The Molecular Structure of Gaseous Bis(trifluoromethyl)selenium Difluoride as determined by Electron Diffraction

Paul L. Baxter, Anthony J. Downs,* Alan M. Forster, and Michael J. Goode
Department of Inorganic Chemistry, University of Oxford, South Parks Road, Oxford OX1 3QR
David W. H. Rankin * and Heather E. Robertson
Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

The structure of gaseous bis(trifluoromethyl)selenium difluoride has been determined by electron diffraction. Hence the predominant species is shown to be the monomer $(CF_3)_2SeF_2$ with the CF_3 ligands occupying the equatorial sites of a framework derived from a trigonal bipyramid. Salient structural parameters (r_a) are: r(Se–F) 182.7(0.5), r(Se–C) 202.2(0.8), and r(C–F) 131.4(0.3) pm; F–Se–F 157.8(3.5), C–Se–C 118.7(1.7), and F–C–Se 108.9(0.4)°. The molecule has C_2 symmetry overall, with the CF_3 groups twisted 19.8(1.1)° away from the positions in which one C–F bond of each group is *anti* with respect to an Se–C bond (corresponding to a conformation having C_{2v} symmetry overall). Comparisons with the structures of related molecules show that the switch from SeF_4 to $(CF_3)_2SeF_2$, unlike that from SF_4 to $(CF_3)_2SF_2$, results in an *increase* in the equatorial bond angle, in keeping with the expectations of the valence shell electron pair repulsion model.

Several diorganoselenium difluorides, R_2SeF_2, have been described, *e.g.* R = alkyl[1] or perfluoroalkyl.[2] Apart from a report of the reactions of Lewis acids with certain of these compounds, little is known about their chemistry, and no definitive structural information has been reported to date. The vibrational spectra of each of the compounds Me_2SeF_2,[3] $(CF_3)_2SeF_2$,[2] and $(C_2F_5)_2SeF_2$ [2] are compatible with a discrete molecular unit having the two organic groups in equatorial sites and the two fluorine atoms in axial sites of a trigonal bipyramid centred on the selenium atom. However, the comparatively low volatility which dialkylselenium difluorides[1] share with selenium tetrafluoride implies strong intermolecular forces in the condensed phases, and there must be some doubt whether the same structural unit is retained in the gaseous as in the condensed phases. The bis(perfluoroalkyl)selenium difluorides are an exception to this pattern, as exemplified by $(CF_3)_2SeF_2$ which has a vapour pressure of *ca.* 35 mmHg (*ca.* 4 650 Pa) at room temperature.[2]

Prompted by the specific interest of two of us in the structural and chemical properties of compounds of the types $RR'EF_2$ and REF_3 (R, R′ = the same or different organic groups; E = S or Se),[4,5] we have exploited the comparative volatility of $(CF_3)_2SeF_2$ to determine the structure of the gaseous molecule by electron diffraction. Hence we have been able to confirm the trigonal-bipyramidal parentage of the molecular framework as well as the equatorial location of the Se–C bonds. The structure invites comparison, not only with that recently determined by electron diffraction for the gaseous $(CF_3)_2SF_2$ molecule,[6] but also with those of other sulphur and selenium compounds including fluorine or CF_3 groups as substituents.

