Preparation of $N(SeCl)_2{}^+X^-$ (X = $SbCl_6$ or $FeCl_4$), $F_3C\overline{CSeNSeC}CF_3{}^+SbCl_6{}^-$, $F_3C\overline{CSeNSeC}CF_3$, $F_3C\overline{CSeSeC}CF_3$ and $F_3C\overline{CSeSeC(CF_3)C(CF_3)SeSeC}CF_3$. Electron Diffraction Study of $F_3C\overline{CSeSeC}CF_3$ and Crystal Structure of the Eight-membered Heterocycle $F_3C\overline{CSeSeC(CF_3)C(CF_3)SeSeC}CF_3$†

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The salts $N(SeCl)_2{}^+SbCl_6{}^-$ **1** and $N(SeCl)_2{}^+FeCl_4{}^-$ **2** were synthesized by reaction of $SeCl_3{}^+X^-$ (X = $SbCl_6$ or $FeCl_4$) with $N(SiMe_3)_3$; **1** was also formed by reaction of Se_2NCl_3 with $SbCl_5$. Reaction of **1** with $SnCl_2$ and F_3CCCCF_3 led to the formation of $F_3C\overline{CSeNSeC}CF_3{}^+SbCl_6{}^-$ **3**. In this reaction the Se_2N^+ cation is a likely intermediate because $SnCl_2$ seems to be essential for chloride abstraction in the first reaction step to generate Se_2N^+ *in situ* which then adds F_3CCCCF_3 to yield **3**. Compound **3** is a useful building block to generate selenium compounds such as $F_3C\overline{CSeNSeC}CF_3$ **4**, $F_3C\overline{CSeSeC}CF_3$ **5** and $F_3C\overline{CSeSeC(CF_3)C(CF_3)SeSeC}CF_3$ **6**. The heterocycle **5** was shown by electron diffraction to have an approximately planar four-membered ring structure. The structure of compound **6** was determined by X-ray crystallography: orthorhombic, space group *Pbca*, a = 10.1920(21), b = 13.0615(20) and c = 22.050(5) Å. In order to rationalize the structures of **5** and the cation $F_3C\overline{CSeNSeC}CF_3{}^+$, *ab initio* calculations were made on model compounds in which the CF_3 groups were replaced by a fluorine atom (*i.e.* $F\overline{CSeSeC}F$ for **5** and $F\overline{CSeNSeC}F^+$ for the cation in **3**). In addition, mass spectrometric experiments were performed in order to examine the structures and stabilities of the unligated cation $F_3C\overline{CSeNSeC}CF_3{}^+$ as well as its neutral counterpart. The existence of the neutral radical **4** was established by means of neutralization–reionization mass spectrometry.

During the last few years significant advances have been made in the area of Se–N chemistry.[1-3] The objective has been the preparation of polymeric $(SeN)_x$ which may exhibit more unusual properties than the superconductor $(SN)_x$. Several Se–N chlorides which are potential building blocks, because they are sources of the SeNSe unit, have been synthesized recently. The first examples of ternary Se–N–Cl cations were $N(SeCl_2)_2{}^+$ and $N(SeCl)_2{}^+$. The former was prepared by reaction of $SeCl_3{}^+AsF_6{}^-$ with $N(SiMe_3)_3$ [equation (1)].[4]

$$6SeCl_3{}^+AsF_6{}^- + 5N(SiMe_3)_3 \longrightarrow 9SiMe_3F + 3AsF_3 + N_2 + 6SiMe_3Cl + 3N(SeCl_2)_2{}^+AsF_6{}^- \quad (1)$$

The $N(SeCl)_2{}^+$ cation was prepared by different reaction pathways as its $GaCl_4{}^-$ or its $SbCl_6{}^-$ salt.[5-7] The salt $N(SeCl)_2{}^+GaCl_4{}^-$ was obtained from the reaction of Se_2NCl_3 with the Lewis acid $GaCl_3$ [equation (2)], whereas $N(SeCl)_2{}^+SbCl_6{}^-$ **1** was prepared by the reaction of $SeCl_3{}^+SbCl_6{}^-$ with $N(SiMe_3)_3$ [equation (3)]. The solid-state structure of the

$$Se_2NCl_3 + GaCl_3 \longrightarrow N(SeCl)_2{}^+GaCl_4{}^- \quad (2)$$

$$2SeCl_3{}^+SbCl_6{}^- + N(SiMe_3)_3 \longrightarrow N(SeCl)_2{}^+SbCl_6{}^- + SbCl_5 + Cl_2 + 3SiMe_3Cl \quad (3)$$

cation $N(SeCl)_2{}^+$ depends on its counter anion. It exists in the crystalline state as either the u isomer ($GaCl_4{}^-$ salt) or the s isomer ($SbCl_6{}^-$ salt), both isomers being essentially identical in their total energy [ΔE(MP2) = 1 kcal mol^{-1}], as shown by *ab initio* computations.[7]

Not only is the $N(SeCl)_2{}^+$ cation of general interest in terms of structure and bonding, it is also a very useful building block in the synthesis of heterocycles like $F_3C\overline{CSeNSeC}CF_3{}^+SbCl_6{}^-$, $F_3C\overline{CSeNSeC}CF_3$, $F_3C\overline{CSeSeC}CF_3$ and $F_3C\overline{CSeSeC(CF_3)C(CF_3)SeSeC}CF_3$. The synthesis of the first by reaction of **1** with $F_3CC{\equiv}CCF_3$ and $SnCl_2$ is very interesting, because the formation of the still

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† *Supplementary data available:* Further details concerning the crystal structure determination may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76012 Eggenstein-Leopoldshafen, Germany, by quoting reference CSD-57857.

Non-SI units employed: $E_h \approx 4.36 \times 10^{-18}$ J, eV $\approx 1.60 \times 10^{-19}$ J, cal = 4.184 J.

unknown Se_2N^+ cation as an intermediate is more than likely. In this paper we summarize the syntheses of the compounds, the results of some structural investigations (electron diffraction, X-ray) and of *ab initio* molecular orbital (MO) calculations for $FCSeNSeCF^+$ and FCSeSeCF. We also present the results of neutralization-reionization mass spectrometry (NRMS) experiments on compound $F_3CCSeNSeCCF_3{}^+SbCl_6{}^-$ which show the existence of $F_3CCSeNSeCCF_3$ and neutral Se_2N as stable compounds in the gas phase. The experiments presented are summarized in Scheme 1.

