Synthesis and structure of triphenylsulfonium tetrafluoroborate

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The crystal and molecular structure of triphenylsulfonium tetrafluoroborate, the simplest representative of aromatic sulfonium salts, was determined. A very weak coordination interaction F→S is observed in one of the two crystallographically independent cation-anion pairs.

Key words: sulfonium salts; crystal and molecular structure.

Interest taken in the research of triarylsulfonium salts, containing BF_4^-, SbF_6^-, PF_6^-, and AsF_6^- as counterions, is due to their capability to effectively generate active initiators of the cationic polymerization (Lewis acids) upon UV-irradiation. A fundamental method for synthesizing these salts is the direct arylation of disulfides by relevant diaryliodonium salts after Nesmeyanov.[1] Previously,[2,3] triarylsulfonium salts with versatile aromatic substituents were studied and a method for synthesizing polyarylenesulfonium salts by direct arylation of poly-*n*-phenylenesulfide was suggested.[4,5] However, works on the structure of low-molecular-weight and polymeric sulfonium salts, which could explain the relative ease of introducing the third aryl substituent at the sulfur atom, have not been published until recently. With the aim of obtaining first-hand data on the structure of polyarylenesulfonium salts we studied the crystal and molecular structure of a model compound, triphenylsulfonium tetrafluoroborate ($Ph_3S^+ \cdot BF_4^-$) (**1**).

Experimental

Compound **1** was synthesized by arylation of Ph_2S with diphenyliodonium tetrafluoroborate by a known procedure.[1] The single crystals with m.p. 186.5—187 °C were obtained from ethanol.

The X-ray diffraction experiment was performed on a Siemens P3/PC diffractometer at 140 K (λ(Mo-Kα), graphite monochromator, θ/2θ-scan, $2\theta_{max} = 48°$). The crystals of compound **1** are monoclinic, $a = 17.716(2)$ Å, $b = 10.419(3)$ Å, $c = 17.705(4)$ Å, $\beta = 93.17(2)°$, $V = 3263(2)$ Å^3, $d_{calc} = 1.426$ g cm^{-3}, $Z = 8$. $C_{18}H_{15}S^+ \cdot BF_4^-$, space group $P2_1/c$. The total number of measured reflections was 4970. The structure was solved by direct methods and refined by the block-diagonal LSM anisotropically for nonhydrogen atoms and isotropically for H atoms located in a difference synthesis. The final values of the reliability factors are $R = 0.051$, $R_w = 0.059$ for 3880 reflections with $I > 3\sigma(I)$.

All calculations were carried out on an IBM PC/AT personal computer using the SHELXTL PLUS program package.[6] The atomic coordinates and thermal parameters are represented in Table 1, and the bond lengths and bond angles are listed in Table 2 and Table 3, respectively.

Results and Discussion

The two crystallographically independent cation-anion pairs of **1** (Fig. 1) differ slightly in mutual positions of the cation and anion. The S(1)...F(1) distance (3.49 Å) in the *B* pair is close to the upper bound estimate of the sum of van der Waals radii for S and F atoms (3.4 Å, see Ref. 7) which allows to suggest a weak coordination interaction F→S. In fact, the C(7*B*)—S(1*B*)—F(1*B*) angle (150°) and a decrease (by ~2°) in the C(7*B*)—S(1*B*)—C(1*B*) and C(7*B*)—S(1*B*)—C(13*B*) angles as compared with C(1*B*)—S(1*B*)—C(13*B*) (see Table 3) indicate a minor tendency of the S(1*B*) atom toward a trigonal-bipyramidal coordination with pseudoequatorial substituents C(1*B*) and C(13*B*); the unshared electron pair (UEP) of the S(1*B*) atom plays the role of the third equatorial substituent. It should be also noted that the "axial" bond S(1*B*)—C(7*B*) in the above-mentioned trigonal-bipyramidal coordination is longer than the equatorial bonds by 0.02 Å, whereas the lengths of the latter correspond most closely to the standard value[8] for C(ar)—S$^+$. All mentioned peculiarities are not observed in the geometry of the cation-anion pair *A*. Thus, the F→S interaction is so weak that it is easily destroyed by packing effects. In the structures with the triarylselenium cations[9—11] the analogous Hal→Se and O→Se interactions are much stronger so that the Se atom has a pronounced pseudotrigonal-bipyramidal or even pseudo-octahedral coordination. The weak F→S interaction in the crystal of **1** is likely to be determined by a weaker donor power of F atom compared with that of Cl, Br, and O atoms.

† Deceased in 1995.

