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Amination of octafluoronaphthalene in liquid ammonia 2,6- and 2,7-Diaminohexafluoronaphthalenes selective preparation

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Abstract

Monoamination of octafluoronaphthalene by liquid ammonia affords 2-aminoheptafluoronaphthalene mainly (isolated yield 85–90%). Diamination of octafluoronaphthalene or amination of 2-aminoheptafluoronaphthalene affords a mixture of isomeric 1,6-, 1,7-, 2,6-, and 2,7-diaminohexafluoronaphthalenes with considerable prevalence of the 2,7-isomer (~70%), thus being the first example of the predominant substitution at position 7 in 2-substituted polyfluoronaphthalenes. The 2,7/2,6 ratio of 2-*X*-heptafluoronaphthalene (*X* = $^{-}$NH, NH_2 and NHAc) amination diminishes with the decrease of electron-donating effect of the substituent; 2,7-diaminohexafluoronaphthalene forms in the reactions of 2-aminoheptafluoronaphthalene or octafluoronaphthalene with excess of $NaNH_2$ in liquid ammonia and 2,6-diaminohexafluoronaphthalene—in the reaction of 2-acetylamidoheptafluoronaphthalene with liquid ammonia followed by acetylamido group hydrolysis. The method of the selective preparation of these diamines based on the reversible transformation of amino group and a convenient technique of their high purity isolation by complexation with crown ether have been elaborated.

Keywords: Octafluoronaphthalene; Diaminohexafluoronaphthalenes; Liquid ammonia; Aminodefluorination; Nucleophilic substitution; Regioselectivity

1. Introduction

The known reactions of octafluoronaphthalene (**1**) with both charged and neutral nucleophiles [1,2] proceed mainly by fluorine displacement at the β-carbon atom (β/α > 9/1). Nucleophilic substitution in β-*X*-heptafluoronaphthalenes or insertion of two substituents into **1** results in the mixture of β,β-disubstituted isomers with the 2,6 being predominant (>75%) [3–8]. Only some of the individual 2,6-disubstituted hexafluoronaphthalenes have been reported (2-methoxy-6-thiomethoxyhexafluoronaphthalene [3], 2-methoxy-6-piperidinohexafluoronaphthalene [4], 1,3,4,5,7,8-hexafluoronaphthalene [5], perfluoro-2,6-diphenylnaphthalene [6]), while 2,7-isomers have not been isolated at all. Diamination of **1** has not been reported, though polyfluoroaromatic diamines and diaminohexafluoronaphthalenes in particular are prospective monomers for condensation polymers, whose physicochemical characteristics depend strongly on the framework as well as presence of fluorine atoms [9].

We have shown [10] the use of liquid ammonia as a reagent/medium system provides for selective preparation of mono- and diaminopolyfluoro(get)arenes with high purity and yields. The present work goals are (i) the investigation of the direct amination of **1** by liquid ammonia or its solutions as the shortest route to diaminohexafluoronaphthalenes; (ii) the development of the methods for 2,6- and 2,7-diaminohexafluoronaphthalenes selective preparation based on the reversible transformation of 2-aminoheptafluoronaphthalene (**2a**); (iii) the elaboration of the procedure for product isolation and purification based on complexation with crown ether.

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Table 1
Experimental conditions and product yields for reactions of octafluoronaphthalene (**1**) with amination reagents

Entry	Reactant amounts		Reaction conditions		Product mixture yields (g)	Product mixture composition (%, GC data)[a]							Product isolated yields (g/% calculated to **1**); purification method
	1 (g)	NH_3 (ml)	Temperature (°C, ±5)	Time (h)		**1**	**2a**	**2b**	**3a**	**3b**	**3c**	**3d**	
1	10.0	50 (liq)	15	9	9.5		95	2	<1				**2a** 8.5/87; crystallization
2	10.0	50 (liq)	90	24	8.0		1		71	12	10	3	**3a** + **3b** (9:1) 6.2/63; complexation
3	5.0	30 (aq)	120	5	4.8	19	72	6	2	<1			
4	5.0	30 (aq)	120	8	4.7	5	81	6	5	1			**2a** 3.0/61; complexation
5[b]	10.0	60 (aq)	130	48	8.6				62	16	8	3	**3a** + **3b** (7:2) 5.9/60; complexation
6[c]	5.0	30 (aq)	110	5	4.7		81	9	1				
7[c]	5.0	30 (liq)	90	5	4.6	4	45		31	5	7	2	
8[d]	2.0	80 (liq)	−55	0.15	1.9	1	64						**2a** 1.0/52; sublimation
9[e]	2.0	80 (liq)	−55	1	1.8				72		4		**3a** 1.1/55; complexation