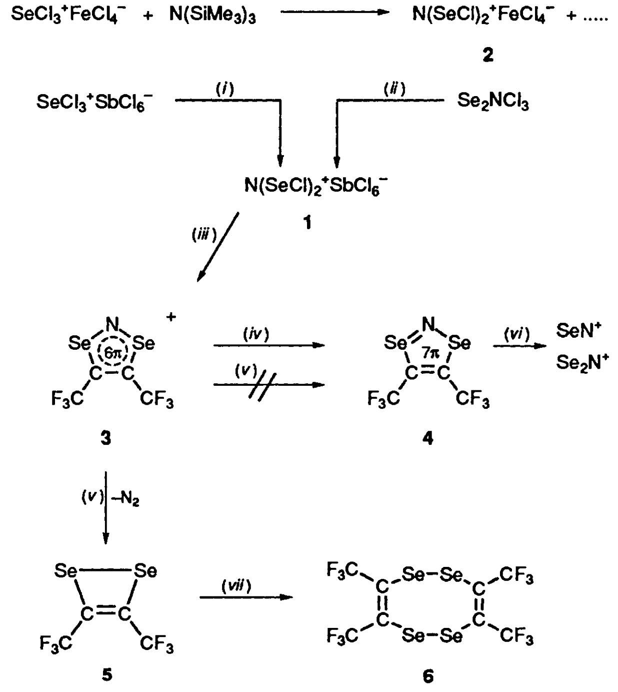
Results and Discussion

The salt $N(SeCl)_2{}^+SbCl_6{}^-$ **1** was obtained by reaction of $SeCl_3{}^+SbCl_6{}^-$ and $N(SiMe_3)_3$ in CCl_4 solution at room temperature. It was shown that the $N(SeCl)_2{}^+$ cation has a different solid-state structure (s isomer, C_s) from that in the previously reported $N(SeCl)_2{}^+GaCl_4{}^-$ salt (u isomer, C_{2v}).[6,7] At the MP2 level the s-shaped isomer is slightly higher in energy than the u-shaped cation (ΔE = 1 kcal mol^{-1}) and it was shown experimentally that only marginal differences in cation–anion interaction can favour either of these species.[7] The compound $N(SeCl)_2{}^+FeCl_4{}^-$ **2** was synthesized in 80% yield from $SeCl_4$, $FeCl_3$ and $N(SiMe_3)_3$ [equations (4) and (5)]. The infrared

$$2SeCl_4 + 2FeCl_3 \longrightarrow 2SeCl_3{}^+FeCl_4{}^- \quad (4)$$

$$2SeCl_3{}^+FeCl_4{}^- + N(SiMe_3)_3 \longrightarrow N(SeCl)_2{}^+FeCl_4{}^- + FeCl_3 + Cl_2 + 3SiMe_3Cl \quad (5)$$

spectrum of **2** shows two strong bands at 933 [ν_{asym}(SeNSe)] and at 432 cm^{-1} [ν_{sym}(SeNSe)] which indicate that the $N(SeCl)_2{}^+$ cation exists in the u-shaped C_{2v} form. The compound $N(SeCl)_2{}^+GaCl_4{}^-$ reported by Dehnicke and co-workers[6] was prepared by a different reaction route from Se_2NCl_3 and $GaCl_3$ [equation (2)]. In order to apply this reaction to the synthesis of **1**, we prepared Se_2NCl_3 from $SeCl_4$ and $N(SiMe_3)_3$.[6,8] The synthesis of $N(SeCl)_2{}^+X^-$ ($X = SbCl_6{}^-$ **1** or $FeCl_4{}^-$ **2**) is possible either by reaction of Se_2NCl_3 with Lewis acids like $SbCl_5$ or $FeCl_3$ or by the reaction of $SeCl_3{}^+X^-$ with $N(SiMe_3)_3$. The latter method is more convenient because the starting material $SeCl_3{}^+X^-$ can easily be synthesized without side-products in nearly quantitative yield whereas the yield in the preparation of Se_2NCl_3 is only 60%.[6]



Scheme 1 (*i*) $N(SiMe_3)_3$; (*ii*) $SbCl_5$; (*iii*) excess of $SnCl_2$, F_3CCCCF_3; (*iv*) NRMS; (*v*) $Na_2S_2O_4$; (*vi*) MS; (*vii*) 0 °C, 7 d

Compound **1** is a very useful building block in heterocyclic selenium chemistry. Its reaction with hexafluorobutyne and $SnCl_2$ led to the formation of the five-membered heterocycle $F_3CCSeNSeCCF_3{}^+SbCl_6{}^-$ **3** [equation (6)]. The cation in

$$N(SeCl)_2{}^+SbCl_6{}^- + SnCl_2 + F_3CC{\equiv}CCF_3 \longrightarrow \underset{\mathbf{3}}{F_3CCSeNSeCCF_3{}^+SbCl_6{}^-} + SnCl_4 \quad (6)$$

3 is the selenium analogue of the well known 4,5-bis(trifluoromethyl)-1,3,2-dithiazolylium cation.[9] It is very likely that the still unknown Se_2N^+ cation is formed during the reaction as an unstable intermediate due to the presence of $SnCl_2$, which acts as a chloride acceptor. Subsequently, it is trapped by cycloaddition to $F_3CC{\equiv}CCF_3$, which leads to the formation of **3**. This statement is supported by the fact that **1** did not react to give **3** in the absence of $SnCl_2$. Another possible reaction pathway in which $F_3CCSe(Cl)NSe(Cl)CCF_3{}^+SbCl_6{}^-$ might have been formed in the first step can be excluded because it should be sufficiently stable to have been isolated. Moreover, no reaction was observed without $SnCl_2$. In addition, the reaction of **1** with $SnCl_2$ (in the absence of F_3CCCCF_3) in order to obtain the Se_2N^+ cation (and $SnCl_4$) led to unidentified decomposition products. In contrast, the reaction of the analogous sulfur cation in $N(SCl)_2{}^+AlCl_4{}^-$ is a convenient method to synthesize $S_2N^+AlCl_4{}^-$ in good yield.[10] This means that $SnCl_2$ is necessary to abstract the chlorine atoms *via* adduct formation (*cf.* ref. 10) and that hexafluorobutyne is essential to stabilize the intermediate for formation of **3**. Unfortunately, the crystals of **3** were not suitable for a structure determination, but the structure of a model compound in which the CF_3 groups are replaced by F atoms has been computed by *ab initio* methods. The geometry was fully optimized at the Hartree–Fock (HF) and correlated MP2 level. The corresponding structures including bond lengths and angles are shown in Fig. 1. Not only at the MP2 level but also at the HF level both the Se–N and the Se–C bond distances are slightly shorter than the sum of the covalent radii for a single bond (Se–N 1.92, Se–C 1.94 Å)[11] which indicates an additional π-bond interaction between the ring atoms (6π-electron aromatic ring).

