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Synthesis and Structure of Reaction Products Obtained from 1,2-Epoxyperfluorobutane and Bifunctional Nucleophilic Reagents

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Abstract—1,2-Epoxyperfluorobutane readily reacts with bifunctional nucleophilic reagents to provide heterocyclic compounds with a pentafluoroethyl substituent. The reaction of this epoxide with thiourea and acetone thiosemicarbazone gave rise to 2-amino-5-pentafluoroethyl-5-fluoro-4(5*H*)-thiazolinone and 2-isopropylidenehydrazono-5-pentafluoroethyl-5-fluoro-4-thiazolidinone respectively. The reaction of 1,2-epoxyperfluorobutane with *o*-phenylenediamine and 2,3-diaminonaphthalene afforded in high yields 3-pentafluoroethyl-2(1*H*)-quinoxalinone and 3-(pentafluoroethyl)benzo[*g*]-2(1*H*)-quinoxalinone. The molecular and crystal structure of the obtained fluorine-containing heterocycles was established by XRD analysis.

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The oxides of terminal fluoroolefins are highly reactive compounds and important intermediates in the syntheses of versatile polyfluorinated functional derivatives and heterocyclic compounds endowed with a wide range of biological activity and with useful technical properties [1–6].

Perfluoroolefins oxides can be regarded as useful building blocks for heterocyclic systems containing fluorine atoms and perfuoroalkyl groups [6–11]. The most thorough investigation was performed on reactions of perfluoroepoxypropane that was an important semiproduct in the fluoroorganic synthesis [1–3, 7–10]. The oxides of higher terminal perfluoroolefins were poorly studied in the heterocyclization reactions [7]. This fact to a large extent originates from the ready isomerization of 1,2-epoxyperfluoroalkanes under the action of nucleophilic reagents with the formation of the derivatives of the corresponding polyfluorinated acids [1, 2, 11].

In extension of the studies in the field of perfluorooxiranes and aiming at the synthesis of new fluorine-containing heterocyclic compounds we studied the reactions of the perfluoroepoxypropane homolog, 1,2-epoxyperfluorobutane (**I**), with a number of bifunctional nucleophiles: thiourea, *o*-phenylenediamine, and also with 2,3-diaminonaphthalene and acetone thiosemicarbazone whose reactions with terminal perfluorepoxides did not appear in publications.

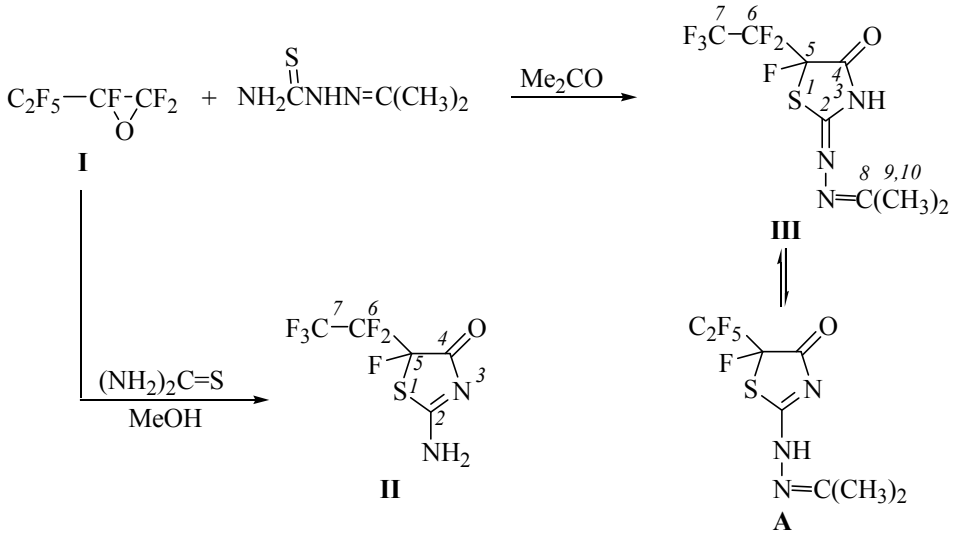
Like the perfluoroepoxypropane, oxirane **I** is a preparatively accessible synthon [12, 13] that can be utilized for the preparation of heterocyclic compounds with a pentafluoroethyl substituent.

