The Direct Synthesis of Arylxenon Trifluoromethanesulfonates via Electrophilic Substitution

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Abstract. The reaction of xenonbis(trifluoroacetate) and trifluoromethanesulfonic acid (triflic acid) gave the new, highly reactive unsymmetrical xenon-oxo species CF₃COOXeOSO₂CF₃. Benzene derivates, containing electron withdrawing substituents such as -F, -CF₃, -Cl or -NO₂ were electrophilic attacked by this intermediate to yield arylxenon trifluoromethanesulfonates. Via this one-pot synthesis trifluoromethanesulfonates with the cations [Xe(2,4,6- $F_3C_6H_2$]⁺, [Xe(2-F-5-NO₂C₆H₃)]⁺, [Xe(2-F-5-CF₃C₆H₃)]⁺ and $[Xe(3,5-(CF_3)_2C_6H_3)]^+$ were prepared. All compounds were characterized by their NMR, mass, and vibrational spectra.

Additionally, several new arylxenon trifluoromethanesulfonates were detected by $^{129}\rm Xe-NMR$ spectroscopy as products of the reaction of $1,3\text{-}F_2C_6H_4$ and further deactivated benzenes with xenontrifluoroacetate trifluoromethane sulfonate. Fluoro substituents in ortho position to xenon significantly increase the thermal stability of the arylxenon trifluoromethanesulfonates obtained.

The molecular structure of $[Xe(2,6-F_2C_6H_3)][OSO_2CF_3]$ was determined by single crystal diffraction methods. The arylxenon unit is weakly coordinated by one oxygen atom of the CF₃SO₃ anion. The salt crystallizes in the triclinic space group P1, a = 880.9(3) pm, b = 1093.9(5) pm, c =1209.8(5) pm, $\alpha = 89.04(4)^\circ$, $\beta = 74.23(3)^\circ$, $\gamma = 86.03(3)^\circ$, Z = 4.

Keywords: Arylxenon trifluoromethanesulfonates; electrophilic aromatic substitution; xenontrifluoroacetate trifluoromethanesulfonate; NMR spectra; X-ray crystal structure

Die direkte Synthese von Arylxenontrifluormethansulfonaten durch elektrophile Substitution

Inhaltsübersicht. Bei der Reaktion von Xenonbis(trifluoracetat) mit Trifluormethansulfonsäure wird die neue, hochreaktive, unsymmetrische Xenon-Sauerstoff-Verbindung CF₃COOXeOSO₂CF₃ erzeugt. Benzolderivate mit elektronenziehenden Substituenten wie F, CF₃, Cl und NO₂ werden von diesem Intermediat unter Bildung von Arylxenontrifluormethansulfonaten elektrophil angegriffen. Über diese Eintopfsynthese wurden Trifluormethansulfonate mit den Kationen [Xe(2,4,6-F₃C₆H₂)]⁺, [Xe(2-F-5-NO₂C₆H₃)]⁺,

Prof. Dr. D. Naumann Institut für Anorganische Chemie Universität zu Köln Greinstraße 6 D-50939 Köln Fax: 02 21/4 70-51 96 $[Xe(2-F-5-CF_3C_6H_3)]^+$ und $[Xe(3,5-(CF_3)_2C_6H_3)]^+$ synthetisiert. Alle Verbindungen wurden durch ihre NMR-, Massenund Schwingungsspektren charakterisiert.

Zusätzlich wurden mehrere neue Arylxenontrifluormethansulfonate als Produkte der Umsetzungen von 1,3- $F_2C_6H_4$ und weiteren desaktivierten Benzolen mit Xenon(trifluoracetat)trifluormethansulfonat anhand der ¹²⁹Xe-NMR-Spektren identifiziert.

Fluorsubstituenten in ortho-Position zu Xenon erhöhen signifikant die thermische Stabilität der Arylxenontrifluormethansulfonate.

Die Molekülstruktur von $[Xe(2,6-F_2C_6H_3)][OSO_2CF_3]$ wurde durch eine Einkristallröntgenstrukturanalyse bestimmt. Die Arylxenoneinheit koordiniert schwach mit einem Sauerstoffatom des CF₃SO₃-Anions. Die Verbindung kristallisiert in der triklinen Raumgruppe mit a = 880.9(3) pm, b = 1093.9(5) pm, c = 1209.8(5) pm, α = 89.04(4)°, β = 74.23(3)°, γ = 86.03(3)°, Z = 4.

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Introduction

At present time, carbon is the element of lowest electronegativity which forms a stable covalent bond to xenon, although the existence of a xenon-boron bond in FXeBF₂ [1] and a xenon-silicon bond in [F₃SiXe]⁺ [2] has been reported. In 1979 *Lagow* et al. reported about the plasma induced reaction of XeF₂ and CF₃-radicals to give Xe(CF₃)₂ but until today the value of these early observations is controversially discussed [3]. In 1989 pentafluorophenylxenon borates were prepared from XeF₂ and B(C₆F₅)₃ and characterized by their NMR spectra being the first compounds with a stable Xe–C-bond [4–6].

In the following years several arylxenon derivatives were prepared via exchange reactions of XeF_2 and triarylboranes [7–9]. Anion exchange reactions were studied which yielded stable compounds in the cases of the hexafluoroarsenate [6], the pentafluorobenzoate [10], the trifluoromethanesulfonate [11] and with anions of CH- and NH-super acids [12]. However, all synthetic approaches had in common that fluorine, chlorine and trifluoromethyl substituted triarylboranes had to be used as aryltransfer reagents. Unfortunately, many of these boranes were unknown and therefore had to be prepared and characterized in advance [13].

Recently we published a communication about the direct synthesis of arylxenon trifluoromethanesulfonates via electrophilic substitution of commercially available F- and CF₃-substituted benzenes [14]. Herein we give detailled informations about some structural features of arylxenon trifluoromethanesulfonates and the reaction mechanism involving the reactive species $CF_3COOXeOSO_2CF_3$.

Results and Discussion

The Preparation of CF₃COOXeOSO₂CF₃

Electrophilic substitution of aromatic systems with compounds of the general formula RI(OR')(OR'')(R = per-, polyfluoroalkyl, alkenyl, alkinyl, aryl; R' = COCH₃, COCF₃, H; R'' = COCH₃, COCF₃, SO₂(4-CH₃C₆H₄), SO₃H, SO₂CF₃) is a common reaction for the synthesis of aryl(organo)iodine(III) species, R(Ar)I(OR'') [15, 16]. *Tyrra, Butler* and *Naumann* observed an electrophilic attack of iodine tris(trifluoroacetate) to pentafluorobenzene in the presence of trifluoromethanesulfonic acid with formation of bis(pentafluorophenyl)iodine trifluoromethanesulfonate [17].

 $I(OCOCF_3)_3 + 2C_6F_5H + CF_3SO_3H$

 \rightarrow [I(C₆F₅)₂]OSO₂CF₃ + 3 CF₃COOH

These results as well as previous observations revealed that mixed substituted iodine(III) intermediates, $I(OCOCF_3)_2OSO_2CF_3$ and $ArI(OCOCF_3)OSO_2CF_3$ are the reactive intermediates within these reaction sequences. But, unfortunately, such an intermediate could not be detected by the means of any kind of spectroscopy.

The suggestion of such a derivative being an intermediate is now supported by our new investigations in xenon chemistry.

The reaction of $Xe(OCOCF_3)_2$ and CF_3SO_3H in e.g. CCl_3F gave a new xenon-oxo species which must be regarded as the xenon analogue to the iodine species mentioned above:

 $Xe(OCOCF_3)_2 + CF_3SO_3H$

 \Rightarrow CF₃COOXeOSO₂CF₃ + CF₃COOH

After adding CF₃SO₃H to xenonbis(trifluoroacetate) in CCl₃F solution at -40 °C, the precipitation of a vellow solid indicated the formation of CF₃COOXeOSO₂CF₃. Using a 1:1-molar ratio of $Xe(OCOCF_3)_2$ and CF_3SO_3H , the equilibrium was still shifted to the left side. The integrative ratio of the signals of Xe(OCOCF₃)₂ and CF₃COOXeOSO₂CF₃ in the ¹²⁹Xe-NMR spectra was 4:1. Using a ten-fold excess of trifluoromethanesulfonic acid, the equilibrium was shifted to the product side and the intensity of the resonance of Xe(OCOCF₃)₂ ($\delta = -700$ ppm, singlet) in ¹²⁹Xe-NMR spectra decreased in favour of the resonance of CF₃COOXeOSO₂CF₃.

The chemical shift of the unsymmetrical substituted intermediate ($\delta = -387$ ppm, singlet, (CF₃CO)₂O) is solvent dependent (Table 1) and comparable to that measured for FXeOCOCF₃ ($\delta = -355$ ppm, CH₃CN) [18]. The shift together with the high reactivity reveals that this compound consists of strongly polarized but covalent molecules. Unsymmetrically substituted covalent xenon-oxo compounds are unknown with the exception of F₅TeOXeOSeF₅ [19]. Strongly ionic xenonoxo compounds e.g. [F₅TeOXe][AsF₆] ($\delta = +200$ ppm) show resonance at significantly higher frequency [20].

Compared with $Xe(OCOCF_3)_2$, the mixed substituted $CF_3COOXeOSO_2CF_3$ appears to be even more explosive in the solid state. Therefore, after some vigorous explosions we stopped our attempts to isolate the pure substance.

The resonance of [FXe][OSO₂CF₃] (δ = +222 ppm, dublet, ¹J(¹²⁹Xe-¹⁹F) = 5728 Hz) was observed in the

Table 1 ¹²⁹Xe-NMR chemical shifts of $Xe(OCOCF_3)_2$ and $CF_3COOXeOSO_2CF_3$ in different solvents.

Xe-O-derivative	$\delta(^{129}\text{Xe})$	solvent	
Xe(OCOCF ₃) ₂	-770	(CF ₃ CO) ₂ O	
	-769	CCl_2FCClF_2	
	-700	CCl ₃ F	
CF ₃ COOXeOSO ₂ C	CF ₃ -387	(CF ₃ CO) ₂ O	
	-267	CCl_2FCClF_2	
	-289	CCl ₃ F	

¹²⁹Xe-NMR spectra of the reaction mixtures after addition of CF_3SO_3H , unless the primary conversion of XeF_2 into the trifluoroacetate had been complete.

The ¹⁹F-NMR spectrum of the mixture Xe(OCOCF₃)₂/CF₃SO₃H in CCl₃F/CH₃CN at -40 °C shows the resonances of CF₃COOH ($\delta = -75.0$ ppm), $(\delta = -77.5 \text{ ppm})$ $Xe(OCOCF_3)_2$ CF₃SO₃H and $(\delta = -70.6 \text{ ppm})$. The resonances of the CF₃CO₂-group and the CF₃SO₃-group of CF₃COOXeOSO₂CF₃ are sharp singlets at $\delta = -69.2$ and -75.6 ppm with an integrative ratio of approximately 1:1. The integrative ratio of Xe(OCOCF₃)₂ and CF₃COOXeOSO₂CF₃ was 1:4.5 in the ¹⁹F-NMR spectrum and 1:4 in the ¹²⁹Xe-NMR spectrum.

Analogously, in the ¹²⁹Xe-NMR spectrum of a mixture of Xe(OCOCF₃)₂ and HOSO₂F in CCl₃F-solution a new resonance at $\delta = -267$ ppm appeared which was assigned to CF₃COOXeOSO₂F. No evidence for disubstituted Xe(OSO₂F)₂ was found. The reactivity of CF₃COOXeOSO₂F is similar to that of the trifluoromethanesulfonate. The compound reacts in a similar manner as the trifluoromethanesulfonate with 1,3,5trifluorobenzene to yield 2,4,6-trifluorophenylxenon fluorosulfate which was detected in the ¹²⁹Xe-NMR spectrum of the reaction mixture.

Reactions of CF₃COOXeOSO₂CF₃ with substituted benzenes

Due to the explosive nature of $Xe(OCOCF_3)_2$ in the solid state, the syntheses of arylxenon trifluoromethanesulfonates were performed in solution or suspension, respectively. Therefore, in a primary step $Xe(OCOCF_3)_2$ was prepared in CCl_3F , converted into $CF_3COOXeOSO_2CF_3$ by addition of CF_3SO_3H and finally reacted with the corresponding fluorobenzene.

