

SYNTHESIS OF TETRAPHENYLSTIBONIUM ALKYL- AND ARYL-SULPHONATES. CRYSTAL STRUCTURE OF TETRAPHENYLSTIBONIUM BENZENESULPHONATE HYDRATE

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Summary

The tetraphenylstibonium sulphonates $\text{Ph}_4\text{SbO}_3\text{SR} \cdot n\text{H}_2\text{O}$ ($n = 1$, $\text{R} = \text{C}_6\text{H}_5$; $n = 0$, $\text{R} = \text{CH}_3$, CF_3 , $\text{CH}_2\text{CH}_2\text{OH}$, $4\text{-CH}_3\text{C}_6\text{H}_4$, $2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3$) have been obtained by neutralization of tetraphenylstibonium hydroxide with the appropriate alkyl- or aryl-sulphonic acid. The crystal structure of tetraphenylstibonium benzenesulphonate hydrate has been determined by single crystal X-ray diffraction. The sulphonate group is unidentately coordinated to antimony, which has a distorted trigonal bipyramidal environment. The rather long Sb–O bond, (2.506(4) Å) and the distortion of the polyhedron around Sb, and the IR data for the sulphonate group are consistent with the assumption of a large ionic bond character in the Sb–O bond. From IR data analogous molecular structures are inferred for the other tetraphenylstibonium sulphonates.

Introduction

Tetraphenylstibonium sulphonates $\text{Ph}_4\text{SbO}_3\text{SR}$ ($\text{Ph} = \text{C}_6\text{H}_5$) have not previously been described. The only example of a tetraorganostibonium sulphonate, $\text{Me}_4\text{SbO}_3\text{-SMe}$ ($\text{Me} = \text{CH}_3$), was obtained as a product of oxidation of $\text{Me}_4\text{SbO}_2\text{SMe}$ [1], but its structure was not determined. We became interested in such compounds during studies on reactions of R_3SbO and sulphonic acids. The products of these reactions were very variable in composition and structure, though in all cases the sulphonate ligand was unidentately bonded, albeit with more or less appreciable ionic bond character [2,3]. There is little information on unidentate bonding of sulphonate ligands in the literature, and it thus seemed of interest to seek other compounds with unidentate sulphonate ligands. We expected to find this type of bonding in tetraphenylstibonium sulphonates, and we report below on the preparation and structural studies of such compounds.

TABLE 1

ANALYTICAL DATA FOR TETRAPHENYLSTIBONIUM ALKYL- AND ARYL-SULPHONATES

Compound	Yield (%)	M.p. (°C)	Microanalytical data (Found (calcd.) (%))		Molecular weight, (Found in CHCl ₃ (calcd.))
			C	H	
Ph ₄ SbO ₃ SCH ₃ (1)	72	258	57.2 (57.17)	4.4 (4.41)	536 (525)
Ph ₄ SbO ₃ SCF ₃ (2)	86	255	52.4 (51.84)	3.6 (3.48)	578 (579)
Ph ₄ SbO ₃ SCH ₂ CH ₂ OH (3)	79	158–160	56.3 (56.24)	4.7 (4.54)	568 (555)
Ph ₄ SbO ₃ SC ₆ H ₅ · H ₂ O (4)	67	98–101	59.8 (59.52)	4.6 (4.50)	599 (605)
Ph ₄ SbO ₃ SC ₆ H ₄ CH ₃ (5)	71	162–165	62.2 (61.92)	4.7 (4.53)	583 (601)
Ph ₄ SbO ₃ SC ₆ H ₃ (NO ₂) ₂ ^a (6)	91	141–143	53.1 (53.20)	3.4 (3.42)	678 (677)

^a Nitrogen analysis: N, found 4.1, calcd. 4.14%.

Experimental

Ph₄SbOH was prepared according to ref. 4. 2,4-Dinitrobenzenesulphonic acid was made by adding small portions of bis(2,4-dinitrophenyl)disulphide [5] to fuming nitric acid at room temperature; after addition of water the surplus acid was removed repeatedly by azeotropic distillation. Other sulphonic acids and solvents were commercial products (Merck, Fluka).

