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Conformationally Controlled Intramolecular Heterocyclization of 2,4-Diaminoperfluoro-4-methyl-2-pentenethiocyanate-3

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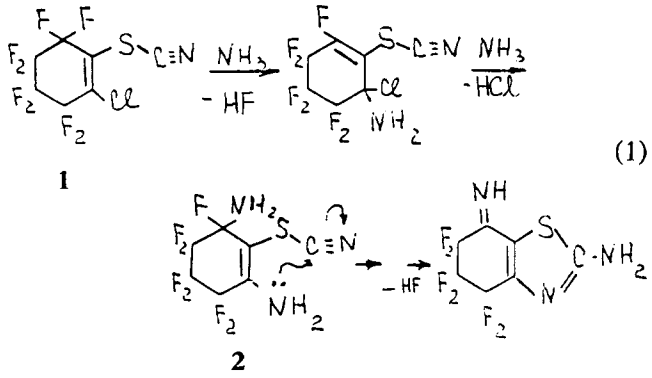
ABSTRACT

Perfluoro-2-methyl-2-pentene-thiocyanate-3 reacts with ammonia to give 2,4-diaminoperfluoro-4-methyl-2-pentenethiocyanate-3 (**4**) *and 2-aminoperfluoro-4,4-dimethyl-4,5-dihydro-5-ethylidene-1,3-thiazole* (**5**). *Compound* **4** *is kinetically stable and at 150°C undergoes rotational isomerization to afford the cyclic isomer 2-amino-4,4-bis(trifluoromethyl)-4,5-dihydro-5-(1-aminoperfluoroethylidene)-1,3-thiazole* (**6**). *Intramolecular cyclizations, resulting in the thiazolines* **5** *and* **6**, *proceed likewise via the Thorpe reaction. For compounds* **4–6**, *X-ray diffraction analyses were undertaken and IR spectra in solution and in solid state were investigated. It is supposed that a high kinetic preference for formation of* **4** *and the fact that it does not undergo spontaneous cyclization in ammonolysis stem from the NH· · ·N intramolecular hydrogen bonding between two amino groups.*

INTRODUCTION

As has been shown earlier, reaction between alicyclic perfluorinated derivatives of the recently reported [1,2] α,β-unsaturated thiocyanate **1** and ammonia involves a series of consecutive "attachment–detachment" stages yielding intermediate **2**. The latter undergoes intramolecular cyclization following the pattern of the Thorpe reaction (Equation 1) [3].



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RESULTS AND DISCUSSION

We now wish to report that the structurally similar acyclic compound **3** [1,2] also reacts with ammonia via Ad–E stages. However, because of the specific stereochemistry of the intermediates and the difference between a mobile aliphatic chain and a rigid ring, the reaction gives products of quite a different class (Scheme 1).

Thus, it turned out that ammonolysis of the α,β-unsaturated thiocyanate **3** led to diaminothiocyanate **4** and aminothiazoline **5**.

The nucleophilic attack of NH_3 at the thiocyanate **3** carbon atom bound to two CF_3 groups is supposed to proceed via the β-aminothiocyanate B. The reaction runs stereospecifically, which is confirmed by the formation of only one (with respect to the double bond) stereoisomer of the final product **5** (viz., the *E* isomer as fixed by X-ray diffraction analysis). Therefore, one can propose that the cis elimination occurring at the first stage proceeds by a concerted mechanism via the transition state A.

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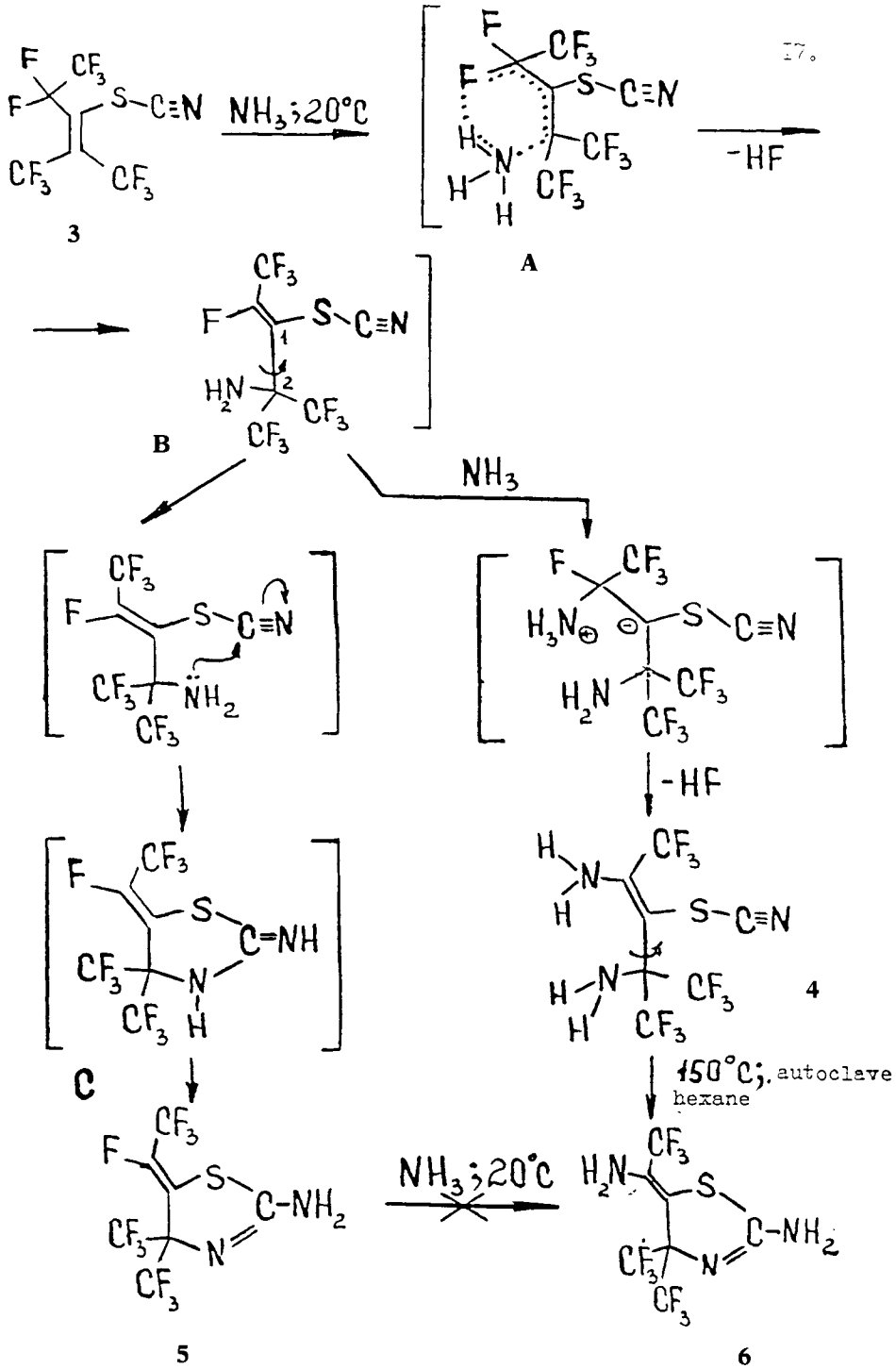


SCHEME 1

It should be noted that the direction of the attack of the NH_3 is not surprising, since the electron-accepting properties of the SCN group are similar to those of $-C(O)CH_3$ and $-S(O)CH_3$ groups. The Hammett σp constants are equal to +0.52 for the SCN group (compared with +0.50 and +0.49 for $C(O)CH_3$ and $S(O)CH_3$ groups, respectively) [4].

Then, two reaction paths seem to be available for the β-aminothiocyanate B. One of them includes nucleophilic addition of NH_3 at the double bond with subsequent elimination of hydrogen fluoride. As a result, only one isomer of the diaminothiocyanate **4** is formed (viz., the *E* isomer as fixed by X-ray diffraction data). Another pathway is the

intramolecular heterocyclization of the Thorpe reaction type, which is effected because rotation around the C(1)–C(2) σ bond is possible. The reaction produces the imine C which then isomerizes to the more stable amine **5**.