Experimental

Synthesis.—Bis(trifluoromethyl) selenide, $(CF_3)_2Se$, obtained by heating selenium with silver trifluoroacetate,[7] was kindly made available by Professor A. Haas and Dr. W. Gombler of the Ruhr-Universität, Bochum. Bis(trifluoromethyl)selenium difluoride, $(CF_3)_2SeF_2$, was prepared on the small scale (10—100 mg) by the interaction of XeF_2 (prepared photochemically by direct interaction of the elements[8]) with liquid $(CF_3)_2Se$; this proceeded slowly but quantitatively at room temperature in accordance with equation (1).[5] However, to produce a sample large enough for electron-diffraction measurements (*ca.* 1 g), it was more convenient to use AgF_2 (Aldrich) as the fluorinating agent. No volatile product resulted from the contact of liquid $(CF_3)_2Se$ with AgF_2 over a period of 6 h at room temperature. However, $(CF_3)_2Se$ vapour (*ca.* 1 g) was found to react with AgF_2 (*ca.* three-fold excess) held at 363 K in a conditioned polytetrafluoroethylene (ptfe) reactor to give $(CF_3)_2SeF_2$ in *ca.* 60% yield. The efficiency of the reaction profited by removal of the $(CF_3)_2SeF_2$ from the reaction mixture at frequent intervals. The $(CF_3)_2SeF_2$ was manipulated in a vacuum system constructed from Teflon-FEP tubing with ptfe couplings and needle valves (Production Techniques Ltd.). Contact with borosilicate glass, even when conditioned, resulted in the immediate formation of solid $(CF_3)_2SeO$. The difluoride was purified by fractional condensation *in vacuo* to give a colourless liquid freezing at *ca.* 258 K; its purity was checked by reference to the i.r. spectrum of the vapour[2] and the ^{19}F n.m.r. spectrum of a $CDCl_3$ solution.[2,9] The material was stored at 77 K in an ampoule made from heat-moulded Teflon-FEP tubing and closed by a ptfe needle valve.

$$(CF_3)_2Se + XeF_2 \longrightarrow (CF_3)_2SeF_2 + Xe \qquad (1)$$

Electron-diffraction Measurements.—Electron-scattering patterns were recorded on Kodak Electron Image plates using the Edinburgh gas diffraction apparatus,[10] with nozzle-to-plate distances of 128 and 286 mm and an accelerating voltage of *ca.* 44 kV. The sample was held at room temperature (295 K) in the Teflon ampoule and gained access to the nozzle of the diffraction apparatus (also maintained at room temperature) *via* a Teflon–stainless-steel pressure coupling and a stainless-steel needle valve. The nozzle-to-plate distances and electron wavelengths are given in Table 1, together with the weighting functions used to set up the off-diagonal weight matrix, the correlation parameters, and final scale factors.

Details of the electron-scattering patterns were collected in digital form using a computer-controlled Joyce-Loebl MDM6 microdensitometer with the scanning program described previously.[11] Calculations, performed on ICL 2972 computers at the Edinburgh Regional Computing Centre, made use of the programs for data reduction[11] and least-squares refinement[12] described elsewhere, the complex scattering factors being those listed by Schäfer *et al.*[13]

Table 1. Nozzle-to-plate distances, weighting functions, correlation parameters, scale factors, and electron wavelengths

Nozzle-to-plate distance/mm	Δs	$s_{\text{min.}}$	sw_1	sw_2	$s_{\text{max.}}$	Correlation, p/h	Scale factor, k[a]	Electron wavelength[b]/pm
	nm^{-1}							
285.6	2	22	40	120	144	0.4805	0.901(11)	5.675
128.4	4	60	80	300	340	0.0972	0.798(16)	5.673

[a] Figures in parentheses are the estimated standard deviations of the last digits. [b] Determined by reference to the scattering pattern of benzene vapour.

Table 2. Portion of the least-squares correlation matrix showing off-diagonal elements greater than 50%

Distance	Angles		Vibrational amplitudes			Scale factor	
r_3	FCSe	θ	u_2	u_9	u_{13}	k_2	
-55	-89						r_2
			55				FCSe
		-75					CSeC
					64		θ
			78	51			u_1
				62			u_2
						54	u_3

