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SYNTHESIS, THERMOLYSIS, AND MASS SPECTROMETRY OF PERFLUORINATED DI- AND TRIAZIDOPYRIDINES

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2,4-Diazido-3,5,6-trifluoropyridine and 2,4,6-triazido-3,5-difluoropyridine were obtained by the reaction of pentafluoropyridine with sodium azide in aqueous acetone. Under the action of electron impact the 2,4-diazidopyridine undergoes sequential fission of the azide groups in positions 2 and 4 of the pyridine ring and ring contraction with the formation of a characteristic $[M\text{-}2N_2\text{-}F]^+$ *ion. On the other hand thermolysis of the same diazide is accompanied by the selective decomposition of its* γ*-azide group with the formation of 4-amino-2-azido-3,5,6-trifluoropyridine. The effect of selective decomposition of the azide groups in 2,4-diazidopyridines on thermolysis and under electron impact is caused by the different distribution of bonding orbital density at the* α*- and* γ*-azide groups respectively in the initial diazide and its radical cation. One of the routes of the triazide decomposition under electron impact is the formation of the* $[M\text{-}N_2]^+$ *ion due to decomposition of the* α*-azide group.*

Keywords: polyazides, fluoropyridines, mass spectral decomposition, thermolysis.

We showed previously that azide groups in positions 2 and 4 of a pyridine ring differed significantly in the distribution of bonding orbital density on the nitrogen atoms, and as a result selectively underwent different types of chemical conversions (cycloaddition of electron-rich [1-4] and electron-poor [4,5] dipolarophiles, addition of nucleophiles to the terminal nitrogen atom [6], and photolysis [7,8]). The selectivity of the decomposition of the azide groups in 2,4-diazidopyridines on thermolysis and on electron impact has not been studied. To carry out such an investigation it was desirable to have perfluorinated model azides which in the process of decomposition should form relatively stable intermediate products. The synthesis of 2,4-diazido-3,5,6-trifluoropyridine and 2,4,6-triazido-3,5-difluoropyridine and their conversions on thermolysis and on electron impact are described in the present study.

The reaction of pentafluoropyridine with sodium azide was carried out in aqueous acetone. It has been established that the interaction of these reactants in aprotic polar solvents stops at the stage of the monoazide **1** formation [9]. Repeated study of this reaction showed that after boiling pentafluoropyridine with sodium azide for 3 days in 10% aqueous acetone (70°C) the main reaction product was the diazidopyridine **3**, the yield of which was 82% after purification. Reaction of compound **3** with an excess of sodium azide at 70°C for two weeks enabled the triazidopyridine **4** to be obtained in 62% yield.

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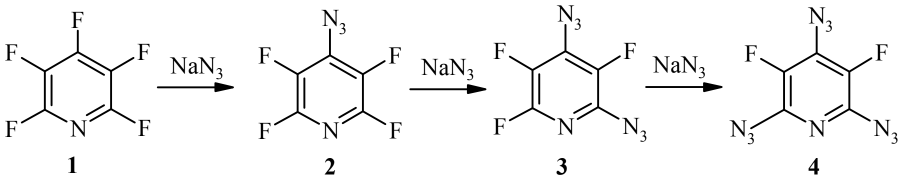


The composition and structure of compounds **3** and **4** were in complete accordance with the data of elemental analysis, IR, ^{13}C and ^{19}F NMR spectroscopy, and mass spectrometry. The presence in the ^{13}C NMR spectrum of compound **3** of five signals for the pyridine ring carbon atoms at 130.5 (m, $C_{(4)}$), 134.7 (dd, $C_{(5)}$, J_{C-F} = 260 and 32), 138.7 (dd, $C_{(6)}$, J_{C-F} = 262 and 32), 139.1 (d, $C_{(3)}$, J_{C-F} = 264), and 144.1 ppm (dd, $C_{(2)}$, J_{C-F} = 13.8 and 2.9 Hz) indicates that the two azide groups in the molecule are located in positions 2 and 4 of the pyridine ring. This was also confirmed by the ^{19}F NMR spectrum of diazide **3** in which signals for three fluorine atoms were present at –25.87 ($F_{(6)}$, J_{65} = 23.7), -82.11 ($F_{(3)}$), and -92.20 ppm ($F_{(5)}$, J_{56} = 23.7 Hz) and which is in good agreement with spectra of the known 2,4-disubstituted derivatives of 3,5,6-trifluoropyridines [10]. Only one signal for the fluorine atoms was present in the ^{19}F NMR spectrum of triazide **4** at -84.00 ppm ($F_{(3)}$,$F_{(5)}$).

