Preparation and Properties of Difluoro(heptafluoroisopropyl)nitrilosulphur

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Difluoro(heptafluoroisopropyl)nitrilosulphur, $NSF_2CF(CF_3)_2$ (I), has been prepared by reacting NSF_3 with C_3F_6 in the presence of CsF at 90 °C; further addition of C_3F_6 gives $(CF_3)_2CFSF{=}NCF(CF_3)_2$. Above 60 °C compound (I) isomerises to $F_2S{=}NCF(CF_3)_2$. Both *cis*- and *trans*-$(CF_3)_2CFSF_4N{=}SF_2$ have been isolated from the reaction between SF_4 and (I) in the presence of HF. Spectroscopic data for the new compounds are presented.

THE only substituted derivatives, $N{\equiv}SF_2X$, of trifluoronitrilosulphur that are known are those which have been prepared by reacting $N{\equiv}SF_3$ with a secondary amine ($X = NEt_2$[1] or NC_5H_{10}[2]) or phenol ($X = OPh$[2]). We have investigated possible routes to derivatives in which a carbon–sulphur bond is formed and have successfully isolated difluoro(heptafluoroisopropyl)nitrilosulphur, $N{\equiv}SF_2CF(CF_3)_2$ (I).

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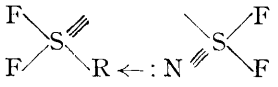
RESULTS AND DISCUSSION

Trifluoronitrilosulphur has been prepared from both $SF_2{=}NC(O)F$ [3] and, under the same conditions, $SF_2{=}NC(O)CF_3$ [4] by oxidative fluorination with silver difluoride. However, we have found that an analogous reaction between $(CF_3)_2CFSF{=}NC(O)CF_3$ and AgF_2 does not produce the expected product but its isomer $SF_2{=}NCF(CF_3)_2$, which has previously been prepared by the reaction of SF_4 and $(CF_3)_2C{=}NH$ in the presence of CsF.[5]

Rosenberg and Muetterties first demonstrated the catalytic effect of CsF on the addition of perfluoropropene to a sulphur–fluorine bond when they produced a mixture of $(CF_3)_2CFSF_3$ and $[(CF_3)_2CF]_2SF_2$ from SF_4 at 150 °C.[6] We have now shown that C_3F_6 and NSF_3 produce $NSF_2CF(CF_3)_2$, (I), in the presence of CsF at 90 °C. While a sample of compound (I) contained in an n.m.r. tube appeared to be indefinitely stable at room temperature, it slowly rearranged to $F_2S{=}NCF(CF_3)_2$ at 80 °C; conversion took place at 90 °C within 20 h. Small traces of $N{\equiv}SF$,[7] SF_4,[8] and OSF_2 [8] were also detected by i.r. spectroscopy when the isomerisation reaction was carried out at 110 °C.

The driving force for the isomerisation appears to be mainly the greater energy of the C–N bond which is formed compared to that of the C–S bond which is broken. It is certainly not due to increased strength of the N–S multiple bond, which appears to be weaker in the product. Since the change in entropy for the reaction should be small, the sum of the bond energies of the product should be larger than that for the reactant. Indeed, when the sums of the energies are calculated, that for the product is found to be slightly greater (by 6 kcal) than that for the reactant, using the following values: $S^{VI}{-}C$, 52;[9] $S^{VI}{-}F$, 79;[9] $S^{VI}{\equiv}N$, 96;[10] R–N, 73;[11] $S^{IV}{-}F$, 82;[9] and $S^{IV}{=}N$, 75 kcal.[10] Although some of the values used are of doubtful accuracy, the free energy for the isomerisation is probably not large.

No attempt has been made to elucidate the mechanism of the isomerisation reaction; however, a reasonable possibility is a two-centered bimolecular Michaelis–Arbusov-type reaction involving an intermediate with a six-membered ring.