We carried out the reaction of compound **I** with thiourea in methanol that provided under mild conditions 2-amino- 5-pentafluoroethyl-5-fluoro-4(5*H*)-thiazolinone (**II**) in a high yield.

1,2-Epoxyperfluorobutane (**I**) reacted in acetone with acetone thiasemicarbazone gave in a good yield 2-isopropylidenehydrazono-5-pentafluoroethyl-5-fluoro-thiazolidin-4-one (**III**). Compound **III** was isolated in the individual state by column chromatography followed by recrystallization from hexane. At the use in this reaction of a proton-donor solvent (methanol) we obtained an intractable mixture of products presumably due to side processes of isomerization and polymerization. The presence in the reaction mixture of the target compound **III** was detected by ^{1}H and ^{19}F NMR spectra.

In order to obtain more complete information on the structure of obtained compounds **II** and **III** we carried

Scheme 1.



out alongside the IR, ^{1}H, ^{13}C, ^{19}F NMR spectral study and elemental analysis also XRD analysis on their single crystals. XRD data confirmed the formation of the thiazolinone ring in the reaction of the terminal perfluoro-oxiranes with thiourea (Scheme 1, Fig. 1) (No published data existed on XRD studies of reaction products of terminal perfluoroolefin oxides with dinucleophiles).

Compound **II** in the crystal according to XRD data exists in the amino-form (Fig. 1, protons are localized by the direct method and refined independently). At the same time the measured length of the exocyclic bond C^1–N^2 1.295(3) Å proved to be shorter that that of endocyclic bonds C^1–N^1 1.312(3) and C^2–N^1 1.341(3) Å indicating the strong delocalization of the electron density in the system of the conjugated bonds. Yet the bond C^2–O^1 1.217(3) Å is close to a standard double bond and it is not involved in the conjugatipon system. The ring is planar with the deviation of atoms from the mean square plane no more than 0.035 Å. About 20% of positions in the crystal are occupied by the molecules of opposite configuration (R/S), therefore the positions of S^1, C^3, and C^4 atoms are disordered, and the position of atoms F^1 and F^2 in the opposite configurations practically coincide. Besides the molecules in the crystal are involved in the system of intermolecular hydrogen bonds (see the table) forming polymer "bands" with an interlayer distance of ~3.8 Å.

At the same time the XRD data showed that in the crystal compound **III** exists as thiazolidinone (Scheme 1, Fig. 2), but in the organic solvents it might be present in a mixture with the tautomeric form **A** as indicated by the broadened signals in the ^{13}C NMR spectrum in the region δ, ppm: 152.35 br.s (C^2) and 164.39 br.d (C^4). The presence in the molecule of the C=N–N=C moiety with a weak conjugation of the double bonds is unambiguously manifested by the distribution of bond distances in this fragment: C^1=N^2 1.260(3), N^2–N^3 1.420(3), N^3=C^6 1.276(3) Å. The prevalence of the imino-form in this case may be due to its stabilization in the system of the intermolecular hydrogen bonds (see the table).

Formerly the reaction of perfluoroepoxypropane with *ortho*-disubstituted arenes afforded analogs of benzo-

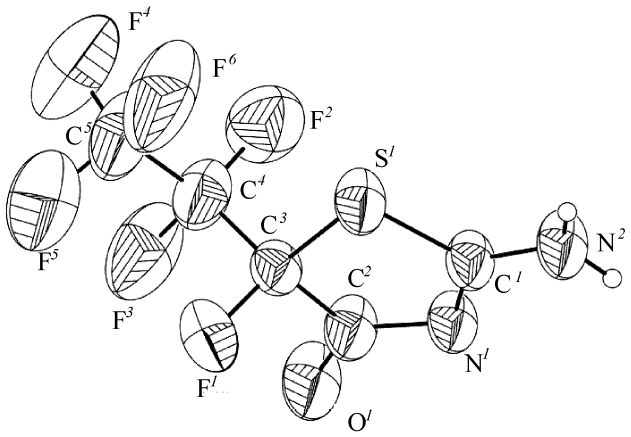


Fig. 1. Molecular structure of thiazolinone **II** represented with thermal ellipsoids of 50% probability.