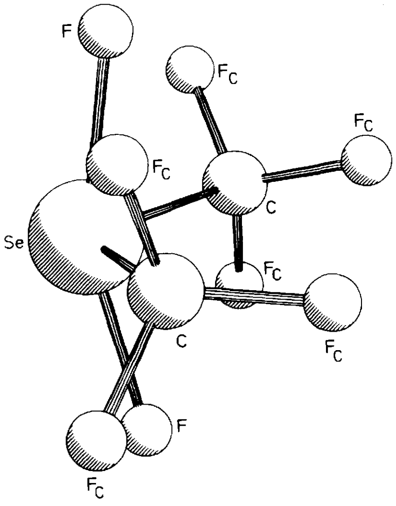

Figure 1. Perspective view of the molecule $(CF_3)_2SeF_2$

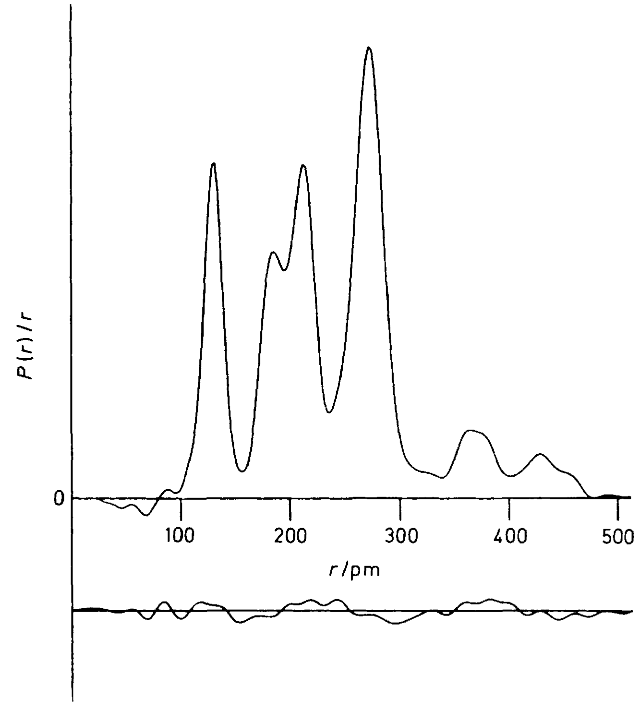

Figure 2. Observed and difference radial-distribution curves, $P(r)/r$ *vs.* r, for $(CF_3)_2SeF_2$. Before Fourier transformation the data were multiplied by $s \cdot \exp[(-0.000\,02\,s^2)/(Z_{Se} - f_{Se})(Z_F - f_F)]$

Structure Refinement

On the evidence of the vibrational[2] and fluorine-19 n.m.r. spectra,[2] bis(trifluoromethyl)selenium difluoride appears to have a molecular framework derived from a trigonal bipyramid with equatorially sited trifluoromethyl and axially sited fluorine substituents. Accordingly we adopted such a model as a basis for calculating electron-scattering intensities, preliminary analysis of the measured intensities ruling out the possibility that the CF_3 groups occupy axial positions [*cf.* the molecules $(CF_3)_nPCl_{5-n}$ ($n = 2$ or 3)[14] and $(CF_3)_nPF_{5-n}$ ($n = 1$ or 2)[15]]. Local C_{3v} symmetry has been assumed for each of the CF_3 groups but allowance has been made for 'tilting' and 'twisting' of these groups. In all, our model involves eight independent geometrical parameters. With reference to Figure 1, these comprise the three bonded distances Se–F, Se–C, and C–F_C (where F_C denotes a fluorine atom of a CF_3 group), and the five angles F_C–C–Se, F–Se–F, C–Se–C, a CF_3 'tilt' angle θ, and a CF_3 'twist' angle φ. Following the example of an earlier electron-diffraction study of the molecule $(CF_3)_2Se$,[16] we have defined θ as the angle in the CSeC plane between the C_3 axis of each CF_3 group and the C–Se bond direction, such that a positive tilt is in the direction away from the other CF_3 group. The mutual orientation of the CF_3 groups is related by φ such that $\varphi = 0$ corresponds to the C_{2v} conformation with four long and two short non-bonded C $\cdots$ F_C distances; the CF_3 groups are then rotated simultaneously about their C_3 axes by the angle φ, in opposite directions from the C_{2v} conformation, so that C_2 molecular symmetry is preserved.