[a] Average values from the results of at least three experiments, the error for the main products does not exceed 2%.
[b] The product mixture contains three additional diaminopentafluoronaphthalenes ~7% in total (M 248, GC–MS data).
[c] EtOH (30 mL) was used as co-solvent. The product mixture contains additional isomeric aminoethoxyhexafluoronaphthalenes ~5% in total (M 295, GC–MS data).
[d] Na (0.35 g) was used for $NaNH_2$ preparation ($NaNH_2$/**1** mole ratio = 2). The product mixture also contains *N,N*-bis(heptafluoro-2-naphthyl)amine, 7% (M 521), 2-amino-7-(N-heptafluoro-2-naphthylamino) naphthalene, 8% (M 518) (GC–MS data), and non-volatile compounds (~20%).
[e] Na (0.85 g) was used for $NaNH_2$ preparation ($NaNH_2$/**1** mole ratio = 5). The product mixture also contains non-volatile compounds (~25%).

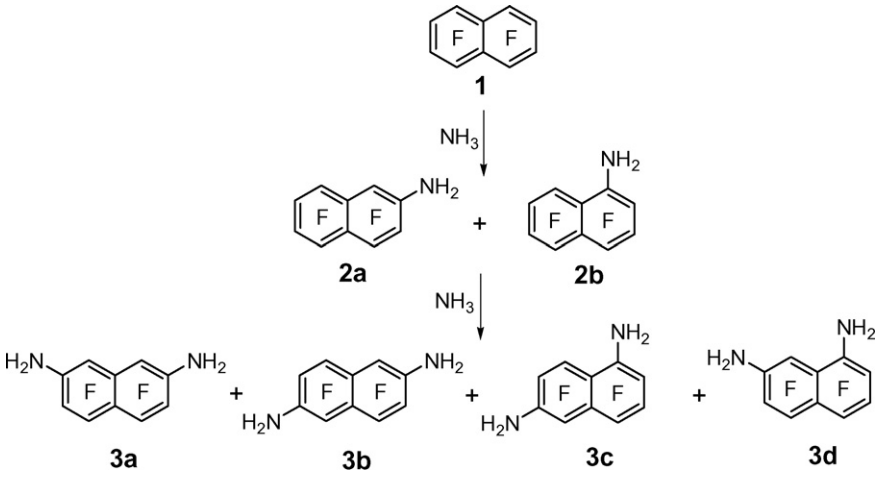
2. Results and discussion

2.1. Amination of octafluoronaphthalene by liquid ammonia and its solutions

The processes were carried out in a steel autoclave under pressure to keep ammonia as a liquid up to ~120 °C ($t_{crit}NH_3$ = 132°C [11]). Both mono- and diamination of **1** by liquid ammonia can be realized selectively due to the large difference in temperature conditions required (Entries 1 and 2, Table 1, Scheme 1). Proportion of β/α substitution in monoamination of **1** is 95/2, and so the major product – **2a** – has been isolated from the product mixture with yield >85% by crystallization. Thus, this mode of **2a** preparation has a clear advantage towards the known method (via amination of **1** by aqueous-ethanolic ammonia), which is characterized by low yield (44%) [4].

Under the optimal conditions of **1** bis-aminodefluorination (Entry 2, Table 1, Scheme 1) content of isomeric diaminohexafluoronaphthalenes is ≥96%, at that 2,7-diaminohexafluoronaphthalene (**3a**) is the major product. The proportions of 2,6-diaminohexafluoronaphthalene (**3b**) and 1,6-diaminohexafluoronaphthalene (**3c**) in the product mixture are considerably lower, and the minor product is 1,7-diaminohexafluoronaphthalene (**3d**). Aminodefluorination of **2a** affords the same result (Entry 1, Table 2), *i.e.* the ratio of diamines **3a–d** does not depend on the identity of starting compound (**1** or **2a**). Isomeric diamines **3a–d** obtained for the first time have been isolated and characterized.

Aqueous or ethanolic ammonia are widespread amination systems for polyfluoroarenes in spite of their lower efficiency as compared with liquid ammonia ([10] and references therein) caused by hydrogen bonding [12]. Actually, amination of **1** by aqueous ammonia occurs at harder conditions. The reaction becomes efficient only at 120 °C, however under this temperature, mono- and diamination processes cannot be separated. Thus, diamination is appreciable at 80% conversion of **1** (Entry 3, Table 1), and an increase of the reaction duration



Scheme 1.