The $F_3CCSNSCCF_3{}^+$ cation can be chemically reduced with an excess of finely ground sodium dithionite in SO_2 at room temperature to give the 7π-electron radical $F_3CCSNSCCF_3$ as a sensitive black-green liquid beneath a blue gas in high yield (88%).[12] The same reaction with the selenium cation in salt **3** did not yield the 7π radical species, but led under dinitrogen elimination to the formation of $F_3CCSeSeCCF_3$ **5**. Compound **5** was obtained in 40% yield as a red liquid (m.p. −15 °C), which has to be stored at liquid-nitrogen temperature in order to prevent dimerization. The compound was previously obtained

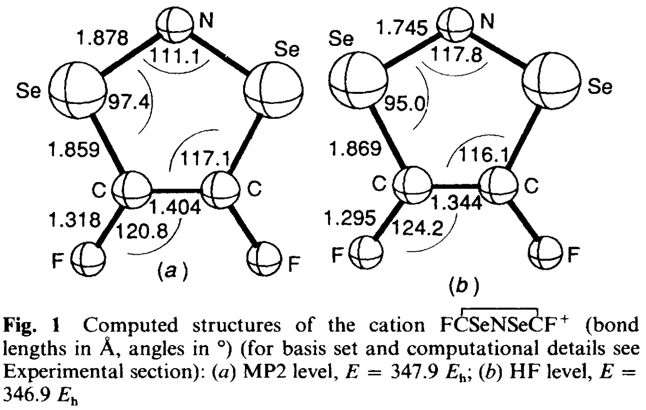


Fig. 1 Computed structures of the cation $FCSeNSeCF^+$ (bond lengths in Å, angles in °) (for basis set and computational details see Experimental section): (*a*) MP2 level, E = 347.9 E_h; (*b*) HF level, E = 346.9 E_h

by refluxing elemental selenium under a flow of N_2 and $F_3CC{\equiv}CCF_3$ [equation (7)] (yield 25%), but the structure was not determined.[13]

$$2Se + F_3CC{\equiv}CCF_3 \longrightarrow F_3C\overline{CSeSeC}CF_3 \quad (7)$$

5

The gas-phase structure of compound **5** was investigated by electron diffraction. The experimental and theoretical molecular intensities and radial distributions are shown in Fig. 2, and the molecular structure including the numbering of the atoms is presented in Fig. 3. The main results of the least-squares procedure are presented in Table 1, and the final molecular parameters with estimated total errors in Table 2. The Se–C bond length is well determined as its contribution at 1.9 Å is well separated from those of the other distances on the radial distribution curve. As to the C=C, C–C and C–F bonds, their lengths obtained using different initial values of Δ(CC) and Δ(CF) were also stable and the differences referring to refinements from different initial values did not exceed the experimental errors.

The C–C bond lengths in compound **5** and the sulfur analogue $F_3C\overline{CSSC}CF_3$ are in good agreement, taking into account the large experimental errors in the structure determination of $F_3C\overline{CSSC}CF_3$.[14] Structural changes in the rest of the molecule as compared with simpler systems suggest considerable electron-density redistribution. This seems to be consistent with the overall structure presented by Scheme 2. According to these resonance structures the Se–Se bond is not expected to be considerably different from a single bond. The length of the C–Se bonds is intermediate between the single C–Se bond in MeSeSeMe[15] and the double C=Se bond in $F_2C{=}Se$.[16]

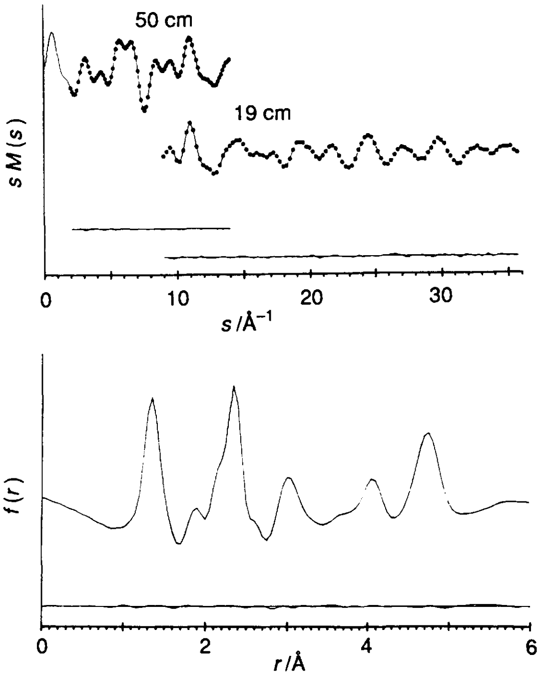


Fig. 2 Experimental (• • •) and theoretical (—) molecular intensities $sM(s)$ and radial distributions $f(r)$. The difference curves are shown below

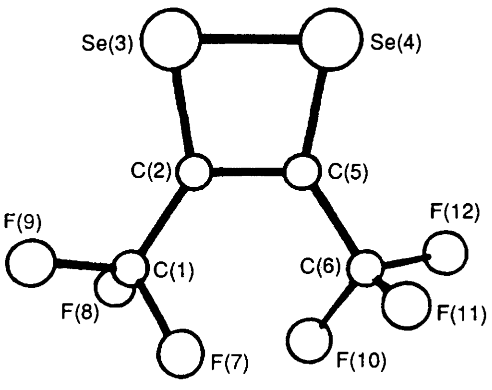


Fig. 3 Molecular structure of compound **5**

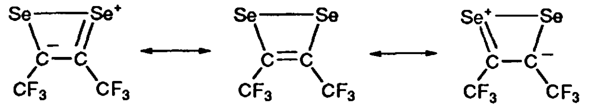
Concerning the vibrational amplitudes, they were grouped together according to the appearance of the respective distances on the radial distribution curve. This grouping is indicated in Table 1. The influence of alternative choices of the fixed differences between vibrational amplitudes belonging to the same group on the other parameters was carefully examined. It was found that the choice of these differences, in a reasonable range, did not influence the structural results beyond experimental error.

The conformation of the molecular skeleton was found to be approximately planar, the Se–C=C–Se and C–C=C–C dihedral angles being 11.3 ± 2 and 8.6 ± 3.4°, respectively. The difference from zero dihedral angles obtained in the electron diffraction analysis may be a consequence of torsional motion, and, accordingly, a planar equilibrium conformation cannot be excluded. However, the C–Se and C–C bonds originating from the same end of the C=C bond turn in the same direction. This may indicate that the deviation of the molecular skeleton from planarity is a real structural feature and not merely a consequence of torsional vibrations.

Torsion of the CF_3 groups around the C–C bonds was also examined. Refinements were made with several initial values of the C=C–C–F(7) torsional angle between 0 and 60°. The smallest R factor was obtained at 27.0°. This might indicate that rotation of the CF_3 groups is considerably restricted.

In addition, the observed tilt decreases the closest contact between Se and F, 3.033(4) Å, which is about 0.32 Å shorter than the sum of the respective van der Waals radii, 3.35 Å. This points to an interaction between Se and F of the CF_3 group as a consequence of electron-density redistribution in accordance with the resonance structures of Scheme 2, where the Se atom has a partial positive charge. Thus electrostatic interaction between the positively charged Se and electron-withdrawing fluorine could make the observed conformation the preferred one. This is facilitated by the electron-density redistribution in the molecular skeleton provided by resonance.

The structure of $F\overline{CSeSeC}F$ as a model compound for **5** was calculated by *ab initio* methods (HF, MP2). The results are shown in Fig. 4. The calculated data nicely support the experimentally obtained (electron diffraction) structural data for **5**.



