67. Structural Studies of Crystalline Pentavalent Organobismuth Compounds

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Respectfully dedicated to Prof. *J.D. Dunitz* on the occasion of his 60th birthday: *Salve Magister 'Via, Veritas, Vita'*

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Summary

The syntheses and X-Ray analyses of three pentavalent organobismuth compounds are described; one of these compounds has a novel diphenylbis(trifluoroacetato)-bismuthate anion with trigonal bipyramidal geometry and a stereochemically active lone pair. Analysis of these structures together with other data from the literature allows a mapping of the reaction coordinate for bismuth polyhedra.

Introduction. – We have recently shown that pentavalent organobismuth reagents are useful for the controlled arylation of enolic systems or their derived enolate anions [1–3]. In particular, the reaction with the appropriate member of a series of tetraarylbismuth carboxylates or sulfonates, Ph_4BiX (X = OAc, $OCOCF_3$, OSO_2 p-$CH_3C_6H_4$, OSO_2CF_3) occurs in an entirely chemospecific and highly regioselective manner [4] *(Scheme, Table 1)*. Thus, under neutral or acidic conditions loss of benzene is observed with resultant *O*-arylation, while under basic conditions loss of the anion $X^{\ominus}$ may be considered to generate a different intermediate leading to arylation at a neighbouring carbon atom.

Scheme. *Controlled Arylation by Tetraarylbismuth Carboxylates or Sulfonates*

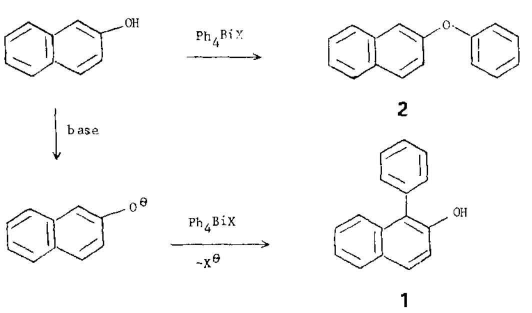
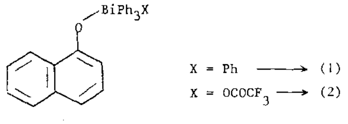


Table 1. *Reaction of Pentavalent Organobismuth Compounds (Ph_4BiX) with β-Naphthol under Neutral* (A) *and Basic* (B) *Conditions*

Reagent Ph_4BiX	Reaction Conditions	Products (% Yield)
X = OAc	A	**1** (25) **2** (26)
	B	**1** (90)
X = $OCOCF_3$	A	**2** (75)
	B	**1** (90)
X = OSO_2-*p*-$CH_3C_6H_4$	A	**2** (42)
	B	**1** (90)
X = OSO_2CF_3	A	No reaction
	B	**1** (86)



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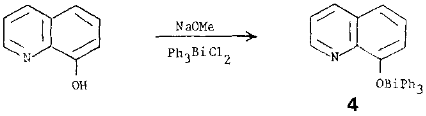
The formation of an organobismuth intermediate possessing a covalent Bi–O bond (*e.g.* **3**) is a logical consequence of this mechanistic rationale, as is the hypothesis that the ionic 'character' of the organobismuth reagent should increase as the group X becomes more electronegative. To examine these hypotheses in more detail, we have determined the geometry around the bismuth atom in three crystalline pentavalent derivatives. We anticipated that a purely covalent intermediate would display the classical trigonal bipyramidal geometry found in triphenylbismuth dichloride [5], while an ionic compound would be expected to show a tetrahedrally disposed tetraphenylbismuthonium cation as observed in the case of the perchlorate salt [6].

Preparation of Organobismuth Derivatives. – Although we have been unable so far to isolate a stable intermediate from the reactions of β-naphthol with pentavalent organobismuth reagents, examination of [7] revealed that the reaction of 8-hydroxyquinoline with triphenylbismuth dichloride under basic conditions gives an orange crystalline compound whose constitution (**4**) suggests the presence of a Bi–O bond (*Eqn 1*). Suitable crystals for X-ray analysis were obtained by slow evaporation from a CH_2Cl_2/MeOH mixture.



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(1)

From the series of tetraphenylbismuth carboxylates and sulfonates we elected to compare the structures of the tosylate and trifluoroacetate derivatives, both of which are readily prepared from pentaphenylbismuth by reaction with one molar equivalent of the appropriate organic acid. Crystals of the 'ionic' tosylate were readily obtained by slow evaporation of a hexane/CH_2Cl_2 solution. However, all efforts to date to prepare a satisfactory crystal of the 'covalent' monotrifluoroacetate failed. Nevertheless, in the course of these attempts it was possible to isolate a beautifully crystalline, but entirely unexpected compound, which was formed as an impurity in the preparation of the monotrifluoroacetate. As microanalytical data served to establish the unlikely empirical formula $Ph_3BiOCOCF_3$, an X-ray analysis of the compound was undertaken *(vide infra)*. The resolution of the structure revealed a tetraphenylbismuthonium cation in association with a diphenylbis(trifluoroacetato)bismuthate anion: $[Ph_4Bi]^+$ $[Ph_2Bi(OCOCF_3)_2]^-$ (**5**).

Subsequent study showed that this derivative can be prepared in good yield by a variety of mechanistically interesting disproportionation reactions which are probably initiated by the formation of a donor-acceptor complex between the appropriate Bi(III) and Bi(V) species (*Eqn. 2* and *3*).

$$\begin{aligned} &\mathrm{Ph_3Bi + CF_3CO_2H} &&\rightarrow \mathrm{Ph_2BiOCOCF_3} \\ &\mathrm{Ph_2BiOCOCF_3 + Ph_4BiOCOCF_3} &&\rightarrow \mathrm{[Ph_4Bi]^+[Ph_2Bi(OCOCF_3)_2]^-} \\ & &&(68\%) \end{aligned} \tag{2}$$

$$\begin{aligned} &\mathrm{Ph_3Bi + 2CF_3CO_2H} &&\rightarrow \mathrm{PhBi(OCOCF_3)_2} \\ &\mathrm{PhBi(OCOCF_3)_2 + Ph_5Bi} &&\rightarrow \mathrm{[Ph_4Bi]^+[Ph_2Bi(OCOCF_3)_2]^-} \\ & &&(86\%) \end{aligned} \tag{3}$$

An alternative preparation involving reaction of the two pentavalent reagents, triphenylbismuth bis(trifluoroacetate) and tetraphenylbismuth mono(trifluoroacetate) at 150°C is also possible (50%). In this instance, however, a series of control experiments indicated that the most probable mechanism involves prior reductive elimination of phenyl trifluoroacetate from the bis(trifluoroacetate) and hence *in situ* generation of diphenylbismuth mono(trifluoroacetate).

