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Low-Temperature Structure of 3-(p-Bromophenyl)thiazolo[3,2-a]pyridinium Tetrafluoroborate

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Abstract. $C_{13}H_9BrNS^+.BF_4^-$, $M_r = 377.99$, monoclinic, $P2_1/n$, $a = 12.200$ (2), $b = 7.633$ (1), $c = 14.664$ (2) Å, $\beta = 97.84$ (1)°; $d_x = 1.855$ Mg m^{-3}, $Z = 4$, λ(Mo $K\alpha_1$) = 0.70926 Å, $\mu = 340.5$ mm^{-1}, m.p. = 489 K. Diffraction data were collected at about 123 K and the structure was refined to $R = 0.052$. The fused thiazole and pyridine rings are quite regular.

Introduction. During an extensive study of the reactions and syntheses of azolium systems (Messmer & Gelléri, 1965; Gelléri & Messmer, 1973), the geometry and aromaticity of the thiazolo skeleton became of interest. A quantum-chemical approach to the behaviour of the title compound led to the X-ray study. The compound was synthesized by a modification of the method of Bradsher & Boliek (1967) from 2-mercaptopyridine and p-bromophenacyl bromide. The condensation of the intermediate product [α-(2-pyridylthio)-4-bromoacetophenone] yielded the title compound which was crystallized as the tetrafluoroborate salt.

Unit-cell parameters and their e.s.d.'s were calculated from diffractometer data using the least-squares technique. 3945 independent reflexions were collected at low temperature (about 123 K) on a Syntex $P2_1$ automatic four-circle diffractometer with monochromated Mo $K\alpha_1$ radiation. 416 reflexions [$I \leq 2\sigma(I)$] were taken as unobserved. No absorption correction was made. The fractional coordinates of Br and S were determined by the Patterson method. Other non-hydrogen atoms were located in a subsequent

Fourier map. The structure was refined by anisotropic least squares using the program *SHELX* (Sheldrick, 1976). H atoms were located from the assumed geometry of the sp^2 C atoms and were refined in one isotropic cycle. The final R values are 0.052 and 0.058 for the observed and all reflexions, respectively. No sign of disorder in the BF_4 group could be detected in the difference maps. The final atomic coordinates are listed in Tables 1 and 2.*

Discussion. A view of the molecule with the atomic numbering is shown in Fig. 1. Bond lengths and angles are given in Tables 3 and 4.

The fused thiazole and pyridine rings are coplanar (the dihedral angle is 4°). The phenyl ring is twisted with respect to the thiazole ring about C(5)—C(10) by 52.0°, which is very close to the value (49.2°) found in 3-phenyltetrazolo[4,5-a]pyridinium tetrafluoroborate (PTPTF; Sasvári, Czugler, Gelléri, Náray-Szabó, Hess & Schwarz, 1979). The main difference between the two structures lies in the endocyclic bond angles of the pyridine rings. These are quite close to 120° in the title compound while two extreme values were observed for PTPTF. The 117.8° at C(9) is, however, the same as in PTPTF (117.3°). The thiazole ring resembles a

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35119 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

number of similar fragments in various compounds (e.g. 3-ethyl-2-methylbenzothiazolium tetrafluoroborate, EMBT; Srenger, 1974; 3-ethyl-2-methyl-6-nitrobenzothiazolium tetrafluoroborate, EMNBT; Srenger & Robert, 1978). The two C–S bonds are

Table 1. Final fractional coordinates ($\times 10^4$) and isotropic B values for the non-hydrogen atoms

Estimated standard deviations are in parentheses.

	x	y	z	B (Å²)
N(1)	5554 (2)	178 (3)	2137 (2)	1·2 (1)
C(2)	4662 (2)	233 (4)	2607 (2)	1·5 (1)
S(3)	4989 (1)	1249 (1)	3661 (1)	1·9 (2)
C(4)	6325 (3)	1597 (4)	3442 (2)	1·6 (2)
C(5)	6520 (3)	991 (4)	2608 (2)	1·5 (1)
C(6)	5487 (3)	−698 (4)	1308 (2)	1·4 (1)
C(7)	4516 (3)	−1495 (4)	955 (2)	1·8 (2)
C(8)	3591 (3)	−1385 (4)	1429 (2)	2·0 (2)
C(9)	3653 (3)	−520 (4)	2254 (2)	1·9 (2)
C(10)	7550 (3)	1106 (4)	2194 (2)	1·3 (1)
C(11)	7556 (3)	1821 (4)	1309 (2)	1·6 (2)
C(12)	8534 (2)	1911 (4)	928 (2)	1·5 (2)
C(13)	9504 (2)	1295 (4)	1430 (2)	1·6 (2)
C(14)	9529 (3)	633 (4)	2317 (2)	1·4 (2)
C(15)	8554 (3)	549 (4)	2697 (2)	1·5 (1)
Br	10856 (1)	1404 (1)	912 (1)	1·9 (1)
F(1)	3041 (2)	2115 (3)	175 (1)	2·2 (1)
F(2)	4677 (2)	3357 (4)	811 (2)	3·9 (2)
F(3)	3176 (2)	3745 (4)	1493 (2)	5·3 (3)
F(4)	3286 (3)	5030 (3)	114 (2)	5·6 (3)
B	3532 (3)	3583 (5)	646 (2)	1·7 (2)

