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Synthesis and Structure of Triphenylbismuth Difluoride

V. V. Sharutin, O. K. Sharutina, I. V. Egorova, T. K. Ivanenko, and V. K. Bel'skii

Blagoveshchensk State Pedagogical University, Blagoveshchensk, Russia

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Abstract — The reaction of triphenylbismuth dichloride with sodium fluoride in acetone leads to formation of triphenylbismuth difluoride in 73% yield. The X-ray diffraction data show that the bismuth atom in the two symmetrically independent molecules of bismuth difluoride has a trigonal-bipyramidal coordination with equatorial fluorine atoms. The Bi–F and Bi–C distances are 2.53(1)–2.59(1) and 2.10(3)–2.22(2) Å, respectively, and the FBiF angle is 175.1(5)°.

It is known that the triphenylbismuth difluoride prepared from triphenylbismuth dibromide and potassium fluoride melts at 127.5°C. At the same time, the reaction of triphenylbismuth dihalide with silver fluoride in benzene evidently leads to another crystal modification which melts at 158.5–159°C [2]. We slightly changed the conditions of synthesis of triphenylbismuth difluoride **I** melting at 127.5°C (reaction of sodium fluoride and triphenylbismuth dichloride in aqueous acetone) and studied its crystal structure.

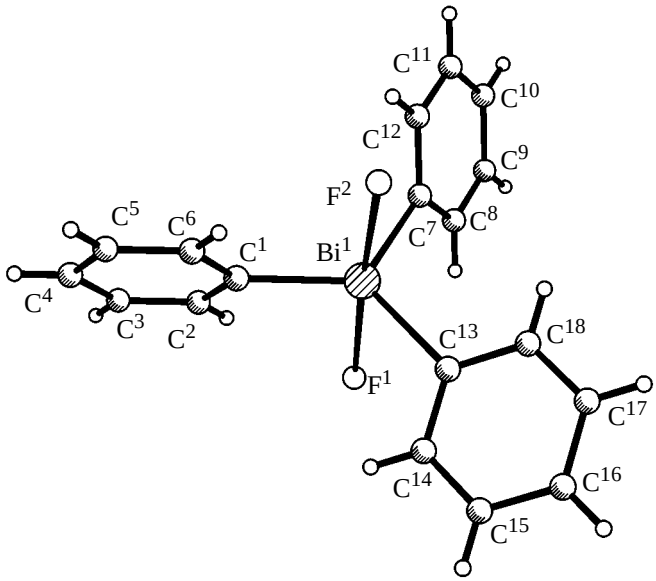
The X-ray diffraction data show that the bismuth atom in the two symmetrically independent molecules of compound **I** has a distorted trigonal-bipyramidal coordination with axial fluorine atoms. The angles between equatorial phenyl substituents are slightly different [113.6(10)°, 118.5(12)°, and 127.9(12)° in molecule A and 118.2(11)°, 120.5(9)°, and 121.3(11)° in molecule B], but axial FBiF angles are practically equal to each other [175.1(5)° and 175.6(5)°]. Note that in the molecule of triphenylbismuth bis(trifluoroacetate) in which the bismuth atom has the coordination number 7 the respective angles are 110.1(3)°, 109.2(3)°, and 140.6(3)° [3].

The bismuth atom in molecule A lies practically in the equatorial plane (the deviation from the plane is 0.001 Å), while in molecule B this deviation is larger (0.017 Å). Both in A and in B, different torsion angles of phenyl rings with respect to the equatorial plane are observed: 72.9°, 67.2°, and 31.6° in A and 115.7°, 35.7°, and 103.5° in B. The spatial arrangement of molecule A of compound **I** is presented in the figure. The atomic coordinates are listed in Table 1, and the bond lengths and bond angles, in Table 2.

EXPERIMENTAL

X-ray diffraction analysis of crystals of triphenylbismuth difluoride (I). The unit cell parameters and the intensities of 1116 unique reflections with $I > 2\sigma(I)$ were measured on an Enraf–Nonius CAD-4 automatic diffractometer (λMoK_α radiation, λ 0.71073 Å, Nb filter, $2\theta/\theta$ scanning). The crystals are orthorhombic; at 20°C, a 9.140(2) Å, b 17.122(3) Å, c 22.339(4); V 3496(1) Å^3; space group $P2_12_12_1$, Z 8, d_{calc} 1.817 g/cm^3. The structure was solved by the heavy atom method and refined anisotropically for non-hydrogen atoms and isotropically for hydrogen atoms to R 0.0386 and R_W 0.1104. All the calculations were carried out using the SHELXL-97 program package [4].

Triphenylbismuth difluoride (I). To a soilution



Overall view of molecule A of compound **I**.