Formal substitution of the fluorine atom at the double exocyclic bond in **5** by the amino-group under the action of NH_3, which would have yielded the thiazoline **6** upon ammonolysis of **3**, was not observed, although, theoretically, one could have expected it. Ammonia was shown to react with fluoroolefins via the Ad–E mechanism [5].

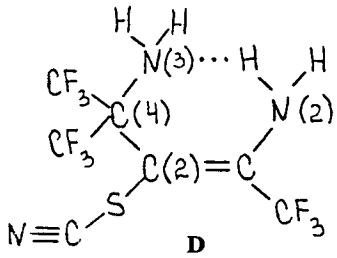
The intramolecular cyclization of the β-aminothiocyanate B seems to proceed slower than the formation of **4** because the latter is the main product of the reaction (the yields of **4** and **5** are 55% and 12%, respectively).

Thus, as follows from the above, diaminothiocyanate **4** is a stable compound, is easily isolated, and does not undergo spontaneous intramolecular heterocyclization into the thiazoline **6**, although, judging by the formation of **5**, this might have been expected.

It has been found that this cyclization, which involves an intramolecular rotation and then conversion of **4** into the thiazoline **6**, may take place on heating (in an autoclave, in hexane solution at 150°C).

It should be noted that a similar route for formation of thiazoline rings by intramolecular cyclization of β-aminothiocyanates has been reported [6,7,8]. In all the cited examples, however, β-aminorhodanides were not isolated, their existence being only implied.

The above data led us to conclude that the diaminothiocyanate **4** is the kinetic product, while the thiazoline **6** is its thermodynamically more stable isomer. It can reasonably be regarded that such a high kinetic preference for formation of **4** can be explained by conformational control; namely, formation of the chelate **D** resulting from intramolecular hydrogen bonding of the NH· · ·N type exists between two amino groups and hinders rotation around the C(2)–C(4) σ bond (see also Figure 1), thus impeding cyclization to **6** under ambient conditions.



D

This conclusion is also supported by an X-ray diffraction investigation of **4** and by the analysis of its IR spectra in solution (for more details, see below).

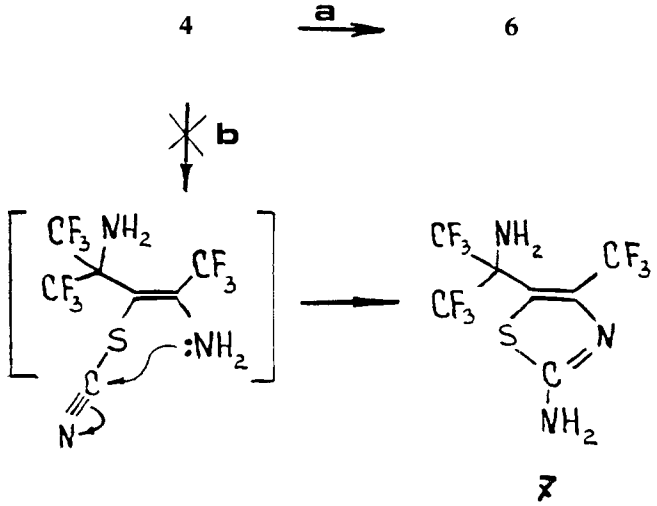
Further evidence for hindered rotation around the σ bond C(2)–C(4) comes from the ^{19}F NMR spectrum of the diaminothiocyanate **4**. The spectrum exhibits broad singlets at $\theta = -5.9$ and -4.3, which speaks for nonequivalence of the CF_3 groups at the saturated carbon atom.

It is noteworthy that compound **4** has two amino groups, $H_2N(2)$ and $H_2N(3)$, at the β-position with respect to the thiocyanate group. Therefore, it might be suggested that the intramolecular heterocyclization proceeds via two directions (Scheme 2).

Path "a" includes participation of the amino group at the saturated carbon atom and eventually leads to the thiazoline **6** (this case is identical to the formation of **5**; see Scheme 1).

On the other hand path "b" might also take place. This reaction implies participation of the other amino group and gives rise to the thiazole **7**. This route is similar to that observed previously [3] in the alicyclic series (see Equation 1, intermediate **2**). It should be noted that a trans arrangement of amino- and thiocyanate groups at the double bond in **4** would not hinder the cyclization, because the double bond is activated by the amino group and, theoretically, isomerization of the *E* isomer into the *Z* isomer (see Ref. [9]) with subsequent intramolecular heterocyclization is possible. Such precedents have been reported in the literature [10]. However, under the conditions stated, path "a" appears to be energetically more favorable, since it yields exclusively the thiazoline **6**.

The structures of compounds **4–6** have been proved by spectral (NMR, MS, IR) methods and by X-ray diffraction analysis. Figures 1, 4, and 5 present the structures of molecules **4–6**. In Tables 1–3 are given the bond lengths and bond angles of the compounds studied. For compounds **4–6**, IR spectra were examined in solution and in the solid state (Figures 3, 6, and 7).



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SCHEME 2

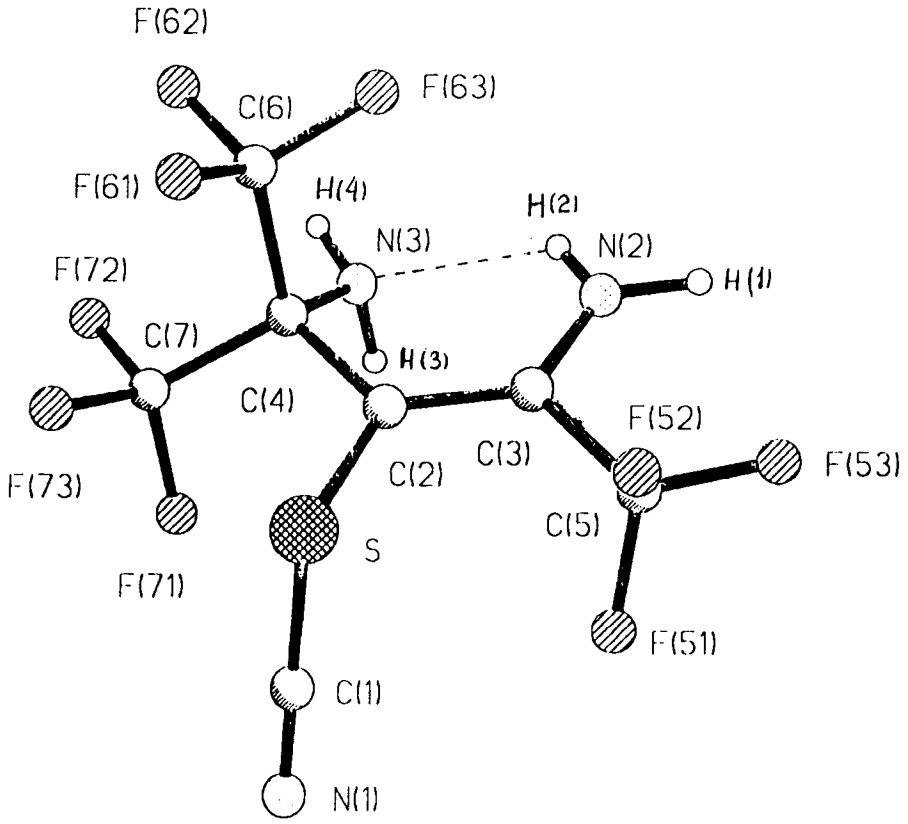


FIGURE 1 Molecular structure of compound **4**.