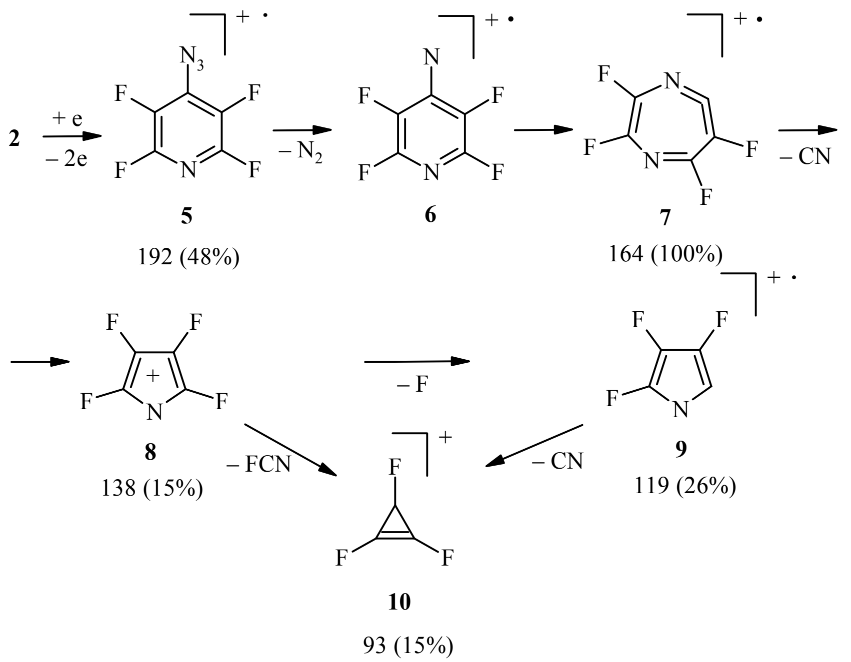
We analyzed the mass spectra of compounds **2**, **3**, and **4** with the aim of studying the selectivity of the breakdown of the azide groups in 2,4-di- and 2,4,6-triazidopyridines under electron impact. For numerous thermolysis and photolysis reactions of 2- and 4-azidopyridines it has been shown that the breakdown mechanisms of these isomers are significantly different. The first stage of the breakdown of 4-azidopyridines is the generation of pyridyl-4-nitrene which under the reaction conditions undergoes rapid ring expansion with the formation of a 1,4-diazacycloheptatetraene intermediate. Reaction of the latter with nucleophiles (water, alcohol, amines) gives various derivatives of 1,4-diazacycloheptatetraene [11]. Derivatives of phenyl azides also undergo analogous conversions [11-13]. It is important to note that the decomposition scheme of phenyl azides under electron impact is practically identical to that under thermolysis and includes the formation of the fairly intense ions M^{+}, $[M-N_2]^{+\cdot}$, and $[M-N_2-CN]^{+}$ [14].

The observed route for the decomposition of azide **2** under electron impact is shown in Scheme 1 which reproduces completely the route of fragmentation for phenyl azides [14]. The same dissociative ionization mechanism also applies to 4-azidotetrachloropyridine [4]. It is evident from the Scheme that the presence in the mass spectrum of the $[M-N_2-CN]^{+}$ ion is a diagnostic indicator for the decomposition of 4-azidopyridines under electron impact and corresponds to the process of splitting off a CN radical from the 1,4-diazacycloheptatetraene molecule **7**.

