 9191.7(15) | 2997.7(7) | 35.4(3) |
| C(142) | 10 476.9(17) | 10 476.9(17) | 2536.2(10) | 51.1(4) |
| C(143) | 11 228(2) | 11 228(2) | 2165.7(13) | 80.7(7) |
| C(144) | 10 710(3) | 10 710(3) | 2245.4(15) | 86.4(8) |
| C(145) | 9436(3) | 9436(3) | 2686.7(13) | 74.7(6) |
| C(146) | 8696(2) | 8696(2) | 3052.3(10) | 53.1(4) |
| B(2) | 6658.0(15) | 2767.9(9) | 1514.6(7) | 28.0(3) |

TABLE 1 (continued)

| Atom | $x$ | $y$ | $z$ | $U_{\text{equiv}}$, Å$^2$ |
|---|---|---|---|---|
| C(211) | 5653.6(13) | 3575.6(8) | 1583.1(7) | 28.8(3) |
| C(212) | 4910.6(14) | 4105.5(8) | 1016.1(7) | 32.4(3) |
| C(213) | 4026.6(15) | 4766.7(9) | 1107.3(8) | 38.5(3) |
| C(214) | 3845.6(16) | 4917.5(9) | 1780.0(8) | 39.6(3) |
| C(215) | 4552.8(16) | 4401.9(9) | 2357.6(8) | 41.1(3) |
| C(216) | 5437.3(16) | 3753.8(9) | 2257.2(7) | 36.6(3) |
| C(221) | 5739.7(14) | 1850.0(8) | 1921.4(7) | 32.6(3) |
| C(222) | 4416.8(16) | 1757.2(10) | 2361.8(8) | 44.2(3) |
| C(223) | 3661(2) | 963.5(12) | 2669.8(11) | 61.6(5) |
| C(224) | 4216(2) | 235.3(11) | 2544.9(11) | 62.5(5) |
| C(225) | 5528(2) | 295.1(10) | 2122.2(10) | 57.5(4) |
| C(226) | 6267.2(18) | 1082.6(9) | 1821.3(9) | 45.2(4) |
| C(231) | 8122.0(14) | 2774.9(8) | 1921.1(7) | 30.6(3) |
| C(232) | 8641.2(16) | 2037.3(9) | 2428.1(7) | 39.0(3) |
| C(233) | 9905.4(19) | 2045.9(13) | 2747.8(9) | 54.5(4) |
| C(234) | 10 711.5(19) | 2793.8(14) | 2568.8(10) | 61.5(5) |
| C(235) | 10 234.5(18) | 3548.0(12) | 2078.7(10) | 55.1(5) |
| C(236) | 8951.8(16) | 3534.7(10) | 1773.1(9) | 41.8(3) |
| C(241) | 7111.1(14) | 2861.0(8) | 631.6(7) | 29.8(3) |
| C(242) | 6214.7(16) | 2519.4(9) | 248.8(7) | 38.5(3) |
| C(243) | 6576.2(18) | 2575.7(10) | −490.2(8) | 47.1(4) |
| C(244) | 7853.5(18) | 2985.3(11) | −882.0(8) | 49.7(4) |
| C(245) | 8740.9(17) | 3349.7(12) | −532.8(8) | 50.9(4) |
| C(246) | 8370.9(15) | 3286.4(10) | 206.9(7) | 40.4(3) |