Parameters of hydrogen bonds in crystals of compounds **II–V**

Compd. no.	D–H	d(D–H), Å	d(H–A), Å	Angle DHA, deg	d(D–A), Å	A
II	N^2–H^1	0.86(3)	2.11(3)	173(3)	2.966(3)	N^1 [–x, –y + 1, –z + 1]
	N^2–H^2	0.78(3)	2.05(3)	141(1)	2.817(3)	O^1 [x, y – 1, z]
III	N^1–H^1	0.81(3)	2.03(3)	171(3)	2.829(3)	O^1 [–x + 1, –y + 1, –z + 2]
IV	N^1–H^1	0.85(2)	1.94(2)	173(2)	2.789(2)	O^1 [–x + 1, –y + 2, –z + 1]
V	N^1–H^1	0.90(3)	1.89(3)	173(3)	2.783(3)	O^1 [–x + 1, –y + 2, –z + 1]

fused compounds [2, 8, 10], but the data on their structure were in some events ambiguous. For instance, the product of the reaction between the perfluoroepoxypropane and *o*-phenylenediaminem was regarded as having either keto [8] or enol form [2, 10]. Analogous products were obtained in [14] from *o*-phenylenediamine and methyl esters of perfluorinated α-ketoacids, and based on spectral data (IR, ^{1}H NMR spectra) they were assigned a structure of an equilibrium mixture of keto and enol forms. In this study a reaction was performed of epoxide **I** with the *o*-phenylenediamine giving in a high yield heterocyclization product **IV**. The XRD analysis demonstrated that in the crystal state 3-pentafluoroethyl-2(1*H*)-quinoxalinone (**IV**) existed in the keto-form (Scheme 2, Fig. 3). Therewith the length of the C–O bond is close to a standard double bond, 1.236(3) Å, and the molecules are bound into dimer by intermolecular hydrogen bonds involving the N–H···C=O moieties (see the table, Fig. 4). The molecular packing is by layers, its interesting feature is the presence of shortened π–π contacts between the carbonyl groups of the neighboring layers σ $O^1\cdots C^1$ [–x, 2 – σ, 1 – z] ~3.2 Å (Fig. 5).

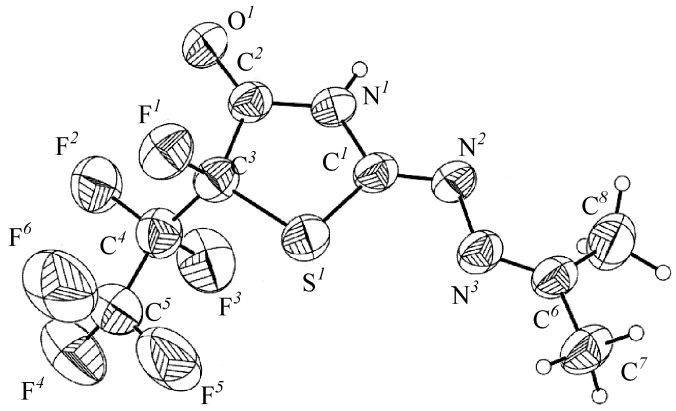


Fig. 2. Molecular structure of thiazolidinone **III** represented with thermal ellipsoids of 50% probability.

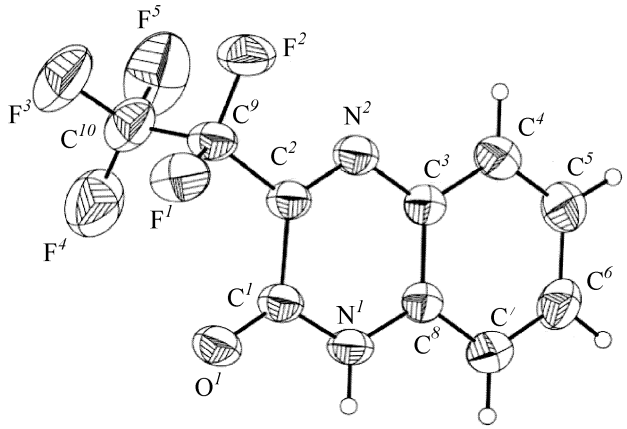


Fig. 3. Molecular structure of quinoxalinone **IV** represented with thermal ellipsoids of 50% probability.