It was also found that no compound (I) was recovered from a sample which had been irradiated in the gas phase by a 450 W high-pressure mercury discharge lamp for 30 min. The greater number of compounds hereby produced together with $SF_2{=}NCF(CF_3)_2$ is indicative of a more complex break-down pattern. Compound (I) was recovered from a sample which had been set aside in contact with water for 1 week at room temperature; under similar circumstances $F_2S{=}NCF(CF_3)_2$ was completely hydrolysed.[4] The only other compound reported to exist both as $F_2S{=}NX$ and NSF_2X is that for which X = F; $SF_2{=}NF$ has only recently been reported [12] while the existence of $N{\equiv}SF_3$ has been established for some time.[13] While the compounds $XN{=}SF_2$ [X = Cl, Br, or I(?)] have been prepared, their corresponding nitrilosulphur derivatives have not been isolated.[14-16]

The thermal instability of compound (I) limited the maximum temperature which could be employed for determination of its preparation. However, at low temperatures the compound was formed only slowly and there was a tendency for more by-products to be formed. Those derived from oligomerisation of C_3F_6 [17] could be reduced by employing an excess of $N{\equiv}SF_3$. On the other hand the formation of fluoro(heptafluoroisopropyl)(heptafluoroisopropylimino)sulphur, $(CF_3)_2CFSF{=}NCF(CF_3)_2$, was inevitable, since it was formed from (I) and C_3F_6 in the presence of CsF at 65 °C, a temperature at which catalytic addition of C_3F_6 to NSF_3 does not take place. Similar reactions between $F_2S{=}NR_f$ ($R_f = CF_3$, C_2F_5, or C_3F_7) and C_3F_6 in the presence of CsF at 80—90 °C have been examined by Dresdner and his co-workers.[18,19] Small quantities of $(CF_3)_2CFCF(CF_3)_2$ and $(CF_3)_2C{=}NCF(CF_3)_2$ were also produced in the preparation of (I). The imine may well have been produced by the mechanism responsible for formation of $CF_3(C_2F_5)C{=}NCF_3$ as the main product of the CsF-catalysed reaction between $CF_3CF{=}CFCF_3$ and $F_2S{=}NCF_3$ above 280 °C.[19]

While it has been shown that $N{\equiv}SF_3$ is capable of adding two molecules of HF at room temperature to produce SF_5NH_2,[20] we were unsuccessful in our attempts at isolating the analogous product, $(CF_3)_2CFSF_4NH_2$, from a mixture of compound (I) and HF. The stabilities of these primary amines may well parallel those of the secondary amines SF_5NHR_f ($R_f = CF_3$, C_2F_5, or C_3F_7),

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where an increase in the chain length of R_f was reported to have a destabilising effect.[21]

Clifford and Zeilenga have shown that $N{\equiv}SF_3$ will undergo reaction with SF_4 in the presence of HF at room temperature to produce $SF_5N{=}SF_2$ with SF_5NH_2 acting as an intermediate.[22] Aminotetrafluoro(heptafluoroisopropyl)sulphur, $(CF_3)_2CFSF_4NH_2$, probably has limited stability since it was possible to isolate both *cis*- and *trans*-(*SS*-difluorothionitrosyl)tetrafluoro(heptafluoroisopropyl)sulphur, $(CF_3)_2CFSF_4N{=}SF_2$, from a mixture of (I), SF_4, and HF by employing somewhat more demanding reaction conditions than those used above. There is no evidence for these two compounds being interconvertible for, after heating the pure isomers for 4 days at 65 °C, no change in their n.m.r. spectra was detected. This is believed to be the first reported case in which both of the possible disubstituted isomers of a compound XSF_4Y have been isolated. *trans*-Isomers have been reported for XSF_4Y where X and Y are two perfluoroalkyl groups,[23-25] but n.m.r. spectra of disubstituted derivatives containing S–O linkages (X, Y = $O{-}SO_2F$,[26] OSF_5,[27] and OCF_3 [28]) showed the presence of only the *cis*-isomers. N.m.r. spectroscopy was again used to determine the structure of the mixed disubstituted derivatives; in $CF_3SF_4NF_2$ [29] and CF_3SF_4Cl [30] the substituents were *trans* to each other while only a *cis*-isomer was characterised for $CF_3OSF_4NF_2$.[31]

N.M.R. Spectra.—The n.m.r. bands for the new compounds [Table 1, Supplementary Publication No. SUP 20892 (9 pp.) *] show asymmetry and poor resolution in the case of $(CF_3)_2CFSF{=}NCF(CF_3)_2$, and do not permit evaluation of coupling constants. The same problem has been observed for similar compounds, where it was proposed to originate from magnetic nonequivalence of the two perfluoromethyl groups.[18,32] The data show that the CF_3 resonance originating from a perfluoroisopropyl group attached to a fluorine-bearing sulphur atom regularly occurs downfield from one attached to a two-co-ordinate nitrogen atom; a similar trend cannot be noted for the CF resonance. The singlet produced by the fluorine atoms attached to sulphur in compound (I), broadened probably due to the presence of the nitrogen's quadrupole moment, appears at *ca.* 25 p.p.m. to lower field than any previously reported value for the chemical shift of NSF_3 or any of its derivatives.[2]