 $XeF_2 + 2CF_3COOH \rightarrow Xe(OCOCF_3)_2 + 2HF$

 $Xe(OCOCF_3)_2 + CF_3SO_3H$

 \Rightarrow CF₃COOXeOSO₂CF₃ + CF₃COOH

 $CF_{3}COOXeOSO_{2}CF_{3} + Ar_{f}H$ $\rightarrow [Ar_{f}Xe]OSO_{2}CF_{3} + CF_{3}COOH$

The benzenes used and the xenon derivatives obtained are listed in Table 2.

After addition of the corresponding benzene the major quantity of CCl_3F and other volatile substances were evaporated in vacuo. When adding 2–3 ml of CH_3CN to the reaction mixture, the formation of the arylxenon trifluoromethanesulfonates could be monitored directly by ¹²⁹Xe-NMR spectroscopy.

The reaction with 1,3- $F_2C_6H_4$

In contrast to the reaction of

 $(2,6-F_2C_6H_3)I(OCOCF_3)_2$ with $1,3-F_2C_6H_4$ in the presence of CF_3SO_3H which exclusively yielded [(2,6-

 $F_2C_6H_3)_2I]OSO_2CF_3$ [21], CF_3COOXeOSO_2CF_3 reacted with this benzene less selectively. The ¹²⁹Xe-NMR spectrum of the reaction mixture showed the resonances of at least five arylxenon derivatives. Due to the general stabilizing effect of two fluorine atoms in ring positions 2 and 6, the formation of the thermodynamically more stable cation $[Xe(2,6-F_2C_6H_3)]^+$ was expected to be favoured. But in this case the formation of the cation $[Xe(2,4-F_2C_6H_3)]^+$ was strongly preferred. The integrative ratio (¹²⁹Xe-NMR spectra) was 10:1 in favour of the 2,4-substituted compound. This result indicates a kinetically controlled reaction, as it is usual in most electrophilic substitutions of aromatic systems with more than one substituent [22].

The other xenon-containing derivatives observed in the NMR spectra might be formed by double electrophilic substitions. In a primary step electrophilic attack by a CF₃CO- or CF₃CO₂-cation might give trifluoroacetoxy- or trifluoroacetato-substituted difluorobenzenes which will be attacked in a second reaction step by the CF₃COOXe-cation or vice versa.

Criteria for selective substitution

The course of the reaction mentioned above allows us to formulate some criteria for successful and selective substitutions:

i) Group-electronegativity of the phenyl group should be increased by electron-withdrawing substituents e.g. -F, -Cl, $-CF_3$, $-NO_2$.

ii) The directing effects of the substituents should be uniform.

These postulates are based on the following observations.

ad i) Adding benzene, C_6H_6 , to a yellow suspension of $CF_3COOXeOSO_2CF_3$ in CCl_3F , the reaction mixture immediately became black and a perceptible xenon pressure was built up. No xenon-containing compounds could be detected in the NMR spectra of the tar. Similar observations were made using toluene, aniline, phenol or biphenyl as reaction partners. Only the presence of chlorine, fluorine, trifluoromethyl, or nitro substituents effects a stabilization of the xenoncarbon bond and allows at least the NMR spectroscopic detection of arylxenon derivatives (Table 2).

ad ii) The general rules for the orientation in electrophilic aromatic substitution reactions of benzenes with more than one substituent can be applied to predict the position of an electrophilic attack of xenon and to prevent the formation of isomeres. The symmetrically substituted molecule 1,3,5-trifluorobenzene selectively reacts with CF₃COOXeOSO₂CF₃ to 2,4,6trifluorophenylxenon trifluoromethanesulfonate (Table 3), which can be isolated as a pure solid. In this case the uniform ortho- (and para-) directing inductive effect of the fluorine atoms leads to the exclusive

ArH	[ArXe] ⁺	$\delta(^{129}\text{Xe})$	$^{3}J(^{129}Xe^{-19}F)$	solvent	temp.
$F \to F \to F$	$F \xrightarrow{F} F$	–1983, t	67	CH ₃ CN	238
		–1853, s		CH ₃ CN	238
F	FXe	-2029, d ^a)	48	CH ₃ CN	238
•	Ke F	2127, t	53	-	
F F ₃ C	Xe CF3	–1868, m –1873, m		CD ₃ CN	238
⟨F	Xe	–1924, s		CH ₃ CN/CH ₂ Cl ₂	223
CI_CI	Xe	–1903, s		CH ₃ CN/CH ₂ Cl ₂	223
	∑Xe	–1849, s		CH ₃ CN	233
O ₂ N O ₂ N	O ₂ N O ₂ N	–1805, s		CH ₃ CN/CH ₂ Cl ₂	233

Table 2 ¹²⁹Xe-NMR data of various arylxenon trifluoromethanesulfonates from the reaction mixtures of CF₃COOXeOSO₂CF₃ and the corresponding benzene (δ in ppm, J in Hz, temperature in K).

^a) Four additional dublets of low intensity were detected at $\delta = -1896, -1952, -1975$ and -1981 ppm.

formation of one isomer. In the cases of 1-fluoro-4-trifluoromethyl-benzene and 1-fluoro-4-nitrobenzene the ortho-directing fluorine and the meta-directing CF_3 or NO_2 group reinforce each other favouring the orthoposition next to fluorine respectively the meta-position to the CF_3 - and NO_2 -group to be attacked by the xenon electrophile. This proposal is supported by the isolation and characterization of the corresponding xenon compounds.

1,3-Bis(trifluoromethyl)benzene is substituted by

xenon in meta position to both CF_3 -groups influenced by the CF_3 -ligand as a strongly meta directing substituent. In analogy 1,3-dinitrobenzene reacts to the 3,5dinitrophenylxenon trifluoromethanesulfonate; however, attempts to isolate this compound failed.

In 1-F-3-CF₃C₆F₄ the directing effects are not uniform. The influence of the fluorine substituent favours an attack in the 2- and 4-position, whereas the influence of the CF₃-group the 5-position [22]. The absence of xenon-satellites surrounding the resonances

Ar _f H	[Ar _f Xe] ⁺	$\delta(^{129}\text{Xe})$	$^{3}J(^{129}Xe^{-19}F)$	$\delta(^{19}\mathrm{F})$	$\delta(^{1}\mathrm{H})$	dec. (°C)
F F	F-Xe	–2083 ^a)	57.1	(F-2,6) -96.2 (F-4) -96.4 (CF ₃ SO ₃) -77.8	(H-3,5) 7.3	+110 (DTA)
F ₃ C-	F F_{3C} F	-1977	48.1	(F-2) –94.8 (CF ₃) –62.1 (CF ₃ SO ₃) –79.0	(H-3) 7.7 (H-4) 8.1 (H-6) 8.5	+75 (DTA)
0 ₂ N-	F O_2N F Xe	–1950 ^a)	47.8	(F-2) –91.8 (CF ₃ SO ₃) –79.0	(H-3) 7.8 (H-4) 8.7 (H-6) 9.1	+88 (DTA)
F ₃ C	F ₃ C F ₃ C	-1816	27.0 ^b)	(CF ₃) –61.7 (CF ₃ SO ₃) –78.1	(H-2,6) 8.7 (H-4) 8.4	-10 to -5

Table 3 ¹²⁹Xe-, ¹⁹F- and ¹H-NMR data and decomposition points of arylxenon trifluoromethanesulfonates (T = 238 K; δ in ppm, J in Hz).

^a) 253 K; ^b) ${}^{3}J({}^{129}Xe-{}^{1}H)$.

of the fluorine atoms bonded directly to the ring in the ¹⁹F-NMR spectrum as well as the complexity of the ¹²⁹Xe-NMR signals suggest that no products with xenon directly neighboured to fluorine are formed. However, the ¹²⁹Xe chemical shifts unambiguously reveal the formation of two arylxenon compounds in a ratio of approximately 15:1, which are suggested to be $[Xe(3-F-5-CF_3C_6H_3)]^+$ and $[Xe(2-CF_3-4-FC_6H_3)]^+$.

As mentioned above, one reason for the high reactivity of the nonsymmetrical disubstituted xenon-oxo compound is its polarisation into a cationic $[CF_3COOXe]^+$ unit and the $CF_3SO_3^-$ -anion Therefore, even strongly deactivated benzenes namely 1,3- $(CF_3)_2C_6H_4$ and 1,3- $(NO_2)_2C_6H_4$ are attacked by this electrophile. Furthermore the "one pot"-reaction proceeds in the presence of the strong acids, CF_3SO_3H , CF_3COOH and HF. A superacidic medium according to

 $HF + HOSO_2CF_3 \rightleftharpoons [H_2F]^+ + OSO_2CF_3^-$

must be suggested to be intermediately formed [23]. Taking into account that the nitration of 1,3-dinitrobenzene by the NO₂⁺-cation only proceeds in superacedic media [24], following *Olah*'s concept for generation of superelectrophiles by proton solvation in superacidic media [25], the [CF₃COOXe]⁺-cation must also be regarded as a strong electrophile in this medium.

No substitution is observed in attempted reactions with the even more deactivated $1,3,5-(CF_3)_3C_6H_3$.



In contrast, 1,3,5-trichlorobenzene which is also deactivated towards an electrophilic attack as the trifluoromethyl derivative but substituted by strongly ortho- and para-directing chlorine atoms, spontaneously reacts with the xenon electrophile to give the arylxenon compound, [Xe(2,4,6corresponding $Cl_3C_6H_3)$]⁺ (detected in the ¹²⁹Xe-NMR spectra of the reaction mixtures), although the van der Waals radii of chlorine and the CF₃-group are of comparable size [26]. Due to the thermal instabilities of chlorophenylxenon derivatives [8], all attempts to isolate 2,4,6-trichlorophenylxenon trifluoromethanesulfonate failed. A stabilization by chlorine substituents in ortho position to xenon appears to be less effective as in comparable fluorophenylxenon salts. Similar observations were made during the attempted preparation of chlorophenylxenon tetrafluoroborates via reactions of XeF_2 and the corresponding boranes [8].

Isolation and characterization of arylxenon compounds

The "one pot reaction" increases the problems in purification of arylxenon trifluoromethanesulfonates. Byproducts e.g. HF, CF_3COOH , probably CF_3CO_2 -substituted benzenes and unreacted starting materials have to be separated. Distillation of the major part of the volatile products at low temperature in vacuo leads to an oily residue containing trifluoroacetic acid and the corresponding arylxenon compound as the major products. Extracting the arylxenon salts with less polar solvents such as dichloromethane, toluene or n-hexane failed.

However, after adding some drops of diethylether to a toluene suspension of the residue, it is partly dissolved and the arylxenon trifluoromethanesulfonates precipitate while cooling. After washing the precipitate several times with cold CH_2Cl_2 and drying in vacuo, the xenon salts are obtained as colourless solids. Neither the ¹H-NMR nor the vibrational spectra give any evidence for a complexation of the arylxenon trifluoromethanesulfonates with diethyl ether in solution or in the solid state.

All compounds are colourless, fine powdered solids which are insoluble in toluene, diethylether and CH_2Cl_2 , but readily soluble in CH_3CN .

For a period of about one hour the arylxenon trifluoromethanesulfonates which are fluorine-substituted in 2-position appear to be partly soluble in water without decomposition, e.g. the resonance of [Xe(2,4,6-F₃C₆H₂)][OSO₂CF₃] is detected in the ¹²⁹Xe-NMR spectrum at δ -2080 ppm. Storing the solution overnight leads to a complete decomposition with evolution of elemental xenon. The remaining yellow residue consists of condensed and hydroxy-substituted aromatics which are identified by their mass spectra, e.g. $[(HOC_6F_3H)(C_6F_3H)OSO_2CF_3]^+$, m/e = 426 or $[(HOC_6F_3H)OSO_2CF_3]^+$, m/e = 296.

NMR spectra of the arylxenon trifluoromethanesulfonates

The NMR data of the isolated compounds are summarized in Tables 3 and 4.