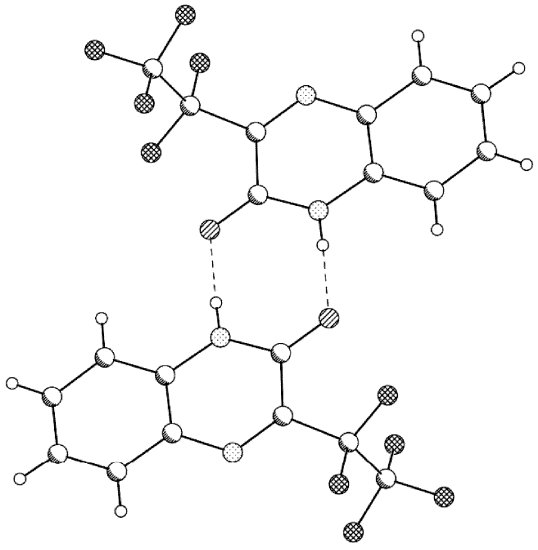


Fig. 4. Intermolecular hydrogen bonds in the crystal of quinoxalinone **IV**.

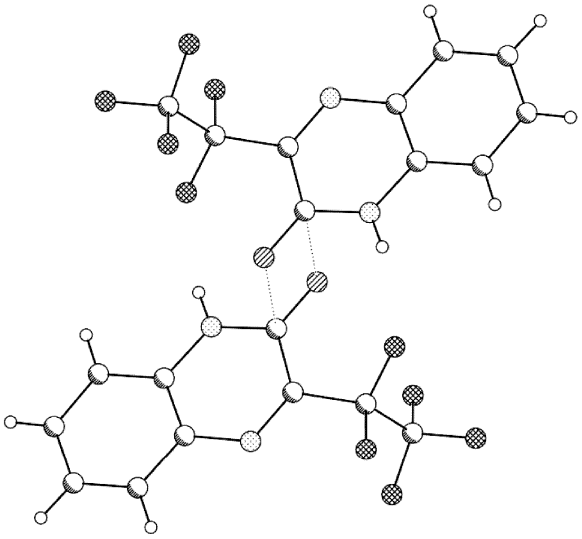


Fig. 5. Intermolecular π–π contacts in the crystal of quinoxalinone **IV**.

Similarly 1,2-epoxyperfluorobutane (**I**) reacted with 2,3-diaminonaphthalene forming 3-(penta-fluoroethyl)-benzo[*g*]-2(1*H*)-quinoxalinone (**V**) (Scheme 2). The structure of compound **V** was proved by XRD analysis PCA (Fig. 6). The fluorine atoms of the trifluoromethyl group suffer strong thermal vibrations that are accounted for in the model by the introduction of disordering of atoms F^1 and F^3 by 2 positions with the occupancy factors 0.7 and 0.3 (the second component is not shown on Fig. 6). Similar to compound **IV** in the crystal of substance **V** the molecules are packed in layers, but the shortened π–π contacts of carbonyl groups present in the packing of quinoxalinone **IV** are lacking in crystals **V**. Apparently the weakening of the π–π interaction compared to compound **IV** results in the increase in the interlayer distance to 3.4 Å. Yet in the packing the system is retained of dimers bound by the hydrogen bonds (see the table), and the difference in the hydrogen bonds parameters in

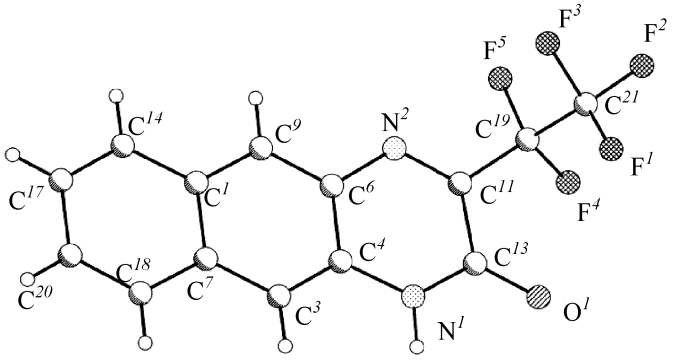


Fig. 6. Molecular structure of benzoquinoxalinone **V**.

compounds **IV** and **V** is practically within the error limits of the measurements.