Characterisation of the *trans*- and *cis*-forms of $(CF_3)_2CFSF_4N{=}SF_2$ was based on interpretation of their n.m.r. spectra. Since the four planar S-fluorine atoms in *trans*-$(CF_3)_2CFSF_4N{=}SF_2$ are all magnetically equivalent a first-order spectrum was obtained. The values for $\delta(SF_4)$ and $\delta(NSF_2)$ lie close to those observed for $F_5SN{=}SF_2$.[33] By using the coupling constants derived from the simpler CF_3 and $N{=}SF_2$ resonances it was possible to interpret the more complex multiplets resulting from the CF and SF_4 groups. The SF_4 group of the *cis*-isomer contains three magnetically different types of fluorine atoms. These resulted in a complex second-order spectrum. A comparison of this spectrum with that of *cis*-$CF_3OSF_4NF_2$,[31] in which the SF_4 group also represents an A_2BC spin system, showed basically the same pattern in the low-field region. The fluorine atom having its resonance at the lowest field (' C ') produced a basic quartet with further irregular fine structure. The distance between these bands (*ca.* 130 Hz) approximated that between the two very complex multiplets which constituted the resonance of the A_2B fluorine atoms. Without a complete analysis of both these resonances and those due to the fluorine atom in the $(CF_3)_2CF$ and NSF_2 groups it is not possible to present further coupling-constant data or indicate which fluorine atoms are B and C.

I.R. Spectra.—The i.r. spectra (SUP 20892) of compound (I) and *cis*- and *trans*-$(CF_3)_2CFSF_4N{=}SF_2$ all show two or three very intense bands in the 1 243—1 297 cm^{-1} region and two weaker peaks at 1 154—1 194 cm^{-1} due to $\nu(CF_3)$ and $\nu(CF)$. The two peaks falling between 944 and 977 cm^{-1} were assigned to $\nu(CC)$ in $[(CF_3)_2CF]_2SF_2$.[34] The presence of two perfluoroisopropyl groups in $(CF_3)_2CFSF{=}NCF(CF_3)_2$ is reflected in the increased number of peaks found in these regions.

Either of the two peaks observed in the spectrum of compound (I) at 1 504 and 1 479 cm^{-1} could be assigned to $\nu(S{=}N)$;[1,2,7] the other peak is probably a combination band whose intensity is enhanced by Fermi resonance. The position of $\nu(S{=}N)$ has been studied in a large number of compounds,[13,19,32,35] and can be assigned to a prominent peak at 1 314 cm^{-1} in *trans*-$(CF_3)_2CFSF_4N{=}SF_2$ (compared with 1 313 cm^{-1} in $SF_5N{=}SF_2$ [3]) which is shifted to a shoulder at 1 300 cm^{-1} in the *cis*-isomer. The shoulder at 1 317 cm^{-1} in $(CF_3)_2CFSF{=}NCF(CF_3)_2$ was similarly assigned. Two strong peaks at 746 and 719 cm^{-1} in the spectrum of (I) were assigned to asymmetric and symmetric SF_2 stretching modes; these are close to the values observed for similar modes in $F_2S{=}NCF(CF_3)_2$.[5] No peak could be definitely assigned

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index Issue (items less than 10 pp. are supplied as full size copies).

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to ν(CS) which has been allotted to bands falling over a wide range of frequencies.[34,36]

The 800—900 cm^{-1} region of $F_2S{=}NCF(CF_3)_2$ and (I) and related compounds [5,37] is generally void of any strong absorption bands. The presence of intense peaks in this vicinity for both isomers of $(CF_3)_2CFSF_4N{=}SF_2$ must therefore result from SF_4 stretching modes. The single band observed at 867 cm^{-1} for the *trans*-isomer falls in the range characteristic of the planar SF_4 stretching vibration in monosubstituted derivatives of SF_6 [38] and also lies close to the value reported for this mode in *trans*-CF_3SF_4Cl.[30] The presence of two bands in the same region at 845 and 874 cm^{-1} for the *cis*-isomer is indicative of this compound's lower symmetry. The possibility of further assigning the remaining bands below this region is limited by the large number of stretching and bending modes expected for both these compounds.