TABLE 1 Bond Lengths (Å) and Bond Angles (°) in Molecule **4**

Bond Lengths			
S–C(2)	1.769(3)	S–C(1)	1.699(3)
F(51)–C(5)	1.329(3)	F(52)–C(5)	1.335(3)
F(63)–C(6)	1.330(3)	F(71)–C(7)	1.335(3)
F(72)–C(7)	1.344(3)	F(62)–C(6)	1.336(3)
F(53)–C(5)	1.332(4)	F(73)–C(7)	1.325(4)
F(61)–C(6)	1.335(4)	C(2)–C(3)	1.367(4)
C(2)–C(4)	1.535(3)	N(1)–C(1)	1.145(4)
C(5)–C(3)	1.528(4)	N(3)–C(4)	1.456(4)
C(3)–N(2)	1.335(4)	C(6)–C(4)	1.534(4)
C(4)–C(7)	1.552(4)		
Bond Angles			
C(2)–S–C(1)	102.3(1)	S–C(2)–C(3)	118.2(2)
S–C(2)–C(4)	118.5(2)	C(3)–C(2)–C(4)	122.5(3)
F(51)–C(5)–F(52)	107.6(2)	F(51)–C(5)–F(53)	106.6(2)
F(52)–C(5)–F(53)	106.2(2)	F(51)–C(5)–C(3)	111.8(2)
F(52)–C(5)–C(3)	112.9(2)	F(53)–C(5)–C(3)	111.4(3)
C(2)–C(3)–C(5)	121.3(3)	C(2)–C(3)–N(2)	126.9(2)
C(5)–C(3)–N(2)	111.7(2)	S–C(1)–N(1)	176.2(3)
F(63)–C(6)–F(62)	106.9(3)	F(63)–C(6)–F(61)	106.7(2)
F(62)–C(6)–F(61)	107.7(2)	F(63)–C(6)–C(4)	111.2(2)
F(62)–C(6)–C(4)	112.0(2)	F(61)–C(6)–C(4)	112.1(3)
C(2)–C(4)–N(3)	109.3(2)	C(2)–C(4)–C(6)	109.4(2)
N(3)–C(4)–C(6)	106.7(2)	C(2)–C(4)–C(7)	113.2(2)
N(3)–C(4)–C(7)	108.7(2)	C(6)–C(4)–C(7)	109.3(2)
F(71)–C(7)–F(72)	106.8(2)	F(71)–C(7)–F(73)	107.6(3)
F(72)–C(7)–F(73)	106.6(2)	F(71)–C(7)–C(4)	109.8(2)
F(72)–C(7)–C(4)	110.2(3)	F(73)–C(7)–C(4)	115.5(2)

TABLE 2 Bond Lengths (Å) and Bond Angles (°) in Molecule **5**

Bond Lengths			
S–C(3)	1.771(4)	S–C(1)	1.758(3)
N(1)–C(3)	1.280(4)	N(1)–C(2)	1.451(4)
F(63)–C(6)	1.327(5)	F(62)–C(6)	1.325(6)
F(53)–C(5)	1.318(5)	F(73)–C(7)	1.321(5)
F(4)–C(4)	1.344(4)	N(2)–C(3)	1.341(4)
F(61)–C(6)	1.318(6)	F(72)–C(7)	1.345(6)
F(51)–C(5)	1.319(6)	F(71)–C(7)	1.313(6)
C(2)–C(1)	1.540(5)	C(2)–C(7)	1.552(6)
C(2)–C(6)	1.558(5)	C(1)–C(4)	1.336(6)
F(52)–C(5)	1.321(5)	C(4)–C(5)	1.474(6)
Bond Angles			
C(3)–S–C(1)	89.3(2)	C(3)–N(1)–C(2)	112.2(3)
S–C(3)–N(1)	118.6(3)	S–C(3)–N(2)	118.0(3)
N(1)–C(3)–N(2)	123.4(4)	N(1)–C(2)–C(1)	109.9(3)
N(1)–C(2)–C(7)	106.1(3)	C(1)–C(2)–C(7)	109.7(3)
N(1)–C(2)–C(6)	105.9(3)	C(1)–C(2)–C(6)	113.0(3)
C(7)–C(2)–C(6)	111.9(3)	S–C(1)–C(2)	108.8(2)
S–C(1)–C(4)	123.5(3)	C(2)–C(1)–C(4)	127.7(3)
F(4)–C(4)–C(1)	120.5(4)	F(4)–C(4)–C(5)	110.1(3)
C(1)–C(4)–C(5)	129.3(3)	F(53)–C(5)–F(51)	105.8(4)
F(53)–C(5)–F(52)	107.4(3)	F(51)–C(5)–F(52)	107.0(4)
F(53)–C(5)–C(4)	112.2(3)	F(51)–C(5)–C(4)	111.5(3)
F(52)–C(5)–C(4)	112.5(4)	F(73)–C(7)–F(72)	106.7(4)
F(73)–C(7)–F(71)	108.6(4)	F(72)–C(7)–F(71)	108.1(3)
F(73)–C(7)–C(2)	109.5(3)	F(72)–C(7)–C(2)	111.5(4)
F(71)–C(7)–C(2)	112.2(4)	F(63)–C(6)–F(62)	106.6(3)
F(63)–C(6)–F(61)	108.1(4)	F(62)–C(6)–F(61)	108.1(4)
F(63)–C(6)–C(2)	112.9(4)	F(62)–C(6)–C(2)	111.1(3)
F(61)–C(6)–C(2)	109.8(3)		

RESULTS AND DISCUSSION

2,4-Diaminoperfluoro-4-methyl-2-pentenethiocyanate-3 (**4**)*: X-ray and IR Studies*

As seen from Figure 1, the amino- and thiocyanate groups are in the trans position with respect to the double bond C(2)=C(3), and the torsional angle SC(2)C(3)N(2) is equal to −170°.

The double bond length is usual and all the atoms at the double bond are coplanar within 0.06 Å. This conformation of **4** is stabilized by a strong intramolecular hydrogen bond N(2)–H(2)···N(3) formed by two amino groups at carbons C(3) and C(4). The parameters of this H bond are as follows: N(2)···N(3) 2.709(3) Å, N(2)–H(2) 0.78(3) Å, H(2)···N(3) 2.17(3) Å, and the angle at H(2) is 127(3)°.

As expected, the bond C(3)–N(2) is substantially shorter than the bond C(4)–N(3). The amino group $H_2N(2)$ is planar within 0.01 Å and coplanar to the double bond (dihedral angle 7.4°). In the second amino group, however, the atom N(3) has a pyramidal configuration and its elevation out of the plane of the adjacent neighbors is equal to 0.266 Å. The dihedral angle between the mean planes of the amino groups in **4** is equal to 111°. This means that their orientation is close to orthogonal. Features of molecular geometry of the compound **4**, mentioned above, obviously occur as a result of the formation of the intramolecular hydrogen bond.

Atoms N(1) of the thiocyanate group in crystal **4** participate as acceptors of two protons thus forming intermolecular H bonds of N–H···N type. (Atoms N(1′) and N(1″) are related to the basis N(1) atom by symmetry operations (X, 1 + Y, Z) (1 − X, 1 − Y, 1 − Z)). The parameters of these bonds are as follows: N(2)–(H1)···N(1′) 3.104Å, H(1)···N(1′) 2.18 Å, angle at H(1) 166°; N(3)–H(3)···N(1″) 3.180 Å, H(3)···N(1″) 2.32 Å, angle at H(3) 156°. Figure 2 shows the projection of crystal **4** onto the bc plane. Because of the presence of these H bonds, the crystal structure is characterized by the endless ribbons of centrosymmetrically bonded molecules elongated along the b axis of the crystal. Atom N(1) participates in the formation of two H bonds, whereas atom H(4) at the N(3) amino group does not.

Other geometrical parameters of structure **4** have expected values [11].

