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**SYNTHESIS AND NMR STUDY OF THE  
N-POLYFLUOROALKYLATION PRODUCT  
OF TRIS(2-AMINOETHYL)AMINE  
WITH 1H,1H,9H-TRIHYDROPERFLUORONAN-1-OL**

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**Abstract:** By the interaction of tris(2-aminoethyl)amine with polyfluorinated alcohol in the presence of catalytic amounts of montmorillonite clay, the corresponding N-polyfluoroalkylation product was synthesized. One-dimensional (<sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F) and two-dimensional heteronuclear (<sup>1</sup>H-<sup>15</sup>N HMBC) methods the structure of the resulting compound was studied by NMR spectroscopy.

**Keywords:** polyfluorinated alcohol, polyethylene polyamines, catalysis, NMR spectroscopy.

**Introduction**

The synthesis of fluorinated amines [1-3] is of interest in connection with the possibility of using same as reagents for producing biologically active compounds, as well as stabilizers of the properties of polymer materials [4]. Catalytic amination of alcohols is carried out at high temperatures in the presence of catalysts based on aluminum, chromium, titanium, vanadium, iron, nickel molybdenum, magnesium oxides, as well as thorium salts and natural aluminosilicates [5].

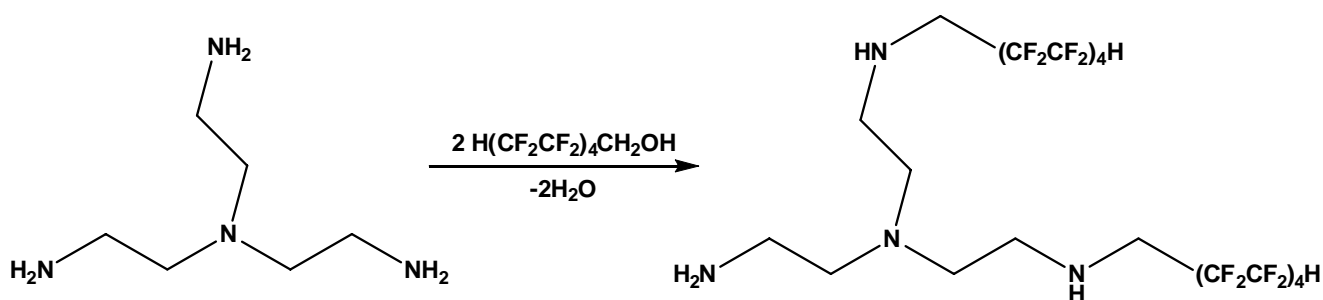
The polyfluorinated alcohols H(CF<sub>2</sub>CF<sub>2</sub>)<sub>n</sub>CH<sub>2</sub>OH, obtained on an industrial scale by reacting tetrafluoroethylene and methanol [6], can be considered as alkylating agents of polyamines,

particularly various isomeric polyalkylene polyamines, which are simultaneously capable of containing amino groups of varying degrees of substitution.

