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Unusual self-condensation of polyfluorinated β-diimines in a medium of perfluorocarbonic acids esters

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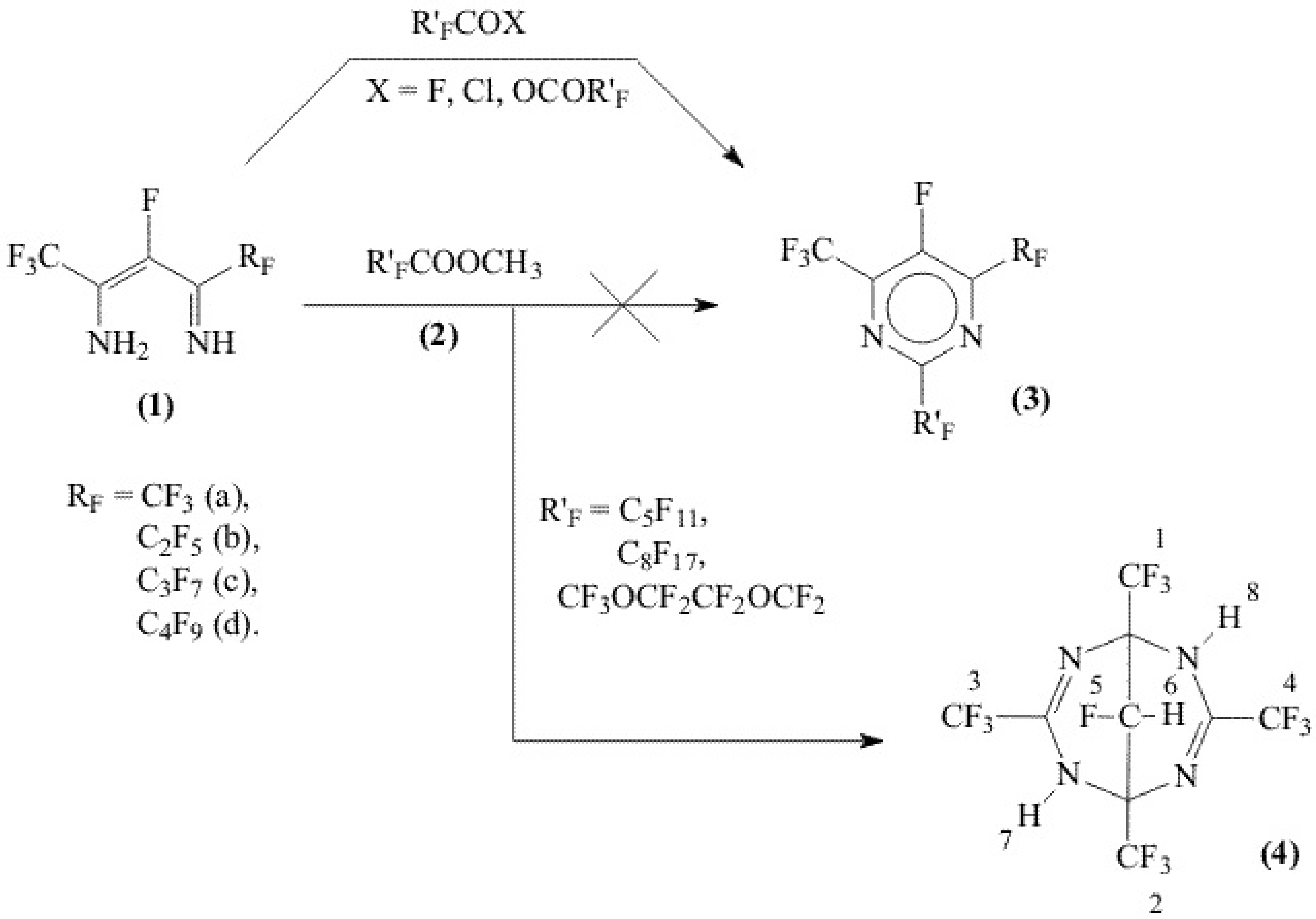
An unusual conversion of polyfluorinated ?-diimines resulted in tetraazabicylo compounds has been found.
Polyfluorinatedβ-diimines (**1**) in reactions with carbonyl compounds [1,2] as well as with acylhalides [3] form pyridines and pyrimidines with fluorine containing substituents.