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Table 1. Atomic coordinates ($\times 10^4$, Å) and equivalent isotropic thermal parameters ($B \times 10^3$, Å^2) in the molecule of triphenylbismuth difluoride

Atom	*x*	*y*	*z*	*B*
Bi^1	5885(2)	4578(1)	4856(1)	69(1)
Bi^2	6477(2)	2253(1)	8026(1)	71(1)
F^1	4995(15)	3321(6)	4320(5)	15(3)
F^2	6985(17)	5779(7)	5363(6)	36(4)
F^3	5371(17)	3365(8)	8619(7)	46(5)
F^4	7394(15)	1095(7)	7410(6)	25(4)
C^1	4780(40)	4240(20)	5640(11)	140(20)
C^2	3640(50)	3710(20)	5594(14)	132(18)
C^3	2880(40)	3475(18)	6100(20)	210(30)
C^4	3260(40)	3780(20)	6659(15)	140(19)
C^5	4400(40)	4314(18)	6705(11)	119(17)
C^6	5160(30)	4546(16)	6196(15)	120(16)
C^7	4780(30)	5344(15)	4233(12)	69(11)
C^8	4370(30)	5060(13)	3674(13)	107(15)
C^9	3610(40)	5538(18)	3277(10)	150(20)
C^{10}	3260(30)	6299(16)	3440(13)	107(15)
C^{11}	3670(40)	6582(12)	3999(14)	120(16)
C^{12}	4430(30)	6105(16)	4395(11)	114(16)
C^{13}	8120(20)	4244(16)	4568(12)	81(13)
C^{14}	8700(30)	3523(14)	4732(12)	107(15)
C^{15}	10110(30)	3324(12)	4567(13)	134(19)
C^{16}	10960(20)	3845(17)	4237(13)	105(14)
C^{17}	10380(30)	4566(15)	4073(11)	108(15)
C^{18}	8960(30)	4765(12)	4239(11)	88(12)
C^{19}	7580(20)	1810(17)	8839(11)	63(11)
C^{20}	8010(40)	2326(13)	9287(16)	150(20)
C^{21}	8820(40)	2059(19)	9771(13)	170(20)
C^{22}	9210(40)	1280(20)	9807(12)	150(20)
C^{23}	8790(40)	760(14)	9359(14)	112(16)
C^{24}	7970(30)	1027(15)	8875(11)	92(13)
C^{25}	4240(30)	1869(14)	7801(13)	75(12)
C^{26}	3180(40)	1761(16)	8240(10)	93(13)
C^{27}	1750(30)	1587(15)	8077(14)	111(15)
C^{28}	1370(30)	1523(15)	7476(16)	113(15)
C^{29}	2430(40)	1632(18)	7037(11)	160(20)
C^{30}	3870(30)	1805(17)	7200(11)	141(19)
C^{31}	7560(30)	3060(16)	7426(14)	94(16)
C^{32}	8130(40)	2847(15)	6873(16)	150(20)
C^{33}	8760(40)	3410(20)	6505(12)	134(19)
C^{34}	8830(40)	4180(20)	6691(16)	160(20)
C^{35}	8250(40)	4395(14)	7244(17)	170(20)
C^{36}	7620(40)	3834(19)	7612(12)	126(18)

of 3.04 g of triphenylbismuth dichloride in 20 ml of acetone, a solution of 0.50 g of sodium fluoride in 20 ml of water was added. The solvent was removed, and the residue was crystallized from petroleum ether.

Table 2. Bond lengths (*d*) and bond angles (ω) in the molecule of triphenylbismuth difluoride

Molecule A		Molecule B	
bond	*d*, Å	bond	*d*, Å
Bi^1–C^1	2.10(3)	Bi^2–C^{31}	2.16(2)
Bi^1–C^7	2.16(2)	Bi^2–C^{25}	2.21(2)
Bi^1–C^{13}	2.22(2)	Bi^2–C^{19}	2.21(2)
Bi^1–F^2	2.55(1)	Bi^2–F^3	2.53(1)
Bi^1–F^1	2.59(1)	Bi^2–F^4	2.55(1)
C^1–C^2	1.39(1)	C^{35}–C^{36}	1.39(1)
angle	ω, deg	angle	ω, deg
$C^1Bi^1C^7$	118.5(1)	$C^{31}Bi^2C^{25}$	118.2(1)
$C^{13}Bi^1C^1$	127.9(1)	$C^{31}Bi^2C^{19}$	121.3(1)
$C^7Bi^1C^{13}$	113.6(1)	$C^{25}Bi^2C^{19}$	129.5(9)
$C^1Bi^1F^2$	92.3(1)	$C^{31}Bi^2F^3$	91.5(1)
$C^7Bi^1F^2$	89.0(8)	$C^{25}Bi^2F^3$	88.4(8)
$C^{13}Bi^1F^2$	88.5(8)	$C^{19}Bi^2F^3$	90.6(9)
$C^1Bi^1F^1$	90.4(1)	$C^{25}Bi^2F^4$	87.2(8)
$C^7Bi^1F^1$	93.4(8)	$C^{19}Bi^2F^4$	91.5(8)
$C^{13}Bi^1F^1$	86.6(7)	$F^3Bi^2F^4$	175.6(5)
$F^2Bi^1F^1$	175.1(5)		

Yield 2.08 g, mp 127.5°C. Found,%: C 44.54; H 3.02. $C_{18}H_{15}BiF_2$. Calculated,%: C 45.19; H 3.14.

ACKNOWLEDGMENT

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