Mass Spectra.—The mass spectrum of compound (I) was run with the ion source operating at its lowest possible temperature (*ca.* 50 °C) to avoid the compound's rearrangement to $F_2S{=}NCF(CF_3)_2$. Several differences between the mass spectra (Table 2, SUP 20892) of these two compounds were apparent. The molecular ions of both $N{\equiv}SF_3$ [39] and (I) were found to be more abundant than those of their respective isomers $F_2S{=}NF$ [17] and $SF_2{=}NCF(CF_3)_2$.[4,5] The more facile elimination of a nitrogen compared to a fluorine atom from $NSF_2CF(CF_3)_2^+$ also paralleled the break-down pattern of NSF_3^+. Several other fragments resulting from S≡N bond cleavage which still retained the C–S bond intact were also present; no appreciable concentration of ions resulting from rupture of the S≡N bond which still retained a C–N bond were observed, however, in the mass spectrum of $F_2S{=}NCF(CF_3)_2$. Ions resulting solely from rupture of the C–N bond in $F_2S{=}NCF(CF_3)_2^+$ and $R_2NSF{=}NCF(CF_3)_2$ (R = Me or Et) [35] were found in very low abundance while those observed for fracture of the C–S bond in $NSF_2CF(CF_3)_2^+$ and $(CF_3)_2CFSF{=}NR'^+$ [R' = $CH_2C(O)CF_3$] [32] were far more plentiful. It seems probable then that the very abundant ion at *m/e* 234 in the mass spectrum of $(CF_3)_2CFSF{=}NCF(CF_3)_2$ had the structure $FSNCF(CF_3)_2^+$ rather than $(CF_3)_2CFSFN^+$.

While the ion at *m/e* 184 formed from both $F_2S{=}NCF(CF_3)_2$ and (I) was presumably derived through loss of a perfluoromethyl radical from the molecular ion, the occurrence of a metastable ion indicated that, regardless of its source, it was able to decompose to CF_4SN^+ (*m/e* 134) and SN^+ through the elimination of CF_2 and C_2F_6 respectively. Only one major ion, $C_2F_4SN^+$ with *m/e* 146, present for $F_2S{=}NCF(CF_3)_2$ was almost absent from the mass spectrum of (I). This may result from the less-dominant role of the (M–F) ion in the cleavage of the latter compound.

The near identity of the mass spectra of the *cis*- and *trans*-isomers of $(CF_3)_2CFSF_4N{=}SF_2$ does not aid assignment of their symmetry. The most apparent difference is the higher abundance of ions with *m/e* 134 and 184 in the spectrum of the *cis*-isomer. Neither compound gave a molecular ion. The abundances of the heavier fragment ions indicate that it probably prefers to undergo simple cleavage at either the C–S bond to produce $C_3F_7^+$ or $F_6S_2N^+$ or at the S–N bond to form $C_3F_{11}S^+$. The ion SF_3^+ was also observed to constitute the base peak in the mass spectrum of $SF_5N{=}SF_2$.[3]

EXPERIMENTAL

Pressure reactions were carried out in Hoke stainless steel cylinders (30 cm^3) fitted with Whitey valves. Gases and volatile liquids were manipulated by using a standard Pyrex vacuum system. Initial separations were made by trap-to-trap distillation generally using traps of −196, −120, −95, and −78 °C. Fluorine-19 n.m.r. spectra were recorded on neat liquids (with CCl_3F as external reference) using a JEOL C-60 H spectrometer. Mass spectra were recorded on a Hitachi–Perkin-Elmer RMU-7 mass spectrometer; values are reported for ions with *m/e* above 30 and refer only to the most abundant isotope. The i.r. spectra, which are reported between 500 and 2 000 cm^{-1}, were run on vapour-phase samples using a Perkin-Elmer 621 spectrophotometer. Elemental analyses were undertaken by Bernhardt. Starting materials were either prepared in the laboratory or obtained commercially.