Throughout the investigation of reactivity of (**1**) we have studied interaction of these compounds with perfluorocarbonic acids esters (**2**).

Esters (**2**) were supposed to be condensed with diimines (**1**), similarly to perfluoroacyhalides, to afford perfluorinated pyrimidines (**3**).



However β-diimine (**1a**) at heating in ester solutions (**2**) was found to form polyfluorinated tetraazabicyclononadiene (**4**). At that esters serves just as a medium in which the observed self-condensation of diimine (**1a**) occurs. No one case of the presence of expected pyrimidines (**3**) in the reaction mass was registered.

The isolated bicyclodiene (**4**) is a white cotton-like substance. We failed to determine its melting temperature because at heating even in a sealed off capillary there was observed full sublimation of the sample (without decomposition).

Three types of signals are observed in the ^{19}F NMR spectrum (d_6-DMSO), two of them belong to CF_3 group (-8.1 and -1.6 ppm) and one to CFH group with a characteristic chemical shift (136.9 ppm from CF_3COOH) and $J_{F\text{-}H}$ = 47 Hz.

In the ^{1}H NNR spectrum there were observed one signal belonging to CFH group (6.0 ppm) and two separate signals of NH groups (10.7 and 11.0 ppm). The composition of the obtained compound (**4**) was also confirmed by the data of mass-spectrometry (M^+; m/z 414) and elemental analysis (see Experimental).

The structure of compound (4) has been finally determined according to X-ray data (Fig.1).