The experimental radial-distribution curve (Figure 2) shows prominent, well defined peaks near 130 and 270 pm associated with the C–F bonded and Se $\cdots$ F_C non-bonded atom pairs respectively. The contributions of the Se–C bonded and shortest $F_C \cdots F_C$ non-bonded atom pairs overlap to give a single strong maximum near 200 pm; scattering from bonded Se–F atom pairs gives rise to the shoulder at *ca.* 180 pm on the flank of this peak. Near 370 and 430 pm there are broad features representing mainly the scattering from non-bonded F $\cdots$ F_C, $F_C \cdots F_C$, and C $\cdots$ F_C atom pairs. Despite appreciable correlation of the parameters defining the Se–C distance, F_C–C–Se angle, and the 'tilt' angle θ, as revealed by the final least-squares correlation matrix (see Table 2), the main features of the structure are reasonably well determined.

Molecular-scattering intensities were calculated by established procedures and the molecular structure was refined on this basis by full-matrix least-squares analysis. No corrections were

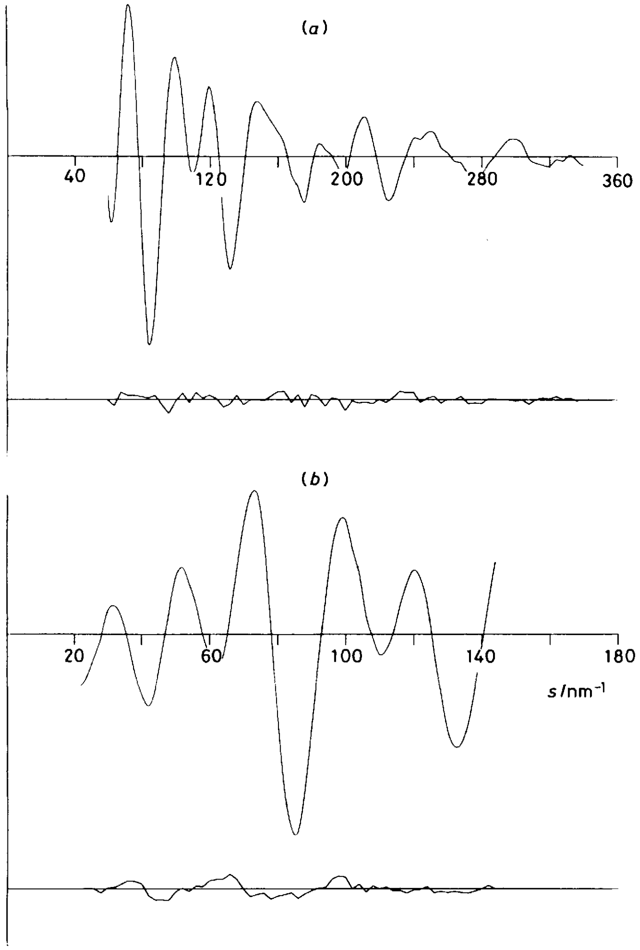

Figure 3. Experimental and final-difference molecular-scattering intensities for $(CF_3)_2SeF_2$; nozzle-to-plate distances (*a*) 128.4 and (*b*) 285.6 mm

Table 3. Molecular parameters for $(CF_3)_2SeF_2$[a]