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Table 1. Atomic coordinates ($\times 10^4$) and thermal parameters ($U_{iso}^{eq} \times 10^3$) in the structure **1**

Atom	*x*	*y*	*z*	$U_{iso}^{eq}/Å^2$	Atom	*x*	*y*	*z*	$U_{iso}^{eq}/Å^2$
S(1*A*)	71.7(5)	555.9(8)	7732.1(5)	22.9(3)	S(1*B*)	4866.4(5)	1018.9(9)	2447.0(5)	25.5(3)
C(1*A*)	−486(2)	1556(3)	7088(2)	23(1)	C(1*B*)	4289(2)	2079(4)	1881(2)	26(1)
C(2*A*)	−245(3)	1620(4)	6361(2)	30(1)	C(2*B*)	4294(2)	1882(4)	1107(2)	30(1)
C(3*A*)	−668(3)	2325(4)	5831(2)	38(1)	C(3*B*)	3853(3)	2668(5)	637(3)	42(2)
C(4*A*)	−1330(3)	2949(4)	6034(2)	36(1)	C(4*B*)	3413(2)	3624(4)	937(3)	35(1)
C(5*A*)	−1554(3)	2868(4)	6764(2)	31(1)	C(5*B*)	3411(2)	3803(4)	1713(3)	30(1)
C(6*A*)	−1130(2)	2165(4)	7314(2)	25(1)	C(6*B*)	3852(2)	3043(4)	2192(2)	27(1)
C(7*A*)	−622(2)	−146(3)	8316(2)	24(1)	C(7*B*)	4243(2)	319(4)	3103(2)	29(1)
C(8*A*)	−1149(2)	−925(4)	7930(2)	30(1)	C(8*B*)	3474(3)	295(4)	2946(3)	38(2)
C(9*A*)	−1684(3)	−1537(4)	8338(2)	34(1)	C(9*B*)	3025(3)	−358(4)	3450(3)	47(2)
C(10*A*)	−1692(3)	−1378(4)	9112(3)	37(1)	C(10*B*)	3346(3)	−954(5)	4073(3)	48(2)
C(11*A*)	−1164(3)	−602(4)	9481(2)	36(1)	C(11*B*)	4109(3)	−928(5)	4214(3)	54(2)
C(12*A*)	−615(3)	14(4)	9081(2)	30(1)	C(12*B*)	4575(3)	−295(4)	3726(3)	42(2)
C(13*A*)	609(2)	1643(3)	8327(2)	23(1)	C(13*B*)	5490(2)	1995(4)	3023(2)	25(1)
C(14*A*)	281(2)	2622(4)	8722(2)	27(1)	C(14*B*)	5265(3)	2638(4)	3661(2)	32(1)
C(15*A*)	743(2)	3433(4)	9153(2)	26(1)	C(15*B*)	5800(3)	3323(4)	4089(2)	38(1)
C(16*A*)	1528(2)	3272(4)	9169(2)	30(1)	C(16*B*)	6552(3)	3358(5)	3894(3)	43(2)
C(17*A*)	1845(2)	2305(4)	8763(2)	32(1)	C(17*B*)	6758(3)	2717(5)	3255(3)	40(2)
C(18*A*)	1393(2)	1469(4)	8333(2)	28(1)	C(18*B*)	6229(2)	2031(4)	2804(2)	30(1)
B(1*A*)	1597(3)	−903(5)	5889(3)	30(1)	B(1*B*)	6612(3)	−82(5)	971(3)	32(2)
F(1*A*)	1801(2)	−429(3)	6600(1)	53(1)	F(1*B*)	6000(2)	715(4)	909(2)	80(1)
F(2*A*)	907(1)	−371(2)	5627(1)	42(1)	F(2*B*)	7087(2)	53(3)	387(2)	56(1)
F(3*A*)	1516(1)	−2229(2)	5934(1)	34(1)	F(3*B*)	6370(2)	−1372(3)	979(1)	52(1)
F(4*A*)	2142(1)	−620(3)	5384(1)	45(1)	F(4*B*)	7012(1)	111(3)	1663(1)	44(1)
H(2*A*)	25(3)	114(4)	626(2)	40(10)	H(2*B*)	461(3)	125(5)	90(3)	50(10)
H(3*A*)	−49(2)	237(4)	527(2)	30(1)	H(3*B*)	379(2)	245(4)	12(3)	40(10)
H(4*A*)	−163(2)	333(3)	564(2)	10(10)	H(4*B*)	309(3)	420(5)	64(3)	50(10)
H(5*A*)	−192(2)	334(4)	687(2)	30(10)	H(5*B*)	316(2)	439(4)	192(2)	20(10)
H(6*A*)	−125(2)	209(3)	780(2)	20(10)	H(6*B*)	384(2)	317(4)	272(3)	40(10)
H(8*A*)	−113(2)	−98(4)	737(3)	40(10)	H(8*B*)	324(3)	55(5)	256(3)	50(20)
H(9*A*)	−203(3)	−207(5)	812(3)	40(10)	H(9*B*)	238(3)	−48(5)	326(3)	70(20)
H(10*A*)	−213(3)	−182(5)	942(3)	60(10)	H(10*B*)	302(2)	−151(4)	434(2)	30(10)
H(11*A*)	−113(3)	−51(4)	1009(3)	50(10)	H(11*B*)	440(3)	−161(6)	463(4)	80(20)
H(12*A*)	−23(3)	42(4)	932(2)	30(10)	H(12*B*)	512(3)	−28(5)	378(3)	70(20)
H(14*A*)	−27(3)	284(5)	875(3)	50(10)	H(14*B*)	472(2)	255(4)	378(2)	30(10)
H(15*A*)	50(3)	413(5)	948(3)	40(10)	H(15*B*)	569(3)	385(5)	456(3)	50(10)
H(16*A*)	182(2)	400(4)	950(2)	40(10)	H(16*B*)	688(3)	376(5)	424(3)	50(10)
H(17*A*)	243(2)	227(4)	880(2)	20(10)	H(17*B*)	723(3)	289(5)	310(3)	60(20)
H(18*A*)	161(2)	79(4)	805(2)	30(10)	H(18*B*)	631(2)	154(4)	237(2)	30(10)

