An unusually strong intramolecular C—H...N hydrogen bond in 3-(α-hydroperfluoroisobutyryl)-2-(α-hydroperfluoroisobutyryl)imino-1,3-thiazolidine

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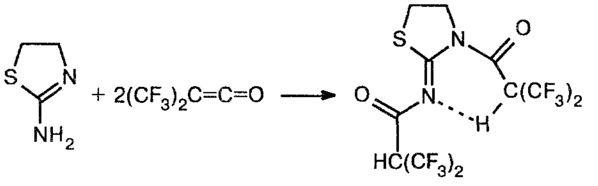
An unusually strong intramolecular C—H...N hydrogen bond with the shortest known H...N distance of 2.00(3) Å has been found by X-ray diffraction analysis.

Key words: unusual hydrogen bonds, X-ray diffraction analysis.

C—H...X hydrogen bonds (X = O, N, *etc.*)[1,2] are usually weak H-bonds; however, they play an important role in other inter- and intramolecular interactions. C—H...N-type H-bonds are poorly studied, less frequently occurring, and weaker than H-bonds of the C—H...O type. We have found an unusually strong (short) intramolecular C—H...N hydrogen bond in 3-(α-hydroperfluoroisobutyryl)-2-(α-hydroperfluoroisobutyryl)imino-1,3-thiazolidine (**1**). Compound **1** was prepared by acylation of 2-aminothiazoline with bis(trifluoromethyl)ketene.



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The molecular structure of **1** is unambiguously determined by X-ray diffraction (XRD) analysis (Fig. 1). It is established that the molecule of **1** contains an unusually short (strong) C(9)—H(9)...N(1) H-bond; interatomic distances: H(9)...N(1) 2.00(3), C(9)—H(9) 1.05(3), and C(9)...N(1) 2.836(3) Å; the C(9)—H(9)...N(1) angle is equal to 135(3)°. The H(9)...N(1) and C(9)...N(1) intramolecular distances in **1** are considerably lower than the corresponding sums of van der Waals radii of the atoms:[3] $R_H + R_N = 2.75$ and $R_C + R_N = 3.25$ Å. The C(9)—H(9)...N(1) H-bond mentioned closes the six-membered cycle of N(1), C(2), N(3), C(3), C(9), and H(9) atoms in the molecule of **1**. As far as we know, this H-bond in the molecule of **1** is the shortest bond of all structurally studied H-bonds of the C—H...N type. A fairly short intramolecular H-bond of the C(sp^3)—H...N(sp^3) type (with a H...N distance of 2.34(3) Å) was previously found in the structure of 4,4-bis(phenylsulfonyl)-2,*N*,*N*-trimethylbutylamine,[4] and another short intramolecular H-bond of the C(arom.)—H...N(sp^2) type (with a H...N distance of 2.23 Å) was found in the structure of (*Z*)-4-benzylidene-2-methyl-5(*4H*)-oxazolone.[5]

The high strength (the unusually short H...N distance) of the C(9)—H(9)...N(1) H-bond in the molecule of **1** can be explained by the especially favorable spatial orientation (to some extent a sterically forced proximity) of the atoms of this H-bond and by the especially "acidic" character of the H(9) atom (as well as the H(6) atom) due to three very electronegative substituents at the C(9) atom (and the C(6) atom): two CF_3 groups and the —C(=O)N fragment.

There is also a considerably shortened S...O(1) contact of 2.652(2) Å in the molecule of **1**, in which a specific noncovalent interaction occurs between S and O(1) atoms.[6]

In the crystalline structure, molecules of **1** are combined in center-symmetric H-dimers by a pair of weak intermolecular H-bonds of the C—H...O type (see Fig. 1); the corresponding distances: C(6)—H(6) 1.05(3), H(6)...O(1') 2.38(3), and C(6)...O(1') 3.260(3) Å; the C(6)—H(6)...O(1') angle is equal to 140(2)°.

The strong intramolecular C(9)—H(9)...N(1) H-bond discussed also exists in solutions of compound **1**, which is confirmed by its ^{1}H NMR spectra recorded in two different solvents (see Experimental). It can be seen from these spectra that in these solvents (acetone-d_6 and $CDCl_3$) the signal of the "acidic" H(9) proton is shifted downfield considerably more than the signal of another "acidic" H(6) proton, which is almost equivalent to the H(9) proton at first sight.

