

X-Ray Studies on Potent New Curariform Agents. Part 2.† The Crystal and Molecular Structure of 3,3'-Thiobis-(2-methyl-1-phenylimidazo-[1,5-*a*]pyridinium) Bistetrafluoroborate(III)

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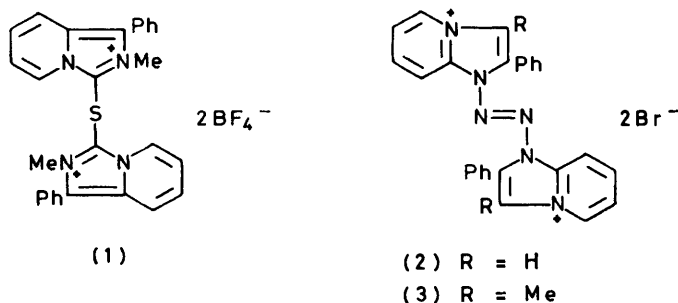
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The structure of the title compound, representative of a new series of powerful and selective neuromuscular blocking agents has been determined by a three-dimensional X-ray analysis. Monoclinic crystals in space group $P2_1/c$ have lattice parameters $a = 15.517(2)$, $b = 14.054(3)$, $c = 13.862(2)$ Å, $\beta = 108.88(1)^\circ$, and $Z = 4$. The structure was solved by centro-symmetric symbolic addition and refined by full-matrix least-squares calculations to $R = 0.080$ for 1 133 reflections. The molecule consists of two identical halves inclined at an angle of 72.8° joined by a sulphide link. Quaternary nitrogen atom separations are all <4.8 Å, and the non-planarity of the molecule is in striking contrast with related compounds which show comparable activity.

COMPETITIVE postsynaptic neuromuscular blockade may be brought about by the presence of substances which combine reversibly with acetylcholine receptors on the postsynaptic membrane surface at sites identified as the motor end-plate.¹ Curariform agents, so-called from the well-known (+)-tubocurarine chloride, are non-depolarising, in that they prevent depolarisation of the motor end-plate solely by competing with acetylcholine for occupation of the receptor sites, and neither the electrical properties of the end-plate nor its permeability to potassium ions is affected. It has been demonstrated² that the maximum number of molecules of (+)-tubocurarine that can occupy receptor sites on each end-plate is of the order of 3 or 4×10^6 , but the nature of the interaction of curariform agents with the receptors is still an open question.³ Early attempts to correlate structural features of suitably active molecules mostly centred around the separation of quaternary nitrogen atoms in the molecule,⁴ and a recent summary⁵ of the molecular criteria necessary, includes a quaternary nitrogen atom interjacency of 10.8(3) Å in a rigid, concave molecule having oxygen atoms suitably disposed to aid orientation. That these criteria are not critical was first shown by the determination^{6,7} of the crystal structure of the near-planar 1,1'-azobis-2-phenylimidazo-[1,2-*a*]pyridinium dibromide (2) whose quaternary nitrogen separation is 7.5 Å in the crystal, and by the demonstration⁸ that (+)-tubocurarine chloride has only one quaternary nitrogen atom.

Our suggestions⁶ that effective neuromuscular blockade can be achieved by single point interaction with acetylcholine receptors, and that considerable variations of conformation are permitted, is further supported by the crystal structure of the title compound (1) whose four possible quaternary nitrogen atom intramolecular separations are <4.80 Å, and whose concave structure is in striking contrast to that of (2). The title compound (1) is one of a series⁹ of bis-quaternaries whose neuro-

muscular potencies and duration of action have been determined¹⁰ in several species, and Table 1 summarises¹¹ some of the results obtained in one species. The related compound 1,1'-azobis-3-methyl-2-phenylimidazo-[1,2-*a*]pyridinium dibromide § (3) is currently used in



clinical practice.¹² A preliminary report based on visually estimated data from the present study has been published.¹³

EXPERIMENTAL

Crystals of (1) were prepared as in ref. 9 and crystallised from nitromethane-ether as pale yellow needles, m.p. 308° (decomp.) (Found: C, 54.5; H, 4.5; N, 8.8; S, 5.4. $[C_{28}H_{24}N_4S]^{2+}2BF_4^-$ requires C, 54.05; H, 3.9; N, 9.0; S, 5.15%), $M = 622.17$.