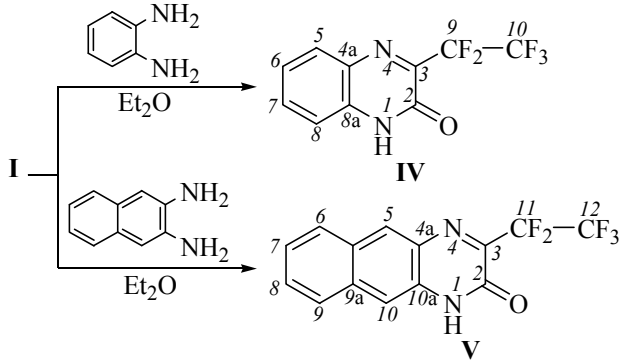
In the reaction mixture of epoxide **I** with *o*-phenylenediamine alongside heterocycle **IV** a small amount of benzimidazole **VI** was detected by ^1H and ^{19}F NMR spectroscopy. The latter compound may result from the competing isomerization reaction of the initial oxirane (Scheme 3). The reaction mixture of epoxide **I** with 2,3-diaminonaphthalene has a more complex compositiuon and contains alongside the prevailing compound **V** benzimidazole **VII** (signals of C_3F_7 group are present in the ^{19}F NMR spectrum) and other fluorine-containing unidentified compounds, but their overall quantity is minor (~10%).

Compounds **IV** and **V** were isolated in the individual state by crystallization from aqueous methanol, analytical sample of quinoxalinone **V** was obtained by recrystallization from a mixture ethyl acetate–hexane.

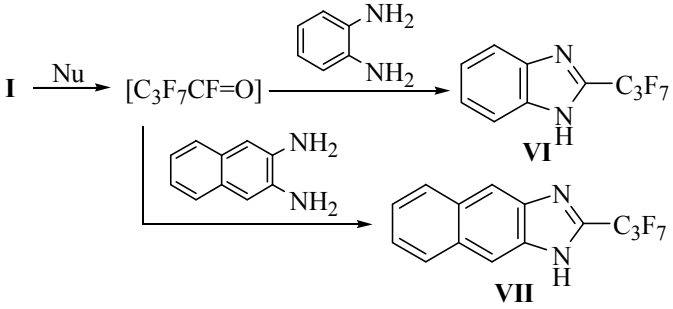
EXPERIMENTAL

^1H, ^{13}C, and ^{19}F NMR spectra were registered on a spectrometer Bruker DRX-400 (400, 100, and

Scheme 2.



Scheme 3.



376 MHz respectively), internal references TMS and C_6F_6. The chemical shifts in the ^{19}F NMR spectra are reported with respect to $CFCl_3$ and are considered as positive in the growing field. The assignment of signals in the ^1H and ^{13}C NMR spectra of compounds **III** and **V** was confirmed by the data of 2D experiments ^1H–^1H NOESY, ^1H–^{13}C HSQC and HMBC. IR spectra from mulls of compounds in mineral oil were recorded on an IR Fourier spectrometer Perkin Elmer Spectrum One. Elemental analyses were performed using analyzer Perkin Elmer PE 2400.

XRD analysis of compounds **II–V** was carried out on an automtic single-crystal diffractometer Xcalibur 3 with CCD detector applying the standard procedure [MOK-radiation, 295(2) K, graphite monochromator, ω-scanning]. The correction for extinction was not done. The structures were solved and refined applying software SHELX-97 [16]. The structures were solved by the direct method and refined in the full-matrix least-squares method in the anisotropic approximation for all nonhydrogen atoms. The hydrogen atoms were revealed from the electron-density differences and they were included in the refinement in the isotropic approximation in the rider model. The hydrogen atoms involved into the hydrogen bonds were solved by the direct method and were included into the refining independently.