The IR spectra of **4** (Figure 3) confirm the presence of a thiocyanate group, the ν_{SCN} frequency being 2168 cm^{-1} for the dilute solution and 2162 cm^{-1} for the crystal sample. The ν_{NH} frequencies at 3508 and 3404 cm^{-1} in the spectrum of the solution (Fig-

TABLE 3 Bond Lengths (Å) and Bond Angles (°) in Molecule **6**

Bond Lengths			
S–C(1)	1.774(2)	S–C(3)	1.758(2)
F(62)–C(6)	1.324(3)	F(63)–C(6)	1.339(3)
F(71)–C(7)	1.327(3)	F(51)–C(5)	1.318(3)
F(61)–C(6)	1.332(3)	N(1)–C(2)	1.445(3)
N(1)–C(3)	1.286(2)	F(72)–C(7)	1.336(3)
F(73)–C(7)	1.322(3)	C(1)–C(2)	1.540(3)
C(1)–C(4)	1.344(3)	F(53)–C(5)	1.335(3)
C(2)–C(6)	1.543(3)	C(2)–C(7)	1.552(3)
F(52)–C(5)	1.313(3)	N(2)–C(3)	1.334(3)
N(3)–C(4)	1.371(3)	C(5)–C(4)	1.514(3)
Bond Angles			
C(1)–S–C(3)	90.4(1)	C(2)–N(1)–C(3)	113.0(2)
S–C(1)–C(2)	107.6(1)	S–C(1)–C(4)	123.1(1)
C(2)–C(1)–C(4)	129.3(2)	N(1)–C(2)–C(1)	110.5(1)
N(1)–C(2)–C(6)	106.4(2)	C(1)–C(2)–C(6)	109.6(2)
N(1)–C(2)–C(7)	105.4(2)	C(1)–C(2)–C(7)	113.2(2)
C(6)–C(2)–C(7)	111.4(2)	F(62)–C(6)–F(63)	107.1(2)
F(62)–C(6)–F(61)	107.5(2)	F(63)–C(6)–F(61)	107.2(2)
F(62)–C(6)–C(2)	109.9(2)	F(63)–C(6)–C(2)	112.8(2)
F(61)–C(6)–C(2)	112.1(2)	F(71)–C(7)–F(72)	106.0(2)
F(71)–C(7)–F(73)	107.7(2)	F(72)–C(7)–F(73)	107.8(2)
F(71)–C(7)–C(2)	111.8(2)	F(72)–C(7)–C(2)	113.4(2)
F(73)–C(7)–C(2)	109.9(2)	F(51)–C(5)–F(53)	105.8(2)
F(51)–C(5)–F(52)	108.0(2)	F(53)–C(5)–F(52)	105.3(2)
F(51)–C(5)–C(4)	112.8(2)	F(53)–C(5)–C(4)	112.8(2)
F(52)–C(5)–C(4)	111.7(2)	S–C(3)–N(1)	117.7(2)
S–C(3)–N(2)	119.0(1)	N(1)–C(3)–N(2)	123.2(2)
C(1)–C(4)–N(3)	128.4(2)	C(1)–C(4)–C(5)	120.4(2)
N(3)–C(4)–C(5)	111.0(2)		

ure 3b) point to the presence of the "free" NH bonds of the $N(3)H_2$ group while the broadened band of the N(2)H bond at 3322 cm^{-1}—to the intramolecular chelate D (see above). (The assignment was made on the basis of comparison with the spectra of compounds **5** and **6** (see below) and with the literature data [12]). In the spectrum of the solid sample (Figure 3a) the latter band remains (a doublet at 3316/3305 cm^{-1}) while the frequencies of the NH bonds of the $N(3)H_2$ group are shifted to 3434 and 3412 cm^{-1}, exhibiting a weak intermolecular H bond. According to X-ray diffraction data, it is the SCN group that participates as a proton acceptor in the formation of the latter H bond. Comparison of the NH· · ·NCS distance (N· · ·N = 3.1–3.2 Å) with van der Waals radii sum ($2r_{vdw}(N)$ = 3.0 Å) proves this interaction to be very weak [13].

2-Aminoperfluoro-4,4-dimethyl-4,5-dihydro-5-ethylidene-1,3-thiazole (**5**) *and 2-Amino-4,4-bis(trifluoromethyl)-4,5-dihydro-5-(1-aminoperfluoroethylidene)-1,3-thiazole* (**6**)*: X-Ray Data and IR-Spectra Analysis*

The isostructural compounds **5** and **6** (Figures 4 and 5) have thiazoline rings planar within 0.05 Å and 0.04 Å, respectively; the amino groups $H_2N(2)$ are virtually coplanar with the heterocycles which contracts the bond lengths, N(2)–C(3). The dihedral angles between the planes of exocyclic double bonds and the planes of heterocycles in **5** and **6** are 9.3° and 6.0°. This means that atoms at double bonds actually lie in the planes of the heterocycles. The double bond lengths C(1)=C(4) have usual values, although a considerable distortion of bond angles at C(1) and C(4) atoms may be observed as compared with the ideal value, 120°. Nevertheless, the sum of bond angles at C(1) and C(4) atoms remains equal to 360°, which means that they retain their planar trigonal coordination. Probably the distortion of bond angles may be attributed to steric factors. Thus in the **5** atom F(4) and fluorine atoms of two CF_3 groups at C(2) repel each other (intramolecular nonbonded contacts are equal to 2.58 Å for F(4) · · · F(63) and 2.73 Å for F(4) · · · F(72)). The intramolecular contact between S and F(52) atoms is equal to 2.75 Å. These distances are considerably shorter than typical for nonbonded contacts of the type F· · ·F and F· · ·S (2.80 and 3.21 Å [14]). In **6**, intramolecular contacts 2.75 Å for S· · ·F(52) and 2.41 Å for H(4)· · ·F(63) and 2.19 Å for H(4)· · ·F(72) are shortened as compared with usual van der Waals contacts (according to Ref. [14], the usual distance H· · ·F is equal to 2.54 Å).

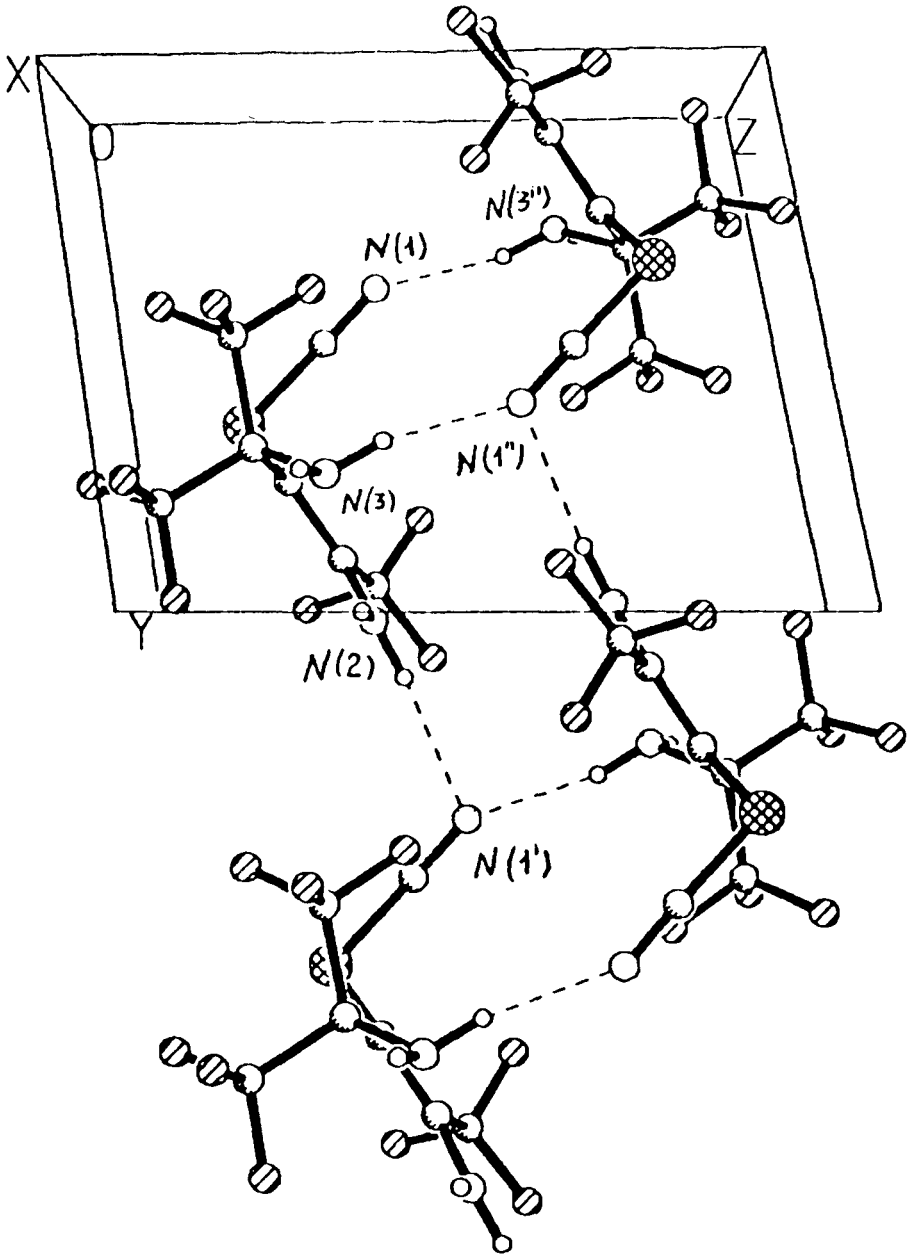


FIGURE 2 Projection of structure **4** on the plane bc. Intramolecular H bond NH· · ·N (see Figure 1) is not shown.