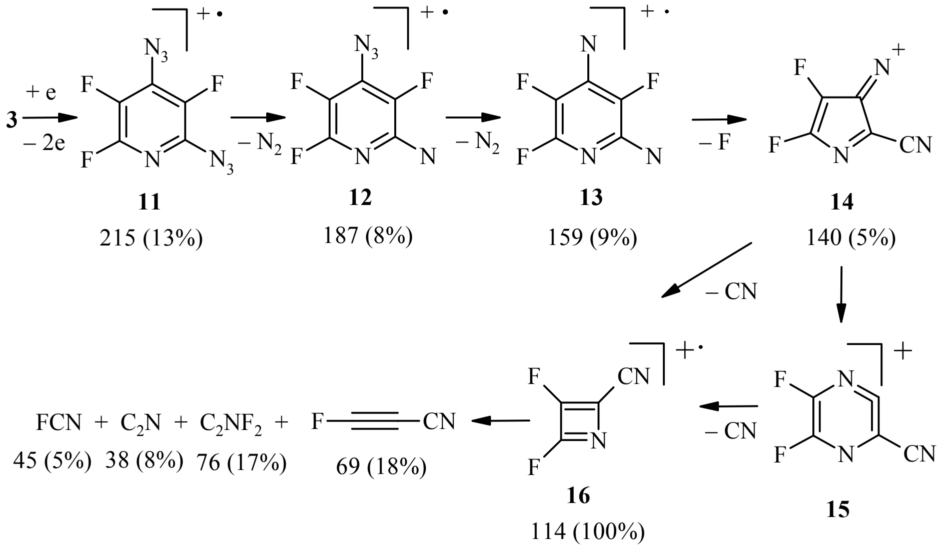
On the other hand the thermal and photochemical decomposition of 2-azidopyridines includes the generation of pyridyl-2-nitrenes, which under the reaction conditions mostly undergo ring contraction with the formation of 2-cyanopyrroles [11-13]. It is evident that in this case decomposition of 2-azidopyridines under electron impact must be characterized by the absence of a peak for the $[M-N_2-CN]^{+}$ ion in the spectrum and the presence of peaks for ions corresponding to the process of the cyano group migration to the β-carbon atom of the pyridine ring. When a fluorine atom is present on this carbon atom the ion $[M-N_2-F]^{+}$ is most probable in the spectrum (Scheme 1).

The route for the decomposition of azide **3** is shown in Scheme 2, the first two stages of which include the sequential elimination of the nitrogen molecule and the formation of the cation radicals **12** and **13**. The absence of a peak for the $[M-2N_2-CN]^{+}$ ion and the presence of a peak for the $[M-2N_2-F]^{+}$ ion indicate that the dinitrene **13** then undergoes ring contraction with the formation probably of ion **14** (or its rearrangement product **15**).

Scheme 1



Scheme 2



Fission of a CN radical from **14** or **15** leads to the most intense ion **16**, the further fragmentation of which gives the ions FCC-CN, C_2NF_2, C_2N, and FCN.

The answer to the problem of which of the azide groups of pyridine **3** loses a molecule of nitrogen first may be obtained from analysis of the geometry of radical cation **11**. It has been shown that the geometry of the azide groups in azides existing in various excited states (singlet, triplet, radical anion), differs significantly from the geometry of azide groups in the ground state [15-17]. It was reasonably expected that the geometric

TABLE 1. Geometric Parameters of the Azide Groups in Pyridines **2-4** and Radical Cations **5**, **11**, and **21** Calculated by the RHF/PM3 and UHF/PM3-SCF* Methods