Structural Results and Geometrical Reaction Coordinates for the Coordination Polyhedra in Pentavalent Organobismuth Compounds. – *8-Hydroxyquinoline Derivative* **4** *(Fig. 1, Table 2)*. The structural analysis of this molecule reveals an essentially trigonal bipyramidal structure with the three phenyl rings occupying the equatorial positions and the bismuth atom exactly in the plane of the three carbon atoms (0.03 Å). As anticipated the Bi-O bond has almost complete covalent character (2.18 Å).

The elegant work of *Dunitz* [8] has indicated that there is a 'strongly preferred orientation' for the reaction between electrophilic and nucleophilic centres in organic

Table 2. *Relevant Bond Distances* (Å) *and Angles* (degrees) *in the 8-Hydroxyquinoline Derivative*

Bi–Cl	2.657(3)	Bi–C(11)	2.168(10)
Bi–O	2.175(7)	Bi–C(21)	2.209(11)
Bi–N(9)	2.807(10)	Bi–C(31)	2.214(11)
Cl–Bi–O	175.1(2)	N(9)–Bi–C(11)	72.8(3)
Cl–Bi–N(9)	116.8(2)	N(9)–Bi–C(21)	76.2(3)
Cl–Bi–C(11)	85.9(3)	N(9)–Bi–C(31)	150.8(3)
Cl–Bi–C(21)	90.6(3)	C(11)–Bi–C(21)	143.1(4)
Cl–Bi–C(31)	92.3(3)	C(11)–Bi–C(31)	110.6(4)
O–Bi–N(9)	67.8(3)	C(21)–Bi–C(31)	106.2(4)
O–Bi–C(11)	94.4(3)	Bi–O–C(1)	124.3(6)
O–Bi–C(21)	92.1(3)		
O–Bi–C(31)	83.0(3)		

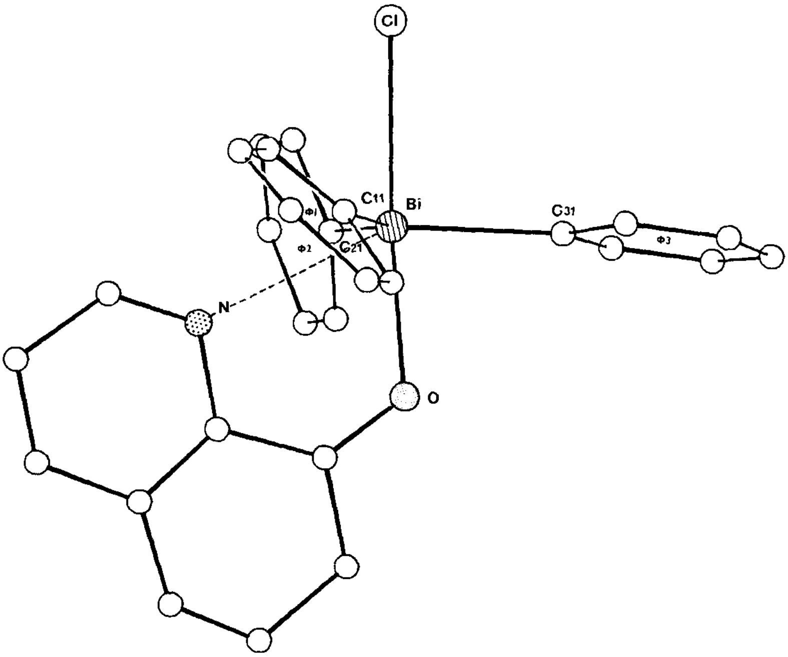

Fig. 1. *8-Hydroxyquinoline derivative*

molecules. In this context, the most interesting feature of the quinoline structure is that the nitrogen atom of the quinoline ring is directed towards the central bismuth atom and placed at a distance of 2.81 Å resulting in a large angular distortion between $\phi 1$ and $\phi 2$ (143°). The constraints imposed by the intramolecularity of the attacking nitrogenous nucleophile upon the electrophilic bismuth centre mean that the angle of attack (a) deviates considerably from the supposedly ideal approach in the equatorial plane which we imagine should exist for the regular bonding transformation of a trigonal bipyramid into an octahedron ($a = 30°$) [9]. Such a structure therefore suggests that considerable angular distortion may occur when the attacking nucleophile cannot adopt the ideal orientation for a minimum energy pathway.

Tetraphenylbismuth Tosylate (Fig. 2, Table 3). In this instance, one oxygen atom of the tosylate counterion is directly opposed to one of the phenyl rings $\phi 4$ (C(41)···Bi···O, 176.5°) and placed at a distance of 2.77 Å from the bismuth atom. The angles between the 'axial' Bi–C(41) bond with 'equatorial' Bi–C bonds range from 98° to 103° (±1) whereas the angles between the equatorial Bi–C bonds themselves lie between 113° and 123° (±1). The bismuth atom is displaced by 0.41 Å (±0.02) from the C(11)–C(21)–C(31) plane. These values differ sharply from the regular tetrahedron observed in the structure of tetraphenylbismuthonium perchlorate [6] ($\widehat{\mathrm{CBiC}}$, 109.3°), where the distance from the bismuth atom to the base of the tetrahedron is 0.73 Å.