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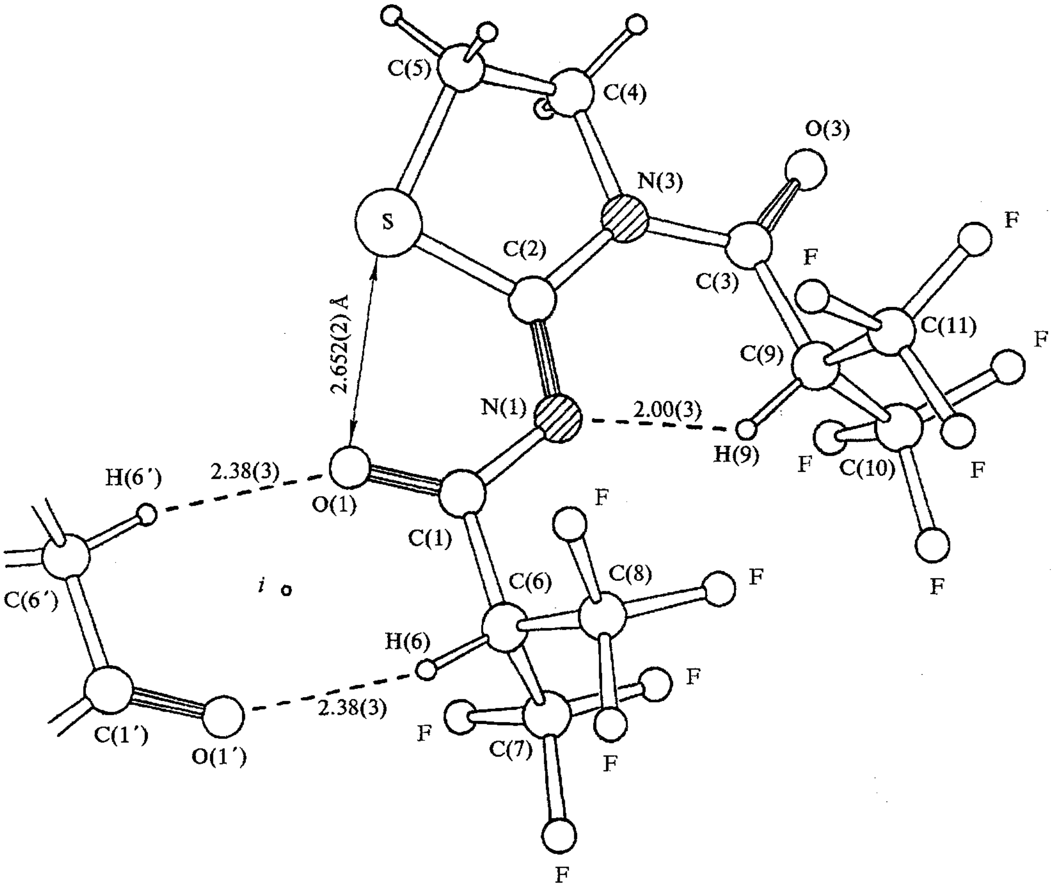

Fig. 1. Structure of the molecule of **1** according to the X-ray diffraction analysis data (the fragment of the adjacent molecule of **1** in the crystal is shown at the left); hydrogen bonds are indicated by dashed lines.

Experimental

^{1}H NMR spectra were recorded on a Bruker CXP-200 instrument (TMS was used as an internal standard).

3-(α-Hydroperfluoroisobutyryl)-2-(α-hydroperfluoroisobutyryl)imino-1,3-thiazolidine (1). A mixture of 1.0 g (0.011 mol) of 2-aminothiazoline and 4.0 g (0.023 mol) of bis(trifluoromethyl)ketene in 20 mL of dehydrated ether was kept for 24 h in a sealed glass tube at 20 °C. Then the tube was opened, the ether was evaporated, and the residue was recrystallized from hexane. Crystalline of substance **1** was obtained (4.2 g, 86 %) with m.p. 66—67 °C. ^{1}H NMR (acetone-d$_6$, δ): 3.52 (t, 2 H, CH_2S); 4.54 (t, 2 H, CH_2N); 5.16 (sept, 1 H, H-6, J_{H-F} = 7.6 Hz); 7.32 (sept, 1 H, H-9, J_{H-F} = 8.2 Hz). ^{1}H NMR ($CDCl_3$, δ): 3.28 (t, 2 H, CH_2S); 4.04 (sept, 1 H, H-6, J_{H-F} = 8 Hz); 4.36 (t, 2 H, CH_2N); 7.02 (sept, 1 H, H-9, J_{H-F} = 8 Hz). The ^{1}H NMR signal at 7.0—7.3 ppm was assigned to the H-9 proton on the basis of the XRD data.

XRD analysis of compound 1 was performed using an automated Enraf-Nonius CAD4-LSI11/02-PDP11/23 diffractometric system (Cu-Kα irradiation, a graphite monochromator). The colorless transparent crystals of **1** are monoclinic: $C_{11}H_6F_{12}N_2O_2S$, mol. weight 458.23, a = 9.203(1), b = 10.349(1), c = 17.299(2) Å, β = 95.74(1)°, V = 1639.3(6) Å^3, Z = 4, d_{calc} = 1.857 g cm^{-3}, spatial group $P2_1/n$. The structure of **1** was decoded by direct methods and refined by the full-matrix least-squares method in the anisotropic (isotropic for H atoms) approximation to R = 0.059 over 2075 independent reflections with $I \geq 3\sigma(I)$. Detailed results of XRD analysis will be published elsewhere.

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