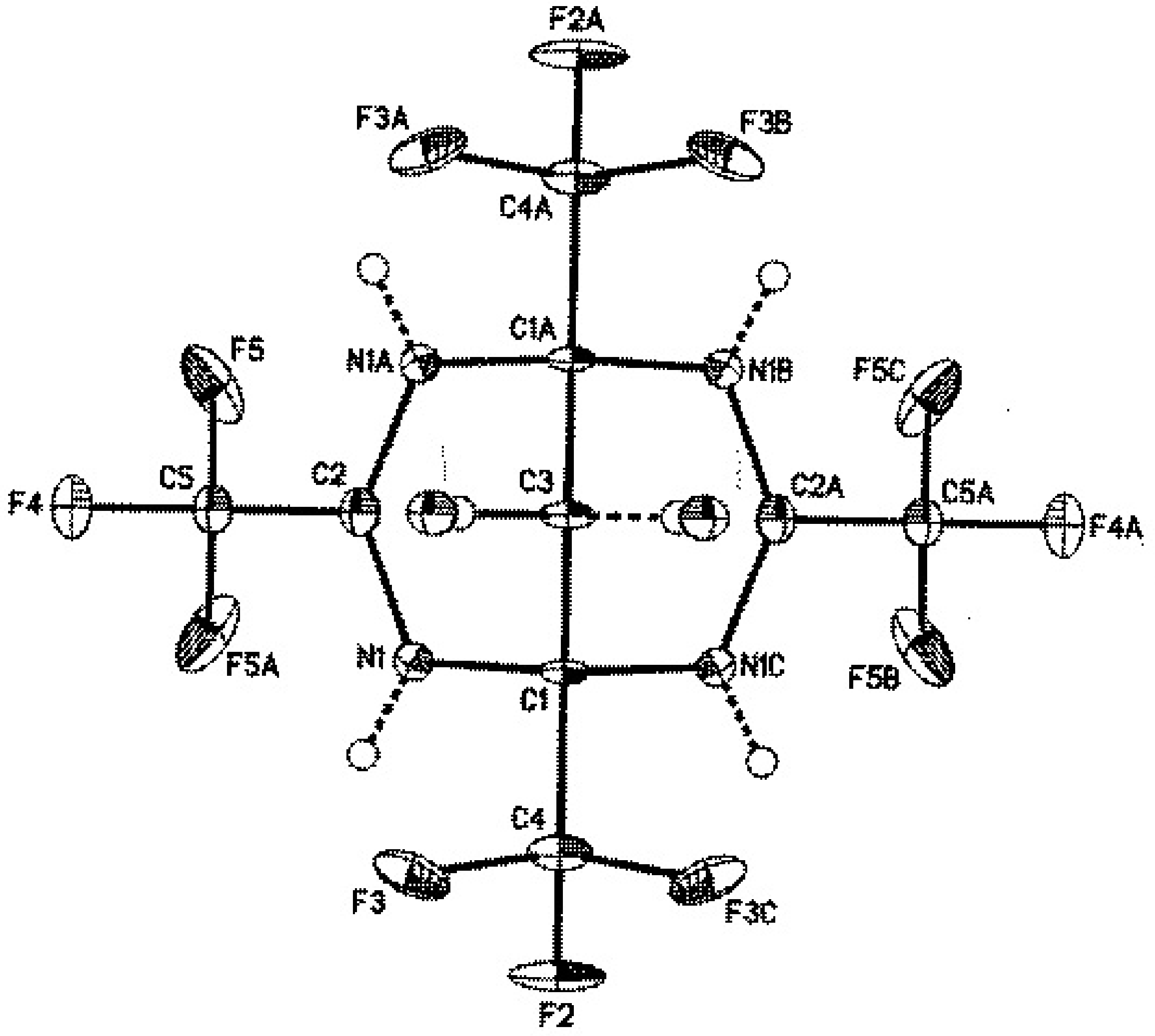


Fig.1. Molecular structure of compound (4) in representation of non-hydrogen atoms by 40%-probabilistic ellipsoids of anisotropic shifts. Alternative positions of disordered H and F atoms are shown in dashed lines.

Experimental

The ^1H and ^{19}F NMR spectra were recorded on a "Bruker AC-200F" spectrometer (200 and 188.3 MHz) with regard to TMS and CF_3COOH accordingly (external standards). The mass spectra were recorded on a VG 7070 E spectrometer at ionizing irradiation of 70 eV.

Monocrystals of compound (**4**) were obtained by crystallization from a benzene-methanol mixture (1:1 ratio). Colorless crystals (**4**) ($C_9H_3N_4F_{13}$, M = 414.15) are rhomb's, space group Cmcm; at T = 100 K: a = 13.686(2), b = 9.5965(18), c = 9.7178(18) Å, V = 1276.3(4)$Å^3$, Z = 4, d_c = 2.155 g/cm ^{3}, F(000) = 808, μ= 0.267 mm $^{-1}$.

The parameters of the unit cell and intensities of 5829 reflections were measured on an automatic Bruker SMART APEX II CCD diffractometer (T = 100 K, λMo$K\alpha$-radiation, graphite monochromator,ψ and ω-scanning, $2\theta \leq 52^{o}$). The structure was determined by the direct method and specified by full matrix least-squares method in anisotropic approximation for non-hydrogen atoms.

The positions of hydrogen atoms were calculated geometrically and were specified in isotropic approximation with fixed positional and heat parameters. The final divergence factors R_1 = 0.056 for 517 independent reflections with $I>2\ \sigma$ and wR_2= 0.153 for all 683 independent reflections, S = 1.010. All the calculations were performed using SHELXTL4 program complex.

A solution of 3.0g of diimine (**1a**) in 12 ml of perfluorocaproic acid methyl ester was boiled with a back flow condenser for 20 minutes. The precipitated residue was separated by filtration, washed with chloroform (3x30 ml) dried under vacuum. There was obtained 1.5g (54%) of compound (**4**).

19F NMR spectrum (DMSO-d6, δ, ppm, J/Hz): -8.1 (d, 6 F, F(1), F(2)); -1.6 (s, 6 F, F(3), F(4)); 136.9 (m, 1 F, F(5)).

1H NMR spectrum: (DMSO-d6, δ, ppm, J/Hz): 6.0 (d, 1 H, H(6), J = 50), 10.7 and 11.0 (both s, 1 H, H(7), H(8)).

Found (%):C, 26.16; H, 0.78; F, 60.51; N, 13.61. $C_9H_9F_{13}N_4$.
Calculated (%):C, 26.10; H, 0.73; F, 59.64; N, 13.53.

Literature

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