Table 2
Experimental conditions and product yields for reactions of **2a** and **2c** with amination reagents

Entry	Reactant amounts		Reaction conditions		Product mixture yields (g)	Product mixture composition (%, GC data)[a]				Product isolated yields (g/% calculated to **1**); purification method
	2a/2c (g)	NH_3 (ml)	Temperature (°C, ±5)	Time (h)		**3a**	**3b**	**3c**	**3d**	
1	**2a** (2.0)	30 (liq)	90	15	1.9	76	11	8	<1	
2	**2a** (2.0)	30 (aq)	130	45	1.9	64	15	10	5	
3[b]	**2a** (2.0)	100 (liq)	−40	1	1.9	93		4		**3a** 1.6/82; complexation
4	**2c** (5.0)	50 (liq)	50	8	3.9[c]	16	76	1	3	**3b** 2.0/47; complexation

[a] Average values from the results of at least three experiments, the error for the main products does not exceed 2%.
[b] Na (0.69 g) was used for $NaNH_2$ preparation ($NaNH_2$/**1** mole ratio = 4).
[c] Weight of the product mixture obtained by acetamido group hydrolysis; mixture weight before hydrolysis was 4.9 g.

results in the accumulation of diamines simultaneously with amination of **1** (Entry 4, Table 1). It should be noted that the β/α ratio of nucleophilic attack on **1** diminishes when liquid NH_3 is replaced by aqueous NH_3. Complete diamination of **1** or amination of **2a** by aqueous ammonia (Entry 5, Table 1 and Entry 2, Table 2 correspondingly) results in the decreased proportion of **3a** in the product mixture as compared with the reaction in liquid ammonia. Together with diaminohexafluoronaphthalenes **3a–d**, three isomeric diaminopentafluoronaphthalenes were found. Formation of hydrodehalogenation products is typical for the reactions of polyfluoroarenes in aqueous ammonia at high temperature and occurs under the action of the reactor material (steel autoclave) and water [13]. Monoamination of **1** in aqueous-ethanolic ammonia is somewhat more effective (compare Entries 6 and 3, Table 1). At the same time the contribution from α-amination increases by ∼1.5 times. Moreover, hexafluoronaphthalenes containing NH_2 and OEt groups are found in the product mixture. In liquid ammonia/ethanol mono- and disubstituted products form in equal amounts even at lower temperature (compare Entries 6 and 7, Table 1), thus testifying to the considerably higher reaction rate in anhydrous medium. However, the product mixture also contains aminoethoxyhexafluoronaphthalenes. The formation of hydro- and ethoxydefluorination products of **1** when reaction is carried out in ammonia/water or ammonia/ethanol mixtures reduces the preparative value of these amination systems.

β-Aminodefluorination of **1** by NH_3 ([4] and this work) is typical for nucleophilic substitution in this substrate [1,2]. Predominance of 2,7 over 2,6 replacement as well as realization of α-replacement in remote ring (1,6 and 1,7) are found for the first time. Obviously it is caused by a difference between electronic effects of fluorine, NH_2 group, and other substituents. To conform this assumption temperature dependence of the regioselectivity of **1** diamination by liquid NH_3 has been experimentally determined. The proportion of the major isomer **3a** in the product mixture has been shown to increase with temperature decrease (Table 3). This indicates the regioselectivity of aminodefluorination in the given temperature interval is controlled by enthalpy of activation, the formation of **3a** being enthalpically preferred than that of **3b** or **3c**. Assuming that the differences of solvation terms contributing to the enthalpy are negligible [5,12], we conclude the aminodefluorination regioselectivity of **1** is controlled by intrinsic structural features of the transition state (TS), namely by the electronic effects of substituents.

Predominance of β-replacement in nucleophilic reactions of **1** and its derivatives is rationalized by the activating electronic effect of two *ortho*-fluorines *versus* one in α-replacement [5,14]. However this effect was shown [14,15] to reduce with decrease of polyfluoroarene electrophilicity followed by the shift of TS to the intermediate. In going from **1** to **2a** the substrate reactivity decreases (compare temperatures in Entries 1, Table 1 and Table 2 correspondingly), therefore, orientation of **2a** amination depends on *ortho*-fluorine effect to a lesser degree. It provides the increase of α-replacement shown by the value (**3a** + **3b**)/(**3c** + **3d**) = 83/13 *versus* **2a/2b** = 95/2.