As is clearly demonstrated in *Fig. 2* there is therefore a considerable flattening of the bismuth tetrahedron in the direction opposite to $\phi 4$ and the molecular configura-

Table 3. *Relevant Bond Distances* (Å) *and Angles* (degrees) *in the Tosylate Derivative*

Bi–O(1)	2.77	O(1)–Bi–C(11)	84
Bi–C(11)	2.24	O(1)–Bi–C(21)	75
Bi–C(21)	2.20	O(1)–Bi–C(31)	79
Bi–C(31)	2.17	O(1)–Bi–C(41)	177
Bi–C(41)	2.22	C(11)–Bi–C(21)	113
S–O(1)	1.46	C(11)–Bi–C(31)	123
S–O(2)	1.45	C(21)–Bi–C(31)	114
S–O(3)	1.45	C(41)–Bi–C(11)	98
S–C(1)	1.81	C(41)–Bi–C(21)	102
σ = 0.03 Å		C(41)–Bi–C(31)	103
		O(1)–S–O(2)	112
		O(1)–S–O(3)	112
		O(2)–S–O(3)	114
		C(1)–S–O(1)	105
		C(1)–S–O(2)	107
		C(1)–S–O(3)	105
		Bi–O–S	166
		σ = 1°	

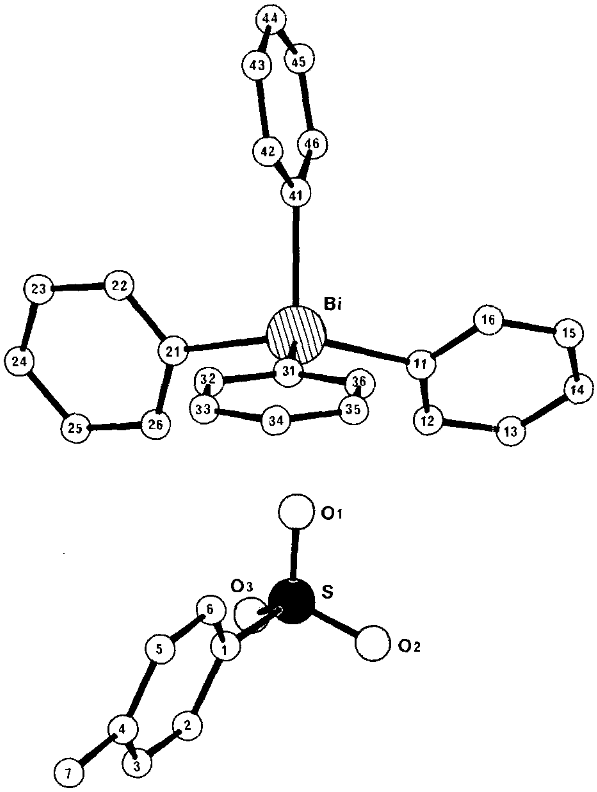

Fig. 2. *Tetraphenylbismuth tosylate*

tion of the bismuth atom therefore tends towards that of a distorted trigonal bipyramid reminiscent of the initial stages in a classical *Walden* inversion.

A comparable distortion has been noted in the case of µ-oxobis(diphenylbismuth)-bis(perchlorate) (**6**) [10] where the metal atom is situated at a distance of 0.3 Å from the basal carbon plane, and the oxygen atom of the perchlorate nucleophile is situated at 2.65 Å and in a *trans*-position with respect to the covalently bonded apical bridging oxygen atom (Bi–O, 2.07 Å). It is also noteworthy that the angle Bi–O–S is rather large (166°) and that the tetrahedron around the sulfur atom of the tosylate counterion is also flattened, this time towards the basal plane of the three oxygen atoms.

Tetraphenylbismuthonium Diphenylbis(trifluoroacetato)bismuthate (**5**) *(Fig. 3, Table 4).* In general terms this molecule may be viewed as a distorted tetraphenylbismuthonium cation and a trigonal bipyramidal anion with a stereochemically active lone pair. The distortion around the tetrahedron is revealed as a slight flattening towards one of the carbonyl oxygen atoms of the trifluoroacetate group bonded to the anionic bismuth atom. The bismuth atom is therefore located closer to the C(11)–C(21)–C(31) face at a distance of 0.55 (±0.03)Å.

In contrast to the other structures, the attacking nucleophilic oxygen atom is at a much greater distance (3.11(±0.03)Å). Moreover, the angle of attack is not directly opposed to $\phi 4$ but is slightly sideways, between $\phi 2$ and $\phi 3$, and closer to $\phi 3$: O(2p)–C(31): 3.18 (±0.03)Å, O(2p)–C(21): 3.35 (±0.03)Å and O(2p)–C(11): 3.49 (±0.03)Å. This leads to an opening of the C(21)–Bi–C(31) and C(11)–Bi–C(31) angles of 114° (±1°) and 120° (±1°), respectively. Unfortunately, the precision of the structure is not sufficiently good to evaluate a possible lengthening of the axial phenyl Bi–C bond opposite to the oxygen approach, as compared with the equatorial Bi–C bond lengths. We do not consider that the relative orientations of the respective elec-

Table 4. *Relevant Bond Distances* (Å) *and Angles* (degrees) *in the Trifluoroacetate Derivative*

Bi(1)–C(11)	2.21(2)	C(11)–Bi(1)–C(21)	108(1)
Bi(1)–C(21)	2.19(2)	C(11)–Bi(1)–C(31)	120
Bi(1)–C(31)	2.23(2)	C(21)–Bi(1)–C(31)	114
Bi(1)–C(41)	2.22(2)	C(41)–Bi(1)–C(11)	109
Bi(1)–O(2p)	3.11(2)	C(41)–Bi(1)–C(21)	101
Bi(2)–C(51)	2.26(2)	C(41)–Bi(1)–C(31)	103
Bi(2)–C(61)	2.24(2)	C(41)–Bi(1)–O(2p)	177
Bi(2)–O(1)	2.38(2)	C(51)–Bi(2)–C(61)	95
Bi(2)–O(1p)	2.41(2)	O(1)–Bi(2)–O(1p)	172
O(1)–C(1)	1.23(3)	O(1)–Bi(2)–C(51)	90
O(2)–C(1)	1.25(3)	O(1)–Bi(2)–C(61)	86
C(1)–C(2)	1.61(5)	O(1p)–Bi(2)–C(51)	84
C(2)–F(1)	1.60(5)	O(1p)–Bi(2)–C(61)	88
C(2)–F(2)	1.08(5)	Bi(2)–O(1)–C(1)	116(2)
C(2)–F(3)	1.25(5)	Bi(2)–O(1p)–C(1p)	112
O(1p)–C(1p)	1.23(3)	O(1)–C(1)–O(2)	123
O(2p)–C(1p)	1.19(3)	O(1p)–C(1p)–O(2p)	132
C(1p)–C(2p)	1.48(3)	O(1)–C(1)–C(2)	110
C(2p)–F(1p)	1.29(5)	O(1p)–C(1p)–C(2p)	113
C(2p)–F(2p)	1.25(5)	O(2)–C(1)–C(2)	125
C(2p)–F(3p)	1.33(5)	O(2p)–C(1p)–C(2p)	114