The ¹²⁹Xe-NMR signal of [Xe(3,5-(CF₃)₂C₆H₃)][OSO₂CF₃] is split into a broadened triplet ($\Delta_{1/2} \approx 10.4$ Hz) which is reduced to a singlet ($\Delta_{1/2} \approx 8.8$ Hz) recording a ¹²⁹Xe{¹H}-NMR spectrum of the same sample. Due to our knowledge it is the first determination of a ³J(¹²⁹Xe – ¹H)-coupling constant in arylxenon compounds; the absolute value of the coupling constant (27 Hz) is in good agreement with that determined for fluoro(hydrogencyanide)xenon hexafluoroarsenate (³J(¹²⁹Xe–¹H) = 26 Hz) [27].

Empirically, the ¹²⁹Xe-NMR chemical shift roughly correlates with the thermal stability of the arylxenon trifluoromethanesulfonates in the solid state (see Table 3) with the exception of that of [Xe(2-F-5-NO₂- C_6H_3)][OSO₂CF₃]. As already published for several arylxenon tetrafluoroborates [7], these effects appear to be independent on the anion. Generally, absorption at highest field is connected with the highest thermal stability of the compound in the solid.

In the ¹³C-NMR spectra the CF₃-groups of the trifluoromethanesulfonate anions are detected at 121.5 ± 1 ppm as quartets with a characteristic coupling constant ¹J(¹⁹F-¹³C) = 319.5 \pm 1 Hz.

The signal of the C-1 atom is symmetrically surrounded by the ¹²⁹Xe satellites showing the same splitting as the inner lines. The absolute values of the ¹J(¹²⁹Xe–¹³C) couplings in [ArXe]⁺ vary between 119 Hz (Ar = C₆F₅) [6] and 72 Hz (Ar = 3,5-(CF₃)₂C₆H₃).

An explanation for the different values of the ${}^{1}J({}^{129}Xe{-}^{13}C)$ couplings in the $[Xe(2,4,6-F_{3}C_{6}H_{2})]^{+}$ and $[Xe(2,6-F_{2}C_{6}H_{3})]^{+}$ -ions cannot be given (Table 4). It has only to be noted that the coupling varies between the two given extrema (104 Hz and 113.1 Hz as well as 99 Hz [7] and 106 Hz [11]) in several NMR experiments without any obvious relation to temperature or concentration.

A typical ¹³C-NMR spectrum is shown in Figure 1 exemplarily for $[Xe(2-F-5-NO_2-C_6H_3)][OSO_2CF_3]$.

Analogously to the effects observed in the ¹²⁹Xe-NMR spectra, the resonance of the C-1-atom is shifted to higher field with increasing stability of the arylxenon trifluoromethanesulfonates in the solid state. However, a direct correlation of ¹³C- and ¹²⁹Xe-NMR chemical shifts does not fit sufficiently. Comparing the ¹³C-NMR shifts of the trifluoromethanesulfonates and the corresponding arylxenon tetrafluoroborates (s. Table 4) the different anions do not appear to influence significantly the electronic character of the arylxenon cations in CH₃CN solution.

Table 4	¹³ C-NMR data of arylxenon(I	() trifluoromethansulfonates	and tetrafluoroborates i	n CD ₃ CN solution (a	§ in ppm, J in
Hz, temp	perature in °C).				

cation	anion	temp.	δ (C-1) ¹ J(¹²⁹ Xe ⁻¹³ C)	δ(C-2)	δ(C-3)	δ(C-4)	δ(C-5)	δ(C-6)	$\frac{\delta(CF_3)}{{}^{1}J({}^{19}F{-}^{13}C)}$	$\delta(OSO_2CF_3)$ ${}^{1}J({}^{19}F_{-}{}^{13}C)$	dec.
Ke F	OSO ₂ CF ₃ ^a)	RT	89.4 106.1	157.5	115.5	138.1	115.5	157.5		121.3 319.1	132
⟨◯ _F ×e	BF4 ^b)	-30	88.8 99.0	156.8	115.2	137.8	115.2	156.8			130
FXe	OSO ₂ CF ₃	-20	84.1 113.1	158.4	105.0	167.5	105.0	158.4		121.4 319.1	110
FXe	BF4 ^b)	-30	83.8 104.0	158.4	105.0	167.8	105.0	158.4			128
CF ₃ -Xe	OSO ₂ CF ₃	-35	103.1 92.0	158.2	121.1	134.4	130.6	131.4	123.0 273.2	121.5 319.4	75
NO ₂ Xe	OSO ₂ CF ₃	-20	102.1 97.1	159.8	120.4	129.5	146.6	132.2		121.5 319.5	88
CF3 Xe	OSO ₂ CF ₃	-35	117.9 72.0	133.7	135.7	128.8	135.7	133.7	122.5 273.2	121.1 318.5	-10- -5

^a) Taken from ref. 11, ^b) taken from ref. 7.

The behaviour of $[Xe(2,6-F_2C_6H_3)]$ -salts in acetonitrile solution

The ¹⁹F- (Figure 2) and the ¹²⁹Xe-NMR spectra of a mixture of equimolar amounts of $[Xe(2,6-F_2C_6H_3)][OSO_2CF_3]$, $[Xe(2,6-F_2C_6H_3)][BF_4]$ and $[Xe(2,6-F_2C_6H_3)][AsF_6]$ show only one well-resolved resonance for the arylxenon cation. This observation indicates a complete dissociation of all three derivatives in CH₃CN solution in terms of solvent devided ion pairs without any cation-anion interaction in solution. Therefore, a coordination of the cation with solvent molecules must be suggested. On the other hand single crystals of the tetrafluoroborate [28] and the trifluoromethanesulfonate have been grown from aceto-

nitrile solutions. In the solid state both compounds are free of complexing acetonitrile and show a significant cation-anion contact (see below).

Mass spectra

EI mass-spectra of $[Xe(Ar_f)][OSO_2CF_3]$ indicate a spontaneous and complete elimination of elemental xenon accompanied by the sulfonation of the aromatic ring.

The fragments detected are those of $Ar_fOSO_2CF_3$ and ions deriving from its decay.

 $[Xe(Ar_{f}][OSO_{2}CF_{3}] \rightarrow [Ar_{f}OSO_{2}CF_{3}]^{+} \rightarrow [Ar_{f}OCF_{3}]^{+} \rightarrow [Ar_{f}O]^{+}$



Fig. 1 ${}^{13}C{}^{1}H$ -NMR spectrum of [Xe(2-F-5-NO₂C₆H₃)]⁺[OSO₂CF₃]⁻ in CD₃CN at 253 K.



Fig. 2 ¹⁹F-NMR spectrum of the mixture of

 $[Xe(2,6-F_2C_6H_3)]^+[X]^-$ (X = OSO₂CF₃, BF₄, AsF₆) in the molar ratio 1:1:1 in CD₃CN at room temperature. Asterisks denote xenon satellites of the ortho-fluorine resonance (δ = -99,1 ppm).



Fig. 3 FAB mass spectrum of $[Xe(2,4,6-F_3C_6H_2)][OSO_2CF_3]$ (dissolved in CF_3COOH/CH_3CN ; BA matrix; m/e: 260/263 $[Xe(2,4,6-F_3C_6H_2]^+; 132 [C_6H_3F_3]^+;$ further peaks are assigned to the matrix and the solvent).

Recently we reported about the first mass-spectrometric detection of an arylxenon cation by the means of FAB-mass spectrometry [29].

Under comparable conditions as used for the detection of $[Xe(2,6-F_2C_6H_3)]^+$ the ion $[Xe(2,4,6-F_3C_6H_2)]^+$ shows the cation peak (m/e = 262 (¹³¹Xe)) with 100% intensity with the typical isotopic pattern of xenon (Figure 3).

Vibrational spectra of fluoroarylxenon trifluoromethanesulfonates

The Raman spectra of $[Xe(2,4,6-F_3C_6H_2)][OSO_2CF_3]$ (Figure 4), $[Xe(2,6-F_2C_6H_3)][OSO_2CF_3]$, $[Xe(2-F-5-NO_2C_6H_3)][OSO_2CF_3]$ and

 $[Xe(2-F-5-CF_3C_6H_3)][OSO_2CF_3]$ were recorded. The frequencies observed and the assignments are listed in Table 5. Frohn reported about a Raman active streching mode of the Xe–C bond in $[Xe(C_6F_5)][AsF_6]$ at 205 cm⁻¹ [30].

The Raman bands of the v(C-I) of the related fluoroiodobenzenes occur in the range of 150–270 cm⁻¹ [31]. As the corresponding arylxenon cations are isoelectronic with the iodobenzenes and the masses are comparable, the v(C-Xe) bands should be observed in the same region as the v(C-I) bands. Indeed, all values measured for the arylxenon trifluoromethanesulfonates vary around $200 \pm 6 \text{ cm}^{-1}$ (Table 6). The different substituents have no significant influence on the frequency of the v(C-Xe) band. As expected, the frequency decreases with increasing mass of the phenyl group.

In the vibrational spectra no evidence is found for complexing CH₃CN in the solids. The absence of a complexing ligand is additionally confirmed by the single crystal structure analysis of $[Xe(2,6-F_2C_6H_3)][OSO_2CF_3]$.



Fig. 4 Raman spectrum of [Xe(2,4,6-F₃C₆H₂)][OSO₂CF₃] at room temperature.

Table 5 Raman frequencies (cm^{-1}) and relative intensities of arylxenon trifluoromethanesulfonates ([X] = OSO₂CF₃) at room temperature.

[Xe(2,4,6- F ₃ C ₆ H ₂)][X]	[Xe(2-F-5- CF ₃ C ₆ H ₃)][X]	$[Xe(2-F-5-NO_2C_6H_3)][X]$	assignment
3076 (1.3)		10 11	v(CH) _{ring}
		1584 (1.6)	$v(CF)_{ring}$
		1353 (10.0)	· · · · · · · · · · · · · · · · · · ·
1242 (1.7)	1229 (2.4)	× ,	$v(CF_3)$
1182 (0.8)			v(CC) _{ring}
. ,		1115 (2.1)	
1024 (6.7)	1027(10.0)	1024 (3.5)	$v(SO_2)$
1008 (1.3)			,
	842 (1.8)		
764 (1.1)	764 (2.5)		$\delta_{as}(CF_3)$
	664 (2.4)	666 (1.5)	$\delta(CC)_{ring}$
562 (4.1)	570 (1.1)	570 (0.3)	$\delta_{\rm s}({\rm CF}_3)$
506 (1.0)	· · ·		$\delta(SO_2)$
. ,	479 (2.2)	458 (1.1)	,
	401 (3.3)		
356 (3.7)	352 (2.0)		various δ
316 (1.2)	318 (2.5)	322 (1.5)	
257 (1.6)		270 (3.5)	
222 (1.4)	236 (7.3)		
203 (10.0)	194 (6.2)	203 (6.7)	v(XeC)
149 (0.7)	166 (5.2)	138 (2.7)	
. ,	119 (6.4)	98 (2.1)	

Different types of anions which weakly coordinate to the arylxenon cation do not influence the v(C-Xe)frequency significantly as shown for $[Xe(2,6-F_2C_6H_3)][OSO_2CF_3]$ (206 cm⁻¹) and $[Xe(2,6-F_2C_6H_3)][BF_4]$ (213 cm⁻¹).

Crystal structure of [Xe(2,6-F₂C₆H₃)][OSO₂CF₃]

For the crystal structure analysis the arylxenon trifluoromethanesulfonate was synthesized according to ref. [29].

Table 6 Raman frequencies of v(XeC) (cm⁻¹) of $[XeAr_{f}][OSO_{2}CF_{3}]$ as a function of the molecular weight (g mol⁻¹) of the substituted phenyl group at room temperature.