The values **3a/3b** (2,7/2,6) for β-replacement and **3c/3d** (1,6/1,7) for α-replacement in **2a** are both >1 and indicate the predominant replacement at pseudo-*meta* positions to amino group. Thus, the regioselectivity of the both routes is in agreement with a stronger electron-donating effect of pseudo-*para*-located NH_2 group relative to fluorine. On the other hand, the reaction of **1** with cyclic amines results in pseudo-*para* (2,6) replacement mainly [4]. There is an analogy in a benzene series; in the reactions of pentafluoroaniline, pentafluoro-*N*-methylaniline and pentafluoro-*N*,*N*-dimethylaniline with *N*-nucleophiles the *meta*/*para* ratio decreases from 7 to 0.07 [16]. A rationalization of these results is based on the conception of

Table 3
Temperature dependence of **3a/3b** and **3a/3c** ratios in the reaction of **1** with liquid NH_3

Entry	Temperature (°C, ±5)	Time (h)	Product mixture composition (%, GC-MS data)		**3a/3b** ratio	**3a/3c** ratio
			Σ aminoheptafluoro naphthalenes **2**	Σ diaminohexafluoro naphthalenes **3**		
1	90	15	14	82	5.6	5.1
2	70	24	50	49	6.5	6.2
3	50	100	14	85	9.9	12.8

steric inhibition of electron-donating resonance effect by the interaction of bulky substituent NR_2 with *ortho*-fluorines. In total these facts indicate NR_2 group is a weaker electron-donor *versus* NH_2 and fluorine. Thus, the regioselectivity of nucleophilic substitution in 2-*X*-heptafluoronaphtalenes is determined by the substituent electronic effect. Taking into account this regularity we have developed methods governing the orientation of aminodefluorination of **2a** based on the reversible transformations of the substituent.

2.2. Selective preparation of 2,7- and 2,6-diaminohexafluoronaphthalenes

Reactions of pentafluoroanisole with nucleophiles result in *para*-replacement of fluorine [17], whereas hydroxylation of pentafluorophenol by KOH/*t*-BuOH or H_2O [17,18] provides *meta*-replacement exclusively. It is caused by ionization of pentafluorophenol hydroxyl group being accompanied by substantial increase of its electron-donating effect. Accordingly the predominant pseudo-*meta*-replacement in **2a** is expected to become exclusive due to ionization of NH_2 group, which can be carried out in liquid ammonia by the action of $NaNH_2$ on **2a** with formation of sodium heptafluoronaphthylamide (**4**).

Interaction of **2a** with four equivalents of $NaNH_2$ in NH_3 at −55 °C in open glass vessel affords products of amination at pseudo-*meta*-positions, the formation of **3a** over **3c** being overwhelming (Scheme 2, Entry 3, Table 2). Thus both negatively charged substituent in amide **4** and nucleophile suppress the pseudo-*para*-amination. In addition, the extent of β-amination increases as against the reaction of **2a** with ammonia (compare **3a/3c** ratio, Entries 3 and 1, Table 2). Obviously it is caused by a shift of TS to the reagent-like state owing to the considerable reaction acceleration in going from neutral (NH_3) to charged (NH_2^-) nucleophile (compare temperatures, Entries 1 and 3, Table 2). According to these data the pathway to the less reactive substrate – **4** *versus* **2a** – affects the reaction rate to a lesser degree.

In order to explore the possibility of sodium amide utilization for the synthesis of **2a** and one-pot synthesis of **3a**, the interaction of **1** with $NaNH_2$ has been investigated. Complete conversion of **1** is achieved by the action of 2.1 equivalent of $NaNH_2$ (Entry 8, Table 1), but in addition to **2a** the product mixture contains *N*,*N*-bis(heptafluoro-2-naphthyl)amine and 2-amino-7-(*N*-heptafluoro-2-naphthylamino)-naphthalene, as well as nonvolatile compounds. This result is evidence for the reaction of **1** with $NaNH_2$ to afford **2a**, followed by its ionization to amide **4**, which competes with $NaNH_2$ in the interaction with highly electrophilic **1**. The formation of considerable amount of by-products in the reaction of **1** with $NaNH_2$ makes it less effective for **2a** preparation than amination of **1** by NH_3. The competition of amide and naphthylamide **4** anions as nucleophiles reacting with **1** was changed in favor of the former by using a fivefold excess. In these conditions the process cannot be interrupted at **2a** formation, and diamines **3a** and **3c** (**3a/3c** = 18/1) formed in total yield ~75% (Entry 9, Table 1). Thus, one-pot synthesis of **3a** directly from **1** can be realized due to the use of the excess of amide anion as aminating reagent.

Decrease of pseudo-*meta*-replacement in **2a** could be achieved by acylation of amino group weakening its electron-donating effect and increasing spatial inhibition of resonance. Similar method was used for tetrafluoro-*para*-phenylenediamine preparation by the reaction of hexafluorobenzene with potassium phthalimide [19].