TABLE 2

Basic interatomic distances in [2,2′-N-Me-Bipy]$^+$[BPh$_4$]$^-$, Å

| Bond | Length | Bond | Length |
|---|---|---|---|
| N(1)−C(6) | 1.337(2) | N(1)−C(2) | 1.343(3) |
| C(2)−C(3) | 1.380(3) | C(3)−C(4) | 1.365(3) |
| C(4)−C(5) | 1.384(2) | C(5)−C(6) | 1.384(2) |
| C(6)−C(7) | 1.488(2) | C(7)−N(8) | 1.362(2) |
| C(7)−C(12) | 1.380(2) | N(8)−C(9) | 1.349(2) |
| N(8)−C(8) | 1.480(2) | C(9)−C(10) | 1.357(2) |
| C(10)−C(11) | 1.380(3) | C(11)−C(12) | 1.382(2) |
| N(13)−C(14) | 1.336(3) | N(13)−C(18) | 1.339(2) |
| C(14)−C(15) | 1.380(4) | C(15)−C(16) | 1.372(4) |
| C(16)-C(17) | 1.381(3) | C(17)−C(18) | 1.384(2) |
| C(18)−C(19) | 1.481(2) | C(19)−N(20) | 1.361(2) |
| C(19)−C(24) | 1.388(2) | N(20)−C(21) | 1.349(2) |
| N(20)−C(20) | 1.484(2) | C(21)−C(22) | 1.359(2) |
| C(22)−C(23) | 1.376(3) | C(23)−C(24) | 1.385(2) |
| B(1)−C(141) | 1.643(2) | B(1)−C(131) | 1.643(2) |
| B(1)−C(121) | 1.648(2) | B(1)−C(111) | 1.650(2) |
| C(111)−C(112) | 1.396(2) | C(111)−C(116) | 1.404(2) |
| C(112)−C(113) | 1.392(2) | C(113)−C(114) | 1.371(3) |
| C(114)−C(115) | 1.385(3) | C(115)−C(116) | 1.393(2) |
| C(121)−C(126) | 1.400(2) | C(121)−C(122) | 1.400(2) |
| C(122)−C(123) | 1.391(2) | C(123)−C(124) | 1.363(3) |
| C(124)−C(125) | 1.382(3) | C(125)−C(126) | 1.393(2) |
| C(131)−C(136) | 1.398(2) | C(131)−C(132) | 1.405(2) |
| C(132)−C(133) | 1.387(2) | C(133)−C(134) | 1.380(2) |
| C(134)−C(135) | 1.382(2) | C(135)−C(136) | 1.398(2) |
| C(141)-C(142) | 1.388(2) | C(141)−C(146) | 1.405(2) |
| C(142)−C(143) | 1.388(2) | C(143)−C(144) | 1.379(3) |
| C(144)−C(145) | 1.367(3) | C(145)−C(146) | 1.378(3) |

TABLE 2 (continued)

| Bond | Length | Bond | Length |
|---|---|---|---|
| B(2)−C(211) | 1.642(2) | B(2)−C(221) | 1.644(2) |
| B(2)−C(231) | 1.650(2) | B(2)−C(241) | 1.653(2) |
| C(211)−C(212) | 1.398(2) | C(211)−C(216) | 1.408(2) |
| C(212)−C(213) | 1.396(2) | C(213)−C(214) | 1.383(2) |
| C(214)−C(215) | 1.384(2) | C(215)−C(216) | 1.385(2) |
| C(221)−C(222) | 1.389(2) | C(221)−C(226) | 1.407(2) |
| C(222)−C(223) | 1.398(2) | C(223)−C(224) | 1.375(3) |
| C(224)−C(225) | 1.370(3) | C(225)−C(226) | 1.382(2) |
| C(231)−C(232) | 1.400(2) | C(231)−C(236) | 1.402(2) |
| C(232)−C(233) | 1.392(2) | C(233)−C(234) | 1.366(3) |
| C(234)−C(235) | 1.388(3) | C(235)−C(236) | 1.394(2) |
| C(241)−C(246) | 1.396(2) | C(241)−C(242) | 1.405(2) |
| C(242)−C(243) | 1.391(2) | C(243)−C(244) | 1.381(2) |
| C(244)−C(245) | 1.376(2) | C(245)−C(246) | 1.390(2) |