It may be noted that the planar $H_2N(3)$ group in **6** is "clamped" between two CF_3 groups at C(2); this is an additional factor (besides the electron conjugation) responsible for its coplanarity with the plane of the heterocyclic ring and double bonds.

Molecules **5** and **6** in the crystal form centrosymmetric dimers E because of hydrogen bond formation. In these bonds of the N–H· · ·N type atoms N(2) of amino groups act as proton donors and imine atoms as proton acceptors. The parameters of the hydrogen bonds are as follows: 2.959 Å and 2.979 Å for N(2)–H(1)· · ·N(1') in **5** and **6** and 2.03 Å and 2.08 Å for H(1)· · ·N(1'), and the angle at hydrogen atoms is 177° and 173°. Thus, these bonds may be considered to be of medium strength. Atoms H(2) of the exocyclic N(2) amino groups do not participate in hydrogen bond formation. The same can be said about the two hydrogens of the N(3) amino group in **6**; this seems to be the result of the shielding of the NH_2 group by CF_3 groups (vide supra).

Other geometrical parameters of **5** and **6** have the expected values close to those cited in the literature for analogous compounds [11,15,16].

The interpretation of the complicated IR pattern of the solid **5** (Figure 6a) is facilitated by X-ray diffraction data, which points to the strong intermolecular H bond of NH· · ·N type. The estimation of this H-bond strength in terms of the vibrational frequency shift according to the Iogansen rule [17] gives the value of $\Delta H \approx 5.5$ kcal/mol. The

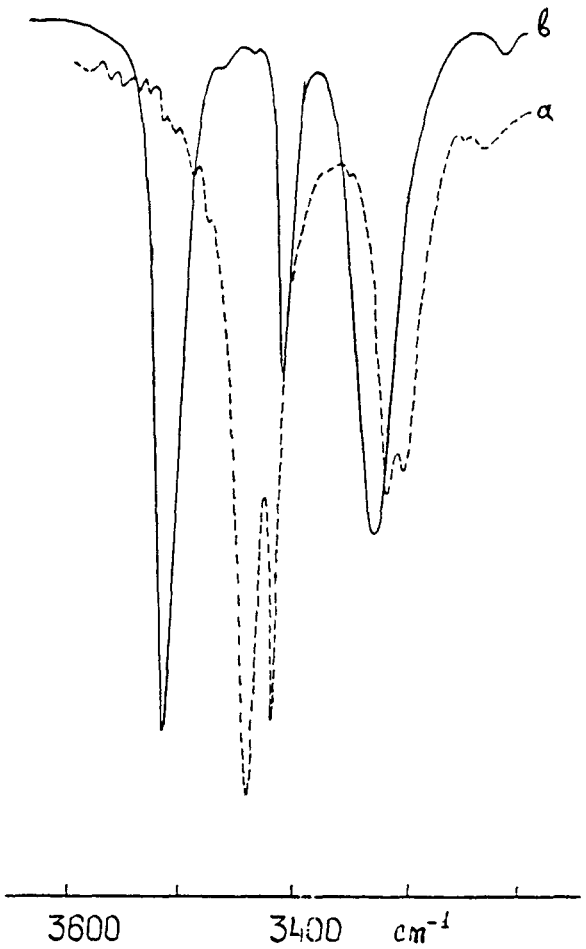
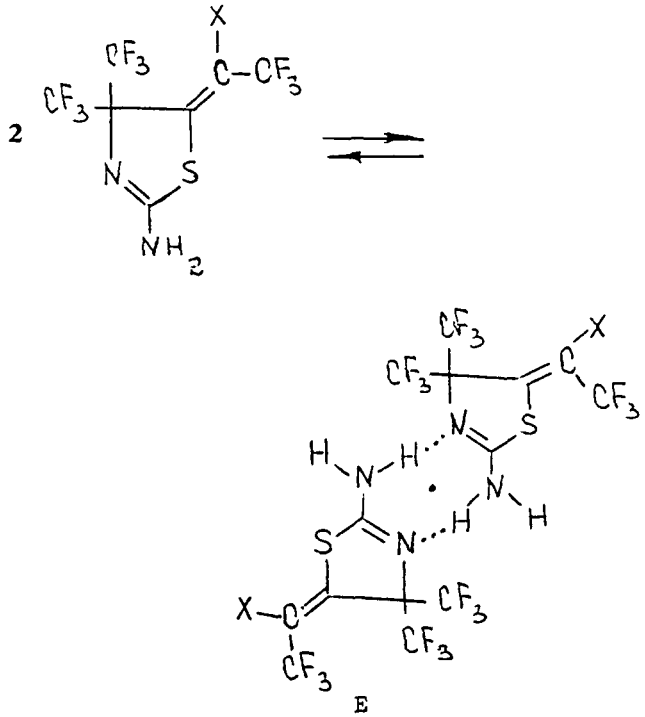


FIGURE 3 IR spectrum of compound **4**: (a) solid sample (fluorolube mull); (b) CCl_4 solution (c = 0.005 mol/l).

narrow γ_{NH} band at 3508 cm^{-1} corresponds to the "free" NH bonds while the broad feature with structure at ~3116 cm^{-1} corresponds to the ν_{NH} in the H complex. The frequencies 3336 and 3264 cm^{-1} are assigned to an overtone and a combination tone of the vibrations, situated in the region 1700–1600 cm^{-1} and enhanced by Fermiresonance [18].

When compound **5** is dissolved in CCl_4 ($c \sim 10^{-3}$ mol/1) its IR spectrum acquires new intense narrow bands at 3524 and 3412 cm^{-1}, pointing to the presence of "free" amino group; the spacing between their frequencies is in accordance with the well-known Bellamy–Williams formula [12]. The intensity of these bands increases on dilution, which proves an equilibrium in solution between the "free" molecules and cyclic dimers E. The presence of unbroken H complexes at such low concentrations of the solution was also observed for related compounds [19].

The comparison of the IR spectra of **5** and **6** allows the conclusion to be reached that the bands at 3528 and 3416 cm^{-1} in the spectrum of compound **6** in solution are associated with the "free" $N(2)H_2$ group. The intense narrow bands at 3540 and 3438 cm^{-1}, also observed in this spectrum, indicate that the second amino group $N(3)H_2$ in solution is "free" as well.



X = F (**5**); NH_2 (**6**)

The IR spectrum of the solid **6** (Figure 7a) shows that the $N(3)H_2$ group remains "free" also in the crystalline state, which is evidenced by the narrow ν_{NH} bands at 3532 and 3424 cm^{-1}. However, the $N(2)H_2$ group in the solid forms a strong H bond of the type N(2)H· · ·N(1′). The narrow ν_{NH} band at 3488 cm^{-1} corresponds to the "free" NH bond (as in the spectrum of **5**), while a broad band near 3110 cm^{-1} corresponds to the ν_{NH} in the H complex. Fermi-enhanced overtones of the vibrations, situated in the 1700–1600 cm^{-1} region, give rise to the bands at 3320 and 3252 cm^{-1} (analogous to those in the spectrum of **5**).

Thus, the behavior of the $N(2)H_2$ group in compound **6** is analogous to that of the only amino group in compound **5**, while the $N(3)H_2$ group is not associated either in solution or in the crystalline state.

EXPERIMENTAL

The ^{19}F and ^{1}H NMR spectra were recorded on a Bruker WP 200 SY (200 MHz) instrument with CF_3CO_2H and TMS as internal standards. The mass spectra were recorded on a chromato-mass-spectrometer VG 70/70 (ionization energy 70 eV). The IR spectra were taken using UR-20 (700–3700 cm^{-1}) and Specord M-80 (2700–3700 cm^{-1}) spectrophotometers; CCl_4 solution concentrations were 0.005–0.001 mol/l, and layer thickness was 1–2 cm.