Table 2. Final fractional coordinates ($\times 10^3$) of the hydrogen atoms with their estimated standard deviations in parentheses

Overall $B = 3·3$ (4) Å².

	x	y	z
H(4)	694 (1)	227 (1)	391 (1)
H(6)	619 (1)	−75 (1)	94 (1)
H(7)	446 (1)	−220 (1)	31 (1)
H(8)	283 (1)	−201 (1)	114 (1)
H(9)	294 (1)	−41 (1)	262 (1)
H(11)	681 (1)	227 (1)	90 (1)
H(12)	855 (1)	250 (1)	26 (1)
H(14)	1031 (1)	20 (1)	269 (1)
H(15)	857 (1)	5 (1)	338 (1)

Table 3. Bond lengths (Å) with their estimated standard deviations in parentheses

N(1)–C(2)	1·366 (4)	C(10)–C(11)	1·409 (4)
N(1)–C(5)	1·423 (4)	C(10)–C(15)	1·407 (4)
N(1)–C(6)	1·381 (4)	C(11)–C(12)	1·386 (5)
C(2)–S(3)	1·726 (3)	C(12)–C(13)	1·387 (4)
C(2)–C(9)	1·392 (4)	C(13)–C(14)	1·393 (4)
S(3)–C(4)	1·723 (3)	C(13)–Br	1·908 (3)
C(4)–C(5)	1·358 (4)	C(14)–C(15)	1·382 (5)
C(5)–C(10)	1·471 (5)	B–F(1)	1·406 (4)
C(6)–C(7)	1·368 (4)	B–F(2)	1·395 (4)
C(7)–C(8)	1·406 (5)	B–F(3)	1·376 (5)
C(8)–C(9)	1·372 (5)	B–F(4)	1·362 (5)

Table 4. Bond angles (°) with their estimated standard deviations in parentheses

| C(2)–N(1)–C(5)	113·9 (2)	C(5)–C(10)–C(15)	119·9 (3)
C(2)–N(1)–C(6)	120·2 (2)	C(11)–C(10)–C(15)	119·0 (3)
C(5)–N(1)–C(6)	125·8 (3)	C(10)–C(11)–C(12)	120·2 (3)
N(1)–C(2)–S(3)	111·2 (2)	C(11)–C(12)–C(13)	119·3 (3)
N(1)–C(2)–C(9)	121·7 (3)	C(12)–C(13)–C(14)	121·7 (3)
S(3)–C(2)–C(9)	127·1 (2)	C(13)–C(14)–C(15)	118·9 (3)
C(2)–S(3)–C(4)	90·7 (1)	C(10)–C(15)–C(14)	120·8 (3)
S(3)–C(4)–C(5)	113·6 (2)	C(12)–C(13)–Br	119·6 (3)
C(4)–C(5)–N(1)	110·5 (3)	C(14)–C(13)–Br	118·5 (3)
C(4)–C(5)–C(10)	128·0 (3)	F(1)–B–F(2)	109·7 (3)
N(1)–C(5)–C(10)	121·5 (2)	F(1)·B–F(3)	110·4 (3)
N(1)–C(6)–C(7)	119·5 (3)	F(1)–B–F(4)	108·6 (3)
C(6)–C(7)–C(8)	119·9 (3)	F(2)–B–F(3)	106·7 (3)
C(7)–C(8)–C(9)	120·8 (3)	F(2)–B–F(4)	109·7 (3)
C(8)–C(9)–C(2)	117·8 (3)	F(3)–B–F(4)	111·8 (3)
C(5)–C(10)–C(11)	121·1 (3)		
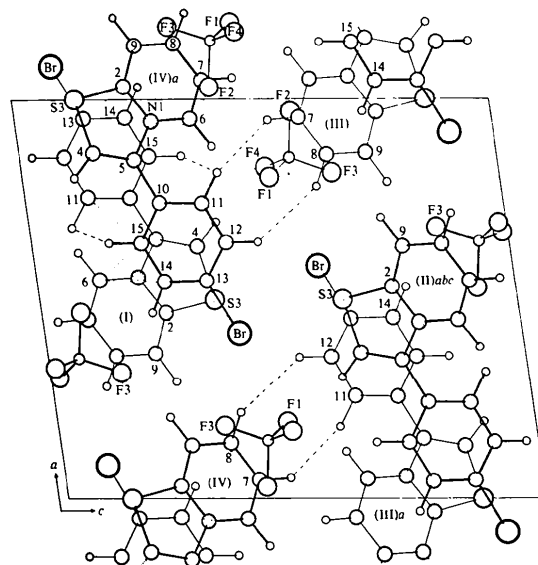
Fig. 1. Orthogonal projection of the unit cell on the plane (010) with the numbering of the atoms. The symmetry-related molecules are assigned by Roman numbers |(I) x,y,z; (II) x̄,ȳ,z̄; (III) ½ + x, ½ − y, ½ + z; (IV) ½ − x, ½ + y, ½ − z] and unit-cell translations are indicated by the letters a, b and c. The shortest intermolecular contacts are given by broken lines for H···H and by dotted lines for all others.
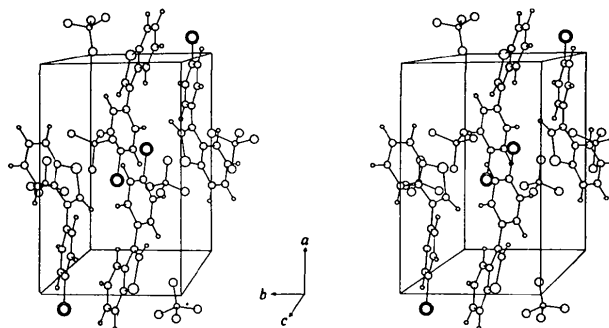