Scheme 2 Resonance structures for compound **5**

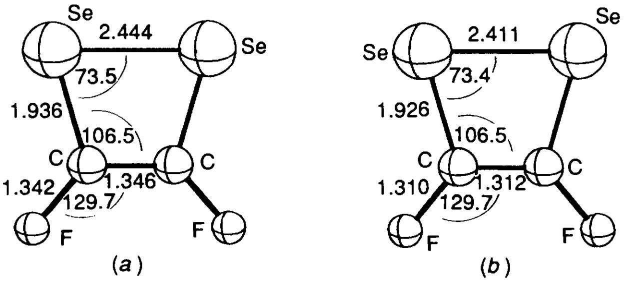


Fig. 4 Geometry-optimized structure of $F\overline{CSeSeC}F$ (bond lengths in Å, angles in °) (for basis set and computational details see Experimental section): (*a*) MP2 level, $E = 293.6\ E_h$; (*b*) HF level, $E = 292.8\ E_h$

Table 1 Results of least-squares electron diffraction refinement of $F_3C\overline{CSeSeC}CF_3$; distances in Å, angles in °

Parameter	r^a	l	Group	Parameter	r^a	l	Group
Independent							
C(2)=C(5)	1.363(5)	0.047(1)	(i)	C(1)–C(2)=C(5)–C(6)	8.6(21)		
C(2)–Se(3)	1.882(1)	0.057(2)	(ii)	F(7)–C(1)–C(2)=C(5)	27.0(12)		
C(2)=C(5)–Se(4)	105.1(2)			Tilt^b	3.4(4)		
C(1)–C(2)=C(5)	130.9(2)			Δ(CC)^c	0.125(4)		
C–C–F (mean)	111.6(1)			Δ(CF)^c	0.023(5)		
Se(3)–C(2)=C(5)–Se(4)	11.3(14)						
Dependent							
C(1)–C(2)	1.488(2)	0.051	(i)	Se(3) ··· F(8)	3.033(4)	0.103	(v)
C–F (mean)	1.340(1)	0.043	(i)	Se(3) ··· F(9)	3.665(6)	0.140	(viii)
Se(3)–Se(4)	2.367(1)	0.047(1)	(iii)	Se(3) ··· F(10)	4.757(10)	0.106	(vii)
C(1) ··· C(5)	2.593(4)	0.068(2)	(iv)	Se(3) ··· F(11)	4.698(13)	0.106	(vii)
C(1) ··· C(6)	3.316(5)	0.118(2)	(v)	Se(3) ··· F(12)	4.758(4)	0.106	(vii)
C(1) ··· F(10)	3.168(9)	0.098	(v)	F(7) ··· F(8)	2.160(1)	0.061	(iii)
C(1) ··· F(11)	3.846(5)	0.072(2)	(vi)	F(7) ··· F(10)	2.811(12)	0.103	(v)
C(1) ··· F(12)	4.510(5)	0.155(3)	(vii)	F(7) ··· F(11)	3.333(10)	0.103	(v)
C(2) ··· F(7)	2.385(6)	0.082	(iii)	F(7) ··· F(12)	4.481(9)	0.186	(vii)
C(2) ··· F(8)	2.316(3)	0.082	(iii)	F(8) ··· F(10)	4.481(9)	0.186	(vii)
C(2) ··· F(9)	2.316(3)	0.082	(iii)	F(8) ··· F(11)	4.866(4)	0.186	(vii)
C(2) ··· F(10)	2.996(10)	0.108	(vi)	F(8) ··· F(12)	5.711(7)	0.135(25)	(ix)
C(2) ··· F(11)	3.297(8)	0.108	(vi)	F(9) ··· F(10)	3.333(10)	0.103	(v)
C(2) ··· F(12)	3.590(5)	0.130(3)	(viii)	F(9) ··· F(11)	4.649(8)	0.186	(vii)
C(1) ··· Se(3)	2.971(4)	0.088	(v)	F(9) ··· F(12)	4.866(4)	0.186	(vii)
C(1) ··· Se(4)	4.079(3)	0.088	(vi)	C(2)–Se(3)–Se(4)	74.27(5)		
C(2) ··· Se(4)	2.594(2)	0.058	(iv)	F–C–F (mean)	107.3(1)		
Se(3) ··· F(7)	4.057(3)	0.089	(vi)				

[a] Least-squares standard deviations in the last digit are given in parentheses. [b] Angle between the C–C bond and direction of the C_3 symmetry axis of the trifluoromethyl group. [c] Δ(CC) = r[C(1)–C(2)] − r[C(2)=C(5)], Δ(CF) = r[C(2)=C(5)] − r(C–F)$_{\text{mean}}$.

Table 2 Bond lengths (r_g in Å), bond angles and torsion angles (°) with estimated total errors for $F_3C\overline{CSeSeC}CF_3$

C=C	1.364 ± 0.007	Se–Se	2.368 ± 0.005
C–C	1.489 ± 0.004	C–F (mean)	1.342 ± 0.003
C–Se	1.884 ± 0.004		
C–Se–Se	74.3 ± 0.1	C–C–F (mean)	111.6 ± 0.3
F–C–F	107.3 ± 0.2	C–C=C–C	8.6 ± 3.4
C=C–Se	105.1 ± 0.3	Se–C=C–Se	11.3 ± 2.0
C–C=C	130.9 ± 0.4	C=C–C–F	27.0 ± 1.9

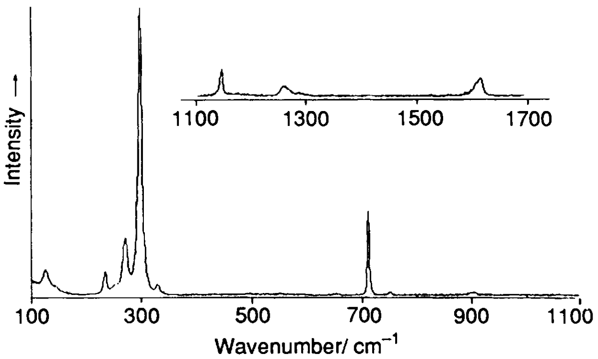


Fig. 5 Raman spectrum of compound **5** (647 nm, 50 mW, 20 °C)

The four-membered heterocycle **5** was also characterized by its Raman spectrum (Fig. 5), which is in agreement with the corresponding infrared spectrum reported in the literature.[13]

Compound **5** is unstable at 0 °C with respect to dimerization. Within 1 week a sample was completely converted into the eight-membered heterocycle **6**, which was isolated in the form of orange crystals, which were neither air nor moisture sensitive. The structure of **6** was determined by X-ray crystallography. Two different views are presented in Fig. 6. The atomic parameters are listed in Table 3, selected bond lengths and angles in Table 4. The molecular structure is a twisted eight-membered ring with four exocyclic CF_3 groups. All bond distances compare well with those expected from a simple σ,π-bonding Lewis representation.