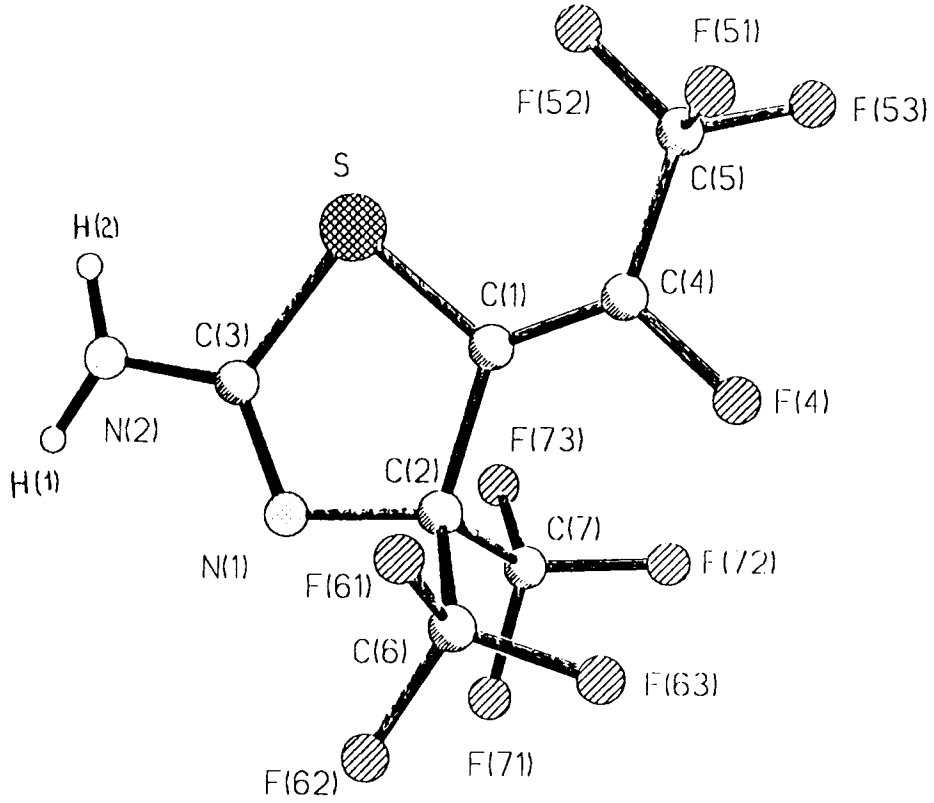


FIGURE 4 Molecular structure of compound **5**.

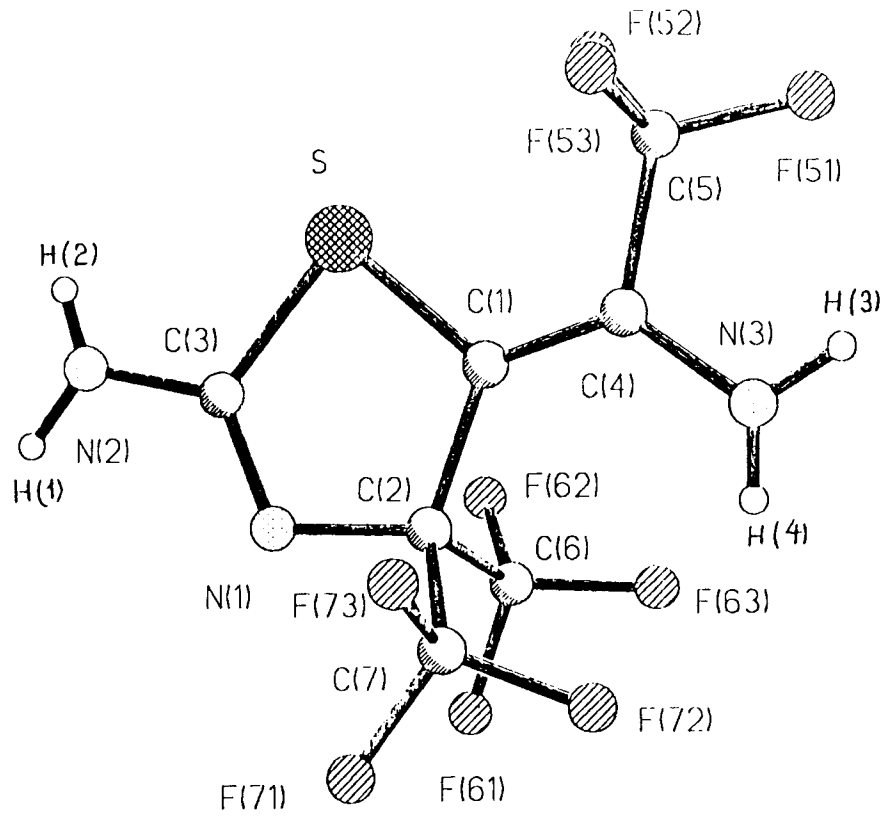


FIGURE 5 Molecular structure of compound **6**.

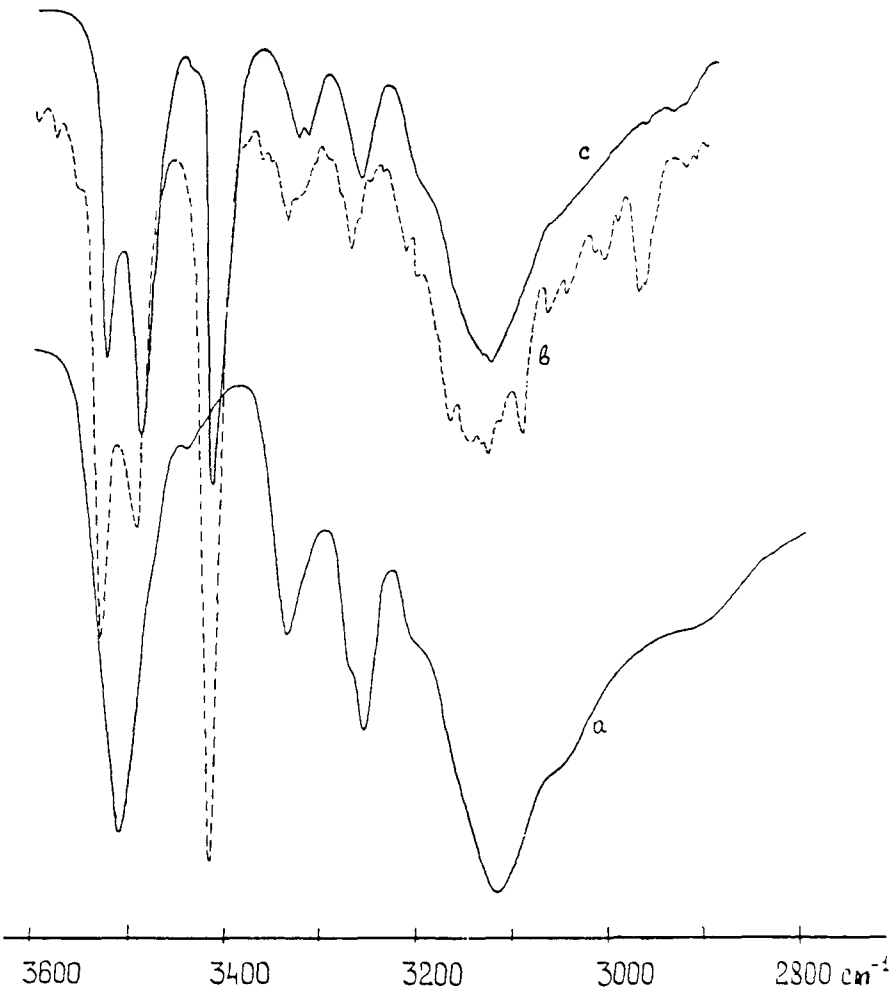


FIGURE 6 IR spectrum of compound **5**: (a) solid sample (fluorolube mull); (b) CCl_4 solution (c = 0.0015 mol/l); (c) CCl_4 solution (c = 0.003 mol/l).