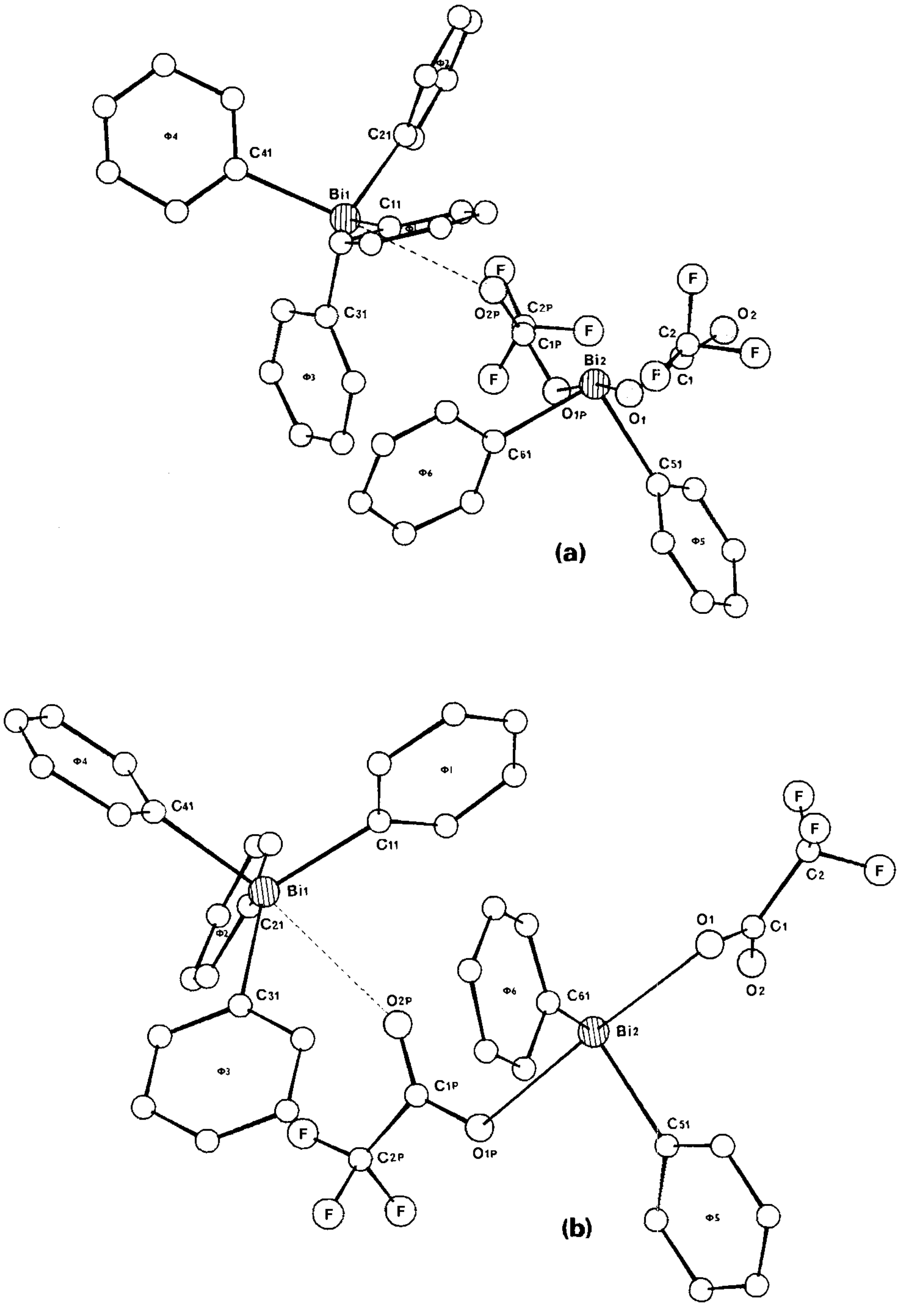

Fig. 3. *Tetraphenylbismuthonium diphenylbis(trifluoroacetato)bismuthate.*
(a) View perpendicular to C(51)-Bi(2)-C(61) plane; (b) view with O-Bi-O axis in the projection plane.

trophilic and nucleophilic centres are influenced by intermolecular forces imposed by the crystalline environment.

Koshland [11] has argued that a 10° misalignment of reactive groups relative to the ideal orientation leads to a large rate decrease. *Menger* [12], on the other hand, prefers to consider a multi-directional transition state theory with a preferred 'cone of reactivity'. In this instance, the deviation of the attacking nucleophilic anion from the standard path is undoubtedly a consequence of the steric constraints imposed by the environment of both the cation and the anion. Although it is tempting to speculate that this structure provides some support for the idea of a 'cone of reactivity', it can equally well be argued that it is an incipient frozen-in stage of an inherently non-productive nucleophilic attack. A much larger data base is required before any refined conclusion can be reached.

The determination of those structures, together with those already in the literature, allow us to follow the deformation of the coordination polyhedron around a bismuth atom and hence to map the reaction coordinate for the transformation of the tetrahedron into the trigonal bipyramid. These changes are most succintly summarized in *Fig. 4*.

We now turn our attention to the remarkable geometry of the diphenylbis(trifluoroacetato)bismuthate anion *(Fig. 5)*, in which the two trifluoroacetate groups adopt the apical positions, and the two phenyl rings, in a propeller fashion, are situated in the equatorial plane passing through the bismuth atom (Bi–O 2.39 (±0.02)Å).

Such a disposition, of course, leaves an empty space (or a phantom ligand) in the equatorial plane, which we interpret as the remaining lone pair of a distorted trigonal bipyramid with dsp^3 bonding around the bismuth atom. The value of the angle between