Parameter	Distance/pm or angle/°	Amplitude/pm	
(*a*) Independent distances and amplitudes			
r_1(Se–F)	182.7(0.5)	u_1	5.4(0.9)
r_2(Se–C)	202.2(0.8)	u_2	6.2(2.3)
r_3(C–F)	131.4(0.3)	u_3	3.6(0.4)
(*b*) Dependent distances and amplitudes			
d_4(F ··· F)	358.6(1.8)		6.2[b]
d_5(C ··· F)	258.9(1.7)		10.2[c]
d_6(Se ··· F_C)	274.1(1.1)	u_6	8.1(0.5)
d_7(Se ··· F_C)	273.8(1.8)		
d_8(Se ··· F_C)	275.5(2.6)		
d_9(F_C ··· F_C)	215.4(0.6)	u_9	5.5(0.5)
d_{10}(C ··· C)	347.9(2.3)		8.0[b]
d_{11}(F ··· F_C)	245.7(1.3)		20.0[b]
d_{12}(F ··· F_C)	372.2(1.3)	u_{12}	10.9(1.6)
d_{13}(F ··· F_C)	317.9(4.1)	u_{13}	16.7(9.1)
d_{14}(F ··· F_C)	379.9(1.3)		10.9[d]
d_{15}(F ··· F_C)	265.4(2.0)		20.0[b]
d_{16}(F ··· F_C)	291.9(4.7)		20.0[b]
d_{17}(C ··· F_C)	422.5(2.3)		10.9[d]
d_{18}(C ··· F_C)	438.0(2.9)		10.9[d]
d_{19}(C ··· F_C)	348.3(2.5)		16.7[e]
d_{20}(F_C ··· F_C)	519.2(2.5)	u_{20}	21.6(11.7)
d_{21}(F_C ··· F_C)	536.4(3.6)		21.6[f]
d_{22}(F_C ··· F_C)	302.4(4.6)		20.0[b]
d_{23}(F_C ··· F_C)	484.2(3.2)		21.6[f]
d_{24}(F_C ··· F_C)	452.6(2.9)		10.9[d]
d_{25}(F_C ··· F_C)	418.0(2.9)		10.9[d]
(*c*) Independent angles			
F_C–C–Se	108.9(0.4)		
F–Se–F	157.8(3.5)		
C–Se–C	118.7(1.7)		
φ, CF_3 'twisting'	19.8(1.1)		
θ, CF_3 'tilting'	0.7(2.1)		

[a] Figures in parentheses are the estimated standard deviations of the last digits. [b] Fixed. [c] Tied to u_6 such that $u_6 = 0.8u$(C ··· F). [d] Set equal to u_{12}. [e] Set equal to u_{13}. [f] Set equal to u_{20}.

applied for 'shrinkage.' All eight of the geometrical parameters used to define the model have yielded to simultaneous refinement. Independent refinement has also been accomplished for the amplitudes of vibration of the Se–F, Se–C, and C–F bonded distances and the shortest F_C ··· F_C non-bonded distance. In addition, we have refined as a single parameter *each* of the following: (*i*) the three Se ··· F_C amplitudes (constrained to be equal) tied to the C ··· F amplitude such that u(Se ··· F_C) = $0.8u$(C ··· F); (*ii*) the amplitudes of the F ··· F_C distances near 370 pm and the C ··· F_C and F_C ··· F_C distances between 410 and 460 pm (all constrained to be equal); (*iii*) the amplitudes of the F ··· F_C distance near 320 pm and the C ··· F_C distance near 350 pm (constrained to be equal); and (*iv*) the amplitudes of the F_C ··· F_C distances between 480 and 540 pm (constrained to be equal). Otherwise we have drawn on the precedents set by the related molecules $(CF_3)_2SF_2$[6] and $(CF_3)_2Se$[16] to fix reasonable values for the remaining amplitudes.

The success of the refinement may be judged overall by reference to the difference between the experimental radial-distribution curve and that calculated on the basis of the optimum model (Figure 2). Figure 3 offers a similar comparison between the experimental and calculated molecular scattering. The structural details and vibrational amplitudes of the optimum refinement, corresponding to $R_G = 0.108$ ($R_D = 0.088$), are listed in Table 3. The estimated standard deviations take into account the effects of correlation and have been increased to allow for systematic errors in the electron wavelength, nozzle-to-plate distance, *etc.*