Crystal Data.—Monoclinic, $a = 15.517(2)$, $b = 14.054(3)$, $c = 13.862(2)$ Å, $\beta = 108.88(1)^\circ$, $D_m = 1.455$ g cm⁻³ (by flotation), $D_c = 1.445$ g cm⁻³, $Z = 4$, $F(000) = 1272$, $\mu = 17.3$ cm⁻¹ for Cu- K_α radiation, $\lambda = 1.5418$ Å. Space group $P2_1/c$ (C_{2h}^5 , No. 14).

Single-crystal Weissenberg equi-inclination photographs and the multiple film technique were used for data collection. Crystals smaller than the optimum size (0.11 cm) were used, and no corrections for absorption were applied. The intensities of 2 344 reflections were estimated visually from layers $hk0-10$ and merged with 674 reflections from layers $h0-3l$ affording 2 388 independent reflections (merging R 0.20). Normalised structure factors were calculated¹⁴ using a temperature factor of 3.3 Å². From 430 $|E|$ values with magnitudes greater than 1.35, the signs of 251 reflections were determined by centrosymmetric symbolic

§ Compound (3) is now marketed under the name Fazadon, B.P., 1,342,713.

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‡ Part I, D. J. Pointer and J. B. Wilford, *J.C.S. Perkin II*, 1972, 2259.

TABLE 1

Comparison of the neuromuscular potencies of some quaternary compounds measured on the tibialis muscle of the anaesthetized cat¹¹

Compound	Dose (mg kg ⁻¹ intravenous)	Mean neuromuscular blockade (%)	Duration of action for 90% recovery (min)
(+)-Tubocurarine chloride	0.1	80	
(1a) ^a	0.4	100	
	0.5	83.5	1.00
	1.0	100	1.50
	2.0	100	9.00
(2)	0.25	23.3	1.00
	0.50	64.04	2.58
	1.00	98.52	6.26
(3)	0.1	12.7	0.87
	0.2	60.4	1.73
	0.4	93.0	2.56

^a The anion in compound (1) is BF₄⁻ and that in (1a) is Br⁻. Compound (1a) was not suitable for X-ray studies.

addition in terms of two symbols. An *E* map using the most probable sign set afforded positions for all atoms except those of one BF₄⁻ anion, subsequently found from an *F*(obs) map phased on the other atom positions. Block-diagonal refinement,¹⁴ initially with isotropic temperature factors, then with anisotropic temperature factors for the cation atoms reduced *R* to 0.122.

A OI P-100 Photoscan microdensitometer¹⁵ was used to re-measure the intensities from layers *h**k*0—10, which were processed by the SHELX system¹⁶ affording 1133 unique reflections (merging *R* 0.052 6). Block diagonal refinement¹⁴ of the atom parameters with isotropic temperature factors gave *R* as 0.128. Full-matrix refinement¹⁷ with sequential variation of layer scale values, atom co-ordinates, and anisotropic temperature factors for all atoms slowly converged with *R* 0.080. A Cruickshank weighting scheme¹⁸ was used in all refinement cycles; the final parameters were *A* = 1.183 3, *B* = -0.047 6, *C* = 0.003 09. Finally, each of the aromatic hydrogen atoms was positioned on the median line through its bonded carbon atom and in the plane of this carbon atom and its two linked neighbours, assuming C-H 1.08 Å.