The compounds were synthesized by stirring a mixture of 5 mmol of tetraphenylstibonium hydroxide and 5 mmol of the appropriate sulphonic acid in 50 ml of methanol at room temperature. The solvent was evaporated after 2 h in vacuo, and the residue recrystallized from a mixture of water and ethanol or a mixture of chloroform and ether. Analytical data are summarized in Table 1.

IR spectra (Nujol) were recorded on a Perkin–Elmer grating spectrometer PE 580 B, and ¹H NMR spectra in CD₃OD on a Perkin–Elmer 90 MHz spectrometer R32 at 37°C. The melting points of the high melting compounds **1** and **2** were determined by DTA, and the others in the usual way. Molecular weights were determined osmotically.

Single crystals of Ph₄SbO₃SPh · H₂O (**4**) were obtained by crystallization from a solution in methanol and chloroform after addition of diethyl ether. A crystal of dimensions 0.15 × 0.26 × 0.39 mm was mounted on a glass fibre and used to obtain cell data and subsequent intensity measurements. Crystal data: mol. wt. 605.35, *a* 13.717(6), *b* 11.613(6), *c* 17.651(7) Å, β 107.86(5)°, *U* 2676.2 Å³, *Z* = 4, *F*(000) = 1184, λ(Mo-K_α) 0.71069 Å, μ(Mo-K_α) 1.2 mm⁻¹. Space group *P*2₁/*c* from systematic absences (*h*0*l* for *l* = 2*n* + 1, and 0*k*0 for *k* = 2*n* + 1).

The intensities of 5254 independent reflexions were measured on a Nonius CAD-4 diffractometer by 2θ/ω-scans and a scan speed of 2.5° min⁻¹. After Lorentz-polarization and absorption correction via ψ-scans 3660 observed *F*_o values (*F*_o > 3σ) were used for the structure determination via Patterson function, Δ*F*

TABLE 2

FINAL FRACTIONAL ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS ($B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$) ($\text{\AA}^2$)

Atom	x	x	z	B_{eq} ($\text{\AA}^2$)
Sb(1)	0.17739(3)	0.20454(3)	0.43292(2)	2.762(7)
S(1)	0.4478(1)	0.2421(1)	0.54952(9)	3.18(3)
O(1)	0.3396(3)	0.2470(4)	0.5422(2)	3.8(1)
O(2)	0.4628(4)	0.1906(6)	0.4801(3)	7.1(1)
O(3)	0.4981(5)	0.3498(5)	0.5705(4)	7.5(2)
O(4)	0.6154(4)	0.4360(5)	0.4627(3)	5.1(1)
C(11)	0.2487(4)	0.2840(5)	0.3566(3)	2.7(1)
C(12)	0.2279(5)	0.2344(6)	0.2808(3)	3.4(1)
C(13)	0.2726(5)	0.2843(6)	0.2271(3)	4.0(1)
C(14)	0.3338(5)	0.3821(6)	0.2486(4)	4.0(1)
C(15)	0.3530(5)	0.4308(6)	0.3244(4)	3.7(1)
C(16)	0.3093(5)	0.3808(6)	0.3791(3)	3.3(1)
C(21)	0.0339(4)	0.1692(5)	0.3460(3)	3.2(1)
C(22)	-0.0057(5)	0.0594(6)	0.3280(4)	3.7(1)
C(23)	-0.1012(5)	0.0435(7)	0.2689(4)	4.6(2)
C(24)	-0.1559(5)	0.1371(8)	0.2295(4)	5.0(2)
C(25)	-0.1164(6)	0.2473(7)	0.2474(5)	5.1(2)
C(26)	-0.0213(6)	0.2633(6)	0.3057(4)	4.6(2)
C(31)	0.2196(5)	0.0365(5)	0.4756(3)	3.1(1)
C(32)	0.1986(6)	-0.0003(6)	0.5436(4)	4.3(2)
C(33)	0.2202(6)	-0.1133(7)	0.5685(4)	5.1(2)
C(34)	0.2620(5)	-0.1883(6)	0.5261(4)	4.5(2)
C(35)	0.2838(5)	-0.1506(6)	0.4572(4)	4.0(2)
C(36)	0.2627(5)	-0.0364(6)	0.4309(4)	3.6(1)
C(41)	0.1223(4)	0.3061(6)	0.5102(3)	3.1(1)
C(42)	0.1699(5)	0.4084(6)	0.5439(4)	3.9(2)
C(43)	0.1273(6)	0.4699(7)	0.5946(4)	4.8(2)
C(44)	0.0408(6)	0.4274(7)	0.6110(4)	5.1(2)
C(45)	-0.0063(6)	0.3266(8)	0.5767(4)	5.4(2)
C(46)	0.0339(5)	0.2648(6)	0.5242(4)	4.1(2)
C(51)	0.5046(4)	0.1482(5)	0.6306(3)	2.9(1)
C(52)	0.5562(5)	0.1941(7)	0.7049(4)	4.2(2)
C(53)	0.5989(6)	0.1172(8)	0.7676(4)	5.4(2)
C(54)	0.5903(6)	0.0003(7)	0.7549(4)	5.1(2)
C(55)	0.5407(5)	-0.0445(6)	0.6801(4)	4.5(2)
C(56)	0.4958(5)	0.0302(6)	0.6172(4)	3.6(1)