Ar _f	М	v(XeC)	
	113	206	
F-OF	131	203	
	140	203	
	163	194	

$$\begin{split} & [Xe(2,6\text{-}F_2\text{C}_6\text{H}_3)][BF_4] + (CH_3)_3\text{SiOSO}_2\text{C}F_3 \\ & \rightarrow [Xe(2,6\text{-}F_2\text{C}_6\text{H}_3)]\text{OSO}_2\text{C}F_3 + (CH_3)_3\text{SiF} + BF_3 \end{split}$$

 $[Xe(2,6-F_2C_6H_3)][OSO_2CF_3]$ crystallizes from CH₃CN solution in triclinic order. The structure consists of two independent ion-pairs with the cation $[Xe(2,6-F_2C_6H_3)]^+$ and the anion $[OSO_2CF_3]^-$ which are connected by short Xe–O-contacts (d(Xe–O) =268.7(9) pm, 282.9(10) pm) without any evidence for a complexation of the arylxenon cation with CH₃CN (Figure 5). In $[Xe(2,6-F_2C_6H_3)][BF_4]$, which crystallizes from CH₃CN in monoclinic order, cation and



Fig. 5 ORTEP drawing of the independent ion-pairs of $[Xe(2,6-F_2C_6H_3)][OSO_2CF_3]$, with 50% probability ellipsoids, hydrogen atoms are omitted.

anion are also weakly coordinated by a nearly linear C-Xe···F bridge $(\varphi(C-Xe···FBF_3) = 167.8^\circ, d(Xe···FBF_3) = 279.3(10) \text{ pm})$ [28].

In comparison, the X-ray structure analysis of $[Xe(C_6F_5)][(C_6F_5)_2BF_2]$ proves the linear coordination of the arylxenon cation with CH₃CN with the discrete unit $[C_6F_5Xe\cdots NCCH_3]^+$ (d(Xe $\cdots N$) = 268.1(8) pm) [6]. In this case the size of the bulky bis(pentafluorophenyl)difluoroborate anion perhaps is decisive for the absence of a direct contact to the arylxenon cation.

In $[Xe(2,6-F_2C_6H_3)][OSO_2CF_3]$ the arrangement of the charges (Xe for the cation, centre of gravity for the anion) shows a fivefold coordination for both,



Fig. 6 Stereo view of the unit cell of $[Xe(2,6-F_2C_6H_3)][OSO_2CF_3].$

cations and anions, and leads to layers perpendicular to [010] with the phenyl group between the layers (Figure 6).

In comparison with the crystal structure of [Xe(2,6- $F_2C_6H_3$][BF₄] the distances and bond angels are nearly identical. The bond lengths d(C-Xe) =207.9(9) pm and 209.2(9) pm correspond with those of comparable compounds [6, 10, 28]. Our proposal that fluorine substituents in 2- and 6-position of the phenyl group significantly increase the thermal stability of arylxenon cations [7] in the solid state by back-donation of electron density from the lone electron pairs of the fluorine atoms, is supported by the crystal structure analysis of $[Xe(2,6-F_2C_6H_3)][OSO_2CF_3]$. Stabilization without any spatial distorsion of the aromatic system is expressed by the distance $d(Xe \cdots F) = 309.8(6) \text{ pm}$ which is more than 12% shorter than the sum of the van der Waals-radii of xenon and fluorine (347 pm) [32]. Although the distance $Hg \cdots F$ in $Hg(C_6F_5)_2$ is more than twice the sum of van der Waals-radii of mercury and fluorine Dallas et al. [33] propose a similar stabilizing effect.

Alcock's model of secondary bonding [32] cannot be applied to this phenomenon in stabilization because significant deformations within the phenyl group are not observed.

Conclusion

The reaction of $Xe(OCOCF_3)_2$ and trifluoromethanesulfonic acid forms the highly reactive species $CF_3OCOXeOSO_2CF_3$, which undergoes electrophilic substitution with different deactivated benzenes to give arylxenon trifluoromethanesulfonates. Applying the rules for the direction of aromatic electrophilic substi-



Fig. 7 Resonances of FXeOCOCF₃ in the ¹⁹F-NMR spectrum of the mixture Xe(OCOCF₃)₂/HOSO₂CF₃ and Cd(CF₃)₂ · 2 CH₃CN in CD₃CN solution at 238 K. **a**: spread XeF signal at $\delta = -121.0$ ppm, **b**: spread CF₃CO₂ signal at $\delta = -71.6$ ppm (⁵J(¹⁹F-¹⁹F) = 5.5 Hz, asterisks denote xenon-satellites).

tution in benzene rings with more than one substituent, it is possible to predict the position of the electrophilic attack of xenon. This new "one-pot reaction" is a convenient route for the synthesis of arylxenon derivatives of strongly deactivated benzenes although the yields are not sufficient. The compounds obtained are saltlike derivatives as the tetrafluoroborates and the hexafluoroarsenates which is shown by the crystal structure analysis as well as the studies in solution.

Thus, the availability of CF₃COOXeOSO₂CF₃ directly from the system Xe(OCOCF₃)₂/HOSO₂CF₃ encouraged us to check the behaviour in reactions with Cd(CF₃)₂ · 2 CH₃CN. Unfortunately both derivatives react via the elimination of difluorocarbene giving FXeOCOCF₃ and Cd(CF₃)OSO₂CF₃. We were able to determine the ⁵J(¹⁹F-¹⁹F) long-range coupling for the first time supporting our proposal of the covalent nature of the Xe–O as well as the Xe–F bond in the molecule FXeOCOCF₃ (Figure 7) [18].

On the basis of these results $CF_3COOXeOSO_2CF_3$ might be regarded as a versatile tool for the synthesis of further new xenon-carbon compounds.

Experimental

Materials. All reactions were carried out in a dry nitrogen atmosphere, using Schlenk techniques. Solvents were purified using standard methods [34]. CCl_3F , CF_3COOH were received from Solvay Fluor und Derivate as gifts. $HOSO_2CF_3$ was purchased from ABCR; all aromatic derivatives from Aldrich. XeF_2 was synthesized by common methods [35]. $[Xe(2,6-F_2C_6H_3)][BF_4]$ was prepared according to ref. [7]. $[Xe(2,6-F_2C_6H_3)][AsF_6]$ was obtained from the tetrafluoroborate in liquid AsF₅ after evaporating BF₃ and excess AsF₅ in quantitative yield. Cd(CF₃)₂ · 2 CH₃CN was synthesized according to ref. [36].

NMR spectra. Nuclear magnetic resonance spectra were recorded on Bruker FT NMR spectrometers AMX 300 (¹⁹F, 282.4 MHz (CCl₃F, ext.); ¹²⁹Xe, 83.3 MHz (1 M XeF₂ in CH₃CN, ext.), ¹³C, 75.5 MHz ((CH₃)₄Si ext.)) and AC 200 (¹⁹F, 188.3 MHz; ¹H, 200.1 MHz ((CH₃)₄Si, ext.); ¹³C(¹H}, 50.3 MHz ((CH₃)₄Si, ext.)). A negative value indicates a shift to high field.

Vibrational spectra. Infrared spectra were recorded on a Perkin-Elmer PE 580 B spectrometer between polyethylene plates or using KBr pellets. The Raman spectra were run on a Jobin Yvon U 1000 spectrometer equipped with an Ar laser (Spectra Physics) operating at 514.5 nm.

Mass spectra. EI mass spectra were recorded on a modified Varian MAT CH5 spectrometer. The FAB mass spectrum was measured on a Varian MAT 731 spectrometer equipped with an Iontech 11 NF FAB cannon. [Xe(2,4,6,-F_3C_6H_2)][OSO_2CF_3] was dissolved in a CH_3CN/CF_3COOH mixture. Elemental xenon was used as the bombarding gas (acceleration voltage 6–8 kV), m-nitrobenzylic alcohol (NBA) was employed as the matrix component.

DTA. The DTA measurements were recorded on a Mettler TA1 thermoanalyzer.

Crystal structure of [Xe(2,6-F₂C₆H₃)][OSO₂CF₃]. CH₃CN was added dropwise to 0.3 g (0.76 mmol) [Xe(2,6-F₂C₆H₃)][OSO₂CF₃] at room temperature until the solution is saturated. During a period of 8 hours the temperature is slowly lowered to $-30 \,^{\circ}$ C; the crystals precipitated were separated from the solvent and dried in a nitrogen stream.

Single-crystal X-ray data of the compound were collected on an Enraf-Nonius CAD4 diffractometer using graphitemonochromatized MoK α -radiation ($\lambda = 71.069$ pm). The cell parameters were determined using 24 reflections in the range $4.81^{\circ} \le \Theta \le 14.58^{\circ}$. Three standard reflections were measured every 7200 seconds to monitor instrument and crystal stability. The correction of intensity based on the standard reflections was -37.6° . Absorption corrections were applied by measuring five PSI-Scan reflections. MolEN programs were used for data reduction [37]. SHELXL93 was