Table 2. Bond lengths (*d*) in cations (*A*) and anions (*B*) in the structure of **1**

Bond	*d*/Å		Bond	*d*/Å		Bond	*d*/Å	
	A	*B*		*A*	*B*		*A*	*B*
S(1)—C(1)	1.799(4)	1.776(4)	C(7)—C(8)	1.388(5)	1.376(6)	C(15)—C(16)	1.400(5)	1.395(7)
S(1)—C(7)	1.804(4)	1.801(4)	C(7)—C(12)	1.364(5)	1.377(6)	C(16)—C(17)	1.375(6)	1.380(7)
S(1)—C(13)	1.785(4)	1.781(4)	C(8)—C(9)	1.379(6)	1.404(7)	C(17)—C(18)	1.383(6)	1.394(6)
C(1)—C(2)	1.381(5)	1.386(5)	C(9)—C(10)	1.382(6)	1.363(7)	B(1)—F(1)	1.382(5)	1.365(6)
C(1)—C(6)	1.383(5)	1.400(5)	C(10)—C(11)	1.373(6)	1.361(8)	B(1)—F(2)	1.398(5)	1.375(6)
C(2)—C(3)	1.380(6)	1.387(6)	C(11)—C(12)	1.392(6)	1.394(7)	B(1)—F(3)	1.392(5)	1.411(6)
C(3)—C(4)	1.404(7)	1.388(6)	C(13)—C(14)	1.383(5)	1.390(5)	B(1)—F(4)	1.383(5)	1.396(5)
C(4)—C(5)	1.375(6)	1.386(6)	C(13)—C(18)	1.400(5)	1.386(6)			
C(5)—C(6)	1.403(6)	1.373(6)	C(14)—C(15)	1.378(5)	1.381(6)			

The similarity between conformations of the *A* and *B* cations lies in the fact that two of the three Ph-rings of each cation are found in nearly close contact; absolute values of the C—S—C—C torsion angles for these rings are 65° and 76°, respectively (in the case of contact the sum equals ~60°).[12]

Table 3. Bond angles (ω) in cations (*A*) and anions (*B*) in the structure of **1**