syntheses and least-squares refinements with anisotropic temperature factors for non-H atoms. H atoms were placed in geometrically (C–H 0.95 Å) calculated positions and included in the final structure-factor calculation with a common isotropic temperature factor. Complex neutral-atom scattering factors were taken from International Tables [6]. Refinement converged with unit weights and 325 refined parameters at $R = 0.034$. In the final refinement cycle the maximum shift over error was less than 0.00 and maximum peak in a final ΔF synthesis was 0.69 e $\text{\AA}^{-3}$. The following programs were used: Enraf–Nonius Structure Determination Package [7], ORTEP II [8] and POP 1 [9]. Final fractional atomic coordinates are listed in Table 2, and intramolecular bond distances and angles in Table 3.

TABLE 3

INTRAMOLECULAR BOND DISTANCES (Å) AND ANGLES (°)

Sb(1)–C(11)	2.104(5)	C(11)–Sb(1)–C(21)	97.6(2)
Sb(1)–C(21)	2.131(5)	C(31)–Sb(1)–C(21)	99.9(2)
Sb(1)–C(31)	2.108(6)	C(41)–Sb(1)–C(21)	97.9(2)
Sb(1)–C(41)	2.111(6)	C(11)–Sb(1)–O(1)	85.9(2)
Sb(1)–O(1)	2.506(4)	C(31)–Sb(1)–O(1)	79.9(2)
S(1)–O(1)	1.451(4)	C(41)–Sb(1)–O(1)	78.6(2)
S(1)–O(2)	1.435(5)	C(21)–Sb(1)–O(1)	176.0(2)
S(1)–O(3)	1.422(6)	C(11)–Sb(1)–C(31)	120.2(2)
S(1)–O(51)	1.777(6)	C(11)–Sb(1)–C(41)	119.8(3)
O(4)–O(3)	2.897(7)	C(31)–Sb(1)–C(41)	113.6(3)
O(4)–O(3')	3.015(7)	Sb(1)–O(1)–S(1)	134.7(3)
O(1)–S(1)–O(2)	110.5(3)		
O(1)–S(1)–C(3)	113.0(3)		
O(1)–S(1)–C(51)	106.3(3)		
O(2)–S(1)–O(3)	113.8(4)		
O(2)–S(1)–C(51)	106.8(3)		
O(3)–S(1)–C(51)	105.8(4)		
O(3)–O(4)–O(3')	93.1(2)		
O(4)–O(3)–O(4')	86.9(2)		

Results and discussion

Tetraphenylstibonium sulphonates $\text{Ph}_4\text{SbO}_3\text{SR}$ were readily obtained by reaction of 1/1 mixtures of Ph_4SbOH and the appropriate sulphonic acid HO_3SR in