TABLE 3

Valence angles φ in $[2,2'\text{-N-Me-Bipy}]^+[\text{BPh}_4]^-$, deg

| Angle | φ | Angle | φ |
|---|---|---|---|
| C(6)−N(1)−C(2) | 116.0(2) | N(1)−C(2)−C(3) | 24.4(2) |
| C(4)−C(3)−C(2) | 118.3(2) | C(3)−C(4)−C(5) | 119.1(2) |
| C(6)−C(5)−C(4) | 118.6(2) | N(1)−C(6)−C(5) | 123.6(2) |
| N(1)−C(6)−C(7) | 116.3(2) | C(5)−C(6)−C(7) | 120.00(14) |
| N(8)−C(7)−C(12) | 118.36(14) | N(8)−C(7)−C(6) | 120.32(13) |
| C(12)−C(7)−C(6) | 121.32(13) | C(9)−N(8)−C(7) | 120.92(13) |
| C(9)−N(8)−C(8) | 117.11(14) | C(7)−N(8)−C(8) | 121.91(14) |
| N(8)−C(9)−C(10) | 121.6(2) | C(9)−C(10)−C(11) | 119.1(2) |
| C(10)−C(11)−C(12) | 119.1(2) | C(7)−C(12)−C(11) | 120.9(2) |
| C(14)−N(13)−C(18) | 116.1(2) | N(13)−C(14)−C(15) | 124.3(2) |
| C(16)−C(15)−C(14) | 118.4(2) | C(15)−C(16)−C(17) | 119.0(2) |
| C(16)−C(17)−C(18) | 118.2(2) | N(13)−C(18)−C(17) | 124.0(2) |
| N(13)−C(18)−C(19) | 115.67(14) | C(17)−C(18)−C(19) | 120.3(2) |
| N(20)−C(19)−C(24) | 118.23(14) | N(20)−C(19)−C(18) | 120.04(12) |
| C(24)−C(19)−C(18) | 121.72(14) | C(21)−N(20)−C(19) | 121.20(13) |
| C(21)−N(20)−C(20) | 117.13(13) | C(19)−N(20)−C(20) | 121.62(13) |
| N(20)−C(21)−C(22) | 121.5(2) | C(21)−C(22)−C(23) | 119.2(2) |
| C(22)−C(23)−C(24) | 119.3(2) | C(23)−C(24)−C(19) | 120.6(2) |
| C(141)−B(1)−C(131) | 109.23(11) | C(141)−B(1)−C(121) | 110.57(10) |
| C(131)−B(1)−C(121) | 108.05(10) | C(141)−B(1)−C(111) | 108.24(10) |
| C(131)−B(1)−C(111) | 110.99(10) | C(121)−B(1)−C(111) | 109.77(10) |
| C(112)−C(111)−C(116) | 114.74(12) | C(112)−C(111)−B(1) | 123.67(12) |
| C(116)−C(111)−B(1) | 121.59(12) | C(113)−C(112)−C(111) | 123.02(14) |
| C(114)−C(113)−C(112) | 120.5(2) | C(113)−C(114)−C(115) | 118.75(14) |
| C(114)−C(115)−C(116) | 120.2(2) | C(115)−C(116)−C(111) | 122.8(2) |
| C(126)−C(121)−C(122) | 114.99(14) | C(126)−C(121)−B(1) | 120.97(12) |
| C(122)−C(121)−B(1) | 124.03(13) | C(123)−C(122)−C(121) | 122.6(2) |
| C(124)−C(123)−C(122) | 120.7(2) | C(123)−C(124)−C(125) | 119.0(2) |
| C(124)−C(125)−C(126) | 120.1(2) | C(125)−C(126)−C(121) | 122.6(2) |
| C(136)−C(131)−C(132) | 115.13(12) | C(136)−C(131)−B(1) | 124.68(11) |
| C(132)−C(131)−B(1) | 120.10(11) | C(133)−C(132)−C(131) | 123.01(13) |
| C(134)−C(133)−C(132) | 120.15(13) | C(133)−C(134)−C(135) | 118.95(12) |
| C(134)−C(135)−C(136) | 120.33(13) | C(135)−C(136)−C(131) | 122.42(12) |
| C(142)−C(141)−C(146) | 114.94(14) | C(142)−C(141)−B(1) | 124.58(12) |
| C(146)−C(141)−B(1) | 120.47(13) | C(141)−C(142)−C(143) | 122.5(2) |
| C(144)−C(143)−C(142) | 120.4(2) | C(145)−C(144)−C(143) | 118.8(2) |
| C(144)−C(145)−C(146) | 120.4(2) | C(145)−C(146)−C(141) | 122.9(2) |
| C(211)−B(2)−C(221) | 109.63(10) | C(211)−B(2)−C(231) | 108.49(9) |
| C(221)−B(2)−C(231) | 110.20(10) | C(211)−B(2)−C(241) | 110.46(10) |
| C(221)−B(2)−C(241) | 107.90(10) | C(231)−B(2)−C(241) | 110.16(10) |
| C(212)−C(211)−C(216) | 115.01(11) | C(212)−C(211)−B(2) | 124.58(11) |
| C(216)−C(211)−B(2) | 120.35(11) | C(213)−C(212)−C(211) | 122.67(12) |
| C(214)−C(213)−C(212) | 120.27(12) | C(213)−C(214)−C(215) | 118.83(12) |