Reactions.— *Fluoro(heptafluoroisopropyl)(trifluoroacetylimino)sulphur with silver difluoride.* The compound $(CF_3)_2CFSF{=}NC(O)CF_3$ (0·453 g, 1·37 mmol) [prepared from the reaction between $(CF_3)_2CFSF_3$ and $CF_3C(O)NH_2$ in the presence of CsF in the manner employed by Glemser for the reaction of SF_4 and $H_2NC(O)NH_2$ [5]] was condensed into an evacuated bomb containing an excess of AgF_2 (Harshaw Chemical Co., technical grade) and set aside at room temperature for 1 day. Trap-to-trap distillation removed $CF_3C(O)F$ (1·23 mmol, identified by its i.r. spectrum).[40] The less-volatile material was similarly divided into two portions. The minor, more volatile fraction was mostly composed of $SF_2{=}NCF(CF_3)_2$, though its mass spectrum was contaminated by peaks arising from $(CF_3)_2CFCF(CF_3)_2$ [41] and $(CF_3)_2C{=}NCF(CF_3)_2$.[42] NSF_3 was also identified by its i.r. spectrum.[7] The i.r. spectrum recorded on the less volatile material showed weak peaks in the carbonyl-stretching region which were not present in the starting material and in addition indicated that $(CF_3)_2CFSF{=}NCF(CF_3)_2$ and $(CF_3)_2CFCF(CF_3)_2$ [36] were also present. There are references in the literature which relate to the reduction of S^{IV} to disulphides.[19] Presumably AgF_2 does not oxidise this disulphide under these conditions [43] although it has been reported to convert CF_3SSCF_3 to CF_3SF_3 and CF_3SF_5 below room temperature.[44]

Trifluoronitrilosulphur with perfluoropropene and caesium fluoride. NSF_3 [3] (43 mmol) and C_3F_6 (33 mmol) (Columbia

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Organic Chemicals Co., Inc.) were condensed into a bomb containing CsF (American Potash and Chemical Corp., dried by heating under vacuum; 1 g) and kept at 90 °C for 3 h. The i.r. spectrum of the most-volatile portion of the products was consistent with a slightly impure sample of NSF_3[7] (*ca.* 16 mmol) containing no C_3F_6.[45] The compound $NSF_2CF(CF_3)_2$, (I), was trapped at −95 °C and $(CF_3)_2CFSF{=}NCF(CF_3)_2$ at −78 °C. Final purification by preparative-scale gas chromatography, using a 14 ft column of dinonyl phthalate (20%) on Anakrom ABS, yielded a pure volatile colourless liquid (21 mmol, *ca.* 80% yield), *difluoro(heptafluoroisopropyl)nitrilosulphur*, (I) [Found: C, 14·1; F, 67·3; N, 5·5; S, 12·6; *M*, 253 (mass spec.). Calc. for C_3F_9NS: C, 14·2; F, 67·6; N, 5·5; S, 12·6%; *M*, 253]. I.r. spectrum: [ν(S=N) and combination bands] 1 504mw, 1 479mw; [$\nu(CF_3)$ and ν(CF)] 1 297s, 1 263vs, 1 194mw, 1 158m; [ν(C–C)] 977m, 950mw; [δ(CF)] 764mw sh; [$\nu_{asym}(SF_2)$ and $\nu_{sym}(SF_2)$] 746m, 719s; [def. modes and ν(C–S)] 624w, 542vw, 520m, and 502mw sh cm^{-1}.

The major impurity removed at this stage was $F_2S{=}NCF(CF_3)_2$. The presence of $(CF_3)_2CFCF(CF_3)_2$ was confirmed by its mass and i.r. spectra;[41] samples examined by n.m.r. spectroscopy were too dilute for the CF resonance to be detected but a doublet in the CF_3 region at 72·3 p.p.m. separated by 8·7 Hz was observed (compared with the literature values of 71·0 p.p.m. and 9·0 Hz).[46] The presence of $(CF_3)_2C{=}NCF(CF_3)_2$ was detected by its mass spectrum.[42] Oligomers of C_3F_6 were identified in some samples by comparing their i.r. and n.m.r. spectra with those of the authentic compounds.