Angle	ω/deg		Angle	ω/deg		Angle	ω/deg	
	A	*B*		*A*	*B*		*A*	*B*
C(1)—S(1)—C(7)	103.3(2)	105.1(2)	S(1)—C(7)—C(8)	114.6(3)	120.8(3)	C(13)—C(14)—C(15)	118.7(4)	118.4(4)
C(1)—S(1)—C(13)	105.2(3)	106.7(2)	S(1)—C(7)—C(12)	123.4(3)	117.0(3)	C(14)—C(15)—C(16)	119.7(4)	120.9(4)
C(7)—S(1)—C(13)	106.1(2)	104.2(2)	C(8)—C(7)—C(12)	121.9(4)	121.9(4)	C(15)—C(16)—C(17)	120.8(4)	119.3(4)
S(1)—C(1)—C(2)	115.5(3)	115.5(3)	C(7)—C(8)—C(9)	118.4(4)	118.0(4)	C(16)—C(17)—C(18)	120.5(4)	121.2(4)
S(1)—C(1)—C(6)	121.0(3)	122.5(3)	C(8)—C(9)—C(10)	120.6(4)	120.6(5)	C(13)—C(18)—C(17)	117.8(4)	117.9(4)
C(2)—C(1)—C(6)	123.4(3)	121.9(4)	C(9)—C(10)—C(11)	119.8(4)	120.4(5)	F(1)—B(1)—F(2)	109.9(4)	113.2(4)
C(1)—C(2)—C(3)	118.3(4)	118.3(4)	C(10)—C(11)—C(12)	120.5(4)	120.8(5)	F(1)—B(1)—F(3)	108.9(3)	109.8(4)
C(2)—C(3)—C(4)	120.2(4)	120.5(4)	C(7)—C(12)—C(11)	118.7(4)	118.3(5)	F(2)—B(1)—F(3)	108.8(3)	107.7(4)
C(3)—C(4)—C(5)	120.0(4)	120.5(4)	S(1)—C(13)—C(14)	122.8(3)	122.9(3)	F(1)—B(1)—F(4)	110.9(4)	110.2(4)
C(4)—C(5)—C(6)	120.8(4)	120.2(4)	S(1)—C(13)—C(18)	114.7(3)	114.9(3)	F(2)—B(1)—F(4)	109.2(3)	110.1(4)
C(1)—C(6)—C(5)	117.2(4)	118.6(4)	C(14)—C(13)—C(18)	122.4(3)	122.2(4)	F(3)—B(1)—F(4)	109.1(3)	105.6(3)

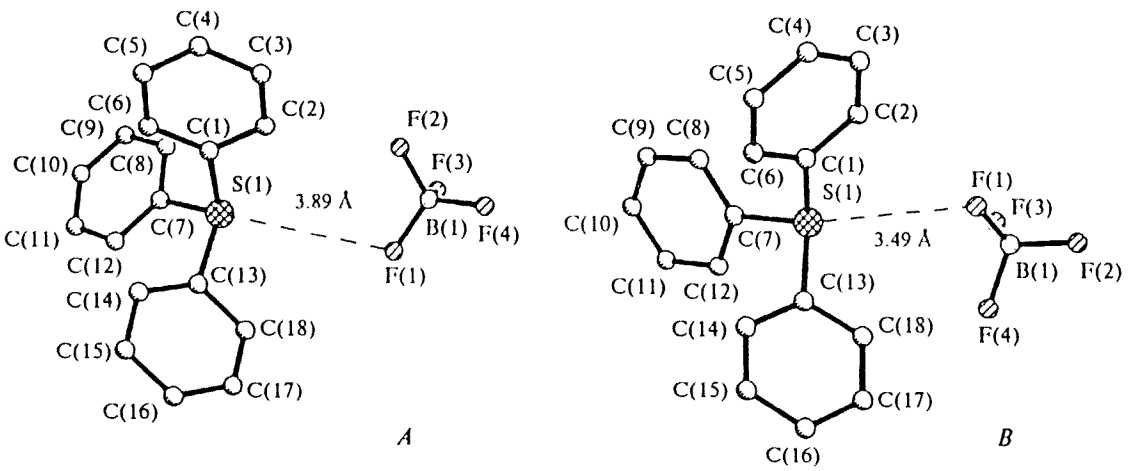

Fig. 1. General view of the cation-anion pairs *A* and *B* in the crystal **1**. The shortest distances F...S are denoted.

The corresponding sums for the third ring are 24° and 97° (*A*) and 21° and 86° (*B*); it means that its position mainly depends on the intermolecular interactions.

An increase in the values of intracyclic angles at the *ipso*-atoms by ~2° compared to the ideal value (120°) and approximately the same increase in the angles at the *ortho*-atoms (see Table 3) can be referred to more detailed characteristics of the molecular geometry of **1**. These deviations are even larger (4—6°) in the Ph_3O^+ cation and are due to the induction effect,[13] which directly depends on the capability of the substituent group to polarize the benzene ring.[14] Since the charge in analogues cations is localized on the chalcogen atom,[13] the O^+ ion, which is smaller in size and located closer to the Ph-rings, has a greater induction capability than S^+ and Se^+. On the contrary, the intracyclic angles at the *ipso*-atoms in neutral phenylenesulfide fragments[15,16] are 1—2° smaller than 120°.

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