RESULTS AND DISCUSSION

The final atomic co-ordinates together with their standard deviations are given in Table 2 and the inter-atomic distances and bond angles calculated from these

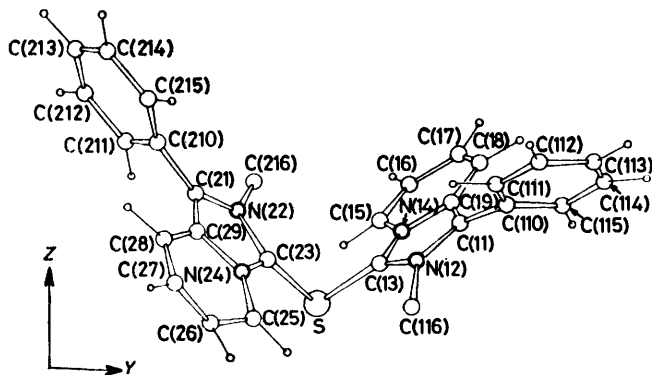


FIGURE 1 Molecular structure of the title compound (1) viewed along the *a* axis, showing the atom numbering system used in the analysis

co-ordinates are listed in Table 3. The atomic numbering scheme is shown in Figure 1 and the hydrogen atoms are numbered as the atoms to which they are attached.

The molecule consists of two chemically indistinguishable halves both bonded to the sulphur atom but which are not crystallographically related, hence there are two distinct measurements of all the molecular parameters. Each imidazo[1,5-*a*]pyridinium ring system is nearly

TABLE 2

Fractional atomic co-ordinates with their estimated standard deviations in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>
S	0.633 5(3)	0.179 1(3)	0.350 0(3)
C(11)	0.727 8(12)	0.421 7(12)	0.485 1(12)
N(12)	0.730 4(8)	0.345 8(9)	0.423 4(9)
C(13)	0.660 9(11)	0.285 2(11)	0.418 2(11)
N(14)	0.612 6(8)	0.321 4(8)	0.474 7(8)
C(15)	0.533 3(12)	0.286 0(14)	0.491 1(14)
C(16)	0.498 3(13)	0.332 3(13)	0.555 8(13)
C(17)	0.541 8(13)	0.420 0(13)	0.606 8(14)
C(18)	0.617 2(12)	0.452 5(12)	0.587 7(12)
C(19)	0.651 6(13)	0.405 1(12)	0.519 4(11)
C(110)	0.795 2(12)	0.496 1(11)	0.516 6(12)
C(111)	0.761 1(15)	0.591 6(14)	0.511 5(17)
C(112)	0.828 1(15)	0.664 6(15)	0.549 7(17)
C(113)	0.917 4(15)	0.644 1(15)	0.585 7(14)
C(114)	0.953 3(14)	0.550 2(14)	0.590 0(14)
C(115)	0.890 6(13)	0.476 5(13)	0.554 2(13)
C(116)	0.793 2(14)	0.336 4(15)	0.364 8(14)
C(21)	0.763 0(12)	-0.017 7(12)	0.539 8(12)
N(22)	0.698 2(9)	0.049 8(9)	0.509 4(9)
C(23)	0.708 7(11)	0.097 6(11)	0.427 2(12)
N(24)	0.779 2(9)	0.055 0(9)	0.408 0(9)
C(25)	0.814 3(16)	0.073 4(14)	0.327 6(16)
C(26)	0.881 1(15)	0.017 9(15)	0.315 8(15)
C(27)	0.923 7(16)	-0.060 1(16)	0.389 8(18)
C(28)	0.884 7(14)	-0.075 2(14)	0.464 7(15)
C(29)	0.815 3(11)	-0.018 8(12)	0.477 6(12)
C(210)	0.771 5(12)	-0.088 1(12)	0.626 0(12)
C(211)	0.854 7(13)	-0.099 2(14)	0.698 3(14)
C(212)	0.863 6(17)	-0.164 9(17)	0.780 8(17)
C(213)	0.789 2(18)	-0.215 1(17)	0.783 1(17)
C(214)	0.705 4(15)	-0.206 4(16)	0.709 2(17)
C(215)	0.696 1(14)	-0.141 7(14)	0.629 6(14)
C(216)	0.630 4(13)	0.076 4(12)	0.560 4(14)
B(1)	0.871 7(16)	0.282 7(16)	0.156 1(15)
F(1)	0.781 2(7)	0.253 6(8)	0.137 0(8)
F(2)	0.923 4(9)	0.218 9(9)	0.224 0(10)
F(3)	0.890 8(10)	0.282 0(10)	0.066 7(9)
F(4)	0.885 0(8)	0.369 1(8)	0.197 4(8)
B(2)	0.450 6(24)	0.385 3(21)	0.191 4(23)
F(5)	0.385 7(12)	0.428 3(13)	0.217 0(13)
F(6)	0.448 8(13)	0.388 4(13)	0.094 2(11)
F(7)	0.487 5(14)	0.317 4(13)	0.244 9(12)
F(8)	0.532 4(21)	0.451 4(23)	0.235 0(28)