The XRD data on compounds **II–V** are deposited into the Cambridge Crystallographic Data Center under the numbers CCDC 744889–744892 respectively. The free access to these data is possible at the address www.ccdc.cam. ac.uk/data_request/cif.

Oxirane **I** was prepared by procedure [13], acetone thiosemicarbazone, by method [15]. The ratio of the reaction products was measured by comparison of the integral intensity of the corresponding signals in the ^{19}F NMR spectra.

The solvents used in the study were purified and dried by standard procedures.

2-Amino-5-pentafluoroethyl-5-fluoro-4(5*H*)-thiazolinone (II). In a flask equipped with a reflux cold finger condenser connected to a cooled trap (–78°C), a gas-inlet tube, and a magnetic stirrer was charged 3.96 g (52 mmol) of thiourea, 45 ml of methanol, and 5.18 g (24 mmol) of oxide **I** was passed into the reaction mixture. The reaction mixture was stirred at room temperature for 3 h, then poured into water (~200 ml), the separated precipitate was filtered off, washed with water, and dried in air. The dry product was dissolved in ether, filtered from insoluble impurities, the solvent was removed, and the residue was recrystallized from aqueous methanol. Yield 4.48 g (74%). Colorless crystals, mp 210–212°C. IR spectrum, ν, cm^{-1}: 3230 (NH), 1710 (C=O), 1650 (C=N). ^1H NMR spectrum (acetone-d_6), δ, ppm: 9.35 br.s (NH_2). ^{13}C NMR spectrum (acetone-d_6), δ, ppm: 177.22 d (C^2, $^3J_{CF}$ 2.4 Hz), 177.00 d (C^4, $^2J_{CF}$ 17.2 Hz), 119.19 q.t.d (C^7, $^1J_{CF}$ 287.5, $^2J_{CF}$ 35.5, $^3J_{CF}$ 0.8 Hz), 111.95 d.d.q.d (C^6, $^1J_{CF}$ 265.7, 260.7, $^2J_{CF}$ 38.0, 34.7 Hz), 107.04 d.d.d.q (C^5, $^1J_{CF}$ 237.9, $^2J_{CF}$ 31.3, 27.86, $^3J_{CF}$ 0.7 Hz). ^{19}F NMR spectrum (acetone-d_6), δ, ppm: 78.49 d.d [3F, F^7, $^4J(F^7,F^5)$ 9.5, $^3J(F^7,F^{6A})$ 0.9 Hz], 117.72 d.d.q [1F, F^{6A}, $^2J(F^{6A},F^{6B})$ 282.4, $^3J(F^{6A},F^5)$ 13.4, $^3J(F^{6A},F^7)$ 0.9], 121.36 d.d (1F, F^{6B}, $^2J(F^{6A},F^{6B})$ 282.4, $^3J(F^{6B},F^5)$ 15.4], 145.04 d.d.q (1F, F^5, $^3J(F^5,F^{6B})$ 15.4, $^3J(F^5,F^{6A})$ 13.4, $^4J(F^5,F^7)$ 9.5 Hz]. Found, %: C 23.84; H 0.81; F 45.00; N 11.38; S 12.51. $C_5H_2F_6N_2OS$. Calculated, %: C 23.81; H 0.79; F 45.24; N 11.11; S 12.70.

XRD analysis of compound **II** was carried out on a crystal fragment (colorless prism) of the size 0.45×0.31×0.25 mm. $C_5H_2F_6N_2OS$, M 252.15, crystal system triclinic, space group P-1, parameters of unit cell: *a* 6.0783(6), *b* 6.7171(7), *c* 11.8302(12) Å, α 95.323(9), β 93.955(8), γ 109.121(9) deg, V 451.85(8) $Å^3$, Z 2, d_{calc} 1.853, μ 0.430 mm^{-1}. Region of scanning $3.23 \le \theta \le 28.28$, overall reflections number 2144 (R_{int} 0.0212), reflections number with $I > 2\sigma(I)$ 1150, the number of refined parameters 171. Final parameters of refinement: R_1 0.0488, wR_2 0.1211 [for reflections with $I > 2\sigma(I)$], R_1 0.0922, wR_2 0.1303 (for all reflections), quality factor S 1.009. The residual peaks of maximum and minimum electron density 0.281 and –0.224 e/$Å^3$.