Com-pound	Group	Bond length, Å			Valence angle, deg ($N_{(\alpha)}$–$N_{(\beta)}$–$N_{(\gamma)}$)
		C–$N_{(\alpha)}$	$N_{(\alpha)}$–$N_{(\beta)}$	$N_{(\beta)}$–$N_{(\gamma)}$	
2	4-N_3	1.4143	1.2796	1.1223	167.99
3	2-N_3	1.4162	1.2808	1.1213	169.22
	4-N_3	1.4159	1.2778	1.1228	167.71
4	2-N_3	1.4180	1.2763	1.1227	169.52
	4-N_3	1.4175	1.2763	1.1233	167.57
	6-N_3	1.4186	1.2773	1.1224	169.62
5	4-N_3	1.3516	1.3491	1.1116	167.67
11	2–N_3	1.3483	1.3438	1.1104	169.56
	4-N_3	1.3926	1.3010	1.1169	168.67
21	2-N_3	1.3603	1.3225	1.1124	169.85
	4-N_3	1.3988	1.2966	1.1178	168.13
	6-N_3	1.3632	1.3199	1.1127	170.00

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* Calculation of the geometry for radical cations **5**, **11**, and **21**.

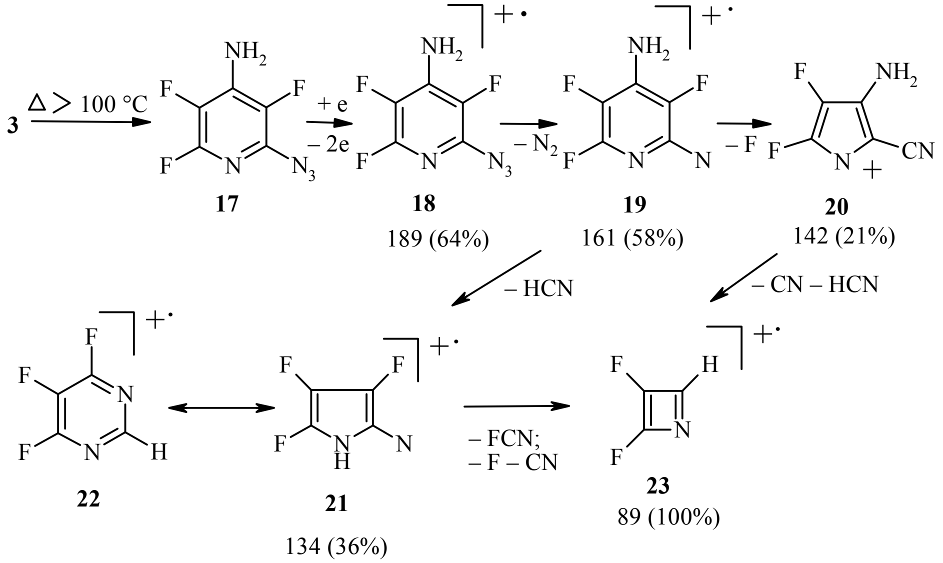
parameters of azide groups for radical cations must also be different from those of the initial azides. In its turn this group of the radical cation, in which the N-N_2 bond is lengthened to a large degree, evidently must also dissociate first. Precisely this rule was observed on photolysis of 2,4-diazidopyridines in [7].

In reality the calculations on the geometry of radical cation **5** by the UHF/PM3-SCF method ($S = 1/2$, $q = +1$) showed (see Table 1) that the N-N_2 bond in this radical is lengthened by 0.07 Å, and the C-N_3 bond is shortened by 0.063 Å (close to the C–N bond length in nitrenes [7]) compared with the analogous parameters in the initial azide molecule. Calculations for radical cation **11** revealed that the N–N_2 bond lengths in its α- and γ-azide groups were lengthened by 0.063 and 0.023 Å respectively but the C–N_3 bonds were shortened by 0.068 and 0.023 Å respectively compared with the analogous bonds in the initial diazide **3**. It follows from these data that fission of the N–N_2 bond in the α azide group of radical cation **11** must occur first. It is most probable that precisely this factor also partially predetermines the further fragmentation of dinitrene **13** along the path of ring contraction with fission of a fluorine radical (Scheme 2). We note that the conclusions of the quantum-chemical investigation of the geometry for radical cation **11** is completely in agreement with empirical data on the effect of the substituent R in azides R–N–N_2 on the stability of their radical cations. Thus, it has been recorded that the strengthening of the conjugation of electron-withdrawing substituents R with the azide group increases the stability of azide radical cations [18]. The γ-azide groups in the molecules of 2,4-diazidopyridines are far more strongly conjugated with the pyridine ring [7], and consequently must be more stable on excitation by electron impact. This also confirms the decomposition scheme of diazide **3**.