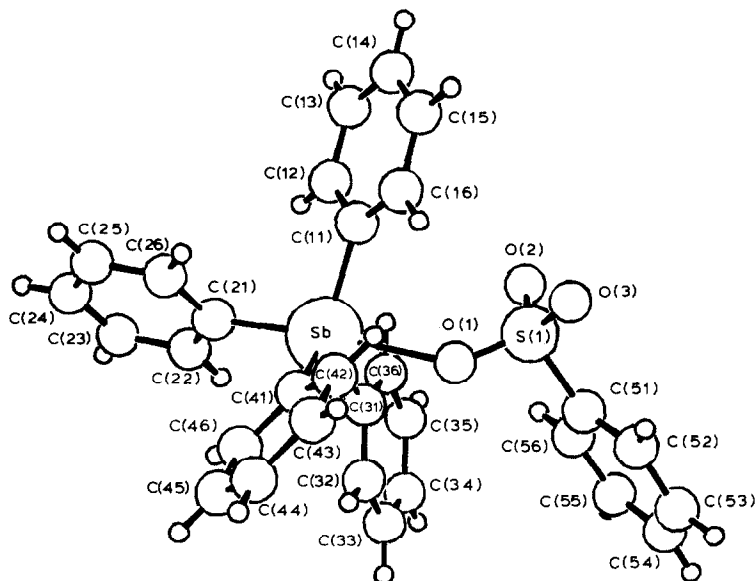


Fig. 1. Structure of a molecule of tetraphenylstibonium benzenesulphonate.

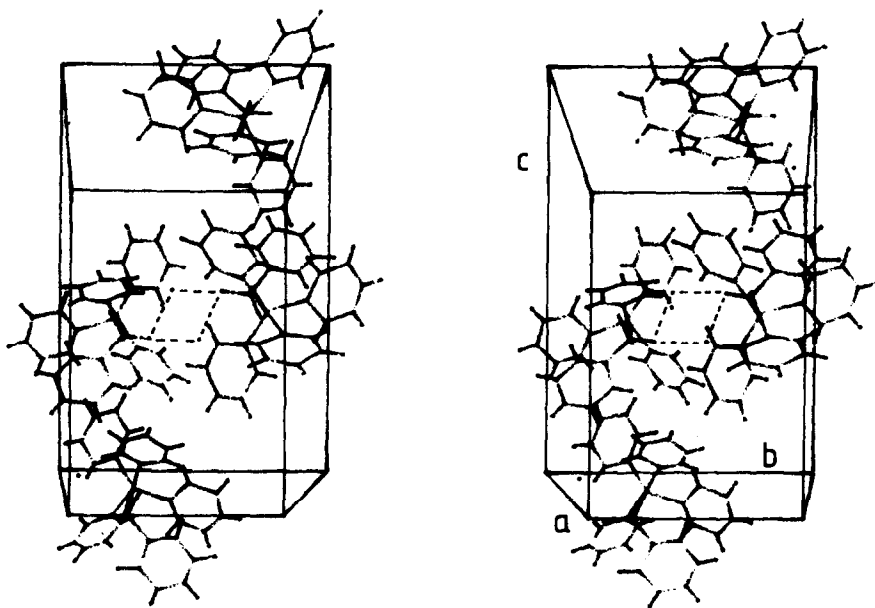
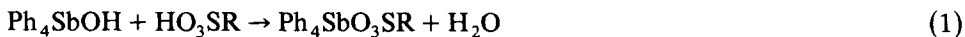


Fig. 2. Unit cell of tetraphenylstibonium benzenesulphonate hydrate. Broken lines indicate hydrogen bonds between O(3) of the sulphonate ligands and O(4) of the water molecules.

methanol according to eq. 1:



The products listed in Table 1 are not sensitive to air or water, and it was not necessary to remove the water produced in the neutralization reaction 1. Except for the slight yellow colour of **6** all are colourless. They are soluble in methanol and chloroform, but insoluble in nonpolar solvents. When **4** is dissolved in chloroform the water of hydration is released and forms a separate phase. The compounds are monomeric in chloroform solution according to molecular weight measurements (see Table 1).

The structure of a molecule of **4** as determined by X-ray diffraction is shown in Fig. 1. Figure 2 shows the unit cell. Molecules of **4** are arranged in the crystal in a quasi dimeric form, two molecules being connected via two water molecules. From the positions of the oxygen atoms of the two water molecules, O(4) and O(4'), hydrogen bonds to O(3) and O(3') are inferred, forming an 8-membered ring (4-oxygen, 4 hydrogen atoms), in the middle of which is the centre of inversion. The distances O(4)–O(3) and O(4)–O(3') are 2.897(7) and 3.015(7) Å, respectively, and are in the range for rather weak hydrogen bonds [10]. Since **4** loses water even on slight warming or on dissolution (*vide supra*), it is evident that water is bonded rather loosely. Sb is surrounded by the four phenyl groups and O(1) to form a distorted trigonal bipyramid, C(11), C(31) and C(41) lying in the equatorial plane, from which Sb is displaced by 0.309 Å in the direction of C(21). This deviation and the values of the three angles C(21)–Sb–C(*i*1) (*i* = 1, 3, 4) indicate a distortion of the Ph₄Sb group towards a tetrahedral structure. The bond distance Sb–C(21) 2.131(5) Å is slightly larger than the mean bond distance for the other three Sb–C