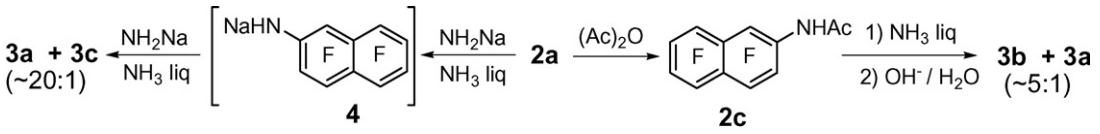
The interaction of 2-acetamidoheptafluoronaphthalene (**2c**) with liquid ammonia affords four isomeric amines with 2-acetamido-6-aminohexafluoronaphthalene (**5**) being predominant. After hydrolysis of the reaction mixture, β,β-diamines **3a** and **3b** have been obtained as the main products (Scheme 2, Entry 4, Table 2). Their ratio (**3a/3b** = 1/5) testifies to the preference of pseudo-*para*-replacement in **2c** amination as against pseudo-*meta* in **2a** amination (**3a/3b** = 7/1, Entry 1, Table 2). Besides the ratio of β/α-replacement products has been enlarged in going from **2a** to **2c** ((**3a** + **3b**)/(**3c** + **3d**) is 9 and 23, Entries 1 and 4 respectively, Table 2). It can be provided by increase of the substrate electrophilicity following by enhancement of *ortho*-fluorines activating effect.

Thus, orientation of amination of **2a** can be governed by the reversible modification of amino group strengthening or weakening its π-donating effect.

2.3. Isolation and structure determination of mono- and diamines

Utilization of direct amination of fluorinated arenes is limited by the complexity of isomeric mono- and/or diamine separation by means of traditional methods. We have elaborated an effective technique of individual polyfluorophenylenediamine isolation from their mixtures [10]. This technique is based on selective complexation of polyfluoroaromatic amines with crown ether, and subsequent decomposition of the complexes obtained by water.

Using this approach, some products of mono- and diamination of **1** have been isolated effectively (≥80% upon their proportion in the mixture) and with rather high purity. Thus, **2a** has been isolated by complexation with 18-crown-6 from the product mixture of unselective amination of **1** by aqueous ammonia (Entry 4, Table 1). Similarly diamine **3a** has been purified from **3c** (Entry 3, Table 2). Using crown ether in deficiency to the total amount of diamines **3a–d** (Entry 4,



Scheme 2.

Table 4
^{19}F NMR spectroscopic data for diamines **3a–3d**

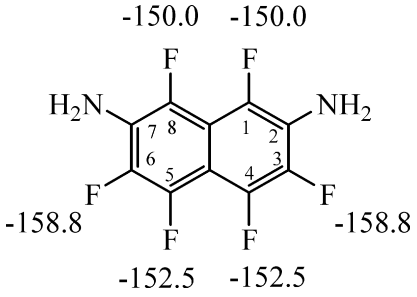
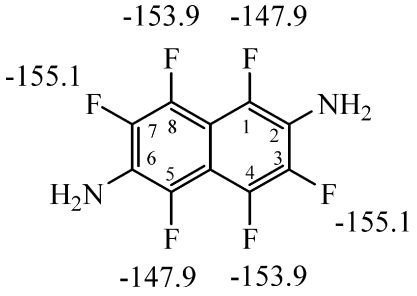
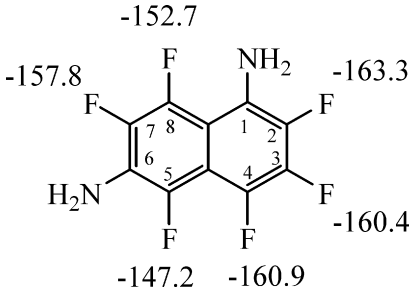
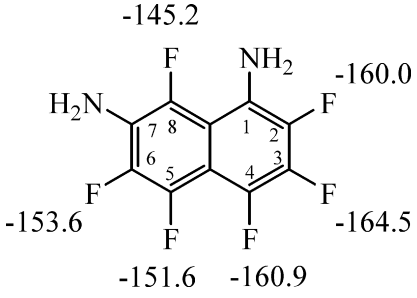
Diamine	Solvent	^{19}F NMR chemical shifts, $CFCl_3$, δ (ppm)	Coupling constants, J (Hz)
3a	Chloroform-*d*		$J(1,3) = J(6,8) = 4.0$ $J(1,4) = J(5,8) = 17.2$ $J(1,5) = J(4,8) \sim 0$ $J(1,6) = J(3,8) = -7.2$ $J(1,8) = 55.0$ $J(3,4) = J(5,6) = -17.2$ $J(3,5) = J(4,6) = 4.2$ $J(3,6) \sim 0$ $J(4,5) = 54.8$
3b	Chloroform-*d*		$J(1,3) = J(5,7) = 4.1$ $J(1,4) = J(5,8) = 15.7$ $J(1,5) = 1.9$ $J(1,7) = J(3,5) = 8.6$ $J(1,8) = J(4,5) = 56.0$ $J(3,4) = J(7,8) = -17.0$ $J(3,7) = 7.3$ $J(3,8) = J(4,7) = -3.6$ $J(4,8) = 1.6$
3c	Chloroform-*d*		$J(2,3) = -20.0$ $J(2,4) = 4.3$ $J(2,5) = -4.2$ $J(2,7) = -2.3$ $J(2,8) = 3.5$ $J(3,4) = -19.1$ $J(3,5) = 3.8$ $J(3,7) = 7.7$ $J(3,8) = -3.4$ $J(4,5) = 61.6$ $J(4,7) = -4.2$ $J(4,8) = 0.7$ $J(5,7) = 7.8$ $J(5,8) = 14.8$ $J(7,8) = -17.2$
3d	Acetone-d_6		$J(2,3) = -19.6$ $J(2,4) = 3.8$ $J(2,5) = -3.8$ $J(2,6) = 6.9$ $J(2,8) = 3.8$ $J(3,4) = -19.3$ $J(3,5) = 3.9$ $J(3,6) = -5.0$ $J(3,8) \sim -2.5$ $J(4,5) = 59.5$ $J(4,6) = 5.0$ $J(4,8) \sim 0.7$ $J(5,6) = -17.0$ $J(5,8) = 14.5$ $J(6,8) = 6.7$