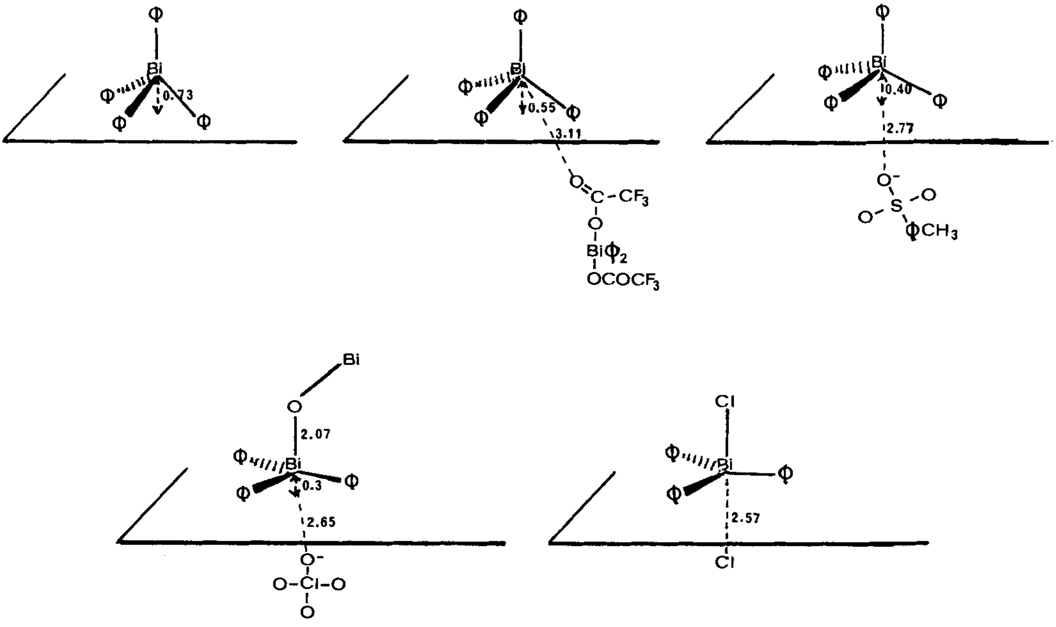

Fig. 4. *Bismuth coordination polyhedron: transformation from tetrahedron to trigonal bipyramid*

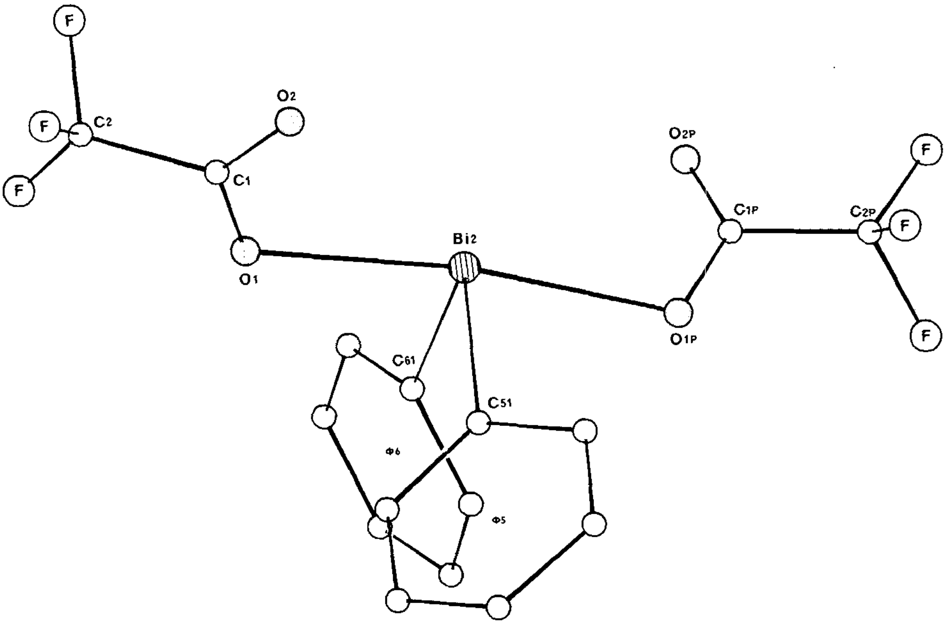

Fig. 5. *Geometrical features of diphenylbis(trifluoroacetato)bismuthate*

the equatorial Bi–C bonds is 95° (±1°), and the two apical oxygen atoms are not aligned with the bismuth atom: O(1)–Bi–O(1p): 172 ±1°. These angular distortions from the ideal trigonal bipyramid are usually explained by the larger spatial requirements of the lone pair [13].

Such a geometry has been observed for group IV elements in the cases of diphenyltellurium dibromide [14] and the analogous selenide [15]. Within group V, *trivalent* diphenylantimony fluoride [16] has been shown to adopt the same trigonal bipyramidal configuration by virtue of forming a fluorine-bridged polymer through the apex. The F–Sb–F angle is 165° (±0.5°) and the C–Sb–C angle is 100° (±0.5°). The tetrafluoroantimonate anion, SbF_4^-, which is found in the crystal structure of KSb_2F_7 [17], exhibits a similar geometry with a 90° (±0.2°) angle between the equatorial bonds and 155° (±0.2°) between the axial bonds. The existence of such a C_{2v}-symmetrical anion has been tentatively suggested for tetrahalogenoantimonate anions [18] and for their diphenylbismuthate congeners [19], Ph_2BiXY^-, on the basis of far IR and *Raman* studies. To our knowledge, however, this is the first structural evidence of a finite anionic species with such a geometry for a group V element.

Experimental Part

General. Melting points (m.p.) were determined using a *Reichert* hot stage apparatus and are uncorrected. IR spectra were run on a *Perkin-Elmer 297* spectrometer and ^{13}C-NMR spectra on a *Bruker WP 60* instrument. Mass spectra were measured on *AEI MS 50* and *MS 9* machines. All solvents and reagents were dried and purified by standard techniques.

Pentaphenylbismuth [20] was prepared by reaction of triphenylbismuth dichloride with phenyl-lithium and used without further purification for the experiments described below. The reaction of the anion of 8-hydroxyquinoline with triphenylbismuth dichloride was performed as described in [7] to give **4** (80%), m.p. 119–124° ([7]: 115–117°), as an orange crystalline solid. Recrystallisation by slow evaporation of a CH_2Cl_2/MeOH solution gave suitable crystals for X-ray analysis.

Tetraphenylbismuth p-*Toluenesulfonate.* A solution of pentaphenylbismuth (16 g, 0,027 mol) in benzene (8 ml) was added dropwise under an Ar atmosphere to a magnetically stirred solution of *p*-TsOH monohydrate (5 g, 0.028 mol) in Et_2O with temperature control maintained by a water bath at 15°. Addition was continued until the purple colouration of pentaphenylbismuth was no longer discharged. The white solid thus formed was filtered, washed with cold Et_2O and dried *in vacuo* to give the title compound (17 g, 0.025 mol) (90%) as a white solid. Recrystallisation from hexane/CH_2Cl_2 gave analytically pure material which was suitable for X-ray analysis, m.p. 155–162°. IR (Nujol): 3050, 1560, 1430 and 1160. ^{13}C-NMR ($CDCl_3$): 143.4 (C(1)); 142.6 (C(a)); 138.2 (C(4)); 135.8 (C(b)); 131.5 (C(c)); 131.3 (C(d)); 127.8 (C(3)); 125.7 (C(2)). MS: 611 (Ph_3BiOTs), 517 (Ph_4Bi), 457 (PhBiOTs), 440 (Ph_3Bi), 380 (BiOTs), 363 (Ph_2Bi), 286 (PhBi), 248 (PhOTs), 209 (Bi), 154 (PhPh). Anal. calc. for $C_{31}H_{27}BiO_3S$: C 54.10, H 4.04, S 4.53; found: C 53.99, H 3.95, S. 4.65.