Discussion

Our analysis of the electron-diffraction pattern leads us first to the conclusion that bis(trifluoromethyl)selenium difluoride exists predominantly as monomeric $(CF_3)_2SeF_2$ in the vapour phase with the two CF_3 groups occupying equatorial sites and the two fluorine atoms axial sites of a framework approximating to a trigonal bipyramid centred on the selenium atom. This is consistent with the inferences drawn from the i.r. spectrum of the vapour and the Raman spectrum of the liquid.[2] It is also in keeping with the suggested order of 'apicophilicity,'[17] F > Cl, Br > CF_3 > OR, SR, NR_2, R, although discrepancies in this order are implied by the molecular structures of the gaseous species $(CF_3)_nPX_{5-n}$ (X = F, n = 1 or 2;[15] X = Cl, n = 2 or 3[14]) determined by electron diffraction. The structure of $(CF_3)_2SeF_2$ resembles that of $(CF_3)_2SF_2$[6] while inviting comparison also with that of $(CF_3)_2Se$.[16] Collation of the dimensions of these and related molecules (Table 4) reveals several noteworthy features reflecting the influences of (*i*) the nature and oxidation state of the central atom and (*ii*) the nature of the substituents.

(*i*) The Se–C bond length increases in the sequence $(CH_3)_2Se$

Table 4. Dimensions of $(CF_3)_2SeF_2$ and some related sulphur and selenium compounds

		Distance/pm		Bond angle/°		
Molecule	Method[a]	$E-F_{ax}$[b]	$E-X_{eq}$[b]	$F_{ax}-E-F_{ax}$[b]	$X_{eq}-E-X_{eq}$[b]	Ref.
$(CF_3)_2SeF_2$	e.d.	182.7	202.2	157.8	118.7	This work
SeF_4	m.s.	177.1	168.2	169.2	100.55	23
$(CF_3)_2Se$	e.d.	—	197.8	—	94.1 or 97.0	16
$(CH_3)_2Se$	m.s.	—	194.3	—	96.2	18
$(CF_3)_2SF_2$	e.d.	168.1	188.8	173.9	97.3	6
SF_4	m.s.	164.6	154.5	173.1	101.5	22
$(CF_3)_2S$	e.d.	—	181.9	—	97.3	20
SeF_6	e.d.	168.8	—	180[c]	90[c]	*c*
O_2SeF_2	e.d.	168.5	157.5	94.1	126.2	*d*
$(F_5Se)_2O$	e.d.	Se–F 166.5 Se–O 169.7	Se–F 168.3	180[e]	90.0	*e*
$(OSeF_4)_2$	e.d.	169.8	Se–F 166.8 Se–O 177.9	175.6	92.4	*f*
$OSeF_2$	m.s.	172.95	157.6	92.2	—	*g*

[a] e.d. = electron diffraction; m.s. = microwave spectroscopy. [b] E = S or Se; X = F, O, CF_3, or CH_3; $E-F_{ax}$ refers to axial and $E-X_{eq}$ to equatorial bonds in a molecule in which the environment of E is related to a trigonal bipyramid or an octahedron. For O_2SeF_2 and $OSeF_2$, which have pseudo-tetrahedral geometries, the axial and equatorial designations do not apply. [c] Assumed value. V. C. Ewing and L. E. Sutton, *Trans. Faraday Soc.*, 1963, **59**, 1241. [d] K. Hagen, V. R. Cross, and K. Hedberg, *J. Mol. Struct.*, 1978, **44**, 187. [e] Assumed value. H. Oberhammer and K. Seppelt, *Inorg. Chem.*, 1978, **17**, 1435. [f] H. Oberhammer and K. Seppelt, *Inorg. Chem.*, 1979, **18**, 2226. [g] I. C. Bowater, R. D. Brown, and F. R. Burden, *J. Mol. Spectrosc.*, 1967, **23**, 272; 1968, **28**, 461.