TABLE 4

COMPARISON OF BOND DISTANCES AND BOND ANGLES (mean values) OF $\text{Ph}_4\text{SbO}_3\text{SPh} \cdot \text{H}_2\text{O}$ AND OF SOME OTHER TETRAORGANOSTIBONIUM COMPOUNDS

Compound	Distances (Å)			Angles (°)			Ref.
	Sb–O	Sb–C _{eq}	Sb–C _{ax}	C _{eq} –Sb–C _{ax}	C _{eq} –Sb–O	C _{ax} –Sb–O	
$\text{Ph}_4\text{SbO}_3\text{SPh} \cdot \text{H}_2\text{O}$ (4)	2.506(4)	2.108(6)	2.131(5)	98.5(2)	81.5(2)	176.0(2)	This work
Ph_4SbOH	2.048	2.131(8)	2.218(5)	93.4(3)	86.7(3)	175.4(2)	[4]
$\text{Ph}_4\text{SbO}_2\text{N}_2\text{CCH}_3$ (1) ^a	2.266	2.122	2.173	96.1	84.1	171.3	
(2) ^a	2.235	2.145	2.176	96.5	83.5	176.8	[11]
$(\text{Ph}_4\text{Sb})_2\text{CO}_3$ ^b	2.257(7)	2.120(12)	2.153(12)	95.2(5)	84.7(4)	176.2(4)	[12]
$\text{Me}_4\text{SbO}_2\text{CC}_6\text{H}_3(\text{OH})(\text{OEt})$	2.890	2.099(12)	2.078(13)	105.9(6)	^c	176.0	[13]
$\text{Me}_4\text{SbOP}(\text{S})\text{Me}_2$ (1) ^a	2.532(4)	2.109(8)	2.150(6)	101.2(3)	^c	^c	
(2) ^a	2.749(4)	2.107(6)	2.144(6)	103.6(3)	^c	^c	[14]

^a Data for molecules 1 and 2, respectively, in the unit cell. ^b Data for the pentacoordinated Sb atom (second Sb atom is hexacoordinated). ^c Values not given.

bonds (2.108(6) Å), as expected for axial bonds in trigonal bipyramids. The angle C(21)–Sb–O(1) with 176.0(2)° is also in accordance with the assumption of an essentially trigonal bipyramidal bond arrangement around Sb.

The distance between antimony and oxygen of the unidentately bonded sulphonate ligand, Sb–O(1) 2.506(4) Å, is markedly longer than the sum of covalent radii (2.11 Å) and also longer than those in other tetraphenylantimony compounds (see Table 4). In $[\text{Ph}_3\text{Sb}(\text{O}_3\text{SCH}_2\text{CH}_2\text{OH})]_2\text{O}$ the Sb–O distance is 2.276(4) Å [2]. This comparison suggests a rather strong ionic character for the Sb–O bond, but the degree of covalency is still apparently strong enough to prevent a tetrahedral configuration for the Ph_4Sb unit.

From a consideration of bond angles (Table 4) of various tetraorganostibonium compounds R_4SbX it appears that the SbC_4 skeleton tends more to be tetrahedral in Me_4Sb compounds than in Ph_4Sb compounds. This implies mainly ionic bonding between antimony and oxygen of the ligand X in Me_4SbX , whereas in Ph_4SbX a more covalent type of bonding, though with appreciable ionic character has to be assumed. Consistent with this assumption is that Sb–O distances (Table 4) are generally longer in cases in which SbC_4 tends to be more tetrahedral. In **4** the Sb–O(1) bond length is intermediate between those of the analogous bonds in Ph_4SbOH , in which Sb has only a slightly distorted trigonal bipyramidal surrounding [4], and in $\text{Me}_4\text{SbO}_2\text{CC}_6\text{H}_3(2\text{-OH})(4\text{-OC}_2\text{H}_5)$ (**7**), which contains a nearly tetrahedral Me_4Sb^+ cation [13]. It is noteworthy that the difference between the Sb–C_{ax} and Sb–C_{eq} bond lengths is largest in Ph_4SbOH , and smallest in **7**. In this respect, also, **4** has an intermediate position. These considerations also support the view that the Sb–O(1) bond has an appreciable ionic character.