planar and the dihedral angle between their least squares planes, from which no atom deviates more than 0.05 Å, is 72.8°. Neither of the phenyl substituents is coplanar with the heterocyclic ring systems, and their least-squares planes make angles of 50.3 and 55.0° with those of the imidazopyridines to which they are bonded. The methyl substituents lie nearly coplanar with the atoms of the heterocyclic rings (Table 5).

The two major contributing canonical forms of the imidazo[1,5-*a*]pyridinium ring system have positive charges on different nitrogen atoms, and consideration of the anion distances from each shows that both have some fluorine neighbours at distances between 3.1 and 3.4 Å (Table 3). Bond lengths in the ring system suggest

TABLE 3

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

(a) Bonded distances

S(1)—C(13)	1.74(1)	S(1)—C(23)	1.73(1)
C(11)—N(12)	1.38(2)	C(21)—N(22)	1.35(2)
C(11)—C(19)	1.43(2)	C(21)—C(29)	1.36(2)
C(11)—C(110)	1.44(2)	C(21)—C(210)	1.52(2)
C(13)—N(12)	1.36(2)	C(23)—N(22)	1.38(2)
C(13)—N(14)	1.35(2)	C(23)—N(24)	1.35(2)
N(12)—C(116)	1.46(2)	N(22)—C(216)	1.49(2)
N(14)—C(15)	1.41(2)	N(24)—C(25)	1.41(3)
N(14)—C(19)	1.37(2)	N(24)—C(29)	1.40(2)
C(15)—C(16)	1.36(3)	C(25)—C(26)	1.35(3)
C(16)—C(17)	1.47(3)	C(26)—C(27)	1.50(3)
C(17)—C(18)	1.36(3)	C(27)—C(28)	1.38(3)
C(18)—C(19)	1.40(2)	C(28)—C(29)	1.39(3)
C(110)—C(111)	1.44(3)	C(210)—C(211)	1.36(3)
C(110)—C(115)	1.43(3)	C(210)—C(215)	1.41(3)
C(111)—C(112)	1.43(3)	C(211)—C(212)	1.44(3)
C(112)—C(113)	1.34(3)	C(212)—C(213)	1.36(3)
C(113)—C(114)	1.43(3)	C(213)—C(214)	1.38(3)
C(114)—C(115)	1.40(3)	C(214)—C(215)	1.40(3)
B(1)—F(1)	1.40(2)	B(2)—F(5)	1.32(4)
B(1)—F(2)	1.36(3)	B(2)—F(6)	1.34(4)
B(1)—F(3)	1.36(3)	B(2)—F(7)	1.23(4)
B(1)—F(4)	1.33(2)	B(2)—F(8)	1.53(5)