Difluoro(heptafluoroisopropylimino)sulphur with perfluoropropane and caesium fluoride. $F_2S{=}NCF(CF_3)_2$ (1·16 g, 4·6 mmol),[5] C_3F_6 (1·93 g, 12·9 mmol), and CsF (2 g) were heated in a bomb at 65 °C for 24 h. The excess of C_3F_6 (1·31 g, 8·8 mmol) was removed and the remaining liquid was distilled from trap to trap. The intermediate fraction compound was a colourless liquid, from which trace impurities were removed by preparative-scale gas chromatography using a 17 ft column packed with n-hexadecane (12%) or Anakrom ABS, characterised as *fluoro(heptafluoroisopropyl)(heptafluoroisopropylimino)sulphur* [Found: C, 17·9; F, 70·5; N, 3·6; S, 8·0; *M*, 396 (vapour density; average of trace readings). Calc. for $C_6F_{15}NS$: C, 17·8; F, 70·7; N, 3·5; S, 7·7%; *M*, 403; v.p. 37 mmHg at 23 °C]. I.r. spectrum: 1 380vw; 1 345mw sh; 1 317m sh; 1 297s; 1 256vs; 1 223m; 1 190m; 1 144m; 1 096m; 1 023m; 988s; 949w; 747w; 728m; 702w; 683m; 668mw sh; 607vw; 561vw; and 541mw cm^{-1}.

Difluoro(heptafluoroisopropyl)nitrilosulphur with hydrogen fluoride. After leaving compound (I) (0·711 g) with an excess of HF in a bomb for 1 week at room temperature, the mixture was distilled into another vessel packed with NaF pellets (Harshaw Chemical Co.) which absorbed the unreacted HF over a period of several hours. A yellowish liquid (0·655 g) was recovered. Most of this material passed through a −78 °C trap and was identified by its i.r. spectrum as unreacted (I) together with some $(CF_3)_2CFCF(CF_3)_2$,[41] $F_2S{=}NCF(CF_3)_2$, and SO_2.[47] The remaining material was chromatographed, using a 14 ft column packed with tricresyl phosphate (15%) on Anakrom ABS, and shown to contain several components. An i.r. spectrum indicated that one compound, which was obtained in trace amounts, gave a peak due to ν(NH) at 3 630 cm^{-1}, but the absence of absorption bands in the 800—900 cm^{-1} region showed that it could not be due to $(CF_3)_2CFSF_4NH_2$. The compounds $(CF_3)_2CFSF{=}NCF(CF_3)_2$, $(CF_3)_2CFSSCF(CF_3)_2$, and $(CF_3)_2CFSSSCF(CF_3)_2$ were identified by their mass spectra. Both the di- and tri-sulphides produced abundant *M* and [$M - C_3F_7$] ions. These would be anticipated from the published mass spectrum of CF_3SSCF_3.[48]

Difluoro(heptafluoroisopropyl)nitrilosulphur with sulphur tetrafluoride and hydrogen fluoride. As excess of HF (*ca.* 50 mmol) was condensed into a bomb containing (I) (1·570 g, 6·2 mmol) and SF_4 (1·769 g, 16·4 mmol) (Matheson Co., purified by low-temperature distillation). After heating the mixture for 3 h at 60 °C the slightly yellow liquid recovered was separated by fractional distillation. The liquid (1·303 g) trapped at −78 °C was mainly composed of the desired product [*ca.* 50% yield based on (I) not recovered]. While both isomers passed a −44 °C bath and were trapped at −65 °C, separation could be achieved by preparative-scale gas chromatography, using a 14 ft column packed into n-hexadecane (12%) on Anakrom ABS. Also removed were traces of $(CF_3)_2CFSF{=}NCF(CF_3)_2$ and $(CF_3)_2CFSSCF(CF_3)_2$. Both g.l.c. and n.m.r. results indicated that the *cis-* and *trans*-isomers were formed approximately in a ratio of 3 : 2. A similar mixture of cis- and trans-(SS-*difluorothionitrosyl)tetrafluoro(heptafluoroisopropyl)sulphur*, existing as a colourless, not very volatile liquid (vapour pressure 15 mmHg at 28 °C), was analysed [Found: C, 10·0; F, 68·7; N, 3·9; S, 17·7; *M* (vapour density; average of five readings) 367; Calc. for $C_3F_{13}NS_2$: C, 10·0; F, 68·5; N, 3·9; S, 17·7%; *M*, 361]. I.r. spectrum: (*trans*-isomer) 1 314s, 1 287s, 1 260s, 1 243vs, 1 178mw, 1 156m, 975m, 949vw, 867vs, 800m, 757vw, 727m, 713m, 692s, 645s, 593vw, 551mw; (*cis*-isomer) 1 300m sh, 1 280vs, 1 263s, 1 245vs, 1 177mw, 1 154m, 970m, 948w, 874s, 845s, 801s, 751s, 726m, 716m, 660w, 597w sh, 583mw, 546w, and 517w cm^{-1}.

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