There are no data in the literature on the selective thermolysis of azide groups in aromatic polyazides. Mainly this is linked with the difficulty of isolating the products of such reactions, formed in low yield and being a complex mixture of many compounds [11]. In the present study we have made attempts to study the thermolysis of diazide **3** by chromato-mass spectrometry. It is assumed that on passing through the chromatographic column at a high temperature the initial diazide will be partially decomposed, and it will be possible to construct a scheme for the thermolysis of a given compound from the mass spectrum of formed products.

Vapors of diazide **3** in a stream of helium were passed through a chromatographic column packed with methylsiloxane at 100°C. The sole product of thermal treatment of diazide **3** under these conditions was aminoazidopyridine **17** the yield of which did not exceed 1% (**3**: R_f 4.60 min; **17**: R_f 5.44 min). The structure of compound **17** was confirmed by its mass spectrum (Scheme 3). The absence in the spectrum of a peak for the $[M\text{-}N_2\text{-}N]^+$ ion, typical for the fragmentation of 4-azidopyridines, and the presence of an intense $[M\text{-}N_2\text{-}F]^+$ ion, characteristic for the decomposition of 2-azido-3-fluoropyridines, convincingly indicate that the azide group in this compound is in position 2 of the pyridine ring. In addition the presence in the spectrum of an intense peak for the $[M\text{-}N_2\text{-}HCN]^{+\cdot}$ ion, typical for the fragmentation of aromatic amines [19], shows the presence of the amino group in position 4 of the pyridine ring in compound **17**.