(b) Interbond angles

C(13)—S(1)—C(23)	103.5(0.8)
N(12)—C(11)—C(19)	105.9(1.4)
N(12)—C(11)—C(110)	125.8(1.5)
C(19)—C(11)—C(110)	128.0(1.5)
C(11)—N(12)—C(13)	109.6(1.3)
C(11)—N(12)—C(116)	125.1(1.4)
C(13)—N(12)—C(116)	125.0(1.4)
S(1)—C(13)—N(12)	128.0(1.2)
S(1)—C(13)—N(14)	123.7(1.2)
N(12)—C(13)—N(14)	108.3(1.3)
C(13)—N(14)—C(15)	129.6(1.4)
C(13)—N(14)—C(19)	109.8(1.3)
C(15)—N(14)—C(19)	120.6(1.4)
N(14)—C(15)—C(16)	119.5(1.7)
C(15)—C(16)—C(17)	120.0(1.7)
C(16)—C(17)—C(18)	118.6(1.7)
C(17)—C(18)—C(19)	120.9(1.6)
N(14)—C(19)—C(11)	106.3(1.4)
N(14)—C(19)—C(18)	120.3(1.5)
C(11)—C(19)—C(18)	133.3(1.6)
C(11)—C(110)—C(111)	116.2(1.6)
C(11)—C(110)—C(115)	122.4(1.5)
C(111)—C(110)—C(115)	121.4(1.7)
C(110)—C(111)—C(112)	116.0(1.9)
C(111)—C(112)—C(113)	121.4(2.1)
C(112)—C(113)—C(114)	123.8(2.0)
C(113)—C(114)—C(115)	116.9(1.8)
C(110)—C(115)—C(114)	120.5(1.7)
N(22)—C(21)—C(29)	110.3(1.5)
N(22)—C(21)—C(210)	124.6(1.5)
C(29)—C(21)—C(210)	124.9(1.6)
C(21)—N(22)—C(23)	109.0(1.3)
C(21)—N(22)—C(216)	126.7(1.4)
C(23)—N(22)—C(216)	124.1(1.4)
S(1)—C(23)—N(22)	126.6(1.2)
S(1)—C(23)—N(24)	126.8(1.3)
N(22)—C(23)—N(24)	105.6(1.4)
C(23)—N(24)—C(25)	128.3(1.5)
C(23)—N(24)—C(29)	111.2(1.4)
C(25)—N(24)—C(29)	120.5(1.5)
N(24)—C(25)—C(26)	119.8(1.9)
C(25)—C(26)—C(27)	121.7(2.0)
C(26)—C(27)—C(28)	115.1(2.0)
C(27)—C(28)—C(29)	123.7(2.0)
N(24)—C(29)—C(21)	103.9(1.4)
N(24)—C(29)—C(28)	119.0(1.6)
C(21)—C(29)—C(28)	136.9(1.7)
C(21)—C(210)—C(211)	118.1(1.6)
C(21)—C(210)—C(215)	120.9(1.6)
C(211)—C(210)—C(215)	120.9(1.7)

TABLE 3 (Continued)

(b) Interbond angles

C(210)—C(211)—C(212)	118.7(1.9)
C(211)—C(212)—C(213)	119.1(2.2)
C(212)—C(213)—C(214)	122.7(2.3)
C(213)—C(214)—C(215)	118.5(2.1)
C(210)—C(215)—C(214)	120.0(1.8)

(c) Some intramolecular non-bonded distances

N(12) ... N(22)	4.40(2)	N(14) ... N(22)	4.02(2)
N(12) ... N(24)	4.18(2)	N(14) ... N(24)	4.81(2)
F(1) ... F(2)	2.20(2)	F(5) ... F(6)	2.29(3)
F(1) ... F(3)	2.25(2)	F(5) ... F(7)	2.16(3)
F(1) ... F(4)	2.25(2)	F(5) ... F(8)	2.23(4)
F(2) ... F(3)	2.25(2)	F(6) ... F(7)	2.22(3)
F(2) ... F(4)	2.19(2)	F(6) ... F(8)	2.15(4)
F(3) ... F(4)	2.21(2)	F(7) ... F(8)	2.03(4)

(d) Some intermolecular non-bonded distances

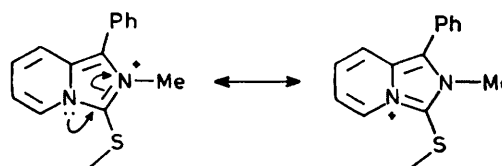
S ... F(7)	2.98(2)		
N(12) ... F(1)	3.14(2)	N(22) ... F(1)	3.31(2)
N(12) ... F(3)	3.19(2)	N(22) ... F(4)	3.41(2)
N(14) ... F(1)	3.04(2)	N(24) ... F(3)	3.26(2)
N(14) ... F(3)	3.26(2)	N(24) ... F(5)	3.14(2)
N(22) ... F(5)	3.44(2)		
N(22) ... F(6)	3.21(2)		

(e) Torsion angles

The torsion angle of the bonded group A—X—Y—B is the angle in the Newman projection between the planes AX₁Y and XYB. It is positive 0 to +180° if clockwise from AX to YB viewed from AX, and negative 0 to -180° if counter-clockwise. The estimated standard deviations of all the angles is ca. 2°