Table 2) allows the isolation of the main component of the mixture—diamine **3b**. Complexation of the diamine mixtures obtained in Entries 2 and 5, Table 1, Entries 1 and 2, Table 2, was used for isolation of the mixtures of β,β-diamines (**3a + 3b**) and α,β-diamines (**3c + 3d**).

As was noted above data about **1** derivatives containing the substituents in both rings are limited to characteristics of some 2,6-disubstituted hexafluoronaphthalenes, 2,7-isomers have been characterized in mixtures with 2,6 isomers by ^{19}F NMR spectroscopy; 1,6- and 1,7-disubstituted hexafluoronaphthalenes have been unknown. For novel individual diamines **3a–3d** comprehensive physical and spectroscopic data were obtained. Location of the substituents was determined by ^{19}F NMR spectra simulation; the spectral

parameters of diamines **3a–3d** are given in Table 4. Assignments and numeric values of the chemical shifts and spin–spin coupling constants are in agreement with the known data for **1** derivatives [3–7].

3. Experimental

3.1. Materials

The following commercial products were used, octafluoronaphthalene (99%), aqueous NH_3 28% (d 0.9 g L^{-1}), 18-crown-6, *tert*-butyl methyl ether (*t*-BuMeO), plates Kieselgel 60 F_{254} (Merck). Liquid NH_3 was used without purification for the reaction in autoclave, and was purified by distillation from $NaNH_2$ suspension for the reaction in the open vessel.

3.2. General

^1H and ^{19}F NMR spectra were recorded on NMR spectrometers Bruker AC-200 (200.13 and 188.28 MHz for ^1H and ^{19}F correspondingly) and AV-300 (300.13 and 282.36 MHz for ^1H and ^{19}F correspondingly) using TMS and C_6F_6 ($\delta = -163$ ppm from CCl_3F) as internal standards; δ are given in ppm relative to CCl_3F, J are given in Hz. The 2D phase sensitive ^{19}F-^{19}F COSY spectra were recorded for the unambiguous assignment of the multiplet splittings. For spectra simulation the program package Xsim/NUMMRIT [20] and the data on the coupling constants in spectrum of octafluoronaphthalene [21] were used. The numeric values of the chemical shifts δ_F and spin-spin coupling constants $J_{F\text{-}F}$ were determined via iterative simulation procedure to fit the data to the experimental spectra. IR spectra were recorded on Bruker Vector-22 instrument. UV spectra were recorded on Fourier spectrometer HP 8453. The precise molecular weights of ions were determined by high resolution mass spectrometry on Finnigan MAT-8200 instrument. GC-MS identification of mixture components was performed using Hewlett Packard G1081A equipment comprising an HP 5890 Series II gas chromatograph and an HP5971 mass selective detector; electron ionization energy of 70 eV; HP5 column (5% of biphenyl and 95% of dimethylsiloxane), 30 m × 0.25 mm × 0.25 μm; with helium as carrier gas, flow rate 1 mL min^{-1}; column temperature programming from 50 °C (2 min) at an increment of 10 °C min^{-1} to 280 °C (5 min); injector temperature 280 °C; ion source temperature 173 °C; data acquisition rate 1.2 scan s^{-1} in the mass range 30–650 amu. Analyses of product mixtures and purity of products were performed on HP 5890 Series II gas chromatograph (thermo conductivity detector); HP5 column (5% of biphenyl and 95% of dimethylsiloxane), 30 m × 0.22 mm × 2.6 μm; with helium as carrier gas, flow rate 1 mL min^{-1}; column temperature programming from 90 °C (2 min) at an increment of 10 °C min^{-1} to 330 °C (5 min); injector temperature 300 °C; detector temperature 320 °C.