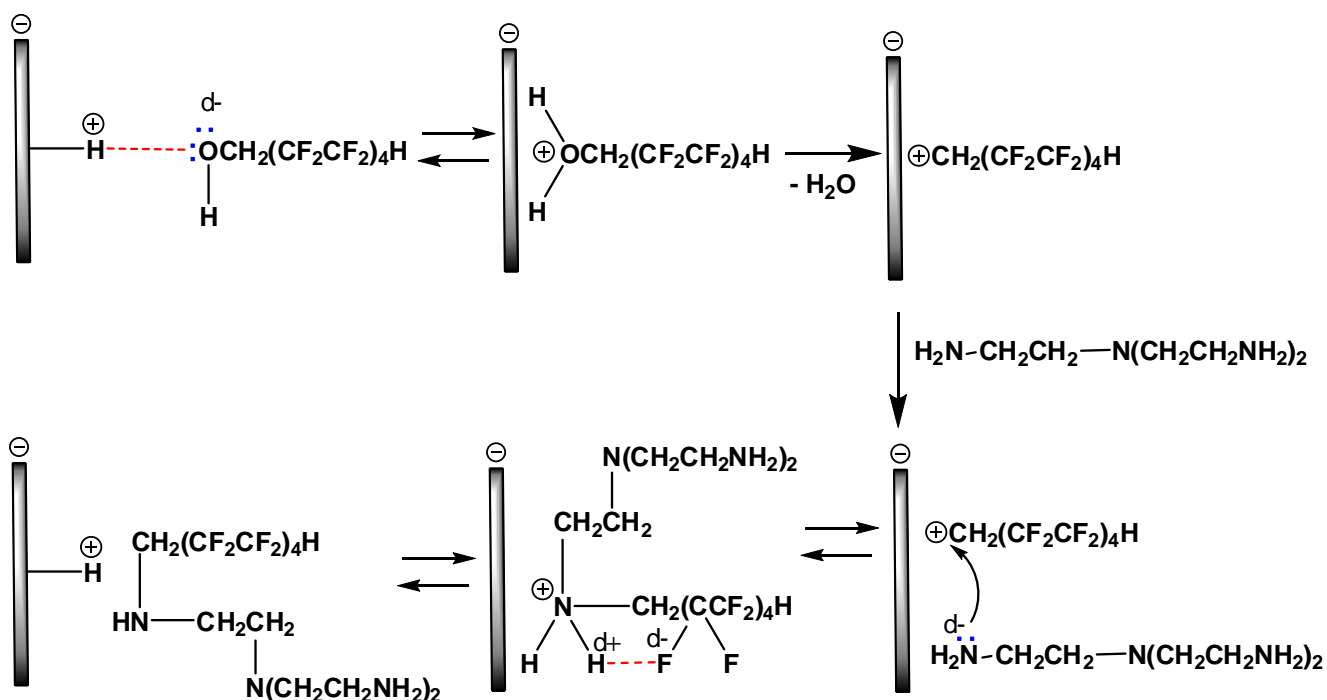
The purpose of the work - catalytic *N*-polyfluoroalkylation of tris(2-aminoethyl) amine with polyfluorinated alcohol ( $n=4$ ) in the presence of highly dispersed montmorillonite clay and study by methods of one-dimensional and two-dimensional NMR spectroscopy of synthesized compound structure.

### Results and discussion

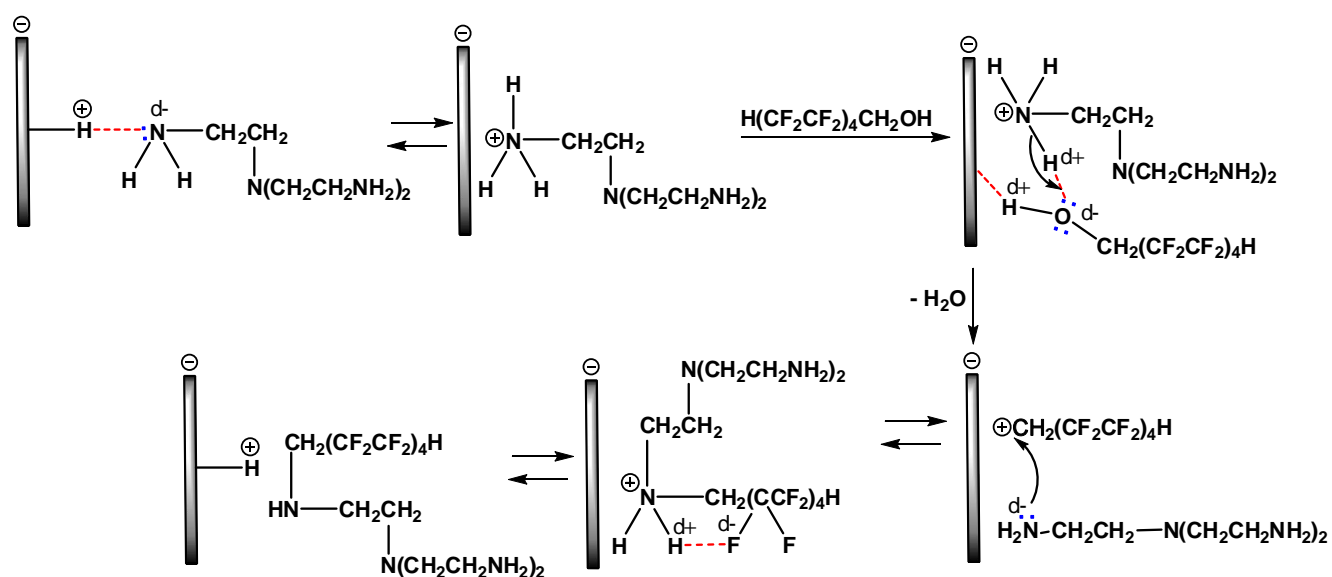
Catalytic *N*-polyfluoroalkylation of tris(2-aminoethyl) amine with 1H,1H,9H-trihydroperfluorononane-1-ol at their molar ratio 1:2 results in production of predominantly product of dialkylation:



Montmorillonite clay, being a Brønsted acid [7-9], facilitates alkylation of tris(2-aminoethyl)amine through initial stages of *O*- and *N*-protonation (only formation of monoalkylation product is shown in schemes 1 and 2). In both cases, a polyfluorinated carbocation is generated, which stability is significantly affected by fluorine atoms having a negative *I*-effect. The formation of intramolecular hydrogen bond in a disubstituted ammonium cation between the  $\text{CF}_2 \cdots \text{H}_2\text{N}^\oplus$  groups favorably affects an increase in its stability.

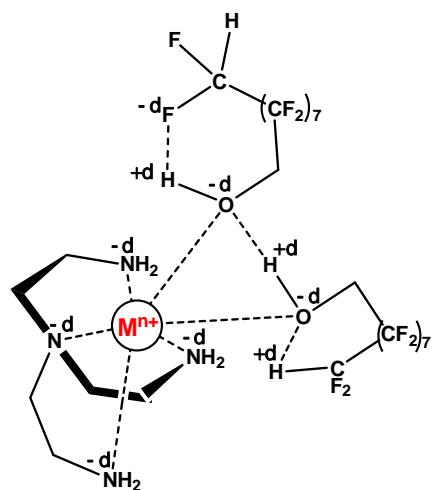


*Scheme 1. The O-protonation mechanism.*

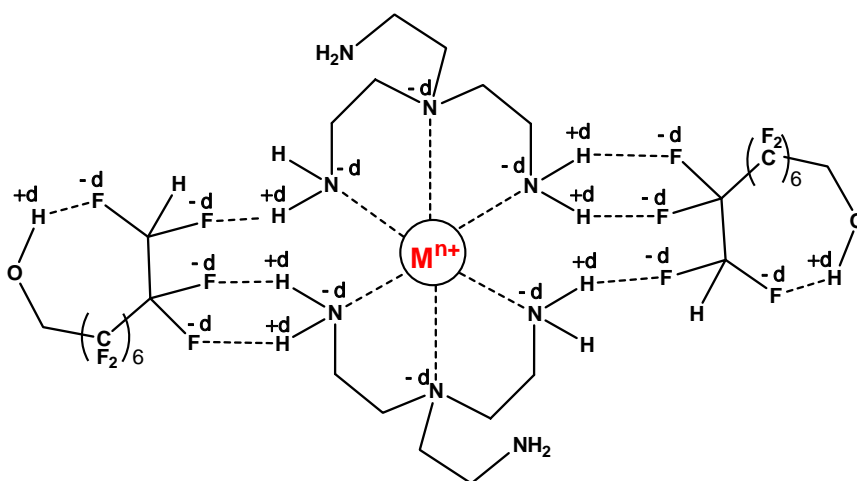


*Scheme 2. The N-protonation mechanism.*

The structural feature of montmorillonite clay is not only Brønsted but also Lewis acidity [7-9], caused by the presence of vacancy-orbital centers  $M^{n+}$  ( $Al^{3+}$ ,  $Fe^{3+}$ ,  $Fe^{2+}$ ,  $Mn^{2+}$ ,  $Ti^{4+}$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$ ,  $Na^+$ ). Formation of donor-acceptor complexes with participation of vacancy orbitals of metal ions can be carried out as with non-divided electron pairs of nitrogen atoms of amino groups of tris(2-aminoethyl)amine and oxygen of hydroxyl groups of 1H,1H,9H-trihydroperfluorononane-1-ol (structure I), and without participation of molecules of polyfluorinated alcohol (structure II).



**Structure I**



**Structure II**

Thus, catalytic *N*-polyfluoroalkylation of tris(2-aminoethyl)amine with 1H,1H,9H-trihydroperfluorononane-1-ol in the presence of montmorillonite clay in a molar ratio of amine and alcohol 1:2 leads to the formation of a disubstituted product. A possible contribution of the Brønsted and Lewis acid sites to the alkylation mechanism is shown.