Tetraphenylbismuth Mono(trifluoroacetate). To a solution of pentaphenylbismuth (2 g, 3.37 mmol) in anh. benzene (5 ml) under an Ar atmosphere was added, dropwise, with stirring, a solution of trifluoroacetic acid (0.384 g, 0.26 ml, 3.37 mmol) in benzene (3 ml) with cooling in a water bath at 15°. After addition was complete, the solvent was removed *in vacuo* and the residue obtained was triturated with pentane, then Et_2O, and finally filtered and dried to give the title compound (1.96 g) (90%). Recrystallisation was accomplished from a toluene/hexane mixture to give very fine needles, m.p. 120–132°. IR ($CHCl_3$): 3050, 1680, 1660. ^{13}C-NMR ($CDCl_3$): 159.62 (C=O); 144.18 (Bi–C); 137.36 (*ortho*-C); 135.87 (*meta*-C); 135.62 (*para*-C); 116.48 (CF_3). MS: 630 ($Ph_4BiOCOCF_3$), 553 ($Ph_3BiOCOCF_3$), 517 (Ph_4Bi), 440 (Ph_3Bi), 399 ($PhBiOCOCF_3$), 363 (Ph_2Bi), 322 ($BiOCOCF_3$), 286 (PhBi), 209 (Bi). Anal. calc. for $C_{26}H_{20}BiF_3O_2$: C 49.52, H 3.17; found: C 49.63, H 3.31.

Diphenylbismuth Mono(trifluoroacetate). A solution of triphenylbismuth (440 mg, 1 mmol) and trifluoroacetic acid (76.5 µl, 1 mmol) in anh. Et_2O (4 ml) was heated to reflux under an Ar atmosphere for 1 h, until all the triphenylbismuth had been consumed (TLC). The mixture was cooled to 0° in an ice bath, filtered, and the white precipitate was washed with cold Et_2O and dried *in vacuo* to give the title compound (320 mg, 67%), m.p. > 350°. IR (Nujol): 3050, 1650, 1600. MS: 399 ($PhBiOCOCF_3$), 363 (Ph_2Bi), 322 ($BiOCOCF_3$), 286 (PhBi), 209 (Bi). Ion molecule interactions also gave rise to peaks at 627 (3Bi), 572 (Ph_2Bi_2) and 495 ($PhBi_2$). Anal. calc. for $C_{14}H_{10}F_3O_2Bi$: C 35.3, H 2.1; found: C 35.37, H 2.17.

Tetraphenylbismuthonium Diphenylbis(trifluoroacetato)bismuthate (**5**). – *Method A.* From pentaphenylbismuth and phenylbismuth bis(trifluoroacetate): A solution of phenylbismuth bis(trifluoroacetate) was generated *in situ* by addition of a solution of trifluoroacetic acid (228 mg, 153 µl, 2 mmol) in anh. Et_2O (1 ml) to a solution of triphenylbismuth (440 mg, 1 mmol) in Et_2O (3 ml) under an Ar atmosphere. The mixture was heated under reflux for 1 h until a homogeneous solution was obtained and the initially formed precipitate of diphenylbismuth mono(trifluoroacetate) had completely redissolved. Analytical TLC confirmed the absence of triphenylbismuth at this stage, but attempted isolation of the product led to decomposition. The mixture was then cooled prior to the addition of a solution of pentaphenylbismuth (594 mg, 1 mmol) in benzene (3 ml), whereupon the title compound crystallised directly from the reaction mixture in the form of plates (950 mg, 86%); m.p. 142–147° (benzene/Et_2O). IR (CH_2Cl_2): 1680, 1180–1120. ^{13}C-NMR ($CDCl_3$): 190.4 (C(11)); 161.7 (C=O); 139.2 (C(1)); 136.8 (C(2')); 135.8 (C(2)); 132.4 (C(4)); 132.3 (C(3)); 131.3 (C(3')); 127.4 (C(4)); 115.9 (CF_3). MS: 589 ($Ph_2Bi(OCOCF_3)_2$), 517 (Ph_4Bi), 418 (Bi_2), 399 ($PhBiOCOCF_3$), 363 (Ph_2Bi). Anal. calc. for $C_{40}H_{30}Bi_2O_4F_6$: C 43.41, H 2.69; found: C 43.17, H 2.7.

Method B. From tetraphenylbismuth mono(trifluoroacetate) and diphenylbismuth mono(trifluoroacetate): a suspension of diphenylbismuth mono(trifluoroacetate) was prepared as described above from triphenylbismuth (440 mg) and trifluoroacetic acid (114 mg, 76.5 µl, 1 mmol) in anh. Et_2O (1 ml). To the cooled mixture was added a solution of tetraphenylbismuth mono(trifluoroacetate) (630 mg, 1 mmol) in anh. benzene (3 ml) whereupon the title compound, identical in all respects with the above sample, crystallised from the reaction mixture (750 mg, 68%).

Method C. From tetraphenylbismuth mono(trifluoroacetate) and triphenylbismuth bis(trifluoroacetate): an intimate mixture of tetraphenylbismuth mono(trifluoroacetate) (315 mg, 0.5 mmol) and triphenylbismuth bis(trifluoroacetate) (333 mg, 0.5 mmol) were heated without solvent under an Ar atmosphere until fusion was complete (145°). The reaction mixture was cooled and the residue recrystallised from benzene/Et_2O to give the title compound (553 mg, 50%).