N(24)—C(23)—S(1)—C(13)	-111
N(22)—C(23)—S(1)—C(13)	+83
N(14)—C(13)—S(1)—C(23)	-101
N(12)—C(13)—S(1)—C(23)	+80
S(1)—C(23)—N(22)—C(216)	+15
S(1)—C(13)—N(12)—C(116)	-5
N(14)—C(13)—N(12)—C(116)	-174
N(24)—C(23)—N(22)—C(216)	-177
C(110)—C(11)—N(12)—C(116)	-11
C(210)—C(21)—N(22)—C(216)	-8

that C(13)—N(14) [1.35(2) Å] and C(23)—N(24) [1.35(2) Å] are the shortest, and probably have some double bond character, whereas C(13)—N(12) [1.36(2) Å] and C(23)—N(22) [1.38(2) Å] are clearly longer, although the differences between them are only of the order of one standard deviation. The bond lengths C(16)—C(17) [1.47(3) Å] and C(26)—C(27) [1.50(3) Å] are significantly longer than each of their adjacent bonds, with differences greater than three standard deviations and each is



represented as a single bond in both canonical forms. Overall, this data suggests a degree of localisation in the bonds of the imidazole ring with the positive charge resident on the bridgehead nitrogen, findings which are compatible with other recent work¹⁹ on comparable structures. The interquaternary nitrogen atom separation, which was formerly thought⁵ to be connected with the mechanism of neuromuscular blockade may be N(14) ... N(24) [4.81(2) Å] although all the N ... N distances are given in Table 3(c).

TABLE 4

	Anisotropic temperature factors (\AA^2) *					
	$10^4 B_{11}$	$10^4 B_{22}$	$10^4 B_{33}$	$10^4 B_{12}$	$10^4 B_{13}$	$10^4 B_{23}$
S	47(3)	34(3)	51(3)	2(3)	5(2)	0(3)
C(11)	36(13)	41(13)	48(14)	1(11)	4(10)	3(11)
N(12)	33(11)	37(11)	52(11)	1(8)	6(8)	2(8)
C(13)	44(14)	33(12)	41(13)	-8(12)	9(10)	-14(9)
N(14)	40(11)	28(9)	34(10)	2(9)	3(7)	4(7)
C(15)	28(13)	64(16)	80(18)	9(12)	8(11)	29(13)
C(16)	56(14)	56(16)	61(16)	-1(13)	24(11)	6(13)
C(17)	53(15)	47(15)	78(16)	22(12)	27(13)	23(12)
C(18)	36(13)	44(14)	61(15)	3(11)	20(11)	19(10)
C(19)	47(14)	42(14)	39(13)	6(12)	6(10)	-2(10)
C(110)	38(13)	35(13)	51(12)	-12(11)	11(10)	-5(9)
C(111)	66(17)	53(17)	115(20)	-16(14)	36(14)	-10(14)
C(112)	60(18)	64(17)	124(22)	-5(16)	15(15)	-35(16)
C(113)	63(19)	64(20)	80(17)	-34(15)	8(14)	-18(13)
C(114)	55(15)	59(17)	71(16)	-12(14)	29(12)	-5(12)
C(115)	46(15)	60(15)	66(14)	-16(14)	20(11)	-3(12)
C(116)	68(17)	77(18)	83(18)	5(14)	45(14)	-12(13)
C(21)	48(15)	38(13)	51(15)	-4(12)	14(11)	-14(11)
N(22)	31(9)	42(10)	56(11)	5(9)	8(9)	2(8)
C(23)	39(12)	24(12)	56(12)	3(10)	10(10)	2(9)
N(24)	43(11)	39(11)	55(12)	-8(9)	13(9)	-8(8)
C(25)	75(17)	73(18)	77(18)	-5(15)	38(14)	-18(14)
C(26)	82(20)	56(17)	96(19)	-7(15)	39(15)	-25(14)
C(27)	79(19)	70(19)	125(25)	13(15)	47(17)	2(17)
C(28)	56(17)	63(19)	98(22)	2(14)	34(15)	-4(14)
C(29)	38(14)	41(14)	52(15)	0(11)	-1(11)	11(11)
C(210)	48(14)	38(13)	47(13)	2(11)	7(10)	8(10)
C(211)	46(15)	69(17)	69(16)	16(13)	1(13)	9(13)
C(212)	90(22)	80(21)	98(21)	9(18)	35(16)	25(16)
C(213)	105(25)	76(21)	99(22)	26(19)	40(19)	30(16)
C(214)	65(18)	80(21)	113(22)	13(15)	24(17)	48(17)
C(215)	47(15)	52(16)	94(18)	-4(13)	23(12)	15(13)
C(216)	60(15)	44(14)	82(16)	22(11)	47(12)	5(11)
B(1)	51(16)	51(16)	48(16)	-12(14)	11(12)	-2(13)
F(1)	57(8)	78(10)	89(9)	-11(7)	16(7)	-17(7)
F(2)	78(11)	74(10)	138(13)	3(9)	11(10)	23(10)
F(3)	121(13)	119(13)	93(12)	-24(11)	56(10)	-12(10)
F(4)	83(10)	56(9)	105(10)	-18(7)	32(8)	-23(8)
B(2)	107(26)	81(24)	107(25)	16(20)	55(20)	17(18)
F(5)	120(15)	175(19)	161(18)	28(13)	72(13)	-25(14)
F(6)	141(15)	192(19)	106(14)	62(15)	41(11)	25(13)
F(7)	179(19)	163(20)	142(18)	70(12)	23(14)	70(15)
F(8)	259(33)	355(46)	444(54)	-132(34)	251(37)	-189(41)