Scheme 3

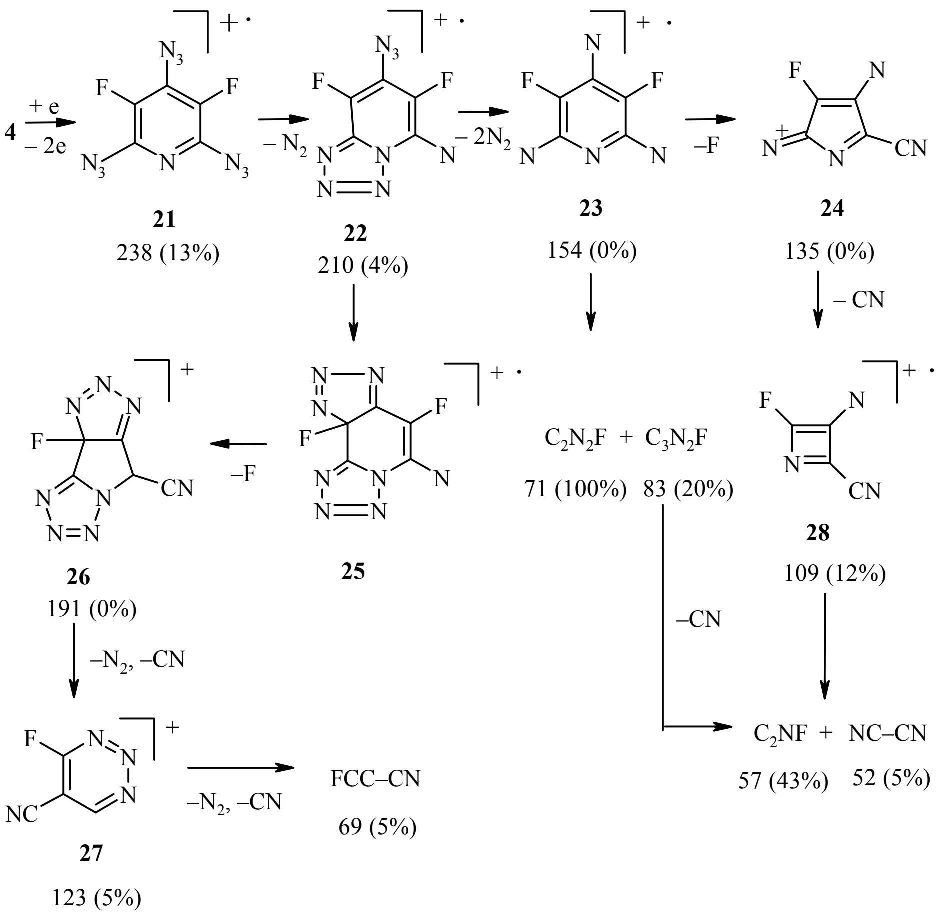


The selectivity of the γ-azide group decomposition on thermolysis of pyridine **3** is in complete agreement with the data of RHF/PM3 calculations of this compound (Table 1), according to which the $N–N_2$ bond in this group is the weakest (it has significantly lower binding orbital density on the $N_{(\alpha)}$ and $N_{(\beta)}$ atoms and as a result a longer distance between these atoms and a lower N–N–N valence angle). In difference to fragmentation by electron impact the azide group in position 4 of the pyridine ring is more labile in the thermal decomposition of 2,4-diazidopyridines.

The main pathways for the fragmentation of triazidopyridine **4** under electron impact are shown in Scheme 4. The first stage of the process is the fission of a molecule of nitrogen and the formation of the $[M\text{-}N_2]^{+\cdot}$ ion.

According to quantum-chemical calculations (Table 1) the azide group at position 2 of the pyridine ring in radical cation **21** must be the most labile. The presence in the spectrum of a peak for the $[M\text{-}N_2]^{+\cdot}$ ion and the absence of peaks for $[M\text{-}2N_2]^{+\cdot}$ and $[M\text{-}3N_2]^{+\cdot}$ ions enables the existence of special pathways to be assumed for the stabilization of the $[M\text{-}N_2]^{+\cdot}$ ion due to the redistribution of chemical bonds in its molecule. The most probable pathway for this stabilization is the formation of tetrazolopyridine **22**, which then undergoes an intramolecular cycloaddition reaction of the γ-azide group at the C=CF double bond with the formation of intermediate **25**. The thermal conversions of α-azido azines in bicyclic tetrazoles of the type **22** have been described in the literature [20,21]. In favor of this hypothesis is the fact that the $[M\text{-}N_2\text{-}N_3\text{-}F\text{-}CN]^+$ ion follows after the $[M\text{-}N_2]^{+\cdot}$ ion in the mass spectrum. Fission of an N_3 radical is a diagnostic characteristic for the decomposition of tetrazoles [18,22]. In addition the $[M\text{-}N_2\text{-}N_3\text{-}F\text{-}CN]^+$ ion formally contains an undissociated –N–N=N fragment, which on a background of fission of F and CN radicals is possible only when this fragment is stabilized by cycloaddition to a double bond (structures **25** and **26**) and subsequent conversion into a heterocyclic system (of type **27**). The $[M\text{-}3N_2\text{-}F\text{-}CN]^{+\cdot}$ ion is displayed after the $[M\text{-}N_2\text{-}N_3\text{-}F\text{-}CN]^+$ ion in the

Scheme 4



mass spectrum and may be formed by the sequence of conversions **22** → **23** → **24** → **28**. We note that the main fragmentation pathway of radical cation **21** lies not through intermediates **27** and **28** but includes decomposition of the radical cation trinitrene **23** to fragments C_2N_2F and C_3N_2F. Such a decomposition pathway was also observed in the mass spectra of 3,5-dichloro-, 3,5-dicyano-, and 3-chloro-5-cyano-substituted triazidopyridines in which the most intense peaks were the peaks of C_2N_2R (100%) and C_3N_2R (30-35%) ions, where R = Cl or CN.