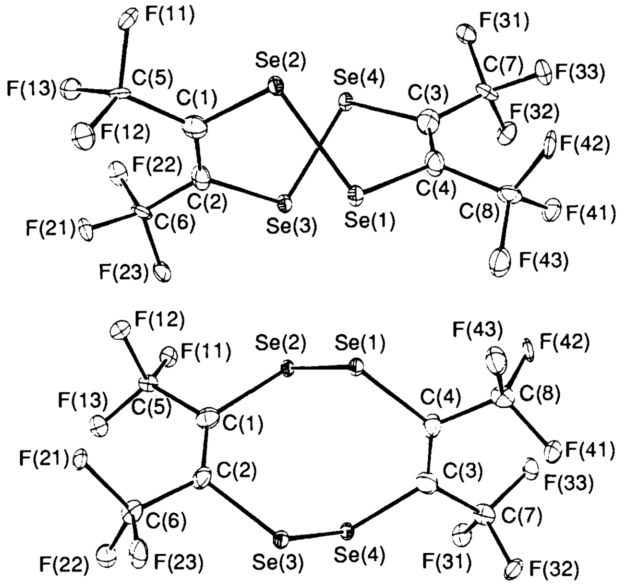


Fig. 6 Two different views[17,18] of the molecular structure of compound **6**

The sulfur analogues of compounds **5** and **6** have been known since the 1960s.[14,19] Monomeric $F_3C\overline{CSSC}CF_3$ is synthesized by refluxing sulfur in the presence of hexafluorobutyne and can easily be converted into the dimer $F_3C\overline{CSSC(CF_3)C(CF_3)SSC}CF_3$ by keeping the monomer at 25 °C for 2 months.[19] The dimer is the thermodynamically more stable at low temperatures, but at elevated temperatures (180–220 °C) it decomposes yielding the monomer.[19] In contrast to the sulfur species, the selenium compound **6** cannot be converted into **5**, but decomposes to give elemental selenium.[13]

In addition, we performed mass spectrometric experiments in order to examine the unimolecular and collision-induced fragmentations of the $F_3C\overline{CSeNSeC}CF_3{}^+$ cation in **3** as well as the stability of its neutral analogue in the gas phase. The NRMS technique has been shown to be a valuable tool for elucidation of the structures of ions and neutral compounds formed in the gas phase.[20–25]

Table 3 Atomic coordinates of compound **6** with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Se(1)	0.443 19(18)	0.021 75(12)	0.160 44(8)
Se(2)	0.255 73(18)	0.023 95(12)	0.101 57(8)
Se(3)	0.453 62(18)	0.260 29(12)	0.097 30(8)
Se(4)	0.264 33(18)	0.267 37(12)	0.154 69(8)
C(1)	0.314 2(16)	0.096 2(11)	0.031 7(8)
C(2)	0.400 5(16)	0.178 0(11)	0.029 6(7)
C(3)	0.313 5(17)	0.192 2(11)	0.225 1(7)
C(4)	0.391 5(16)	0.105 7(11)	0.226 4(7)
C(5)	0.256 9(17)	0.046 4(12)	−0.024 6(8)
C(6)	0.459 4(18)	0.220 8(13)	−0.027 3(8)
C(7)	0.258 1(19)	0.243 6(13)	0.281 5(9)
C(8)	0.450 6(19)	0.063 0(13)	0.285 7(8)
F(11)	0.138 8(10)	0.006 3(7)	−0.011 7(4)
F(12)	0.332 3(10)	−0.031 3(6)	−0.045 1(4)
F(13)	0.239 5(10)	0.110 3(7)	−0.070 9(4)
F(21)	0.486 9(9)	0.146 9(7)	−0.067 6(4)
F(22)	0.384 7(10)	0.289 2(7)	−0.054 2(5)
F(23)	0.574 1(10)	0.265 8(8)	−0.015 2(5)
F(31)	0.141 7(10)	0.285 8(7)	0.266 6(4)
F(32)	0.332 1(11)	0.316 8(7)	0.303 0(4)
F(33)	0.231 6(10)	0.176 0(7)	0.325 7(4)
F(41)	0.480 5(10)	0.137 8(7)	0.325 1(4)
F(42)	0.370 4(11)	−0.002 6(7)	0.313 2(4)
F(43)	0.561 9(11)	0.013 6(8)	0.273 0(5)

Table 4 Selected bond lengths (Å) and angles (°) of compound **6**

Se(1)–Se(2)	2.310(3)	C(5)–F(11)	1.343(19)
Se(1)–C(4)	1.896(15)	C(5)–F(12)	1.350(19)
Se(2)–C(1)	1.901(16)	C(5)–F(13)	1.329(19)
Se(3)–Se(4)	2.309(3)	C(6)–F(21)	1.342(19)
Se(3)–C(2)	1.918(15)	C(6)–F(22)	1.315(21)
Se(4)–C(3)	1.905(16)	C(6)–F(23)	1.336(21)
C(1)–C(2)	1.385(22)	C(7)–F(31)	1.349(22)
C(1)–C(5)	1.519(23)	C(7)–F(32)	1.307(21)
C(2)–C(6)	1.499(24)	C(7)–F(33)	1.342(21)
C(3)–C(4)	1.381(22)	C(8)–F(41)	1.343(20)
C(3)–C(7)	1.52(3)	C(8)–F(42)	1.330(21)
C(4)–C(8)	1.543(24)	C(8)–F(43)	1.335(21)
Se(2)–Se(1)–C(4)	101.2(5)	F(11)–C(5)–F(13)	106.7(13)
Se(1)–Se(2)–C(1)	101.7(5)	F(12)–C(5)–F(13)	107.0(13)
Se(4)–Se(3)–C(2)	102.3(5)	C(2)–C(6)–F(21)	111.7(13)
Se(3)–Se(4)–C(3)	101.9(5)	C(2)–C(6)–F(22)	113.5(14)
Se(2)–C(1)–C(2)	127.6(12)	C(2)–C(6)–F(23)	110.4(15)
Se(2)–C(1)–C(5)	109.3(10)	F(21)–C(6)–F(22)	108.1(15)
C(2)–C(1)–C(5)	123.1(14)	F(21)–C(6)–F(23)	105.4(13)
Se(3)–C(2)–C(1)	125.8(12)	F(22)–C(6)–F(23)	107.3(14)
Se(3)–C(2)–C(6)	109.2(11)	C(3)–C(7)–F(31)	108.0(15)
C(1)–C(2)–C(6)	124.8(14)	C(3)–C(7)–F(32)	113.9(15)
Se(4)–C(3)–C(4)	126.1(12)	C(3)–C(7)–F(33)	112.2(13)
Se(4)–C(3)–C(7)	109.9(11)	F(31)–C(7)–F(32)	107.2(13)
C(4)–C(3)–C(7)	123.9(15)	F(31)–C(7)–F(33)	105.6(14)
Se(1)–C(4)–C(3)	128.1(12)	F(32)–C(7)–F(33)	109.5(16)
Se(1)–C(4)–C(8)	109.4(11)	C(4)–C(8)–F(41)	111.9(13)
C(3)–C(4)–C(8)	122.5(14)	C(4)–C(8)–F(42)	112.3(15)
C(1)–C(5)–F(11)	109.7(14)	C(4)–C(8)–F(43)	109.2(14)
C(1)–C(5)–F(12)	112.1(13)	F(41)–C(8)–F(42)	108.3(14)
C(1)–C(5)–F(13)	114.2(12)	F(41)–C(8)–F(43)	107.1(15)
F(11)–C(5)–F(12)	106.7(12)	F(42)–C(8)–F(43)	107.8(13)

The metastable ion (MI) mass spectrum of $F_3C\overline{CSeNSeC}CF_3{}^+$ (Fig. 7) is dominated by the loss of hexafluorobutyne (100%), corresponding to the formal cycloreversion product of the [2 + 3] addition of the $SeNSe^+$ dipole to the alkyne. The only other unimolecular fragmentation exhibits very low intensity and corresponds to the loss of a neutral SeN unit (1%). The CA (collisional activation) mass spectrum of $F_3C\overline{CSeNSeC}CF_3{}^+$ (Fig. 8) is similar to the MI spectrum; additional peaks are due to the losses of a N or a F atom, the elimination of a CF_3 group, and fragments originating from further decomposition of $Se_2N^{\bullet +}$, *i.e.* $Se_2{}^{\bullet +}$ and SeN^+. The simple dissociation pattern and the low intensities of the radical losses are completely in line with the aromatic character of cationic $F_3C\overline{CSeNSeC}CF_3{}^+$.