### Experimental part

Tris(2-aminoethyl)amine (95%, Keyingchem, China) is purified by distillation and has the following characteristics: boiling point 114°C (15 mm Hg),  $d$  0.976 g·ml<sup>-1</sup>,  $n_D^{20}$  1.497. Polyfluorinated alcohol 1H,1H,9H-trihydroperfluorononane-1-ol ( $\geq 90\%$ , HaloPolymer, Perm) has mp 68-70°C. Calcined montmorillonite clay ( $\geq 98\%$ , JSC B-Clay, Kazakhstan) has a specific surface area of 595 m<sup>2</sup>·g<sup>-1</sup> (in water) and 64 m<sup>2</sup>·g<sup>-1</sup> (nitrogen), a cation exchange capacity of 100 mg·eq/100 g and is presented in the form of a mixture of three main fractions: 50-100 nm – 10 wt.%, less than 1  $\mu$ m – 80 wt.%, less than 10  $\mu$ m – 10 wt.%.

**The method of synthesis.** 1 ml (6.67 mmol) of tris(2-aminoethyl)amine and 5.77 g (13.3 mmol) 1H,1H,9H-trihydroperfluorononane-1-ol in the presence of catalytic amounts of montmorillonite (0.1 mg) was dispersed at ultrasound frequency of 40 kHz in a sealed glass ampoule at 80°C for 2 hours, followed by heating to 120°C for 6 hours. The starting reagents were separated from the reaction product by extraction of the cooled *i*-PrOH at -6°C +1°C with further fractional vacuum distillation of the extract. Yield is 2.27 g (35%), yellow oil,  $R_f$  = 0.71,  $t$  of boiling 133 - 136°C (15 mm Hg).

**NMR spectrum <sup>1</sup>H** [CDCl<sub>3</sub>],  $\delta$ , ppm: 1.56 br.s (2H, H<sub>2</sub>N), 2.43-2.90 m (12H, CH<sub>2</sub>CH<sub>2</sub>), 4.01 t (4H, CH<sub>2</sub>CF<sub>2</sub>,  $J$  = 14.8 Hz), 6.07 tt (2H, HCF<sub>2</sub>,  $J_1$  = 4.8 Hz,  $J_2$  = 51.6 Hz), 7.29 s (2H, HNCH<sub>2</sub>).

**NMR spectrum**  $^{13}\text{C}$  [ $\text{CDCl}_3$ ],  $\delta$ , ppm: 38.66-39.75 ( $\text{CH}_2\text{NH}_2$ ), 41.65 ( $\text{CH}_2\text{CF}_2$ ), 46.01 d ( $\text{CH}_2\text{NHCH}_2\text{CF}_2$ ,  $J = 8.1$  Hz), 49.22-59.56 ( $\text{NCH}_2\text{CH}_2\text{NH}$ ), 60.98 ( $\text{NCH}_2\text{CH}_2\text{NH}_2$ ), 104.67-114.00 ( $\text{CF}_2$ ). **NMR spectrum**  $^{19}\text{F}$  [ $\text{CDCl}_3$ ],  $\delta$ , ppm: -121.83 – -122.40 m ( $\text{CF}_2$ ), -123.70 – -129.76 m ( $\text{CF}_2\text{CH}_2$ ), -137.21 d ( $\text{CF}_2\text{H}$ ,  $J = 48.9$  Hz). **NMR spectrum**  $^{15}\text{N}$  ( $^1\text{H}$ - $^{15}\text{N}$  HMBC) [ $\text{CDCl}_3$ ],  $\delta$ , ppm: 18 ( $\text{NH}_2$ ), 30 ( $\text{NH}$ ), 43 ( $\text{NCH}_2$ ). **Found, %:** C 29.41; H 2.26; N 5.50.  $\text{C}_{24}\text{H}_{22}\text{F}_{32}\text{N}_4$ . **Calculated, %:** C 29.58; H 2.28; N 5.57.  $M$  974.41.

NMR spectra were recorded at room temperature on a Bruker AVANCE III HD (400 MHz) device in  $\text{CDCl}_3$  ( $^1\text{H}$  – 400.17 MHz,  $^{13}\text{C}$  – 161.99 MHz,  $^{19}\text{F}$  – 376 MHz), using tetramethylsilane as an internal standard. The chemical shifts of the  $^{19}\text{F}$  cores are defined relative to  $\text{CFCl}_3$  and the  $^{15}\text{N}$  nuclei relative to liquid ammonia as an external standard. Elemental analysis was carried out on a CHNS/O Euro EA3100 analyzer. TLC was carried out on Sorbfil plates (Russia), eluent is chloroform-acetone (1:1).

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