Attempts to study the selective thermolysis of the azide groups of triazide **4** by chromato-mass spectrometry were unsuccessful. At temperatures below 100°C triazide **4** did not undergo thermal conversions, while at higher temperatures it decomposed into low molecular fragments and products of their dimerization. Thermal decomposition and mass spectral breakdown of the azide groups in 2,4-di- and 2,4,6-triazidipyridines occurs selectively as also a whole series of other reactions with the participation of these groups. The azide groups in position 4 of the pyridine ring are more labile on thermolysis as a result of the lower bonding orbital density on these groups. On the other hand the azide groups in the α position of the pyridine ring are the more labile in the azide radical cations formed on excitation of azides by electron impact. Calculation of the geometry for the azide radical cations by the PM3 method may be used successfully for diagnosing the sequential breakdown of azide groups of aromatic polyazides under electron impact and for a more reliable interpretation of the mass spectral breakdown for such compounds.

EXPERIMENTAL

The IR spectra were recorded on a Specord M 80 instrument in nujol, and the ^{13}C NMR spectra on a Bruker AM 400 instrument (100.6 MHz) in $CDCl_3$ solution. The ^{19}F NMR spectra were recorded on a Bruker AC 200 instrument (188.3 MHz) in $CDCl_3$ solution with $C_6H_5CF_3$ as internal standard. Mass spectra were recorded on a Finnigan MAT-90 instrument at an ionization energy of 70 eV. Analysis of the products of thermolysis of azides was carried out on a Hewlett-Packard 5890 spectrometer (mass detector Hewlett-Packard 5970, ionization energy 70 eV, chromatographic column EC-5, sorbent methylsiloxane containing 5% phenyl substituents and having a porosity of 0.25 μm, carrier gas was helium, temperature of passing samples through the column 100°C, solvent dichloromethane). A check on reactions was effected by TLC on Silufol UV 254 plates.

Calculation of the geometry and electronic properties of compounds **3-4** and of radical cations **5**, **11**, and **21** was carried out by the semiempirical PM3 method [23], with the Spartan set of programs [24]. The molecular structures of compounds were calculated with full optimization of the geometric parameters. Pentafluoropyridine from Aldrich was used in the work.

4-Azido-2,3,5,6-tetrafluoropyridine (2). A solution containing pyridine **1** (1.69 g, 10 mmol) and sodium azide (0.65 g, 10 mmol) in 10% aqueous acetone (100 ml) was stirred at room temperature for 12 h, after which the solvent was distilled off in vacuum at room temperature. The residue was redistilled in a Kugelrohr apparatus (0.01 mm Hg, 25°C), cooling the condensate with ice. Azide **2** was obtained as a colorless oily liquid. Yield 1.46 g (76%). IR spectrum, ν, cm^{-1} 2130, 2100 (N_3), 1640, 1620, 1585, 1500 (C=C, C=N), 1345 (N_3), 1285, 1220 (C–N), 1000 (C–F). ^{13}C NMR spectrum, δ, ppm, *J* (Hz): 132.1 (m, $C_{(4)}$); 135.3 (m, $C_{(3)}$, $C_{(5)}$, $^1J_{C\text{-}F}$ = 262, $^2J_{C\text{-}F}$ = 30); 143.5 (m, $C_{(2)}$, $C_{(6)}$, $^1J_{C\text{-}F}$ = 245, $^2J_{C\text{-}F}$ = 30). Mass spectrum, *m/z* (I_{rel}, %): M^+ 192 (48), $[M\text{-}N_2]^{+\cdot}$ 164 (100), $[M\text{-}N_2\text{-}CN]^+$ 138 (15), $[M\text{-}N_2\text{-}CN\text{-}F]^+$ 119 (26), $[M\text{-}N_2\text{-}CN\text{-}F\text{-}CN]^+$ 93 (15), 78 (13), 70 (19). The other spectral characteristics corresponded to literature data [9].