The most interesting feature of the NR mass spectrum of $F_3C\overline{CSeNSeC}CF_3{}^+$ (Fig. 9) corresponds to the peak at m/z = 336 (for the $^{80}Se_2$ isotopomer) which corresponds to re-ionized neutral $F_3C\overline{CSeNSeC}CF_3$ **4**, thus establishing the intrinsic stability of neutral $F_3C\overline{CSeNSeC}CF_3{}^{\bullet}$ in the gas phase. As compared to the MI and CA mass spectra, the NR spectrum exhibits a much richer fragmentation pattern. This is not only due to the multicollision event in the NR experiment, but also reflects the decreased stability of the neutral species. However, the fragments in the NR spectrum are in line with the cyclic structure of $F_3C\overline{CSeNSeC}CF_3{}^+$, as evidenced by the signals corresponding to the heteroatom backbone, *i.e.* Se_2N^+, $Se_2{}^+$, SeN^+ and Se^+, and those of the hexafluorobutyne moiety, *i.e.* $C_4F_4{}^{\bullet +}$, $C_4F_3{}^+$, $C_3F_3{}^+$, $C_3F_2{}^{\bullet +}$, $CF_3{}^+$ and C_3F^+, respectively.

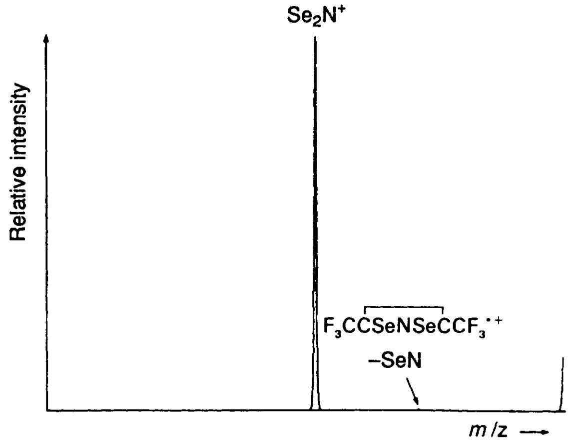


Fig. 7 The MI mass spectrum of $F_3C\overline{CSeNSeC}CF_3{}^+$

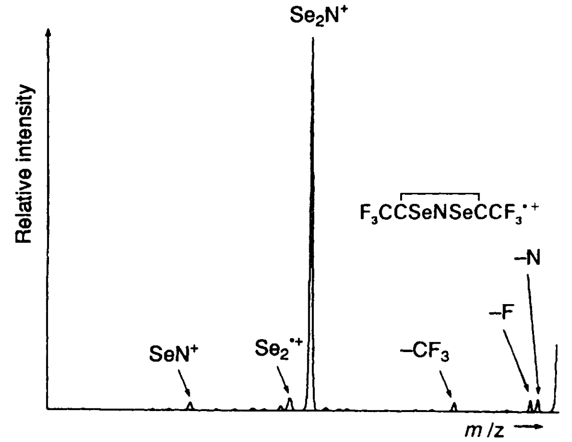


Fig. 8 The CA mass spectrum of $F_3C\overline{CSeNSeC}CF_3{}^+$

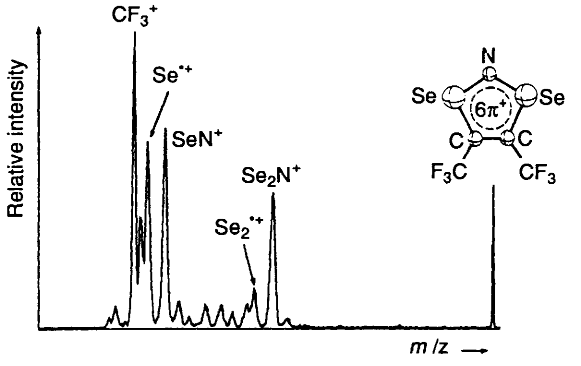


Fig. 9 The NR mass spectrum of $\mathrm{F_3C\overline{CSeNSeC}CF_3{}^+}$

According to the analysis of the isotopomers of $\mathrm{F_3C\overline{CSeNSeC}CF_3{}^+}$, the signal for the re-ionized hexafluorobutyne molecule is almost negligible. We note in passing that the Se_2N^+ cation, which is also formed upon electron impact, does also exhibit an intense recovery signal in its NR spectrum, and thus the elusive neutral $Se_2N^{\bullet}$ molecule is stable within the μs time-scale of the mass spectrometric experiment.*

Experimental

The reactions were carried out in glass vessels in an inert-gas atmosphere (N_2, dry-box). The salt $SeCl_3{}^+SbCl_6{}^-$ was directly prepared from $SeCl_4$ and $SbCl_5$ and $(SeCl)_2N^+SbCl_6{}^-$ was synthesized as described in the literature and purified by recrystallization from SO_2.[7] The compounds $N(SiMe_3)_3$, $SnCl_2$, $SbCl_5$ and $FeCl_3$ (all from Aldrich) were used as received, $Na_2S_2O_4$ (Merck) was dried over P_4O_{10} and F_3CCCCF_3 (Fluorochem) was used after distillation; CCl_4 (Merck, dried over P_4O_{10}), SO_2 (Messer Griesheim, stored over CaH_2), CH_2Cl_2 (Merck, stored over P_4O_{10}) and $CFCl_3$ (Merck, stored over P_4O_{10}) were used after distillation.

Infrared spectra were recorded using a Perkin-Elmer 580B or a Nicolet Magna spectrometer, Raman spectra using a Jobin Yvon Ramanor U 1000 spectrometer equipped with a Spectra Physics krypton-ion laser (647.09 nm), ^{13}C NMR spectra using a Bruker WH 270 instrument (67.9 MHz) and referred to $SiMe_4$ and ^{77}Se NMR spectra with a Bruker ARX 400 spectrometer (76.31 MHz) and referred to Me_2Se. Routine mass spectra were recorded on a Varian MAT 311 A instrument (electron impact, 70 eV), MI, CI and NR spectra with a modified VG ZAB/HF/AMD large-scale four-sector spectrometer of BEBE configuration (B = magnetic sector, E = electric sector).[27,28] The carbon and nitrogen analyses were performed by the TU Berlin service.