 Table 7
 Crystal data and details of data collection and structure refinement

Formula weight 393.45 g mol ⁻¹ Crystal system triclinic Space group P1 Lattice parameters a = 880.9(3) pm α = 89.04(4)° b = 1093.9(5) pm β = 74.23(3) c = 1209.8(5) pm γ = 86.03(3) 1.1192(8) nm ³ Formula units/unit cell Z = 4 d _{calc} 2.335 g cm ⁻³ t _{dealc} (Mo K α) 3.327 mm ⁻¹ F(000) 736 Crystal size (0.30 × 0.20 × 0.10) mm ³ Scan mode 3 $\omega/2\theta$ Scan mode 3 $\omega/2\theta$ Scan mode 3 $\omega/2\theta$ Scan rate 4.12-8.24° min ⁻¹ 2 θ range 4.82° ≤ 2 θ ≤ 49.94° Ranges of hkl 0 ≤ h ≤ 6, -12 ≤ k ≤ 12, -13 ≤ 1 ≤ 14 Number of measured reflections Number of unique 3128 reflections Number of unique 3128 reflections Absorption correction Ψ -Scan Transmission min/max 54.88/99.90 Decay -37.6% Correction (anisotrop) 0.9877/1.9059 min/max Reflections observed 2153 (1 > 2 σ (1)) Number of parameters 309 Weights w = 1/[σ^2 (F_o^2) + (0.0861 (F_o^2 + 2 F_o^2)/3)] S = [Σ w($ F_o ^2 - F_c ^2$) ² / 1.093 (n - p)] ^{1/2} R ₁ = Σ F_o - $ F_c ^2$) ² / 0.1191 Σ w($ F_o ^2$) ^{1/2} Max. shift/esd -0.001 $d\rho$ min/max -0.905/1.143 10 ⁶ e ⁻ pm ³	Compound	$[Xe(2,6-F_2C_6H_3)][OSO_2CF_3]$
Crystal system triclinic Space group PI Lattice parameters $a = 880.9(3) \text{ pm } \alpha = 89.04(4)^{\circ}$ $b = 1093.9(5) \text{ pm } \beta = 74.23(3)$ $c = 1209.8(5) \text{ pm } \gamma = 86.03(3)$ 1.1192(8) nm ³ Formula units/unit cell $Z = 4$ d_{calc} 2.335 g cm ⁻³ u_{calc} (Mo K α) 3.327 mm ⁻¹ F(000) 736 Crystal size (0.30 × 0.20 × 0.10) mm ³ Scan mode $3\omega/2\theta$ Scan width (1.25 + 0.35 tan θ)° Apertur $4 \cdot (1.6 + 1.0 \tan \theta) \text{ mm}$ Scan rate 4.12–8.24° min ⁻¹ 2 θ range 4.82° $\leq 2\theta \leq 49.94^{\circ}$ Ranges of hkl $0 \leq h \leq 6, -12 \leq k \leq 12, -13 \leq 1 \leq 14$ Number of measured 3128 reflections Number of unique 3128 reflections Ψ -Scan Transmission min/max 54.88/99.90 Decay -37.6% Correction (anisotrop) 0.9877/1.9059 min/max Reflections observed 2153 ($1 > 2\sigma(1)$) Number of parameters 309 Weights $w = 1/[\sigma^2(F_o^2) + (0.0861 (F_o^2 + 2F_o^2)/3)]$ $S = [\Sigmaw(F_o ^2 - F_c ^2)^2/ 1.093$ $w = 1/[\sigma^2(F_o^2) + (0.0861 (F_o^2 + 2F_o^2)/3)]$ $S = [\Sigmaw(F_o ^2 - F_c ^2)^2/ 0.1191$ $\Sigmaw(F_o ^2)^{1/2}$ Max. shift/esd -0.001 $d\rho$ min/max -0.905/1.143 10 ⁶ e ⁻ pm ³	Formula weight	$393.45 \text{ g mol}^{-1}$
Space group P1 Lattice parameters $a = 880.9(3) \text{ pm}$ $\alpha = 89.04(4)^{\circ}$ $b = 1093.9(5) \text{ pm}$ $\beta = 74.23(3)$ $c = 1209.8(5) \text{ pm}$ $\gamma = 86.03(3)$ Cell Volume $1.1192(8) \text{ nm}^3$ Formula units/unit cell $Z = 4$ d_{calc} 2.335 g cm^{-3} W_{calc} (Mo K α) 3.327 mm^{-1} F(000) 736 Crystal size $(0.30 \times 0.20 \times 0.10) \text{ mm}^3$ Scan mode $3\omega/2\theta$ Scan mode $3\omega/2\theta$ Scan mode $3\omega/2\theta$ Scan rate $4.12-8.24^{\circ} \text{ min}^{-1}$ 2θ range $4.82^{\circ} \le 2\theta \le 49.94^{\circ}$ Ranges of hkl $0 \le h \le 6, -12 \le k \le 12,$ $-13 \le 1 \le 14$ Number of measured reflections 3128 reflections $4.88/99.90$ Decay -37.6% Correction (anisotrop) $0.9877/1.9059$ min/max Reflections observed 2153 Reflections observed 2153 (I > 2\sigma(I)) 1.093 $m = 1/[\sigma^2(F_0^2) + m_0^2/3)]$ Number of parameters 309 $8e[E_0 = [F_0$	Crystal system	tr <u>i</u> clinic
Lattice parameters $a = 880.9(3) \text{ pm} \alpha = 89.04(4)^{\circ}$ $b = 1093.9(5) \text{ pm} \beta = 74.23(3)$ $c = 1209.8(5) \text{ pm} \gamma = 86.03(3)$ Formula units/unit cell $Z = 4$ d_{calc} 2.335 g cm^{-3} u_{calc} (Mo K α) 3.327 mm^{-1} F(000) 736 Crystal size $(0.30 \times 0.20 \times 0.10) \text{ mm}^{3}$ Scan mode $3\omega/2\theta$ Scan width $(1.25 + 0.35 \tan \theta)^{\circ}$ Apertur $4 \cdot (1.6 + 1.0 \tan \theta) \text{ mm}$ Scan rate $4.12 - 8.24^{\circ} \min^{-1}$ $2\theta \text{ range}$ $4.82^{\circ} \le 2\theta \le 49.94^{\circ}$ Ranges of hkl $0 \le h \le 6, -12 \le k \le 12,$ $-13 \le 1 \le 14$ Number of measured 3128 reflections Number of unique 3128 reflections W -Scan Transmission min/max $54.88/99.90$ Decay -37.6% Correction (anisotrop) $0.9877/1.9059$ min/max Reflections observed 2153 $(I > 2\sigma(I))$ Number of parameters 309 Weights $w = 1/[\sigma^{2}(F_{o}^{2}) + (0.0861(F_{o}^{2} + 2F_{o}^{2})/3)]$ $S = [\Sigmaw(F_{o} ^{2} - F_{c} ^{2})^{2}/$ 1.093 $mR_{1} = \Sigma F_{o} - F_{c} /\Sigma F_{o} $ 0.0508 $wR_{2} = [\Sigmaw(F_{o} ^{2} - F_{c} ^{2})^{2}/$ 0.1191 $\Sigmaw(F_{o} ^{2})^{2} ^{1/2}$ Max. shit/tesd -0.001 $d\rho \min/max$ $-0.905/1.143 10^{6} \text{ e}^{-} \text{ pm}^{3}$	Space group	P1
$b = 1093.9(5) \text{ pm} \beta = 74.23(3)$ $c = 1209.8(5) \text{ pm} \gamma = 86.03(3)$ Formula units/unit cell $Z = 4$ d_{calc} 2.335 g cm^{-3} $u_{calc} (Mo K\alpha)$ 3.327 mm^{-1} F(000) 736 Crystal size (0.30 × 0.20 × 0.10) mm ³ Scan mode 3 $\omega/2\theta$ Scan mode 3 $\omega/2\theta$ Scan mode 3 $\omega/2\theta$ Scan mode $3\omega/2\theta$ Scan mode $3\omega/2\theta$ Scan rate 4.12-8.24° min ⁻¹ 2 θ range 4.82° $\leq 2\theta \leq 49.94^{\circ}$ Ranges of hkl 0 $\leq h \leq 6, -12 \leq k \leq 12,$ -13 $\leq 1 \leq 14$ Number of measured reflections Number of unique 3128 reflections Absorption correction Fransmission min/max Reflections observed (1 > 2 σ (I)) Number of parameters 309 Weights $w = 1/[\sigma^2(F_0^2) + (0.0861(F_0^2 + 2F_0^2)^2/) (0.1191)$ Sw($ F_0 ^2 - F_c ^2 / (0.1191)$ Sw($ F_0 ^2 - F_c ^2 / (0.1191)$ Sw($ F_0 ^2 - F_c ^2 / (0.1191)$ Max. shift/esd -0.001 $d\rho \min/max$ -0.905/1.143 10 ⁶ e ⁻ pm ³	Lattice parameters	$a = 880.9(3) \text{ pm}$ $\alpha = 89.04(4)^{\circ}$
$c = 1209.8(5) \text{ pm} \gamma = 86.03(3)$ Cell Volume Formula units/unit cell $J_{calc} = 2.335 \text{ g cm}^{-3}$ $J_{calc} = 2.54 \text{ g cl}^{-3}$ $J_{calc} = 2.54 \text{ g cl}^{-$		$b = 1093.9(5) \text{ pm}$ $\beta = 74.23(3)^{\circ}$
Cell Volume 1.1192(8) nm ³ Formula units/unit cell $Z = 4$ d_{calc} 2.335 g cm ⁻³ u_{calc} (Mo K α) 3.327 mm ⁻¹ F(000) 736 Crystal size (0.30 × 0.20 × 0.10) mm ³ Scan mode $3\omega/2\theta$ Scan rate $4.12-8.24^{\circ}$ min ⁻¹ 2θ range $4.82^{\circ} \le 2\theta \le 49.94^{\circ}$ Ranges of hkl $0 \le h \le 6, -12 \le k \le 12,$ $-13 \le 1 \le 14$ Number of measured reflections 3128 reflections $4.88/99.90$ Decay -37.6% Correction (anisotrop) $0.9877/1.9059$ min/max $8eflections observed$ 2153 (I > $2\sigma(I))$ 1093 Number of parameters 309 Weights $w = 1/[\sigma^2(F_o^2) + (0.0861(F_o^2 + $		$c = 1209.8(5) \text{ pm}$ $\gamma = 86.03(3)$
Formula units/unit cell $Z = 4$ d_{calc} 2.335 g cm ⁻³ u_{calc} (Mo K α) 3.327 mm ⁻¹ F(000) 736 Crystal size (0.30 × 0.20 × 0.10) mm ³ Scan mode $3\omega/2\theta$ Scan width (1.25 + 0.35 tan θ)° Apertur $4 \cdot (1.6 + 1.0 tan \theta) mmScan rate 4.12–8.24° min-12\theta range 4.82° \leq 2\theta \leq 49.94^{\circ}Ranges of hkl 0 \leq h \leq 6, -12 \leq k \leq 12, -13 \leq l \leq 14Number of measured 3128reflectionsAbsorption correction \Psi-ScanTransmission min/max 54.88/99.90Decay -37.6%Correction (anisotrop) 0.9877/1.9059min/maxReflections observed 2153(l > 2\sigma(I))Number of parameters 309Weights w = 1/[\sigma^2(F_o^2) + (0.0861(F_o^2 + 2F_o^2)/3)]S = [\Sigma w(F_o ^2 - F_c ^2)^2/ 0.1191\Sigma w(F_o ^2)^2 ^{1/2}Max. shift/esd -0.001d\rho min/max -0.905/1.143 106 e- pm3$	Cell Volume	$1.1192(8) \text{ nm}^3$
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Formula units/unit cell	$\mathbf{Z} = 4$
u_{calc} (Mo K α) 3.327 mm^{-1} F(000) 736 Crystal size $(0.30 \times 0.20 \times 0.10) \text{ mm}^3$ Scan mode $3\omega/2\theta$ Scan width $(1.25 + 0.35 \tan \theta)^{\circ}$ Apertur $4 \cdot (1.6 + 1.0 \tan \theta) \text{ mm}$ Scan rate $4.12-8.24^{\circ} \min^{-1}$ 2θ range $4.82^{\circ} \le 2\theta \le 49.94^{\circ}$ Ranges of hkl $0 \le h \le 6, -12 \le k \le 12, -13 \le 1 \le 14$ Number of measured 3128 reflections 3128 reflections $4.88/99.90$ Decay -37.6% Correction (anisotrop) $0.9877/1.9059$ min/max $8eflections observed$ Reflections observed 2153 $(I > 2\sigma(I))$ $8 = [\Sigmaw(F_0 ^2 - F_c ^2)^2/$ Number of parameters 309 Weights $w = 1/[\sigma^2(F_0^2) + (0.0861 (F_0^2 + 2 F_0^2)/3)]$ $S = [\Sigmaw(F_0 ^2 - F_c ^2)^2/$ 1.093 $(n - p)^{1/2}$ 0.0508 $wR_2 = [\Sigmaw(F_0 ^2 - F_c ^2)^2/$ 0.1191 $\Sigmaw(F_0 ^2)^2]^{1/2}$ -0.001 $Ap \min/max$ $-0.905/1.143 \ 10^6 e^- pm^3$	d _{calc}	2.335 g cm^{-3}