TABLE 3 (continued)

| Angle | φ | Angle | φ |
|---|---|---|---|
| C(214)–C(215)–C(216) | 120.28(13) | C(215)–C(216)–C(211) | 122.93(12) |
| C(222)–C(221)–C(226) | 114.84(13) | C(222)–C(221)–B(2) | 125.04(12) |
| C(226)–C(221)–B(2) | 120.10(12) | C(221)–C(222)–C(223) | 122.4(2) |
| C(224)–C(223)–C(222) | 120.4(2) | C(225)–C(224)–C(223) | 119.2(2) |
| C(224)–C(225)–C(226) | 119.9(2) | C(225)–C(226)–C(221) | 123.3(2) |
| C(232)–C(231)–C(236) | 114.91(13) | C(232)–C(231)–B(2) | 123.53(12) |
| C(236)–C(231)–B(2) | 121.57(11) | C(233)–C(232)–C(231) | 123.0(2) |
| C(234)–C(233)–C(232) | 120.3(2) | C(233)–C(234)–C(235) | 119.2(2) |
| C(234)–C(235)–C(236) | 120.0(2) | C(235)–C(236)–C(231) | 122.6(2) |
| C(246)–C(241)–C(242) | 114.91(12) | C(246)–C(241)–B(2) | 123.82(11) |
| C(242)–C(241)–B(2) | 121.26(12) | C(243)–C(242)–C(241) | 122.62(14) |
| C(244)–C(243)–C(242) | 120.28(14) | C(245)–C(244)–C(243) | 118.83(13) |
| C(244)–C(245)–C(246) | 120.4(2) | C(245)–C(246)–C(241) | 122.97(14) |

atoms other than 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 can be obtained from the authors by request.

## RESULTS AND DISCUSSION

The complex structure is ionic. Crystals are built of two crystallographically independent organic cations (N-Me-Bipy)$^+$ and two crystallographically independent anions $(BPh_4)^-$. 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, they possess chamfered conformation with dihedral angles between the plains of pyridine rings 53.0 and 53.1°, respectively. Pyridine rings are practically flat, while the rings containing Me group are more crimped. Mean square deviations for four rings containing N(1) (ring 1), N(8) (ring 2), N(13) (ring 3), and N(20) (ring 4) are 0.001, 0.003, 0.001, and 0.004 Å, respectively. The atoms C(8) and C(20) of methyl groups are bent to neighbouring pyridinium rings 1 and 3, their deviations from mean square planes of rings 2 and 4 are larger: 0.083 and 0.087 Å, respectively. CNC angles at unprotonated nitrogen atoms N(1) and N(13), which are 116.0(2) and 116.1(2)°, are much smaller than those for N(8) and N(20) containing Me group, which are 120.92(13) and 121.20(13)°. *Cis*-conformation of the only crystallographically independent cation (2,2′-Bipy) in the [2,2′-Bipy]$^+$[BPh$_4$]$^-$ salt (**2**) is characterized by the twisting of Py rings which is only 5.2° [1].