* In the form: $T = \exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

TABLE 5

Least-squares planes given in the form $lX' + mY' + nZ' = d$ where X' , Y' , and Z' are co-ordinates in \AA . Deviations (\AA) of atoms from the planes are given in parentheses

Plane (1) Imidazo[1,5- <i>a</i>]pyridinium ring system (1)	$-0.3490X + 0.5260Y - 0.7755Z = -5.031$
[C(11) 0.032, N(12) -0.012, C(13) -0.039, N(14) 0.004, C(15) 0.030, C(16) 0.004, C(17) -0.020, C(18) -0.025, C(19) 0.026]	
Plane (2) Imidazo[1,5- <i>a</i>]pyridinium ring system (2)	$-0.4873X - 0.6388Y - 0.5954Z = -8.64$
[C(21) -0.006, N(22) 0.048, C(23) 0.003, N(24) -0.040, C(25) -0.019, C(26) 0.041, C(27) 0.003, C(28) 0.012, C(29) -0.042]	
Plane (3) Phenyl ring (1)	$0.3810X + 0.1133Y - 0.9176Z = -1.598$
[C(110) -0.011, C(111) 0.009, C(112) -0.003, C(113) -0.003, C(114) 0.002, C(115) 0.005]	
Plane (4) Phenyl ring (2)	$0.4304X - 0.7252Y - 0.5374Z = 0.438$
[C(210) -0.009, C(211) 0.010, C(212) -0.001, C(213) -0.008, C(214) 0.008, C(215) 0.001]	

TABLE 6

Calculated hydrogen atom positions *

	X	Y	Z
H(15)	0.501	0.222	0.452
H(16)	0.439	0.305	0.570
H(17)	0.514	0.458	0.658
H(18)	0.651	0.516	0.626
H(111)	0.689	0.607	0.481
H(112)	0.806	0.737	0.549
H(113)	0.965	0.702	0.613
H(114)	1.026	0.537	0.619
H(115)	0.914	0.404	0.555
H(25)	0.788	0.132	0.276
H(26)	0.904	0.030	0.251
H(27)	0.981	-0.101	0.385
H(28)	0.909	-0.134	0.516
H(211)	0.913	-0.059	0.694
H(212)	0.928	-0.174	0.840
H(213)	0.796	-0.264	0.845
H(214)	0.648	-0.249	0.712
H(215)	0.631	-0.133	0.571

* Hydrogen atoms are numbered according to the atom to which they are bonded.