Syntheses.—$N(SeCl)_2{}^+SbCl_6{}^-$ **1** *from* Se_2NCl_3. The compound $SbCl_5$ (0.392 g, 1.311 mmol) was added to a solution of Se_2NCl_3 (0.365 g, 1.311 mmol) in SO_2 and stirred for 2 h at room temperature. After pumping off the solvent, orange crystals (0.72 g, 95%) were obtained which were spectroscopically and analytically identified to be the recently described $N(SeCl)_2{}^+SbCl_6{}^-$.

$N(SeCl)_2{}^+FeCl_4{}^-$ **2**. The compounds $SeCl_4$ (1.000 g, 4.53 mmol) and $FeCl_3$ (0.735 g, 4.53 mmol) were stirred in CCl_4 (150 cm^3) for 2 h and $N(SiMe_3)_3$ was added dropwise to the reaction mixture and stirred for another 2 h. The precipitated orange solid was filtered off, washed with CCl_4 and dried in vacuum. After recrystallization from SO_2 **2** was obtained as red needles (0.80 g, 80%) (Found: N, 3.00. Cl_6FeNSe_2 requires N, 3.15%). IR (pure compound between KBr plates): ν_{max} 933s [ν_{asym}(SeNSe)], 800s, 481s, 432vs [ν_{sym}(SeNSe)], 428s [ν(SeCl)], 418s cm^{-1} [ν(SeCl)]. Raman (20 mW, −50 °C): 434(2) [ν_{sym}(SeNSe)], 397(10) [ν(SeCl)], 381(1) [ν(SeCl)], 373(1) [$\nu_3(FeCl_4{}^-)$], 332(4) [$\nu_1(FeCl_4{}^-)$], 314(1), 128(5) [γ(SeCl)], 113(4) [δ(SeCl)]. EI mass spectrum: *m*/*z* 254 (15.9, $Fe_2Cl_4{}^+$), 230 (12, $Se_2Cl_2{}^+$), 193 (13, Se_2Cl^+), 161 (14, $FeCl_3{}^+$), 150 (84, $SeCl_2{}^+$), 126 (15, $FeCl_2{}^+$), 115 (100, $SeCl^+$), 91 (11, $FeCl^+$) and 70 (45%, $Cl_2{}^+$).

Se_2NCl_3 (cf. *ref.* 6). A solution of $N(SiMe_3)_3$ (2.200 g, 9.40 mmol) in CH_2Cl_2 (20 cm^3) was added dropwise to a suspension of $SeCl_4$ (4.100 g, 18.70 mmol) in CH_2Cl_2 (30 cm^3). The reaction mixture was refluxed for 12 h and the solution was filtered off from unreacted $SeCl_4$ and concentrated to 10 cm^3. Cooling to 5 °C yielded after 2 d a first fraction of crystals which were not used for further experiments. The second and third fractions of crystals of Se_2NCl_3 (1.30 g, 50%) were used for further experiments.

$\mathrm{F_3C\overline{CSeNSeC}CF_3{}^+SbCl_6{}^-}$ **3**. The compound $F_3CC{\equiv}CCF_3$ (0.926 g, 5.72 mmol) was condensed at −196 °C onto a frozen suspension of **1** (2.750 g, 4.76 mmol) and $SnCl_2$ (0.903 g, 4.76 mmol) in SO_2 (7 cm^3). After warming to room temperature the mixture was stirred for 5 d. It changed from red to light brown. After separation of insoluble by-products the solvent and volatile products were pumped off yielding a white solid which gave, after recrystallization, fine, colourless needles of compound **3** (2.13 g, 67%), decomp. > 155 °C (Found: C, 7.15; N, 2.25. $C_4Cl_6F_6NSbSe_2$ requires C, 7.20; N, 2.10%). IR (KBr pellet): ν_{max} 1595w, 1530w, 1260s, 1185vs [ν(CF)], 1025m, 890vw, 718m, 688m, 639w, 600w, 370m, 335s, 304w cm^{-1} [$\nu_3(SbCl_6)$]. Raman (50 mW, 20 °C): 885(1), 714(2), 636(1), 486(1), 401(1); 334(10), 288(2), 171(4) cm^{-1} [$\nu_1(SbCl_6{}^-)$]. EI mass spectrum: *m*/*z* 336 (32, $F_3CCSeNSeCCF_3$), 228 (51, $SbCl_3{}^+$), 193 (100, $SbCl_2{}^+$), 174 (35, Se_2N^+), and 158 (13%, $SbCl^+$). ^{13}C NMR (CD_3CN): δ 121.9 [2 C, q, ^1J(CF) 278, 4 CF_3] and 184.9 [2 C, q, ^2J(CF) 44 Hz, 2*C*CF_3].

$\mathrm{F_3C\overline{CSeNSeC}CF_3}$ **4**. Compound **4** was generated and identified from **3** by means of NRMS. Briefly, **3** was admitted to the ion source *via* the solid probe inlet system (probe tip temperature 160 °C) and subsequently ionized by a beam of electrons having 70 eV kinetic energy in an EI source (repeller voltage *ca.* 30 V). The ions of interest were accelerated to 8 keV kinetic energy and mass-selected by means of B(1)/E(1) at a resolution of $m/\Delta m \approx 3000$. Unimolecular fragmentations occurring in the field-free region preceding the second magnet were recorded by scanning B(2); the spectra so-obtained will be referred to as MI spectra. For collisional activation the 8 keV ions were collided with helium (80% transmission); the fourth sector was not used in this study. For NRMS experiments the precursor ions were mass-selected by means of B(1) and subjected to a double-collision experiment. Neutralization was performed by collision with xenon (85% transmission); the remaining ions were deflected by a 1000 V potential, the beam of fast neutral compounds was subsequently reionized by collision with oxygen (85% transmission), and the so-formed ions were analysed by scanning E(1). Due to the relatively low vapour pressure of **3**, the NRMS experiments were performed with the first two sectors only, and the resolution was reduced to $m/\Delta m \approx 2000$; both these modifications were necessary to obtain a sensitivity sufficient for the two-stage collision experiments. The signals of $\mathrm{F_3C\overline{CSeNSeC}CF_3{}^+}$ for the ^{78}Se, ^{80}Se and ^{82}Se isotopomers were slightly contaminated by isobaric $SbH_nCl_6{}^+$ (n = 0–2) ions, stemming from thermolysis of **3** and its subsequent reactions with background water present in the mass spectrometer. These contaminations amount to less than 1% of the ion flux, evaluated on the basis of the characteristic losses of $Cl^{\bullet}$ in the spectra of authentic $SbH_nCl_6{}^+$ formed in the ionization of $SbCl_5$. According to this analysis the contribution of neutral SbH_nCl_6 to the recovery signal in the NR spectrum amounts to less than 2%. Unfortunately, the thermal stabilities of $\mathrm{F_3C\overline{CSeNSeC}CF_3{}^+}$ salts with other counter ions, *e.g.* $AlCl_4{}^-$ and $AsF_6{}^-$, were not sufficient for

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* *Note added at proof:* Condensation of a microwave discharge excited stream of argon–nitrogen–selenium gave SeN, Se_2N and Se_2N^+, which were characterised by IR spectroscopy.[26]

NRMS experiments. All spectra were accumulated and processed on-line with either the VG 250/11 or the AMD-Intectra data system; five to 20 scans were averaged to improve the signal-to-noise ratio.