The IR spectra of crystalline substances were recorded in KBr pellets and in fluorolube mulls.

X-ray Diffraction Study of Compounds **4–6**

X-ray diffraction studies of monocrystals **4** and **5** were carried out at 163 K on an automatic diffractometer Syntex $P2_1$ (Mo Kα radiation, graphite monochromator, $\theta/2\theta$ scan, $2\theta \leq 60°$), and for **6** the diffraction data were obtained at 213 K on an automatic "Siemens R3m" diffractometer (Mo Kα radiation, graphite monochromator, $\theta/2\theta$ scan, $2\theta \leq 52°$). The crystals of **4** are triclinic: at 163 K, a = 7.497(1), b = 8.098(2), c = 10.048(2) Å, α = 79.22(3), β = 85.33(3), γ = 73.64(3)°, V = 574.7(2) Å^3, d_{calc} = 1.925 g/cm^3, z = 2, space group $P\bar{1}$. The crystals of **5** and **6** are monoclinic: at 163 K and 213 K, a = 8.944(2) and 8.961(2) Å, b = 10.716(2) and 10.985(2) Å, c = 11.950(2) and 11.754(2) Å, β = 104.87(3) and 104.81(3)°, V = 1107.0(4) and 1118.6(4) Å^3, d_{calc} = 2.017 and 1.978 g/cm^3, z = 4, space group $P2_1/n$.

While comparing the unit cell parameters of crystals **5** and **6** and their structural formulas, which differ only in that a fluorine atom is replaced by an amino group at C(4), it can be seen that these crystals are isostructural.

At 163 K and 213 K for compounds **4–6**, 2621, 2988, and 2517 independent reflections were measured. In further calculations and structure refinement 2177, 2241, and 2267 reflections with $|F| > 4\sigma(F)$ were used. The structures were solved by a direct method and refined in a block-diagonal anisotropic–isotropic (atoms H) approximation; the absorption correction was not used. The final refinement converged to R = 0.0386 (**4**), 0.0577 (**5**), and 0.0375 (**6**), R_w = 0.0441, 0.0628, and 0.0379. All calculations were carried out on PC/AT computer using the SHELX PLUS program. Tables 4 through 6 give coordinates of nonhydrogen atoms of the structures and their equivalent temperature factors.

E-2,4-Diaminoperfluoro-4-methyl-2-pentenethiocyanate-3 (**4**), *E-2-Aminoperfluoro-4,4-dimethyl-4,5-dihydro-5-ethylidene-1,3-thiazole* (**5**) Dry gaseous NH_3 was passed through a solution of 1.77 g of perfluoro-2-methyl-2-pentenethiocyanate-3 [2] in 5

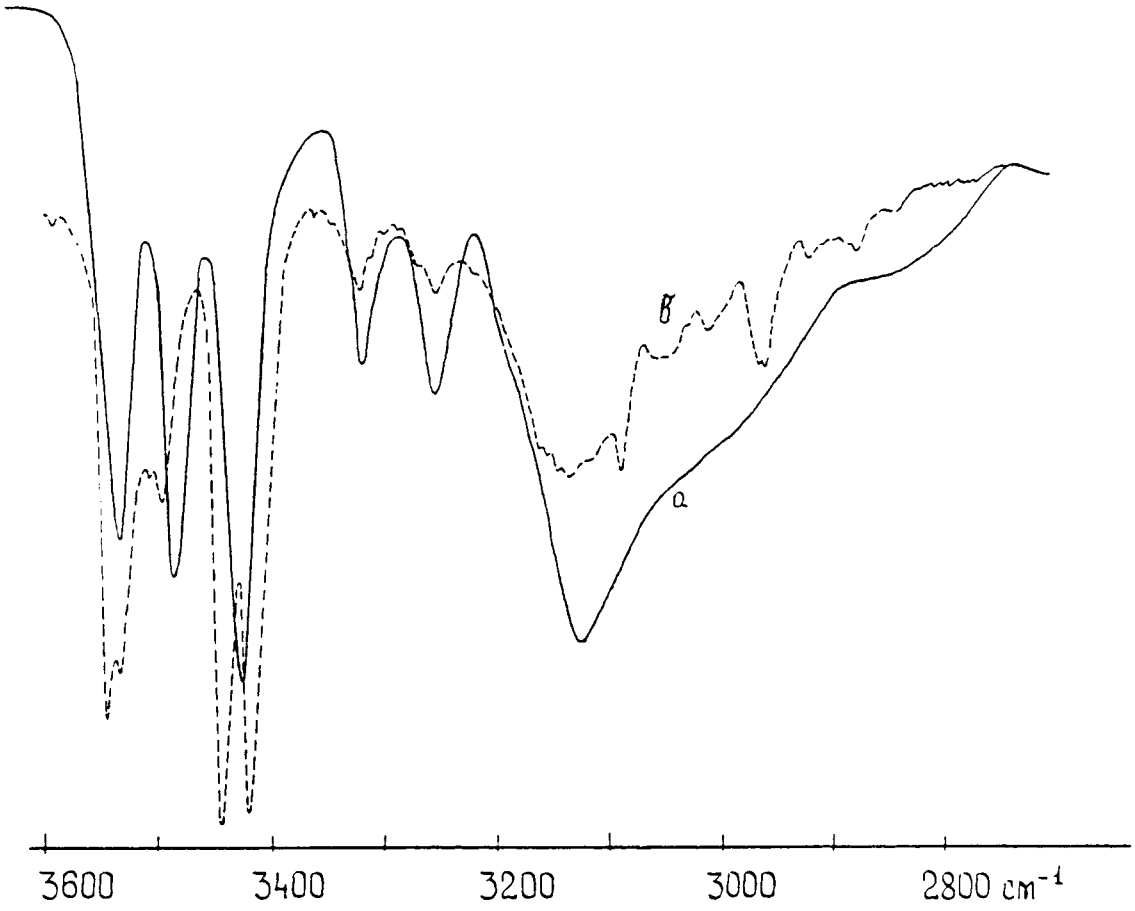
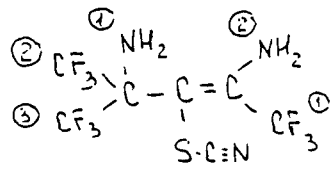


FIGURE 7 IR spectrum of compound **6**: (a) solid sample (fluorolube mull); (b) CCl_4 solution (c = 0.0012 mol/l).

mL of hexane to the end of the exothermic reaction, a temperature of approximately 20°C being maintained. Then water was added and extraction was carried out with ether. The ether extract was dried over $MgSO_4$ and concentrated in vacuo. The residue was washed with 10 mL of hexane and filtered off. Yield: 0.96 g (55.2%) of practically pure **4**, mp 64–67°C. Recrystallization from a hexane–ether mixture gave 0.87 g (50.0%) **4**, mp 69–71°C. The filtrate was evaporated in vacuum and 0.35 g (20%) of the residue was sublimated in 0.5 mm vacuum at approximately 150°C and then recrystallized from pentane–ether mixture. Yield: 0.21 g (12.0%) **5**, mp 106–108°C. **4**: Found: C, 25.43; H, 1.27; F, 51.28; N, 13.03; S, 9.68%. $C_7H_4F_9N_3S$. Calc.: C, 25.23; H, 1.21; F, 51.32; N, 12.61; S, 9.62%. MS, m/z, relative intensity, species: 333, 63.7, M^+; 272, 17.1, $C_6F_9N_2H^+$; 264, 100.0 $(M-CF_3)^+$; 244, 66.3 $(M-CF_3-HF)^+$; 225*, 2.6 (264 → 244); 217, 31.7 $(M-CF_3-HF-HCN)^+$; 194, 10.1, $C_4F_6S^+$; 190; 19.9 $(M-CF_3-HF-2HCN)^+$; 175, 11.3 $(M-2CF_3-HF)^+$; 170, 4.0, $C_5F_5NH^+$; 96, 14.3, $C_2F_3NH^+$; 69, 26.6, CF_3^+. IR (KBr): 1625 s ($\nu_{C=C}$, δ_{NH_2}), 2162 s (ν_{SCN}), 3305 s, 3316 s, 3412 s, 3434 s, (ν_{NH_2}), cm $^{-1}$. ^1H NMR ($CDCl_3$): δ = 2.37 (s, NH_2^1); 6.96 (bs, NH_2^2), intensity ratio 1:1. ^{19}F NMR ($CDCl_3$): δ = −13.35 (s, CF_3^1), −5.9 (bs, CF_3^2), −4.3 (bs, CF_3^3), intensity ratio 1:1:1. **5**: Found: C, 25.06; H, 0.56;