(r_s 194.3 pm),[18] $(CF_3)_2Se$ (197.8 pm),[16] $(CF_3)_2SeF_2$ (202.2 pm). The S–C bond length shows a similar trend, *viz.* $(CH_3)_2S$ (r_s 180.2 pm),[19] $(CF_3)_2S$ (181.9 pm),[20] $(CF_3)_2SF_2$ (188.8 pm).[6] Thus, there is a significant lengthening of the bond to carbon as the oxidation number of the Group 6 atom E (=S or Se) increases from 2 [in $(CF_3)_2E$] to 4 [in $(CF_3)_2EF_2$]; if the electronegativity of the centre E were the dominant influence, experience leads us to expect just the opposite change.[21]

(*ii*) Comparisons involving the pairs of molecules EF_4[22,23] and $(CF_3)_2EF_2$[6] (E = S or Se) show attenuation of the axial E–F bond, by about 4—6 pm, as CF_3 replaces F in the equatorial sites. Similar changes are exhibited by molecules of the type R_nPF_{5-n} (R = Me, n = 1—3;[24] R = CF_3, n = 3[15]), and are interpreted by VSEPR (valence shell electron pair repulsion) arguments[25] in terms of the increased steric demands made within the valence shell of the central atom by the electron pairs forming the bonds to the less electronegative CH_3 or CF_3 groups. Gaseous $(CF_3)_2SeF_2$ contains the longest Se–F bond to be characterized to date (see Table 4).

(*iii*) Although not particularly well determined, the C–Se–C angle in $(CF_3)_2SeF_2$ is, at 118.7°, markedly greater than the corresponding parameter in $(CF_3)_2Se$ (94.1 or 97.0° depending on the conformation).[16] It is also markedly greater than the value of 100.55° deduced by microwave measurements for the equatorial F–Se–F angle in SeF_4.[23] Rather surprisingly the analogous sulphur compounds show the following trend: $(CF_3)_2S$, $(CF_3)_2SF_2$ (both 97.3°)[6,20] < SF_4 (101.5°);[22] this cannot be reconciled with simple electronegativity arguments.[25]

(*iv*) Problems of correlation mean that the measured F–Se–F angle in $(CF_3)_2SeF_2$ is subject to considerable uncertainty [157.8(3.5)°]. Even so, its magnitude is appreciably less than 169.2°, the value deduced for the axial F–Se–F angle in SeF_4.[23] The corresponding angles in $(CF_3)_2SF_2$[6] and SF_4[22] are 173.9 and 173.1° respectively. Thus, whereas the equatorial bond angle of $(CF_3)_2SeF_2$ departs appreciably less than that of $(CF_3)_2SF_2$ from the form of a regular trigonal bipyramid, the reverse holds for the axial bond angles. There are few, if any, direct analogies but the increased bending of the axial F–E–F moiety (E = S or Se) as the atomic number of E increases parallels variations in the dimensions of the molecules H_2E,[25] MF_3 (M = N, P, or As),[25] and XF_5 (X = Cl, Dr, or I).[26]

The CF_3 groups in $(CF_3)_2SeF_2$ have dimensions in line with those in other trifluoromethyl derivatives.[6,14—16,20,21] The C–F bond length (131.4 pm) lies at the short end of the range spanned by such derivatives (131—134 pm). It is appreciably shorter, we note, than the C–F distance in $(CF_3)_2Se$ (133.3 pm), possibly because of the increased electronegativity of the tetravalent selenium centre.[21] The angular dimensions of CF_3 groups do not appear to vary significantly from molecule to molecule, the F–C–F bond angle falling consistently within the range 108—110°. The angle of 'tilt' of the CF_3 groups in $(CF_3)_2SeF_2$ is zero within experimental error, a finding consistent with the properties deduced from the electron-diffraction patterns of related molecules, *e.g.* $(CF_3)_2SF_2$.[6] In contrast to the behaviour of $(CF_3)_2Se$ which gives a double-minimum *R*-factor plot,[16] $(CF_3)_2SeF_2$ gives a single-minimum plot with a well defined angle of 'twist' of the CF_3 groups of 19.8(1.1)°.

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