F(000) 736 Crystal size $(0.30 \times 0.20 \times 0.10) \text{ mm}^3$ Scan mode $3\omega/2\theta$ Scan width $(1.25 + 0.35 \tan \theta)^\circ$ Apertur $4 \cdot (1.6 + 1.0 \tan \theta) \text{ mm}$ Scan rate $4.12-8.24^\circ \min^{-1}$ 2θ range $4.82^\circ \le 2\theta \le 49.94^\circ$ Ranges of hkl $0 \le h \le 6, -12 \le k \le 12,$ $-13 \le 1 \le 14$ 128 reflections 3128 reflections 3128 reflections $4.88/99.90$ Decay -37.6% Correction (anisotrop) $0.9877/1.9059$ min/max $8eflections observed$ Reflections observed 2153 $(I > 2\sigma(I))$ $8 = [\Sigmaw(F_o ^2 - F_c ^2)^2/$ Number of parameters 309 Weights $w = 1/[\sigma^2(F_o^2) + (0.0861 (F_o^2 + 2F_c^2)/3)]$ S = $[\Sigmaw(F_o ^2 - F_c ^2)^2/$ 1.093 $(n - p)^{1/2}$ 0.0508 wR_2 = $[\Sigmaw(F_o ^2 - F_c ^2)^2/$ 0.1191 $\Sigmaw(F_o ^2)^2]^{1/2}$ 0.001 $\Delta p \min/max$ -0.001	u_{calc} (Mo K α)	3.327 mm^{-1}
Crystal size $(0.30 \times 0.20 \times 0.10) \text{ mm}^3$ Scan mode $3\omega/2\theta$ Scan width $(1.25 + 0.35 \tan \theta)^\circ$ Apertur $4 \cdot (1.6 + 1.0 \tan \theta) \text{ mm}$ Scan rate $4.12-8.24^\circ \min^{-1}$ 2θ range $4.82^\circ \le 2\theta \le 49.94^\circ$ Ranges of hkl $0 \le h \le 6, -12 \le k \le 12,$ $-13 \le 1 \le 14$ $-13 \le 1 \le 14$ Number of measured 3128 reflections 3128 reflections $4.88/99.90$ Decay -37.6% Correction (anisotrop) $0.9877/1.9059$ min/max Reflections observed Reflections observed 2153 $(I > 2\sigma(I))$ $w = 1/[\sigma^2(F_o^2) + (0.0861(F_o^2 + 2F_c^2)/3)]$ Number of parameters 309 Weights $w = 1/[\sigma^2(F_o^2) + (0.0861(F_o^2 + 2F_c^2)/3)]$ S = $[\Sigma w(F_o ^2 - F_c ^2)^2/$ 1.093 $(n - p)^{1/2}$ 0.0508 $wR_2 = [\Sigma w(F_o ^2 - F_c ^2)^2/$ 0.1191 $\Sigma w(F_o ^2)^2]^{1/2}$ -0.001 $\Delta p \min/max$ $-0.905/1.143 10^6 e^- pm^3$	F(000)	736
Scan mode $3\omega/2\theta$ Scan width $(1.25 + 0.35 \tan \theta)^{\circ}$ Apertur $4 \cdot (1.6 + 1.0 \tan \theta) \text{ mm}$ Scan rate $4.12-8.24^{\circ} \min^{-1}$ 2θ range $4.82^{\circ} \le 2\theta \le 49.94^{\circ}$ Ranges of hkl $0 \le h \le 6, -12 \le k \le 12, -13 \le 1 \le 14$ Number of measured 3128 reflections Number of unique 3128 reflections Absorption correction Ψ -Scan Transmission min/max $54.88/99.90$ Decay -37.6% Correction (anisotrop) $0.9877/1.9059$ min/max Reflections observed 2153 $(I > 2\sigma(I))$ Number of parameters 309 Weights $w = 1/[\sigma^2(F_o^2) + (0.0861(F_o^2 + 2F_c^2)/3)]$ $S = [\Sigma w(F_o ^2 - F_c ^2)^2/ 1.093$ $(n - p)]^{1/2}$ $R_1 = \Sigma F_o - F_c /\Sigma F_o 0.0508$ $wR_2 = [\Sigma w(F_o ^2 - F_c ^2)^2/ 0.1191$ $\Sigma w(F_o ^2)^2]^{1/2}$ Max. shift/esd -0.001 $d\rho \min/max -0.905/1.143 10^6 e^- pm^3$	Crystal size	$(0.30 \times 0.20 \times 0.10) \text{ mm}^3$
Scan width $(1.25 + 0.35 \tan \theta)^{\circ}$ Apertur $4 \cdot (1.6 + 1.0 \tan \theta) \text{ mm}$ Scan rate $4.12-8.24^{\circ} \text{ min}^{-1}$ $2\theta \text{ range}$ $4.82^{\circ} \le 2\theta \le 49.94^{\circ}$ Ranges of hkl $0 \le h \le 6, -12 \le k \le 12,$ $-13 \le 1 \le 14$ Number of measured 3128 reflections Number of unique 3128 reflections Absorption correction Ψ -Scan Transmission min/max $54.88/99.90$ Decay -37.6% Correction (anisotrop) $0.9877/1.9059$ min/max Reflections observed 2153 $(I > 2\sigma(I))$ Number of parameters 309 Weights $w = 1/[\sigma^2(F_o^2) + (0.0861(F_o^2 + 2F_c^2)/3)]$ $S = [\Sigma w(F_o ^2 - F_c ^2)^2/ 1.093$ $(n - p)]^{1/2}$ $R_1 = \Sigma F_o - F_c /\Sigma F_o 0.0508$ $wR_2 = [\Sigma w(F_o ^2 - F_c ^2)^2/ 0.1191$ $\Sigma w(F_o ^2)^2]^{1/2}$ Max. shift/esd -0.001 $\Delta \rho \min/max -0.905/1.143 10^6 e^- pm^3$	Scan mode	$3\omega/2\theta$
Apertur $4 \cdot (1.6 + 1.0 \tan \theta) \text{ mm}$ Scan rate $4.12-8.24^{\circ} \min^{-1}$ 2θ range $4.82^{\circ} \le 2\theta \le 49.94^{\circ}$ Ranges of hkl $0 \le h \le 6, -12 \le k \le 12, -13 \le l \le 14$ Number of measured 3128 reflections 3128 reflections $4 \cdot (8/9) = 80$ Number of unique 3128 reflections $4 \cdot 8/99.90$ Decay -37.6% Correction (anisotrop) $0.9877/1.9059$ min/max Reflections observed Reflections observed 2153 (I > $2\sigma(I)$) $8 = 1/[\sigma^2(F_o^2) + (0.0861(F_o^2 + 2F_o^2)/3)]$ Number of parameters 309 Weights $w = 1/[\sigma^2(F_o^2) + (0.0861(F_o^2 + 2F_o^2)/3)]$ S = $[\Sigma w(F_o ^2 - F_c ^2)^2 / 1.093$ $(n - p)^{1/2}$ R_1 = \Sigma F_o - F_c / \Sigma F_o 0.0508 wR_2 = $[\Sigma w(F_o ^2 - F_c ^2)^2 / 0.1191$ $\Sigma w(F_o ^2)^2]^{1/2}$ Max. shift/esd -0.001 $\Delta \rho$ min/max $-0.905/1.143 10^6 e^- pm^3$	Scan width	$(1.25 + 0.35 \tan \theta)^{\circ}$
Scan rate $4.12-8.24^{\circ} \text{ min}^{-1}$ 2θ range $4.82^{\circ} \le 2\theta \le 49.94^{\circ}$ Ranges of hkl $0 \le h \le 6, -12 \le k \le 12, -13 \le 1 \le 14$ Number of measured 3128 reflections 3128 Number of unique 3128 reflections $4.88/99.90$ Decay -37.6% Correction (anisotrop) $0.9877/1.9059$ min/max Reflections observed Reflections observed 2153 (I > $2\sigma(I)$) 309 Weights $w = 1/[\sigma^2(F_o^2) + (0.0861(F_o^2 + 2F_o^2)/3)]$ S = $[\Sigmaw(F_o ^2 - F_c ^2)^2/$ 1.093 $(n - p)$] ^{1/2} 0.0508 $wR_2 = [\Sigmaw(F_o ^2 - F_c ^2)^2/$ 0.1191 $\Sigmaw(F_o ^2)^2$] ^{1/2} -0.001 $\Delta\rho$ min/max $-0.905/1.143 10^6 e^- pm^3$	Apertur	$4 \cdot (1.6 + 1.0 \tan \theta) \text{ mm}$
2θ range $4.82^{\circ} \le 2\theta \le 49.94^{\circ}$ Ranges of hkl $0 \le h \le 6, -12 \le k \le 12, -13 \le l \le 14$ Number of measured 3128 reflections 3128 Number of unique 3128 reflections 3128 Absorption correction Ψ -Scan Transmission min/max $54.88/99.90$ Decay -37.6% Correction (anisotrop) $0.9877/1.9059$ min/max Reflections observed Reflections observed 2153 (I > $2\sigma(I)$) 309 Weights $w = 1/[\sigma^2(F_o^2) + (0.0861(F_o^2 + 2F_o^2)/3)]$ S = $[\Sigma w(F_o ^2 - F_c ^2)^2/$ 1.093 $(n - p)$] ^{1/2} $R_1 = \Sigma F_o - F_c /\Sigma F_o $ $R_1 = \Sigma F_o - F_c ^2 ^2/2/$ 0.1191 $\Sigma w(F_o ^2)^2$] ^{1/2} -0.001 Max. shift/esd -0.001 $\Delta\rho$ min/max $-0.905/1.143 \ 10^6 e^- pm^3$	Scan rate	$4.12-8.24^{\circ} \text{ min}^{-1}$
Ranges of hkl $0 \le h \le 6, -12 \le k \le 12,$ $-13 \le 1 \le 14$ Number of measured 3128 reflections 3128 Number of unique 3128 reflections Ψ -ScanTransmission min/max $54.88/99.90$ Decay -37.6% Correction (anisotrop) $0.9877/1.9059$ min/maxReflections observedReflections observed 2153 $(I > 2\sigma(I))$ $W = 1/[\sigma^2(F_o^2) + (0.0861 (F_o^2 + 2 F_c^2)/3)]$ Number of parameters 309 Weights $w = 1/[\sigma^2(F_o^2) + (0.0508 (H_o^2)^2 - F_c ^2)^2/(1.093)$ $n - p)]^{1/2}$ 0.0508 $W_2 = [\Sigma W(F_o ^2 - F_c ^2)^2/(0.1191)$ $\Sigma W(F_o ^2)^2]^{1/2}$ -0.001 Max. shift/esd -0.001 $\Delta \rho$ min/max $-0.905/1.143 \ 10^6 \ e^- \ pm^3$	2θ range	$4.82^\circ \le 2\theta \le 49.94^\circ$
$\begin{array}{rl} -13 \leq 1 \leq 14 \\ 3128 \\ \text{reflections} \\ \text{Number of unique} \\ 3128 \\ \text{reflections} \\ \text{Absorption correction} \\ \text{Absorption correction} \\ \text{Transmission min/max} \\ \text{Selections observed} \\ 3128 \\ \text{Correction (anisotrop)} \\ 0.9877/1.9059 \\ \text{min/max} \\ \text{Reflections observed} \\ 2153 \\ (I > 2\sigma(I)) \\ \text{Number of parameters} \\ 309 \\ \text{Weights} \\ \mathbf{w} = 1/[\sigma^2(\mathbf{F}_o^2) + (0.0861(\mathbf{F}_o^2 + 2\mathbf{F}_o^2)/3)] \\ \text{Se} [\Sigmaw(\mathbf{F}_o ^2 - \mathbf{F}_c ^2)^2 / 1.093 \\ (n - p)]^{1/2} \\ \text{R}_1 = \Sigma \mathbf{F}_o - \mathbf{F}_c \Sigma \mathbf{F}_o \\ \text{Max. shift/esd} \\ -0.001 \\ \Delta \rho \min/max \\ -0.905/1.143 \ 10^6 \ e^- \ pm^3 \\ \end{array}$	Ranges of hkl	$0 \le h \le 6, -12 \le k \le 12,$
Number of measured 3128 reflections 3128 Number of unique 3128 reflections 3128 Absorption correction Ψ -Scan Transmission min/max 54.88/99.90 Decay -37.6% Correction (anisotrop) 0.9877/1.9059 min/max Reflections observed Reflections observed 2153 (I > $2\sigma(I)$) Number of parameters Weights $w = 1/[\sigma^2(F_o^2) + (0.0861(F_o^2 + 2F_o^2)/3)]$ S = $[\Sigma w(F_o ^2 - F_c ^2)^2 / 1.093$ 1.093 (n - p)]^{1/2} 0.0508 $wR_2 = [\Sigma w(F_o ^2 - F_c ^2)^2 / 0.1191$ 0.0508 $\Sigma w(F_o ^2)^2]^{1/2}$ -0.001 $\Delta \rho$ min/max -0.905/1.143 10 ⁶ e ⁻ pm ³	C	$-13 \le 1 \le 14$