F, 56.55; N, 8.38; S, 9.68%. $C_7H_2F_{10}N_2S$. Calc.: C, 25.01; H, 0.60; F, 56.52; N, 8.33; S, 9.54%. MS, m/z, relative intensity, species: 336, 19.0, M^+; 317, 11.5 $(M-F)^+$; 267, 100.0 $(M-CF_3)^+$; 217, 23.6 $(M-C_2F_5)^+$; 175, 19.2 $(M-C_2F_5-CNNH_2)$; 69, 21.6 CF_3^+. IR (KBr): 1540 w, 1610 s, 1670 sh, 1685 s ($\nu_{C=C}$; $\nu_{C=N}$;

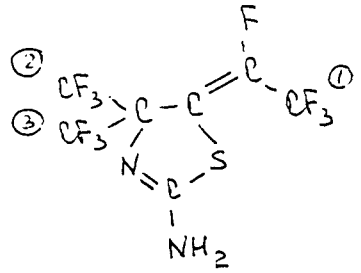


TABLE 4 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for Structure **4**

	x	y	z	U(eq)[a]
S	3731(1)	6456(1)	1859(1)	25(1)
F(51)	1770(2)	8195(2)	4174(2)	31(1)
F(52)	1199(2)	9941(2)	2271(2)	36(1)
F(63)	7023(2)	9760(2)	650(2)	39(1)
F(71)	7609(2)	4140(2)	3239(2)	40(1)
F(72)	9923(2)	4618(2)	1966(2)	42(1)
F(62)	9441(2)	7691(3)	339(2)	42(1)
F(53)	1774(2)	10861(2)	4000(2)	43(1)
F(73)	7494(2)	4451(2)	1076(2)	44(1)
F(61)	6766(2)	7693(3)	−304(2)	42(1)
C(2)	5169(3)	7563(3)	2428(2)	19(1)
N(1)	3482(4)	3808(3)	4107(3)	38(1)
C(5)	2259(4)	9497(3)	3355(3)	26(1)
N(3)	8266(3)	7526(3)	3042(3)	27(1)
C(3)	4337(3)	9014(3)	2990(2)	21(1)
N(2)	5158(4)	10152(3)	3301(3)	27(1)
C(1)	3636(4)	4877(4)	3218(3)	28(1)
C(6)	7629(4)	8045(4)	675(3)	30(1)
C(4)	7260(3)	7029(3)	2071(3)	22(1)
C(7)	8056(4)	5041(4)	2067(3)	31(1)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 6 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for Structure **6**

	x	y	z	U(eq)[a]
S	1365(1)	6015(1)	945(1)	24(1)
F(62)	4139(2)	8200(1)	1148(1)	44(1)
F(63)	4934(2)	8379(1)	3020(1)	45(1)
F(71)	6564(1)	5236(2)	3004(1)	48(1)
F(51)	−51(2)	7662(2)	3865(1)	51(1)
F(61)	6406(2)	7587(2)	2033(2)	52(1)
N(1)	4324(2)	5717(2)	1171(2)	22(1)
F(72)	5774(2)	6303(2)	4242(1)	53(1)
F(73)	4524(2)	4700(2)	3502(1)	53(1)
C(1)	2586(2)	6513(2)	2303(2)	20(1)
F(53)	−510(2)	7250(2)	2050(1)	56(1)
C(2)	4266(2)	6380(2)	2220(2)	22(1)
F(52)	−166(2)	5821(2)	3284(2)	77(1)
N(2)	2760(2)	4928(2)	−538(2)	27(1)
N(3)	2872(2)	7260(2)	4305(2)	42(1)
C(6)	4951(2)	7650(2)	2109(2)	32(1)
C(7)	5295(2)	5649(2)	3257(2)	34(1)
C(5)	333(2)	6912(2)	3112(2)	31(1)
C(3)	2981(2)	5519(2)	483(2)	20(1)
C(4)	2049(2)	6913(2)	3203(2)	25(1)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

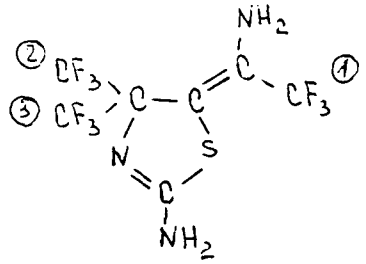
δ_{NH_2}), 3116 s, 3264 m, 3336 m, 3508 s (ν_{NH_2}), cm^{-1}. ^1H NMR ($CDCl_3$): δ = 6.4 (s, NH_2). ^{19}F NMR ($CDCl_3$): δ = −8.8 (d, CF_3^1), −5.8 (d, $CF_3^{2,3}$), 34.1 (hept q, CF); $^3J_{FF}$ = 10.0, $^5J_{FF}$ = 26.0 Hz.

TABLE 5 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for Structure **5**

	x	y	z	U(eq)[a]
S	1424(1)	1012(1)	6036(1)	32(1)
N(1)	4398(3)	709(3)	6206(2)	25(1)
F(63)	5874(4)	1098(4)	9261(2)	76(1)
F(62)	6680(3)	137(3)	7972(2)	59(1)
F(53)	264(3)	2815(2)	8849(3)	57(1)
F(73)	4168(4)	3237(2)	6342(3)	61(1)
F(4)	3204(3)	1968(3)	9325(2)	57(1)
N(2)	2781(4)	46(3)	4480(3)	35(1)
C(3)	3043(4)	547(3)	5540(3)	25(1)
F(61)	4661(4)	−516(3)	8439(2)	67(1)
F(72)	4956(4)	3303(3)	8189(3)	68(1)
F(51)	388(4)	892(3)	9216(3)	79(2)
F(71)	6456(3)	2619(3)	7178(3)	68(1)
C(2)	4356(4)	1301(3)	7290(3)	28(1)
C(1)	2675(4)	1380(3)	7388(3)	27(1)
F(52)	−456(3)	1505(4)	7479(3)	80(1)
C(4)	2185(5)	1685(4)	8319(3)	34(1)
C(5)	596(5)	1727(4)	8459(3)	40(1)
C(7)	5016(5)	2635(4)	7249(4)	44(1)
C(6)	5411(5)	494(5)	8263(3)	46(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

E-2-Amino-4,4-bis(trifluoromethyl)-4,5-dihydro-5-(1-aminoperfluoroethylidene)-1,3-thiazole (**6**). Compound **4**, 0.24 g, was heated for 7 h in an autoclave at 150°C in 75 mL of anhydrous hexane. The solid contents of the autoclave mixture were filtered off and 0.04 g of **6** were obtained, mp 160°C. The autoclave was washed with anhydrous ether and the extract was added to the filtrate. Removal of the solvent yielded 0.16 g of residue, which was



recrystallized from hexane–ether mixture. Yield: 0.09 g **6**, mp 158.5–160.5°C. Yield of **6** 54.2%. Found: C, 25.43; H, 1.33; F, 50.67%. $C_7H_4F_9N_3S$. Calc.: C, 25.23; H, 1.21; F, 51.32%. IR (KBr): 1600 s, 1620 sh, 1650 sh, 1670 s ($\nu_{C=C}$, $\nu_{C=N}$, δ_{NH_2}), 3108 s, 3252 m, 3320 m, 3424 s, 3488 s, 3532 s (ν_{NH_2}). ^1H NMR ($CDCl_3$): 5.7 (s, NH_2^1), 4.4 (s, NH_2^2). ^{19}F NMR ($CDCl_3$): −9.2 (s, CF_3^1), −7.6 s ($CF_3^{2,3}$), intensity ratio 1:2.

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