Each tetraphenylborate anion $(BPh_4)^-$ has in fact plain 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) (ring 7), and C (241) (ring 8) are 0.007, 0.007, 0.003, 0.005, 0.003, 0.004, 0.020, and 0.008 Å, respectively. The seventh phenyl ring is thus the most crimped one. The deviations of boron atoms from the

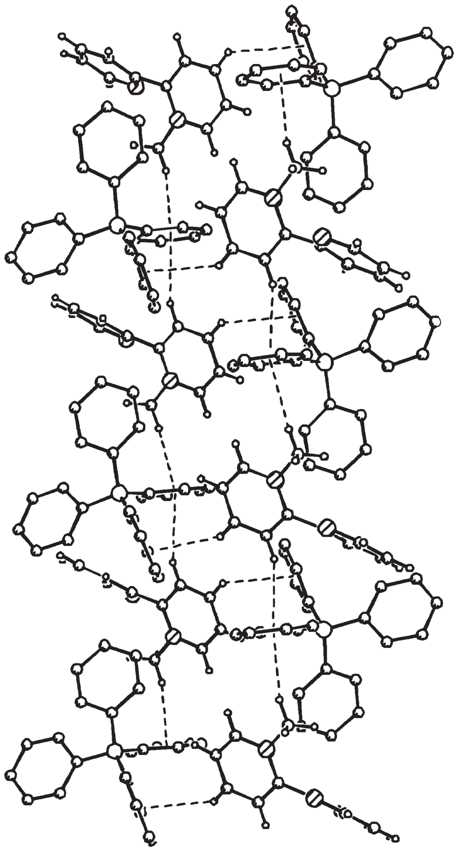

Fig. 3. Fragments of ion pairs packing in the crystal lattice of compound **1**. The contacts C—H...π are shown with dashed lines.

mean square planes of phenyl rings of each anion are more substantial and are 0.030, 0.084, 0.074, 0.050; −0.060, −0.067, −0.117, 0.031 Å, respectively. Dihedral angles between the planes of phenyl rings fall within the ranges 64.8−116.7 and 65.2−117.7° for the anions with the participation of B(1) and B(2), respectively. B—C bond lengths fall within a narrow range 1.642(2)−1.653(2) Å, with a mean of 1.647(2) Å. Tetrahedral angles C—B—C in the anions are within the range 107.90(10)−110.99(10)°, with a mean of 109.47(10)°.

Figure 3 shows a fragment of ion pairs packing in the lattice of **1**. The edge-to-face interactions of aromatic fragments of the cations containing Me group, with Ph rings of the anions $(BPh_4)^-$ are observed in the system [4−7]. The contacts C—H…π corresponding to these interactions are marked with dashed lines. The distances from H atoms to the centroids of Ph rings and the angles at H fall within the ranges 2.59−2.87 Å and 122−170°, respectively. These geometric parameters of hydrogen bonds for the interactions C−H…π occur in the structures of tetraphenylborates present in the Cambridge crystal structure database. These interactions can be responsible for charge transfer and photochromic behaviour of compound **1** which is exhibited as the increase of pink colour intensity when the crystals are kept in light.

## CONCLUSION

Low-temperature X-ray structural investigation of compound **1** showed that edge-to-face interactions exist between the aromatic fragments of cations and aromatic fragments of anions. These interactions can be responsible for charge transfer, photochromic behaviour, and possibly for some other functional properties of this compound.

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