reflections 3128 Number of unique 3128 reflections Absorption correction Ψ -Scan Transmission min/max 54.88/99.90 Decay -37.6% Correction (anisotrop) 0.9877/1.9059 min/max Reflections observed 2153 Reflections observed 2153 (I > $2\sigma(I)$) Number of parameters 309 Weights w = $1/[\sigma^2(F_o^2) + (0.0861 (F_o^2 + 2 F_o^2)/3)]$ S = $[\Sigma w(F_o ^2 - F_c ^2)^2 / 1.093$ R_1 = $\Sigma F_o - F_c /\Sigma F_o $ 0.0508 wR ₂ = $[\Sigma w(F_o ^2 - F_c ^2)^2 / 0.1191$ $\Sigma w(F_o ^2)^2]^{1/2}$ -0.001 -0.905/1.143 10 ⁶ e ⁻ pm ³	Number of measured	3128
Number of unique 3128 reflections Absorption correction Ψ -Scan Transmission min/max 54.88/99.90 Decay -37.6% Correction (anisotrop) 0.9877/1.9059 min/max Reflections observed 2153 Reflections observed 2153 (I > $2\sigma(I)$) Sumber of parameters 309 Weights $w = 1/[\sigma^2(F_o^2) + (0.0861(F_o^2 + 2F_o^2)/3)]$ Second (I = 2)/(S = 2F_o^2)/3)] S = $[\Sigma w(F_o ^2 - F_c ^2)^2 / 1.093$ 0.0508 WR2 = $[\Sigma w(F_o ^2 - F_c ^2)^2 / 0.1191$ Sw(F_o ^2)^2]^{1/2} 0.001 -0.001 Max. shift/esd -0.001 -0.905/1.143 10 ⁶ e ⁻ pm ³	reflections	
reflections Absorption correction Ψ -Scan Transmission min/max 54.88/99.90 Decay -37.6% Correction (anisotrop) 0.9877/1.9059 min/max Reflections observed 2153 (I > 2 σ (I)) Number of parameters 309 Weights w = 1/[σ^2 (F_o^2) + (0.0861 ($F_o^2 + 2 F_c^2$)/3)] S = [Σ w(F_o ² - F_c ²) ² / (n - p)] ^{1/2} R ₁ = Σ F_o - F_c Σ F_o 0.0508 wR ₂ = [Σ w(F_o ² - F_c ²) ² / Max. shift/esd -0.001 $\Delta \rho$ min/max -0.905/1.143 10 ⁶ e ⁻ pm ³	Number of unique	3128
Absorption correction Ψ -Scan Iransmission min/max 54.88/99.90 Decay -37.6% Correction (anisotrop) 0.9877/1.9059 min/max Reflections observed 2153 Reflections observed 2153 (I > 2 σ (I)) Number of parameters 309 Weights w = 1/[σ^2 (F_o^2) + (0.0861 ($F_o^2 + 2 F_c^2$)/3)] S S = [Σ w($ F_o ^2 - F_c ^2$) ² / 1.093 (n - p)]^{1/2} R_1 = $\Sigma F_o - F_c / \Sigma F_o $ 0.0508 wR ₂ = [Σ w($ F_o ^2 - F_c ^2$) ² / Max. shift/esd -0.001 -0.001 $\Delta \rho$ min/max -0.905/1.143 10 ⁶ e ⁻ pm ³	reflections	
Transmission min/max 54.88/99.90 Decay -37.6% Correction (anisotrop) 0.9877/1.9059 min/max Reflections observed 2153 Reflections observed 2153 (I > $2\sigma(I)$) Solution Number of parameters 309 Weights w = $1/[\sigma^2(F_o^2) + (0.0861(F_o^2 + 2F_c^2)/3)]$ S = $[\Sigma w(F_o ^2 - F_c ^2)^2 / 1.093$ 1.093 (n - p)]^{1/2} 0.0508 wR ₂ = $[\Sigma w(F_o ^2 - F_c ^2)^2 / 0.1191$ 0.0508 $\Sigma w(F_o ^2)^2]^{1/2}$ -0.001 Max. shift/esd -0.001 $\Delta \rho$ min/max -0.905/1.143 10 ⁶ e ⁻ pm ³	Absorption correction	Ψ-Scan
Decay -37.6% Correction (anisotrop) 0.9877/1.9059 min/max Reflections observed 2153 (I > 2 σ (I)) Number of parameters 309 Weights w = 1/[σ^2 (F_o^2) + (0.0861 (F_o^2 + 2 F_c^2)/3)] S = [Σ w(F_o ² - F_c ²) ² / 1.093 (n - p)] ^{1/2} R ₁ = Σ F_o - F_c Σ F_o 0.0508 wR ₂ = [Σ w(F_o ² - F_c ²) ² / 0.1191 Σ w(F_o ²) ²] ^{1/2} Max. shift/esd -0.001 $\Delta \rho$ min/max -0.905/1.143 10 ⁶ e ⁻ pm ³	Transmission min/max	54.88/99.90
Correction (anisotrop) 0.9877/1.9059 min/max Reflections observed 2153 (I > $2\sigma(I)$) Number of parameters 309 Weights $w = 1/[\sigma^2(F_o^2) + (0.0861 (F_o^2 + 2 F_o^2)/3)]$ S = $[\Sigma w(F_o ^2 - F_c ^2)^2 / 1.093$ (n - p)] ^{1/2} R ₁ = $\Sigma F_o - F_c /\Sigma F_o $ 0.0508 wR ₂ = $[\Sigma w(F_o ^2 - F_c ^2)^2 / 0.1191$ $\Sigma w(F_o ^2)^2$] ^{1/2} Max. shift/esd -0.001 $\Delta \rho \min/max$ -0.905/1.143 10 ⁶ e ⁻ pm ³	Decay	-37.6%
min/max Reflections observed 2153 (I > $2\sigma(I)$) Number of parameters 309 Weights $w = 1/[\sigma^2(F_o^2) + (0.0861 (F_o^2 + 2 F_c^2)/3)]$ S = $[\Sigma w(F_o ^2 - F_c ^2)^2 / 1.093$ (n - p)] ^{1/2} R ₁ = $\Sigma F_o - F_c /\Sigma F_o 0.0508$ wR ₂ = $[\Sigma w(F_o ^2 - F_c ^2)^2 / 0.1191$ $\Sigma w(F_o ^2)^2$] ^{1/2} Max. shift/esd -0.001 $\Delta \rho \min/max$ -0.905/1.143 10 ⁶ e ⁻ pm ³	Correction (anisotrop)	0.9877/1.9059
Reflections observed 2153 (I > $2\sigma(I)$) 309 Number of parameters 309 Weights $w = 1/[\sigma^2(F_o^2) + (0.0861 (F_o^2 + 2 F_c^2)/3)]$ S = $[\Sigma w(F_o ^2 - F_c ^2)^2 / 1.093$ 1.093 $(n - p)$] ^{1/2} 0.0508 $wR_2 = [\Sigma w(F_o ^2 - F_c ^2)^2 / 0.1191$ 0.1191 $\Sigma w(F_o ^2)^2$] ^{1/2} -0.001 $\Delta \rho$ min/max -0.905/1.143 10 ⁶ e ⁻ pm ³	min/max	
$\begin{array}{ll} (I > 2\sigma(I)) \\ \text{Number of parameters} & 309 \\ \text{Weights} & w = 1/[\sigma^2(F_o^2) + \\ & (0.0861 \ (F_o^2 + 2 \ F_c^2)/3)] \\ \text{S} = [\Sigma w(F_o ^2 - F_c ^2)^2 / \\ (n - p)]^{1/2} & 1.093 \\ \text{R}_1 = \Sigma F_o - F_c /\Sigma F_o & 0.0508 \\ wR_2 = [\Sigma w(F_o ^2 - F_c ^2)^2 / \\ 0.1191 \\ \Sigma w(F_o ^2)^2]^{1/2} & 0.1191 \\ \Sigma w(F_o ^2)^2]^{1/2} & 0.001 \\ \text{Max. shift/esd} & -0.001 \\ \Delta\rho \ \text{min/max} & -0.905/1.143 \ 10^6 \ \text{e}^- \ \text{pm}^3 \end{array}$	Reflections observed	2153
Number of parameters Weights $ \begin{aligned} & Weights & W = 1/[\sigma^2(F_o^2) + (0.0861 (F_o^2 + 2 F_c^2)/3)] \\ & S = [\Sigma W(F_o ^2 - F_c ^2)^2 / 1.093 \\ & (n - p)]^{1/2} \\ & R_1 = \Sigma F_o - F_c /\Sigma F_o & 0.0508 \\ & wR_2 = [\Sigma W(F_o ^2 - F_c ^2)^2 / 0.1191 \\ & \Sigma W(F_o ^2)^2]^{1/2} \\ & Max. shift/esd & -0.001 \\ & \Delta \rho \min/max & -0.905/1.143 10^6 e^- pm^3 \end{aligned} $	$(I > 2\sigma(I))$	
Weights $w = 1/[\sigma^{2}(F_{o}^{2}) + (0.0861 (F_{o}^{2} + 2 F_{c}^{2})/3)]$ $S = [\Sigma w(F_{o} ^{2} - F_{c} ^{2})^{2}/ 1.093$ $(n - p)]^{1/2}$ $R_{1} = \Sigma F_{o} - F_{c} /\Sigma F_{o} 0.0508$ $wR_{2} = [\Sigma w(F_{o} ^{2} - F_{c} ^{2})^{2}/ 0.1191$ $\Sigma w(F_{o} ^{2})^{2}]^{1/2}$ Max. shift/esd -0.001 $\Delta \rho \min/max -0.905/1.143 10^{6} e^{-} pm^{3}$	Number of parameters	309
$(0.0861 (F_o^2 + 2 F_c^2)/3)]$ $S = [\Sigma w(F_o ^2 - F_c ^2)^2 / 1.093$ $(n - p)]^{1/2}$ $R_1 = \Sigma F_o - F_c /\Sigma F_o 0.0508$ $wR_2 = [\Sigma w(F_o ^2 - F_c ^2)^2 / 0.1191$ $\Sigma w(F_o ^2)^2]^{1/2}$ Max. shift/esd -0.001 $\Delta \rho \text{ min/max} -0.905/1.143 \ 10^6 \text{ e}^- \text{ pm}^3$	Weights	$w = 1/[\sigma^2(F_0^2) +$
$S = [\Sigma w(F_0 ^2 - F_c ^2)^2 / 1.093$ $(n - p)]^{1/2}$ $R_1 = \Sigma F_0 - F_c / \Sigma F_0 0.0508$ $wR_2 = [\Sigma w(F_0 ^2 - F_c ^2)^2 / 0.1191$ $\Sigma w(F_0 ^2)^2]^{1/2}$ Max. shift/esd -0.001 $\Delta \rho \text{ min/max} -0.905 / 1.143 \ 10^6 \text{ e}^- \text{ pm}^3$		$(0.0861 (F_2^2 + 2 F_2^2)/3)]$
$\begin{array}{ll} (n-p)^{1/2} & 10^{10} - - - - - - - $	$S = [\Sigma w (F_0 ^2 - F_0 ^2)^2)$	1.093
$\begin{aligned} & R_1 = \mathcal{E}[F_o - F_c] / \mathcal{E}[F_o] & 0.0508 \\ & wR_2 = [\mathcal{E}w(F_o ^2 - F_c ^2)^2 / & 0.1191 \\ & \mathcal{E}w(F_o ^2)^2]^{1/2} \\ & Max. \ shift/esd & -0.001 \\ & \Delta\rho \ min/max & -0.905/1.143 \ 10^6 \ e^- \ pm^3 \end{aligned}$	(n-p)] ^{1/2}	
$wR_{2} = \left[\sum w(F_{0} ^{2} - F_{c} ^{2})^{2} \right] 0.1191$ $\sum w(F_{0} ^{2})^{2} = \frac{1}{2} \frac$	$\mathbf{R}_1 = \boldsymbol{\Sigma} \mathbf{F}_0 - \mathbf{F}_0 \boldsymbol{\Sigma} \mathbf{F}_0 $	0.0508
$\sum w(F_0 ^2)^2]^{1/2} = -0.001$ Max. shift/esd -0.001 $\Delta \rho \min/\max$ -0.905/1.143 10 ⁶ e ⁻ pm ³	$wR_2 = [\Sigma w(F_0 ^2 - F_c ^2)^2/$	0.1191
Max. shift/esd -0.001 $\Delta \rho$ min/max $-0.905/1.143 \ 10^6 \ e^- \ pm^3$	$\Sigma w(F_0 ^2)^2 ^{1/2}$	
$\Delta \rho \min/\max$ -0.905/1.143 10 ⁶ e ⁻ pm ³	Max. shift/esd	-0.001
▲ 	Δρ min/max	-0.905/1.143 10 ⁶ e ⁻ pm ³
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used for least-squares calculation [38]. The linear absorption coefficients, scattering factors for all the atoms, and the anomalous-dispersion corrections were taken from the usual source [39]. The structure was solved by direct methods (SHELXS86) and Fourier synthesis [40]. The refinement was done by full matrix least-squares procedures using anisotropic thermal parameters. The H atoms were placed in idealized position with one thermal parameter for all H atoms of one molecule. Further details are given in Table 7.