Fig. 2. Stereoscopic diagram of the unit-cell contents.

Table 5. *The shortest intermolecular distances* (Å) *with their e.s.d.'s in parentheses; the corresponding sum of the van der Waals radii is given in brackets*

The symmetry positions are (I) x,y,z; (II) $\bar{x},\bar{y},\bar{z}$; (III) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (IV) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ and shifts parallel to the crystallographic axes are indicated by the letters *a,b,c*, with signs.

From atom at (I)	To atom				From atom at (I)	To atom				From atom at (I)	To atom		
C(2)	C(13)	IV(a,−b)	3·416 (4)	|3·40|	H(8)	H(12)	II(a)	2·50 (2)		F(2)	C(7)	II(a)	3·224 (4)
C(4)	C(14)	IV(a)	3·391 (5)		H(11)	H(15)	IV(a)	2·44 (2)		F(3)	C(9)	IV	3·129 (4)
	C(15)	IV(à)	3·461 (5)		F(1)	H(4)	III(−a,−c)	2·18 (1)	|2·55|	F(4)	C(7)	I(b)	3·211 (4)
C(5)	C(15)	IV(a)	3·508 (5)			H(6)	II(a)	2·25 (1)		F(1)	Br	I(−a)	3·058 (2) |3·30|
C(6)	C(14)	IV(a, −b)	3·453 (5)		F(2)	H(7)	II(a)	2·25 (1)		F(3)	Br	I(−a)	3·357 (2)
	C(15)	IV(a,−b)	3·352 (5)			H(14)	IV(a)	2·61 (1)		Br	Br	II(a)	3·820 (2) |3·90|
C(7)	C(14)	IV(a,−b)	3·431 (5)		F(3)	H(9)	IV	2·12 (1)			S(3)	III(−c)	3·779 (2) |3·80|
C(8)	C(14)	IV(a, −b)	3·560 (5)			H(14)	IV(a)	2·34 (1)			S(3)	IV(a)	3·913 (2)
C(11)	C(15)	IV(a)	3·549 (5)		F(4)	H(7)	I(b)	2·55 (1)			C(2)	IV(a)	3·745 (3) |3·65|
C(7)	H(11)	II(a)	3·03 (1)	|2·90|		H(11)	II(a,b)	2·53 (1)			C(9)	IV(a)	3·559 (3)
C(8)	H(14)	IV(a,−b)	3·13 (1)			H(15)	III(−a,−c)	2·62 (1)		S(3)	C(4)	IV(a)	3·718 (3) |3·55|
C(11)	H(15)	IV(a)	2·89 (1)		F(1)	C(4)	III(−a,−c)	3·218 (4)	|3·05|		H(12)	III(−a)	3·27 (1) |3·15|
H(7)	H(11)	II(a)	2·19 (2)	|2·40|		C(6)	II(a)	3·192 (4)					

equal and nearly the same as those in thiophene (1·718 Å; Bak, Christensen, Hansen & Rastrup-Andersen, 1956) and *N*-(3-phenylbenzo[*b*]thien-2-yl)thiobenzamide (1·739 and 1·742 Å; Argay & Kálmán, 1973) while these bonds are significantly different in EMBT and EMNBT (1·734, 1·698 and 1·738, 1·687 Å).

The geometry of the BF_4^- anion seems to be fairly regular. Small distortions are connected with the positions of F(3) and F(4) which have considerably higher thermal motion than the other heavy atoms.

The molecules in the crystal are arranged in two columns parallel to the twofold screw axes (Fig. 1). Thus, each phenyl ring is sandwiched between two thiazole rings and *vice versa*. In this arrangement the sandwiched thiazole and phenyl rings are almost parallel to each other (the dihedral angle is 4·6°) forming angles of 28·4 and 23·8° with the (010) plane. Several intermolecular close contacts are formed and molecules in the columns are held together mainly by C⋯C van der Waals forces (Table 5). The BF_4^- ions are also present in the columns and take part in F⋯H contacts within and between the columns. No van der

Waals approach to the N(1) atom has been found, unlike in PTPTF where an F⋯N(pyridinium) weak ionic bond (2·86 Å) was reported. A stereoscopic view of the unit cell is depicted in Fig. 2.

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