TABLE 7

Comparison of some torsion angles of the title compound (1) and (+)-tubocurarine dibromide²¹

Compound (1)	
N(24)-C(23)-S(1)-C(13)	-111
N(22)-C(23)-S(1)-C(13)	+83
N(14)-C(13)-S(1)-C(23)	-101
N(12)-C(13)-S(1)-C(23)	+80
(+)-Tubocurarine dibromide	
C(24)-C(28)-O(29)-C(30)	-122
C(27)-C(28)-O(29)-C(30)	+62
C(17)-C(12)-O(11)-C(9)	+104
C(13)-C(12)-O(11)-C(9)	-77

The geometry of the sulphur linkage is clearly shown in Figure 1, and the C-S bonded distance of 1.74(1) Å with a C-S-C bond angle of 103.5(8)° compare well with values recently reported²⁰ for a sulphur bridge between sp^2 hybridised carbon atoms.

The conformational requirements of the molecule around the flexible sulphur link are given in Table 3(e) in terms of the torsion angles defined as in ref. 5. It seems reasonable to compare the N-C-S-C linkage in the present structure with the C-C-O-C links in (+)-tubocurarine dibromide.²¹ Both linkages in the latter have angles of similar magnitude but opposite signs; the N-C-S-C link in the title compound compares closely with one of them (Table 7).

The two fluoroborate(III) groups occupy non-comparable sites within the lattice and the atom positions of one are much more clearly defined than the other, whose atom temperature factors are markedly higher. The mean B-F distances of 1.36(2) Å in the best determined anion compared with 1.35(4) Å in the other, are less meaningful than the mean F...F non-bonded distances [2.23(1) and 2.18(4) Å, respectively] since the boron atoms are the least well determined atoms in the structure.

Figure 2 is a projection down the *a* axis. The fluoroborate(III) anions are in planes perpendicular to the *c*

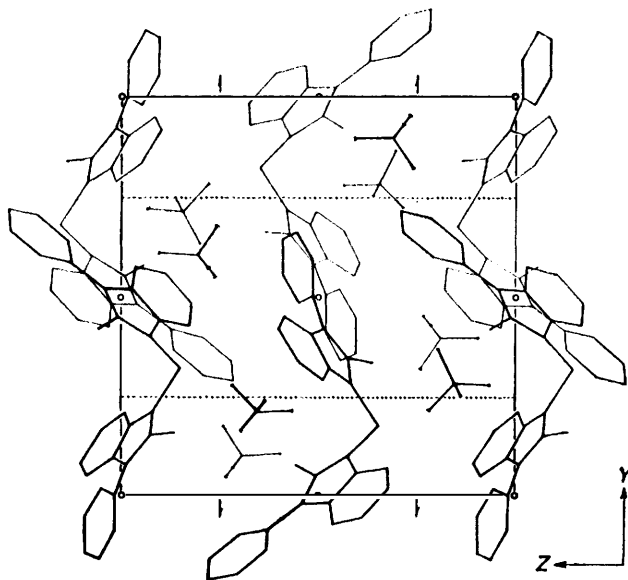


FIGURE 2 The molecular packing viewed along the *a* axis

axis, while the organic cations span the (001) and (002) planes. Adjacent molecules associated with each plane are related by the centres of symmetry sited at the cell-face centres, and the cell centre. Within the layers, in planes normal to the *c* axis, the anions are related by screw axes, with the better defined group lying within the V shape geometry of the cation imposed by the C-S-C bond angle. This anion has two fluorine atoms [F(1) and F(3)] closely associated and nearly equidistant from all four nitrogen atoms of one cation (Table 3) hence the anion is quite strongly held in the crystal lattice. Conversely the other anion is less obviously associated with one cation, and only F(5) and F(6) lie within 3.5 Å of any nitrogen atom. One fluorine atom of this anion makes a significantly short contact with the sulphur atom, S...F(7), 2.98(2) Å, and although the three atoms B(2)-F(7)...S are not collinear, this measurement adds to the weight of evidence²² in favour of a value near 1.72 Å for the van der Waals radius of sulphur.

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