3.3. Synthetic procedures

3.3.1. 2-Acetamidoheptafluoronaphthalene (**2c**)

It was obtained in 87% yield through acylation of **2a** by acetic anhydride in benzene. Mp 210-211 °C. IR (KBr): ν 3210 (NHAc), 1690 cm^{-1} (Ac); ^1H NMR (acetone-d_6): δ 2.22 (s, 3H, Me), 9.36 (br.s, 1H, NH); ^{19}F NMR (188.28 MHz, acetone-d_6): δ −156.7 (t, 1F, J = 17, F_7), −155.4 (t, 1F, J = 17, F_6), −149.3 (dt, 1F, J = 57, J = 17, F_4), −147.0 (dt, 1F, J = 57, J = 17, F_5), −145.5 (dt, 1F, J = 66, J = 17, F_8), −139.3 (d, 1F, J = 17, F_3), −125.5 (dt, 1F, J = 66, J = 17, F_1); HRMS calcd. for $C_{12}H_4OF_7N$: 311.0181, found: 311.0180.

3.3.2. Typical procedure for the reaction of **1**, **2a** and **2c** with liquid or aqueous NH_3

A steel autoclave was charged with substrate and the necessary quantity of liquid or aqueous NH_3, reaction mixture was heated up to the given temperature upon stirring by rotation of autoclave and kept under these conditions for the necessary time. On completion, the autoclave was cooled, NH_3 was evaporated and products were extracted with *t*-BuMeO. The extract was dried with $MgSO_4$, the solvent was evaporated. The product mixture was purified by sublimation in vacuum and analyzed by NMR, GC, GC–MS. Reactant amounts, reaction conditions, yields and compositions of product mixtures are listed in Tables 1–3. Methods of isolation of compounds obtained for the first time are given in Sections 3.3.5 and 3.3.6.

By amination of **2c** (Entry 4, Table 2) mixture of isomeric acetamidoaminohexafluoronaphthalenes (96%, GC–MS and NMR ^{19}F) was obtained. The major component is 2-acetamido-6-aminohexafluoronaphthalene (**5**), which has the followed signals in ^{19}F NMR spectrum of the mixture (188.28 MHz, acetone-d_6): δ −152.8 (dm, 1F, J = 56, F_5), −152.6 (m, 1F, F_7), −150.0 (dm, 1F, J = 64, F_8), −147.1 (dm, 1F, J = 56, F_4), −143.0 (m, 1F, F_3), −127.4 (dm, 1F, J = 64, F_1).

3.3.3. Typical procedure for the reaction of **1** and **2a** with $NaNH_2$ in liquid NH_3

To liquid NH_3 in open glass vessel at −60 °C upon stirring was added Na and, after a dark blue solution was formed, $FeCl_3$ (catalytic amount); the mixture was stirred until discoloration. To a suspension of $NaNH_2$ thus obtained, substrate was added and the mixture was stirred at the given temperature for the necessary time. NH_4Cl (2 g) was added to the reaction mixture and NH_3 was evaporated. Products were extracted from the solid residue with *t*-BuMeO and solvent was evaporated. Product mixture was analyzed as described above. Reactant amounts, reaction conditions, yields and compositions of product mixtures are listed in Tables 1 and 2.

3.3.4. Hydrolysis of **2c** amination products

To the product mixture (4.9 g, Entry 4, Table 2) water (6 ml) and 35% aqueous solution of NaOH (20 ml) were added, and the reaction mixture was stirred under reflux for 3 h. The reaction mixture was diluted with water; the precipitate was filtered, washed with water and dried. The mixture of diaminohexafluoronaphthalenes (3.9 g) was obtained.

3.3.5. Mono- and diamine isolation by complexation with 18-crown-6

*3.3.5.1. 2-Aminoheptafluoronaphthalene (**2a**).* Product mixture (4.7 g, 17 mmol) (Entry 3, Table 1) was refluxed in pentane (100 mL) for 0.5 h and the undissolved residue was filtered (0.3 g, diaminohexafluoronaphthalenes **3a**–**3d**). To the filtrate a solution of 18-crown-6 (2.1 g, 8 mmol) in pentane (15 mL) was added and the mixture was stirred for 1 h. The precipitate formed was filtered, washed with pentane and dried. Complex of amine **2a** with 18-crown-6 (4.5 g) was obtained. The complex was shaken with a mixture of *t*-BuMeO (25 mL) and water (25 mL). The organic layer was washed with water (4× 20 mL), dried with $MgSO_4$ and the solvent was evaporated. Amine **2a** (3.0 g, 11 mmol, GC purity 98%) was obtained. Yield 61%, mp 73–74 °C; literature [22]; mp 70–71 °C.