The bond distances and angles within the phenyl groups bonded to antimony and to sulphur are in the usual range and are not listed in detail.

The IR data for the O_3S group are listed in Table 5 together with the ^1H NMR data. The NMR spectra are as expected, and need not be discussed.

The IR data are of interest because only a few spectra of organometal sulphonates have been presented previously. Bidentate bridging sulphonate groups are present in

TABLE 5

CHARACTERISTIC IR VIBRATIONS OF THE SO_3 GROUP, AND ^1H NMR CHEMICAL SHIFTS (In CD_3OD) FOR TETRAPHENYLSTIBONIUM ALKYL- AND ARYL-SULFONATES

(vs very strong, v strong, b broad; D duplet, M multiplet, S singlet, T triplet)

Compound	IR (cm^{-1})			^1H NMR (ppm)	
	$\nu_{\text{as}}(\text{SO}_2)$	$\nu_{\text{s}}(\text{SO}_2)$	$\nu(\text{SO})$	Ph(-Sb)	Sulphonate
1	1230 vs	1155 vs	1037 vs	7.76(M)	2.63(S) (CH_3)
2	1275 vs, b	1145 vs, b	1035 vs	7.72(M)	–
3	1236 s	1157vs	1031vs	7.72(M)	3.85(T) ($\text{OCH}_2\text{CH}_2\text{S}$); 2.95(T) ($\text{OCH}_2\text{CH}_2\text{S}$)
4	1250 vs	1150 vs	1010 vs/993 vs	7.75(M)	7.33(M) (<i>m</i> -H and <i>p</i> -H; <i>o</i> -H superimposed)
5	1250 s	1160 vs	1010 vs/1000 vs	7.68(M)	7.11(D) (<i>m</i> -H; <i>o</i> -H superimposed) 2.29(S) (CH_3)
6	1258 vs	1212 vs/1192 vs	1027 vs	7.68(M)	8.37–8.03(M) ($\text{C}_6\text{H}_3(\text{NO}_2)_2$)

some organotin compounds [15], while tridentate coordination was inferred for some organothallium compounds [16]. No IR data have previously been reported for unidentate sulphonates such as **4**, $\text{Ph}_4\text{BiO}_3\text{SC}_6\text{H}_4\text{CH}_3$ [17] (which has recently been shown by X-ray methods to have a similar structure to **4**), and $\text{Me}_3\text{SnO}_3\text{SC}_6\text{H}_5 \cdot \text{H}_2\text{O}$ [18]). From the structure of **4** it follows that the O_3S group has local C_s symmetry, and therefore three SO stretching vibrations are to be expected in the IR spectrum, and three such bands are present (see Table 5); $\nu(\text{SO})$ is split into two bands at 1010 and 993 cm^{-1} ; the assignment is supported by comparison with data for sulphonic acid esters [19] in which $\nu(\text{SO})$ is found at about 700–800 cm^{-1} . The shift to higher wave numbers in **4** is to be expected since the S–O(1) bond should have a higher bond order because of the ionic character of the O(1)–Sb bond. Similarly the shift of $\nu_{\text{as}}(\text{SO}_2)$, found at 1250 cm^{-1} in **4** and at about 1350 cm^{-1} in sulphonic acid esters, can be correlated with the lower multiple bond character in the S–O(2) and S–O(3) bonds as compared with the esters.

The $\nu(\text{SO}_2)$ and $\nu(\text{SO})$ bonds for the other sulphonic acid derivatives **1**, **2**, **3**, **5** and **6** appear at similar positions (Table 5). The higher values in **2** and **6** are to be associated with the electron-withdrawing effect of the fluoro and nitro substituents in the organo group of the sulphonate ligand.

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