Table 5. *Crystal Data and Recording Conditions*

Derivative	8-Hydroxyquinoline	Tosylate	Trifluoroacetate
	$C_{27}H_{21}BiClNO$	$C_{31}H_{27}BiO_3S$	$C_{40}H_{30}Bi_2F_6O_4$
System	monoclinic	monoclinic	monoclinic
Space-group	$P2_1/n$	$C2/c$	$P2_1/c$
Cell dimensions (Å)	$a = 19.908(9)$	$a = 21.082(9)$	$a = 9.884(5)$
	$b = 9.436(5)$	$b = 15.488(8)$	$b = 21.215(9)$
	$c = 13.088(7)$	$c = 17.620(8)$	$c = 18.556(8)$
	$\beta = 106.602(4)°$	$\beta = 108.3(4)°$	$\beta = 95.1(4)°$
	$V = 2356$ Å^3	$V = 5462$ Å^3	$V = 3875$ Å^3
Absorption coefficient	$\mu = 72$ cm^{-1}	$\mu = 62$ cm^{-1}	$\mu = 87$ cm^{-1}
Scan width	1.20°	1.20°	1.30°
Scan speed	0.03° s^{-1}	0.24° s^{-1}	0.10° s^{-1}
Maximum number of scans	1	10	7
Number of measured reflections	6057	5982	4702
Number of intensities[a]) $I > 3\sigma(I)$	3087	2518	3259

[a]) The intensities were corrected for absorption with DIFABS procedure [21].

Table 6. *Atomic Coordinates* (× 10^4) *with e.s.d.'s in Parentheses and Equivalent Isotropic Thermal Parameter* U_{eq} *for* $C_{27}H_{21}BiClNO$

Atom	X	Y	Z	U_{eq}
Bi	4572 (1)	6337 (1)	7381 (1)	33 (1)
Cl	3971 (2)	5035 (3)	5547 (2)	42 (4)
O	4997 (4)	7319 (7)	8935 (5)	37 (11)
C(1)	5642 (6)	7945 (10)	9271 (8)	40 (17)
C(2)	5829 (6)	8637 (14)	10273 (8)	52 (19)
C(3)	6508 (8)	9251 (13)	10664 (10)	54 (23)
C(4)	6988 (7)	9196 (13)	10100 (10)	41 (21)
C(5)	6813 (6)	8596 (13)	9071 (9)	63 (20)
C(6)	7269 (6)	8515 (14)	8413 (11)	63 (21)
C(7)	7064 (7)	7909 (15)	7445 (11)	83 (25)
C(8)	6397 (7)	7290 (13)	7109 (9)	77 (22)
N(9)	5942 (5)	7346 (9)	7679 (7)	39 (14)
C(10)	6128 (6)	7954 (11)	8670 (9)	48 (17)
C(11)	5267 (5)	4520 (10)	7746 (9)	38 (16)
C(12)	5592 (6)	3948 (11)	7037 (8)	47 (17)
C(13)	6032 (6)	2785 (12)	7311 (9)	64 (19)
C(14)	6157 (7)	2250 (11)	8368 (11)	78 (22)
C(15)	5863 (6)	2799 (12)	9078 (9)	70 (19)
C(16)	5431 (6)	3969 (11)	8790 (8)	57 (19)
C(21)	4418 (5)	8413 (12)	6567 (9)	43 (18)
C(22)	4500 (6)	9610 (11)	7164 (8)	38 (18)
C(23)	4389 (7)	10965 (12)	6652 (12)	65 (22)
C(24)	4202 (8)	10999 (13)	5622 (11)	76 (24)
C(25)	4127 (9)	9816 (13)	5023 (10)	107 (30)
C(26)	4230 (7)	8493 (13)	5505 (9)	88 (23)
C(31)	3645 (5)	6000 (9)	7964 (7)	35 (15)
C(32)	3183 (6)	7077 (12)	7895 (9)	48 (19)
C(33)	2624 (7)	6907 (14)	8352 (10)	59 (22)
C(34)	2556 (7)	5665 (17)	8885 (11)	83 (25)
C(35)	3008 (8)	4556 (13)	8887 (10)	64 (22)
C(36)	3576 (7)	4728 (11)	8446 (9)	59 (20)

The above two reagents were individually heated to 145° and the progress of the decomposition monitored by IR spectroscopy for the formation of phenyl trifluoroacetate. In this way it was found that decomposition of the bis(trifluoroacetate) led to formation *in situ* of diphenylbismuth mono(trifluoroacetate).

Crystal Structure Determinations. – The intensities were recorded on an automatic four-circle *Philips* diffractometer up to $-\theta \leqslant 28°$ with molybdenum radiation (monochromatised by graphite). The crystal data and recording conditions are listed in *Table 5*.

The three structures were solved by heavy-atom techniques. For the case of tetraphenylbismuthonium diphenylbis(trifluoroacetato)bismuthate, the cell volume did not correspond to an integral multiple of the expected formula weight. The *Patterson* function showed two bismuth atoms in the asymmetric unit and the successive *Fourier* series their two different surroundings.

The structures were refined (local version of SHELX [22] on *C11 Honeywell Bull* Computer) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were located theoretically. The final *R* factors are: 5.0% for tetraphenylbismuth tosylate; 5.3% for tetraphenylbismuthonium diphenylbis(trifluoroacetato)bismuthate and 5.3% for the 8-hydroxyquinoline derivative.

The atomic coordinates are listed in *Tables 6, 7* and *8*. The complete lists of bond distances, valency angles and observed and calculated structure factors are deposited with the *British Lending Library*.

Table 7. *Atomic Coordinates* (× 10^4) *with e.s.d's in Parentheses and Equivalent Isotropic Thermal Parameter* U_{eq} *for* $C_{31}H_{27}BiO_3S$