*3.3.5.2. 2,7-Diaminohexafluoronaphthalene (**3a**).* To a solution of diamines **3a** and **3c** (Entry 3, Table 2) (1.9 g, 7 mmol) in *t*-BuMeO (10 mL) a solution of 18-crown-6 (1.8 g, 6.8 mmol) in *t*-BuMeO (10 mL) was added. The mixture was stirred at room temperature for 1 h. The precipitate formed was filtered, washed with *t*-BuMeO and dried. A complex of diamine **3a** with 18-crown-6 (3.2 g) was obtained. The complex was shaken up with a mixture of *t*-BuMeO (30 mL) and water (30 mL). The organic layer was washed with water (4× 20 mL), dried with $MgSO_4$, and solvent was evaporated.

2,7-Diaminohexafluoronaphthalene (**3a**) (1.6 g, 6 mmol, GC purity 99%). Yield 82%, mp 235–238 °C (decompos.). UV (EtOH): λ_{max} (log ε) 223 (0.6), 253 (2.5) nm; IR (KBr): ν 3520 and 3422 cm^{-1} (NH_2); ^1H NMR (chloroform-*d*): δ 4.07 (br.s, NH_2); ^{19}F NMR see Table 4; HRMS calcd. for $C_{10}H_4F_6N_2$: 266.0279, found: 266.0283.

*3.3.5.3. 2,6-Diaminohexafluoronaphthalene (**3b**).* 2,6-Diaminohexafluoronaphthalene was obtained from a mixture of diaminohexafluoronaphthalenes **3a**–**3d** (Entry 4, Table 2) (3.9 g, 15 mmol) by complexation with 18-crown-6 (2.0 g, 7.6 mmol) according to the procedure described in Section 3.3.5.2.

2,6-Diaminohexafluoronaphthalene (**3b**) (2.0 g, 7.6 mmol, GC purity 97%). Yield 47%, mp 234–235 °C (decompos.). UV (EtOH): λ_{max} (log ε) 234 (3.0), 289 (1.1), 301 (1.3) nm; IR (KBr): ν 3509 and 3414 cm^{-1} (NH_2); ^1H NMR (chloroform-*d*): δ 3.97 (br.s, NH_2); ^{19}F NMR see Table 4; HRMS calcd. for $C_{10}H_4F_6N_2$: 266.0279, found: 266.0275.

3.3.6. Separation of diaminohexafluoronaphthalene 3a-d mixture

A solution of diaminohexafluoronaphthalenes **3a**–**3d** (9.0 g, 34 mmol, Entry 4, Table 1) was treated with a solution of 18-crown-6 (9.0 g, 34 mmol) according to the procedure described in Section 3.3.5.2. The precipitate was decomposed by water and the mixture of diamines **3a** and **3b** (~9:1) was obtained (6.6 g, 24 mmol, yield 60%). Anal. Calcd. for $C_{10}H_4F_6N_2$: C, 45.7; H, 1.57; N, 10.6. Found: C, 45.1; H, 1.50; N, 10.5.

The filtrate was shaken up with water (40 mL). The organic layer was washed with water, dried with $MgSO_4$, *t*-BuMeO was evaporated. The mixture of diamines **3c** and **3d** thus obtained was separated by thin-layer chromatography, eluent hexane–ethyl acetate (4:1 by volume).

1,6-Diaminohexafluoronaphthalene (**3c**) (R_f 0.49). GC purity: 94%, mp 195–200 °C (decompos.). UV (EtOH): λ_{max} (log ε) 230 (2.9), 254 (2.6), 304 (0.6), 349 (0.4) nm; IR (KBr): ν 3509 and 3397 cm^{-1} (NH_2); ^1H NMR (chloroform-*d*): δ 4.09 (br.s, C_6NH_2), 4.53 (br.s, C_1NH_2); ^{19}F NMR see Table 4; HRMS calcd. for $C_{10}H_4F_6N_2$: 266.0279, found: 266.0277.

1,7-Diaminohexafluoronaphthalene (**3d**) (R_f 0.31). GC purity: 98%, mp 200–202.5 °C. UV (EtOH): λ_{max} (log ε) 224 (2.0), 249 (1.8), 316 (0.6) nm; IR (KBr): ν 3498 and 3428 cm^{-1} (NH_2); ^1H NMR (chloroform-*d*): δ 4.02 (br.s, C_7NH_2), 4.50 (br.s, C_1NH_2); ^{19}F NMR see Table 4; HRMS calcd. for $C_{10}H_4F_6N_2$: 266.0279, found: 266.0285.

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