$\mathrm{F_3C\overline{CSeSeC}CF_3}$ **5**. A solution of compound **3** (1.920 g, 2.88 mmol) and $Na_2S_2O_4$ (2.510 g, 14.42 mmol) in SO_2 (7 cm^3) was stirred for 2 d at room temperature. The solvent was pumped off at −50 °C and the orange-red residue, which melts at −15 °C to give a red liquid, was condensed into a vessel held at −20 °C. The product (0.37 g, 40%) was stored at −196 °C to prevent dimerization, m.p. −15 °C. Raman (50 mW, 20 °C): 1616(1) [ν(C=C)], 1285(1), 1259(1), 1144(1) [ν(C=F)], 901(1), 751(1), 712(3), 651(1), 329(1), 297(10), 270(2), 250(1), 233(1) and 124(1) cm^{-1}. EI mass spectrum: *m/z* 322 (M^+, 100), 303 (18, *M* −F), 160 (32, *M* − F_3CCCCF_3), 143 (16, $F_3CCCCF_2^+$), 93 (10, F_3CCC^+) and 69 (11%, CF_3^+). NMR ($CDCl_3$): ^{13}C, δ 117.9 [2 C, q, ^1J(CF) 272, 2 CF_3], 124.4 [2 C, q, ^2J(CF) 21 Hz, 2CCF_3]; ^{77}Se, δ 682.2 [2 Se, q, ^3J(SeF) 2.3 Hz].

$\mathrm{F_3C\overline{CSeSeC(CF_3)C(CF_3)SeSeC}CF_3}$ **6**. Within 1 week compound **5** (0.30 g, 0.94 mmol) slowly dimerized at 0 °C and quantitatively yielded the air- and moisture-stable compound **6** (0.30 g, 100%). Single crystals suitable for X-ray diffraction study were grown by recrystallization from $CFCl_3$, m.p. 142 °C (Found: C, 15.00. $C_8F_{12}Se_4$ requires C, 15.00%). IR (KBr pellet): 1562s [ν(C=C)], 1230vs, 1179s, 1148 (sh), 1130s, 969m, 850m, 809m, 681s, 671 (sh), 595m, 554w, 528m, 460w, 358w, 331m and 270m. Raman (50 mW, 20 °C): 1559(3) [ν(C=C)], 1243(1), 1170(1), 1137(1), 966(1), 843(1), 801(1), 678(3), 667(1), 591(1), 553(1), 518(1), 456(1), 329(2), 310(9), 264(10), 214(3), 182(5), 152(7), 128(10) and 108(7) cm^{-1}. NMR ($CDCl_3$): ^{13}C, δ 120.6 [4 C, q, ^1J(CF) 278 Hz, 4 CF_3] and 131.4 (4 C, m, 4 F_3CC); ^{77}Se, NMR: δ 378 (4 Se, m).

Electron Diffraction Structure Determination of $\mathrm{F_3C\overline{CSeSeC}CF_3}$.—The electron diffraction photographs of the sample were recorded with two nozzle-to-plate distances, 19 and 50 cm, in a modified EG-100A apparatus[29,30] with a membrane-nozzle system at room temperature.[31] The experimental molecular intensity range was 2.000–14.000 $Å^{-1}$ with step 0.125 $Å^{-1}$ for the 50 cm nozzle-to-plate distance, and 9.00–35.75 $Å^{-1}$ with step 0.25 $Å^{-1}$ for the 19 cm nozzle-to-plate distance.

The analysis was carried out by applying the least-squares method to the molecular intensities.[32] Electron scattering factors were taken from available compilations.[33,34] A preliminary model of C_2 symmetry was chosen on the basis of the reported structure of 3,4-bis(trifluoromethyl)dithiete.[14] The C_2 symmetry axis bisects both the C=C and Se–Se bonds in this model. Models having C_{2v} or C_s symmetry, or no symmetry at all, were also tested. The best agreement with the experimental data was achieved for the C_2 symmetry model. The CF_3 groups had local C_3 symmetry. The following independent parameters described the molecular geometry: C–Se and C=C bond lengths; Δ(CC) (difference between C–C and C=C bond lengths); Δ(CF) (difference between the C=C and mean C–F bond lengths); C=C–Se, C–C=C and mean C–C–F bond angles. Torsional angles were also refined as independent parameters: Se–C=C–Se, C–C=C–C and C=C–C–F(7) with 0° corresponding to *syn* orientation. In the final stages of the analysis a tilt of the C_3 symmetry axes from the direction of the C–C bonds was introduced.

Crystal Structure Determination of Compound **6**.—Orange crystals were obtained from a solution of compound **6** in $CFCl_3$ at room temperature (see above).

Crystal data. $C_8F_{12}Se_4$, *M* = 639.91, orthorhombic, space group *Pbca*, *a* = 10.1920(21), *b* = 13.0615(20), *c* = 22.050(5) Å, *U* = 2935.4(10) $Å^3$, *Z* = 8, D_c = 2.896 g cm^{-3}, *F*(000) = 2334.11. Orange crystal, dimensions 0.30 × 0.38 × 0.50 mm, μ(Mo-Kα) = 10.02 mm^{-1}, λ(Mo-Kα) = 0.7093 Å.

Data collection and processing. Rigaku AFC 6S diffractometer using the routine DIFRAC,[35] ω–2θ scan mode ($2\theta_{max}$ = 45.9°), *T* = −170 °C, graphite-monochromated Mo-Kα radiation; 2757 unique reflections measured, 1779 with $I_{net} > 2.5\sigma(I_{net})$ used for calculations, absorption corrections made using DIFABS[35,36] (maximum, minimum transmission factors = 0.096 921, 0.021 194).

Structure analysis and refinement. The structure was solved by direct methods and refined by full-matrix least-squares analysis to residuals of *R* = 0.061, *R'* = 0.068 for 1312 reflections [$I \geqslant 2.5\sigma(I_{net})$] (2043 total) and 218 parameters. All atoms were assigned anisotropic thermal parameters. Scattering factors were taken from ref. 33 and corrected for anomalous dispersion.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Computational Methods.—The computations were carried out with the Gaussian 92[37] program using the 6-31 + G* basis set for nitrogen, fluorine and carbon. For selenium a (ECP28MWB)[38] quasi-relativistic pseudo-potential and the following basis set was used: Se, (5s5p)/[3s3p]-DZ + p (extended with a single *d* function, d_{exp} = 0.338).[39] The geometries for the $\mathrm{F\overline{CSeNSeC}F^+}$ cation and for the neutral $\mathrm{F\overline{CSeSeC}F}$ were fully optimized at the HF level employing standard procedures.[40] In addition, the geometries were fully optimized at the electron-correlated second-order Møller–Plesset level [MP2(full)].

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