2,4-Diazido-3,5,6-trifluoropyridine (3). A solution containing pyridine **1** (1.69 g, 10 mmol) and sodium azide (2.6 g, 40 mmol) in 10% aqueous acetone (200 ml) was stirred at room temperature for 6 h, then boiled for 72 h. The solvent was distilled off in vacuum at room temperature, the residue washed with water, dried in the air, and chromatographed on a column with aluminum oxide using diethyl ether–petroleum ether, 2 : 98 as eluent. The product was purified further in a Kugelrohr apparatus (0.01 mm Hg, 25°C), cooling the condensate with ice. Diazide **3** was obtained as a colorless oily liquid. Yield 1.76 g (82%). IR spectrum, ν, cm^{-1}: 2140, 2105 (N_3), 1625, 1615, 1485, 1430 (C=C, C=N), 1380, 1340 (N_3), 1280, 1240 (C–N), 1000 (C–F). ^{19}F NMR spectrum, δ, ppm, *J* (Hz): -25.87 (t, $F_{(6)}$, J_{65} = 23.7); -82.11 (d, $F_{(3)}$); -92.20 (d, $F_{(5)}$, J_{56} = 23.7). ^{13}C NMR spectrum, δ, ppm, *J* (Hz): 130.5 (m, $C_{(4)}$); 134.7 (dd, $C_{(5)}$, $^1J_{C\text{-}F}$ = 260, $^2J_{C\text{-}F}$ = 32); 138.7 (dd, $C_{(6)}$, $^1J_{C\text{-}F}$ = 262, $^2J_{C\text{-}F}$ = 32); 139.1 (d, $C_{(3)}$, $^1J_{C\text{-}F}$ = 264); 144.1 (dd, $C_{(2)}$, $^2J_{C\text{-}F}$ = 13.8, $^3J_{C\text{-}F}$ = 2.9). Mass spectrum, *m/z* (I_{rel}, %): M^+ 215 (13), $[M\text{-}N_2]^+$ 187 (8), $[M\text{-}2N_2]^+$ 159 (9), $[M\text{-}2N_2\text{-}F]^+$ 140 (5), $[M\text{-}2N_2\text{-}F\text{-}CN]^+$ 114 (100), 93 (5), 88 (9), 83 (5), 76 (17), 74 (6), 71 (9), 69 (18), 64 (16), 62 (10), 57 (14), 38 (10). Found, %: C 27.62; N 45.84. $C_5F_3N_7$. Calculated, %: C 27.91; N 45.58.

2,4,6-Triazido-3,5-difluoropyridine (4). A solution containing pyridine **1** (1.69 g, 10 mmol) and sodium azide (2.6 g, 40 mmol) in 10% aqueous acetone was stirred at room temperature for 6 h, then boiled for 2 weeks. The solvent was distilled off in vacuum at room temperature, the residue washed with water, dried in the air, then chromatographed on a column with aluminum oxide using diethyl ether–petroleum ether, 2 : 98 as eluent. The compound was further purified by distillation in a Kugelrohr apparatus (0.01 mm Hg, 28°C), cooling the condensate with ice. Triazide **4** was obtained as a colorless oily liquid. Yield 1.48 g (62%). IR spectrum, ν, cm^{-1}: 2168, 2140, 2108 (N_3), 1628, 1615, 1485, 1432, 1400 (C=C, C=N), 1380, 1340 (N_3), 1280, 1238 (C–N), 1000 (C–F). ^{19}F NMR spectrum: -84.0 ppm. ^{13}C NMR spectrum, δ, ppm, *J* (Hz): 147.2 (dd, $C_{(2)}$, $C_{(6)}$, $J_{C\text{-}F}$ = 14 and 3); 138.7 (d, $C_{(3)}$, $C_{(5)}$, $J_{C\text{-}F}$ = 264); 135.0 (m, $C_{(4)}$). Mass spectrum, *m/z* (I_{rel}, %): M^+ 238 (13), $[M\text{-}N_2]^+$ 210 (4), $[M\text{-}N_2\text{-}N_3\text{-}F\text{-}CN]^+$ 123 (5), $[M\text{-}3N_2\text{-}F\text{-}CN]^+$ 109 (12), 83 (20), 71 (100), 69 (5), 57 (43), 52 (5), 50 (5), 43 (5), 38 (9). Found, %: C 25.43; N 58.61. $C_5F_2N_{10}$. Calculated, %: C 25.21; N 58.82.

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