The final functional coordinates of the non-hydrogen atoms are given in Table 8. A selection of bond distances and angles involving the xenon atoms is given in Table 9.

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Table 8 Fractional atomic coordinates and equivalent isotropic ^a) displacement parameters for $[Xe(2,6-F_2C_6H_3)][OSO_2CF_3].$

Atom	X	у	z	U(eq)
Xe1	0.42355(8)	0.59961(6)	0.35099(5)	0.0548(3)
C11	0.5242(13)	0.7485(9)	0.2569(8)	0.054(3)
C12	0.4405(14)	0.8614(10)	0.2687(9)	0.058(3)
C13	0.5065(15)	0.9581(11)	0.2073(11)	0.073(4)
C14	0.6549(15)	0.9425(11)	0.1362(10)	0.075(4)
C15	0.7426(14)	0.8326(10)	0.1248(8)	0.059(3)
C16	0.6755(13)	0.7366(9)	0.1862(8)	0.053(3)
F11	0.2955(8)	0.8715(6)	0.3400(6)	0.090(2)
F12	0.7531(8)	0.6251(6)	0.1805(6)	0.079(2)
O11	0.3129(12)	0.4136(8)	0.4909(8)	0.104(3)
S1	0.2803(3)	0.2946(2)	0.4592(2)	0.0501(7)
O12	0.2773(11)	0.2848(11)	0.3451(6)	0.111(4)
O13	0.3637(10)	0.2005(9)	0.5045(7)	0.097(3)
C17	0.0825(16)	0.2855(11)	0.5420(9)	0.072(4)
F13	-0.0161(10)	0.3659(8)	0.5123(8)	0.130(3)
F14	0.0633(10)	0.2868(10)	0.6504(6)	0.129(3)
F15	0.0249(9)	0.1779(8)	0.5230(7)	0.109(3)
Xe2	0.07423(9)	0.41535(6)	0.17798(6)	0.0611(3)
C21	-0.0336(12)	0.2550(8)	0.2433(7)	0.042(2)
C22	-0.1819(12)	0.2633(8)	0.3140(7)	0.044(2)
C23	-0.2521(13)	0.1574(10)	0.3598(8)	0.056(3)
C24	-0.1658(14)	0.0468(9)	0.3334(9)	0.060(3)
C25	-0.0190(14)	0.0396(9)	0.2617(9)	0.063(3)
C26	0.0524(13)	0.1434(9)	0.2160(8)	0.053(3)
F21	-0.2594(8)	0.3733(5)	0.3381(5)	0.076(2)
F22	0.1978(7)	0.1405(6)	0.1466(5)	0.073(2)
O21	0.2457(11)	0.6285(9)	0.1424(6)	0.099(3)
S2	0.2204(3)	0.7028(2)	0.0512(2)	0.0488(7)
O22	0.1118(11)	0.6594(12)	0.0028(8)	0.135(5)
O23	0.2028(14)	0.8268(8)	0.0731(10)	0.152(5)
C27	0.4077(18)	0.6838(11)	-0.0579(10)	0.074(4)
F23	0.5183(11)	0.7118(14)	-0.0257(7)	0.181(6)
F24	0.4013(10)	0.7456(8)	-0.1503(5)	0.109(3)
F25	0.4309(11)	0.5701(8)	-0.0960(8)	0.144(4)

^a) For anisotropic atoms, the U value is U_{eq} , calculated as $U_{eq} = 1/3 \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i a_j$.

Table 9 Selected Bond Distances (pm) and Selected Bond Angles (°) of $[Xe(2,6-F_2C_6H_3)][OSO_2CF_3]$.

Xe1-C11	207.9(9)	Xe2-C21	209.2(9)
Xe1-011	268.7(9)	Xe2-O21	282.9(10)
Xe1–F12	309.8(6)	Xe2-F21	310.8(6)
Xe1-F11	312.0(7)	Xe2–F22	311.9(6)
C11-Xe1-O11	173.0(3)	C21-Xe2-O21	165.1(3)
S1–O11–Xe1	127.6(5)	S2-O21-Xe2	113.6(5)
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Caution! In the solid state $Xe(OCOCF_3)_2$ and CF₃COOXeOSO₂CF₃ are explosive even at low temperature (>-40 °C) especially on mechanical strain. However, no problems appeared in preparation and handling of these compounds in CCl₃F solutions or suspensions. In this medium $Xe(OCOCF_3)_2$ decomposes slowly at temperatures above -10 °C and CF₃COOXeOSO₂CF₃ above -40 °C. Before starting the isolation procedure of the arylxenon compounds the reaction mixtures had to be checked by ¹²⁹Xe-NMR spectroscopy on eventually remaining CF3COOXeOSO2CF3 and Xe(OCOCF₃)₂.

Preparation of CF₃COOXeOSO₂CF₃; general procedure. 0.61 g (3.6 mmol) XeF₂ were suspended in 30 ml CCl₃F at -15 °C, 550 µl (7.2 mmol) CF₃COOH were added and stirred for three hours. Cooling down the reaction vessel to -40 °C and adding dropwise freshly destilled 320 µl (3.6 mmol) HOSO₂CF₃ the voluminous and pale yellow precipitate of Xe(OCOCF₃)₂ became bright yellow, indicating the formation of CF₃COOXeOSO₂CF₃. After one hour additional stirring the benzene was added in small portions. For the NMR-control of the system Xe(OCOCF₃)₂/HOSO₂CF₃, the solvent volume was reduced by vacuum distillation at -40 °C (5 ml) and 2–3 ml cold (-35 °C) CH₃CN were added.

Scaling up to 1.2 g (7 mmol) XeF₂ did not bear any problems.

Preparation and isolation of 2,4,6-trifluorophenylxenon trifluoromethanesulfonate. CF3COOXeOSO2CF3 was prepared in CCl₃F solution in a PTFE-vessel as described above: 1.1 g (6.5 mmol) XeF_2 and 1.48 g (13 mmol) CF_3COOH were mixed in 30 ml CCl₃F at -15 °C. The mixture was stirred for three hours. 0.98 g (6.5 mmol) HOSO₂CF₃ were added dropwise at -40 °C and stirring was continued for one hour. The yellow precipitate of CF3COOXeOSO2CF3 disappeared after dropwise addition of 0.86 g (6.5 mmol) pure 1,3,5- $F_3C_6H_3$. The yellow solution was warmed to -20 °C and the solvent was distilled off in vacuo (3 hours). 5 ml cold (-30 °C) CH₃CN were added to check by 129 Xe-NMR whether Xe(OCOCF₃)₂ and CF₃COOXeOSO₂CF₃ had reacted completely. The remaining solvent was distilled off at -10 °C and the oily brown residue was suspended in 20 ml cold (-50 °C) toluene (two phases). Diethylether was added dropwise until the mixture became homogeneous. While storing overnight on dry-ice, a white solid precipitated, which was filtered at low temperature, washed several times with cold CH₂Cl₂ (30 ml) and dried in vacuo at room temperature. The yield of spectroscopical pure [Xe(2,4,6- $F_2C_6H_3$][OSO₂CF₃] was about 15% relative to XeF₂.

Preparation of CF₃- and NO₂-substituted arylxenon trifluoromethanesulfonates. The preparation of $[Xe(2-F-5-(CF_3)C_6H_3)][OSO_2CF_3]$, $[Xe(2-F-5-(NO_2)C_6H_3)][OSO_2CF_3]$ and $[Xe(3,5-(CF_3)_2C_6H_3)][OSO_2CF_3]$ was identical with the procedure described above.

Only in the case of 3,5-bis(trifluoromethyl)phenylxenon trifluoromethanesulfonate, which decomposes at temperatures $>-5^{\circ}$ C, the reaction mixture was held on a temperature not exceeding -30 °C:

Ar _f H	XeF ₂	CF ₃ COOH	HOSO ₂ CF ₃	yield (%)
1-F-4-NO ₂ -	C ₆ H ₄ :			
0.49 g (3.5 mmol)	0.59 g (3.5 mmol)	0.8 g (7.0 mmol)	0.52 g (3.5 mmol)	0.15 g (10.2)
1-F-4-CF ₃ -C	C ₆ H ₄ :			
0.71 g (4.3 mmol)	0.73 g (4.3 mmol)	0.98 g (8.6 mmol)	0.65 g (4.3 mmol)	0.28 g (14.7)
1,3-(CF ₃) ₂ -0	C ₆ H ₄ :			
0.76 g (3.6 mmol)	0.61 g (3.6 mmol)	0.82 g (7.2 mmol)	0.54 g (3.6 mmol)	0.21 g (11.0)

For NMR data see Tables 3 and 4.

Arylxenon trifluoromethanesulfonates, which could not be isolated (Table 2), were generated via the "one-pot" procedure in CCl₃F solution as described above. On the basis of 0.3 g (1.8 mmol) XeF₂ the other components were added according to stoichiometry.

The aromatic compounds (ArH) were added dropwise at -40 °C to the CCl₃F-solution. At this temperature all volatile compounds were distilled off in vacuo until 3–5 ml of the mixture remained. The same amount of cold CH₃CN was added and the mixtures were analyzed by their ¹²⁹Xe- and ¹⁹F-NMR spectra.

Preparation of [Xe(2,4,6-F₃C₆H₂)][OSO₂F]. 0.42 g (2.5 mmol) XeF₂ were suspended in 20 ml CCl₃F at -20 °C. 0.57 g (5 mmol) CF₃COOH were added. The mixture was stirred for 3 hours. The temperature was lowered to -40 °C and after adding 0.25 g (2.5 mmol) HOSO₂F a yellow, voluminous solid precipitated. The solvent volume was reduced in vacuo, the solid was dissolved in some ml of cold $(-35 \,^{\circ}\text{C})$ CH₃CN and analysed by ¹²⁹Xe-NMR spectroscopy: δ $(^{129}Xe) = -692 \text{ ppm}$, s, $(Xe(OCOCF_3)_2)$ and δ $(^{129}Xe) =$ -267 ppm, s (CF₃COOXeOSO₂F). When adding 0.33 g (2.5 mmol) 1,3,5-F₃C₆H₃ to the system Xe(OCOCF₃)₂/ HOSO₂F in CCl₃F at -40 °C the precipitate disappeared and the solution became pale yellow. The solvent was distilled off in vacuo and the remaining 5 ml were mixed with 5 ml cold CH₃CN. [Xe(2,4,6-F₃C₆H₂)][OSO₂F]: δ (¹²⁹Xe) = $-2092 \text{ ppm}, {}^{3}\text{J}({}^{129}\text{Xe}{}^{-19}\text{F}) = 54 \text{ Hz}.$

The reaction of CF₃COOXeOSO₂CF₃ with

 $Cd(CF_3)_2 \cdot 2 CH_3CN$. To a suspension of

CF₃COOXeOSO₂CF₃ in CCl₃F at -40 °C a solution of Cd(CF₃)₂ · 2 CH₃CN was added dropwise. The reaction mixture immediately became light-yellow and a colourless solid suggested to be Cd(OSO₂CF₃)₂ or CdF₂ precipitated. The ¹⁹F-NMR spectrum of the reaction mixture showed the resonances of FXeOCOCF₃ (δ = -121.0 ppm, q, ⁵J(¹⁹F-¹⁹F) = 5.5 Hz, ¹J(¹²⁹Xe-¹⁹F) = 5471 Hz, XeF; δ = -71.6 ppm, d, ⁵J(¹⁹F-¹⁹F) = 5.5 Hz, CF₃), Cd(CF₃)₂ · 2 CH₃CN, [CdCF₃]⁺, CF₃COOH, Xe(OCOCF₃)₂, CF₃SO₃CF₂H (δ = -73.2 ppm, t, ⁵J(¹⁹F-¹⁹F) ≈ 3 Hz, CF₃; δ = -82.6 ppm, q, ⁵J(¹⁹F-¹⁹F) ≈ 3 Hz,

 ${}^{2}J({}^{19}F-{}^{1}H) = 66.6 \text{ Hz}, \text{ CF}_{2}H)$, XeF₂, HF and a CF₂HN-derivative ($\delta = -101.4 \text{ ppm}$, d, ${}^{2}J({}^{19}F-{}^{1}H) = 61.0 \text{ Hz}$) among further low-intensity resonances between -74 and -80 ppm.

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