Atom	*X*	*Y*	*Z*	U_{eq}
Bi	4588 (1)	2823 (1)	5311 (1)	48 (1)
S(1)	3422 (1)	1411 (2)	3325 (2)	51 (5)
O(1)	3726 (3)	1969 (4)	4009 (4)	69 (13)
O(2)	3919 (3)	1003 (5)	3029 (4)	95 (15)
O(3)	2944 (4)	817 (5)	3469 (4)	99 (15)
C(1)	2937 (4)	2131 (8)	2548 (6)	36 (18)
C(2)	2751 (5)	1829 (7)	1748 (8)	39 (19)
C(3)	2329 (6)	2398 (10)	1164 (6)	36 (20)
C(4)	2096 (7)	3207 (10)	1263 (12)	104 (36)
C(5)	2312 (6)	3452 (7)	2074 (9)	68 (22)
C(6)	2711 (5)	2933 (9)	2697 (6)	43 (20)
C(7)	1665 (6)	3749 (8)	597 (7)	104 (25)
C(11)	5233 (4)	2951 (8)	4521 (6)	51 (17)
C(12)	5173 (4)	2376 (6)	3886 (7)	55 (18)
C(13)	5604 (5)	2505 (7)	3437 (6)	63 (20)
C(14)	6043 (5)	3190 (8)	3598 (7)	84 (20)
C(15)	6083 (5)	3741 (7)	4234 (7)	56 (19)
C(16)	5672 (5)	3607 (7)	4690 (6)	56 (18)
C(21)	3689 (5)	3633 (7)	4930 (6)	46 (17)
C(22)	3664 (5)	4278 (7)	4393 (7)	54 (18)
C(23)	3091 (6)	4767 (7)	4124 (7)	90 (22)
C(24)	2564 (6)	4638 (9)	4409 (9)	82 (28)
C(25)	2591 (7)	4019 (11)	4966 (10)	113 (30)
C(26)	3171 (6)	3502 (8)	5230 (7)	94 (22)
C(41)	5228 (5)	3564 (8)	6349 (6)	59 (18)
C(42)	5108 (5)	4397 (8)	6460 (7)	61 (21)
C(43)	5545 (7)	4902 (8)	7027 (8)	83 (24)
C(44)	6142 (7)	4518 (9)	7502 (8)	68 (26)
C(45)	6283 (5)	3669 (10)	7406 (8)	79 (24)
C(46)	5819 (6)	3180 (7)	6830 (7)	84 (21)
C(31)	4442 (5)	1608 (7)	5849 (7)	47 (19)
C(32)	4294 (6)	1655 (8)	6546 (8)	90 (23)
C(33)	4204 (5)	885 (11)	6909 (7)	80 (24)
C(34)	4272 (6)	101 (9)	6594 (9)	80 (26)
C(35)	4422 (5)	81 (9)	5898 (9)	86 (25)
C(36)	4494 (5)	829 (9)	5508 (6)	65 (20)

Table 8. *Atomic Coordinates* (× 10^4) *with e.s.d's in Parentheses and Equivalent Isotropic Thermal Parameter* U_{eq} *for* $C_{40}H_{30}Bi_2F_6O_4$

Atom	*X*	*Y*	*Z*	U_{eq}
Bi(1)	8818 (1)	3761 (1)	2814 (1)	48 (1)
Bi(2)	3044 (1)	2900 (1)	1141 (1)	49 (1)
C(11)	9456 (16)	2770 (7)	2728 (7)	52 (26)
C(12)	10801 (16)	2586 (8)	2867 (9)	54 (29)
C(13)	11161 (17)	1978 (8)	2872 (10)	47 (30)
C(14)	10226 (23)	1513 (10)	2709 (12)	111 (47)
C(15)	8878 (21)	1676 (8)	2564 (10)	67 (36)
C(16)	8407 (14)	2323 (7)	2566 (9)	58 (28)
C(21)	10167 (14)	4217 (8)	3659 (8)	59 (27)
C(22)	10655 (15)	3874 (7)	4255 (10)	40 (27)
C(23)	11406 (15)	4145 (10)	4830 (9)	54 (31)
C(24)	11689 (20)	4769 (10)	4803 (11)	55 (39)
C(25)	11253 (20)	5100 (8)	4224 (14)	75 (41)
C(26)	10479 (18)	4857 (9)	3641 (10)	66 (34)
C(31)	8409 (15)	4346 (8)	1817 (8)	51 (29)
C(32)	7712 (15)	4876 (9)	1892 (9)	65 (31)
C(33)	7393 (18)	5247 (8)	1293 (13)	94 (39)
C(34)	7799 (22)	5046 (11)	626 (11)	111 (43)
C(35)	8444 (19)	4498 (10)	588 (11)	84 (39)
C(36)	8744 (16)	4099 (7)	1190 (10)	52 (29)
C(41)	6857 (16)	3803 (8)	3315 (10)	54 (31)
C(42)	6927 (16)	3819 (10)	4042 (9)	68 (35)
C(43)	5732 (25)	3871 (15)	4340 (12)	140 (57)
C(44)	4536 (26)	3917 (16)	3991 (17)	155 (67)
C(45)	4480 (21)	3915 (16)	3274 (15)	198 (61)
C(46)	5655 (22)	3824 (11)	2872 (11)	105 (48)
C(51)	4074 (15)	3082 (9)	121 (9)	69 (29)
C(52)	3957 (17)	2671 (9)	− 462 (13)	68 (39)
C(53)	4605 (22)	2806 (11)	−1085 (12)	117 (44)
C(54)	5292 (25)	3337 (13)	−1102 (13)	127 (51)
C(55)	5419 (20)	3749 (10)	− 560 (16)	105 (46)
C(56)	4812 (19)	3640 (9)	89 (11)	68 (35)
C(61)	1004 (16)	2704 (8)	562 (9)	59 (29)
C(62)	113 (20)	2319 (7)	858 (8)	51 (29)
C(63)	− 1195 (20)	2211 (9)	558 (11)	63 (38)
C(64)	− 1628 (17)	2568 (9)	− 18 (11)	42 (36)
C(65)	− 801 (19)	2996 (9)	− 352 (9)	58 (32)
C(66)	542 (18)	3047 (9)	− 33 (10)	67 (36)
O(1)	3463 (12)	1803 (5)	1036 (6)	58 (21)
C(1)	4477 (22)	1600 (11)	1400 (11)	67 (42)
O(2)	5434 (15)	1949 (6)	1641 (9)	120 (33)
C(2)	4594 (23)	847 (19)	1289 (30)	305 (95)
F(1)	4640 (25)	781 (8)	2152 (8)	209 (43)
F(2)	3640 (21)	616 (7)	1346 (17)	184 (53)
F(3)	5807 (18)	739 (7)	1497 (15)	345 (52)
O(1P)	2502 (12)	4009 (5)	1068 (6)	74 (21)
C(1P)	2065 (18)	4202 (8)	1630 (11)	46 (29)
O(2P)	1512 (9)	3946 (5)	2091 (5)	66 (18)
C(2P)	2136 (30)	4895 (11)	1700 (15)	131 (50)
F(1P)	1595 (19)	5243 (6)	1185 (8)	151 (37)
F(2P)	1897 (18)	5139 (18)	2290 (7)	247 (38)
F(3P)	3390 (16)	5110 (7)	1660 (10)	168 (38)

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