2-Isopropylidenehydrazono-5-pentafluoroethyl-5-fluoro-4-thiazolidinone (III). In a flask equipped with a reflux cold finger condenser connected to a cooled trap (–78°C), a gas-inlet tube, and a magnetic stirrer was charged 1.32 g (10 mmol) of acetone thiosemicarbazone, 1.7 g (20 mmol) of $NaHCO_3$, 30 ml of acetone, and at stirring was passed through 2.38 g (11 mmol) of oxirane **I**. The reaction mixture was stirred at room temperature for 2 h, then the precipitate was filtered off, the filtrate was poured into ice water, the separated precipitate was filtered off and dried in air. The reaction product was isolated by column chromatography (SiO_2, eluent hexane–acetone 2.5:1) followed by recrystallization from hexane. Yield 2.2 g (72%). Colorless crystals, mp 98–99°C. IR spectrum, ν, cm^{-1}: 3102, 3165 (NH), 1747 (C=O), 1653 (C=N). ^1H NMR spectrum (acetone-d_6), δ, ppm: 11.9 br.s

(NH), [2.10 s (3H), 2.08 s (3H), H^9, H^{10}]. ^{13}C NMR spectrum (acetone-d_6), δ, ppm: 169.55 s (C^8), 164.39 br.d (C^4, $^2J_{CF}$ 20 Hz), 152.35 br.s (C^2), 119.08 q.t.d (C^7, $^1J_{CF}$ 288.0, $^2J_{CF}$ 35.1, $^3J_{CF}$ 1.0 Hz), 111.83 d.d.q.d (C^6, $^1J_{CF}$ 265.8, 261.9, $^2J_{CF}$ 38.2, 35.1 Hz), 99.49 d.d.d (C^5, $^1J_{CF}$ 233.3, $^2J_{CF}$ 29.7, 27.9 Hz), 24.78 s, 18.86 s (C^9, C^{10}). ^{19}F NMR spectrum (acetone-d_6), δ, ppm: 78.98 d.d [3F, F^7, $^4J(F^7, F^5)$ 9.6, $^3J(F^7, F^{6A})$ 0.8 Hz], 119.42 d.d.q [1F, F^{6A}, $^2J(F^{6A}, F^{6B})$ 283.1, $^3J(F^{6A}, F^5)$ 14.9, $^3J(F^{6A}, F^7)$ 0.8 Hz], 121.77 d.d [1F, F^{6B}, $^2J(F^{6A}, F^{6B})$ 283.1, $^3J(F^{6B}, F^5)$ 15.9 Hz], 143.50 m (1F, F^5). Found, %: C 31.34; H 2.35; F 37.31; N 13.55; S 10.45. $C_8H_7F_6N_3OS$. Found, %: C 31.27; H 2.28; F 31.27; N 13.68; S 10.42.

XRD analysis of compound **III** was carried out on a crystal fragment (colorless prism) of the size 0.52 × 0.49 × 0.43 mm. $C_8H_7F_6N_3OS$. M 307.23, crystal system triclinic, space group P-1, unit cell parameters: *a* 6.4645(7), *b* 9.6686(12), *c* 10.1911(16) Å, α 89.886(12), β 88.030(11), γ 73.907(11) deg, V 611.63(14) Å^3, Z 2, d_{calc} 1.668, μ 0.336 mm^{-1}. Region of scanning 2.96 ≤ θ ≤ 28.30, overall reflections number 2959 (R_{int} 0.0141), reflections number with I > 2σ(I) 2013, the number of refined parameters 176. Final parameters of refinement: R_1 0.0481, wR_2 0.1561[for reflections with $I > 2\sigma(I)$], R_1 0.0682, wR_2 0.1683 (for all reflections), quality factor S 1.006. The residual peaks of maximum and minimum electron density 0.372 and –0.394 e/Å^3.

3-Pentafluoroethyl-2(1*H*)-quinoxalinone (**IV**). In a flask equipped with a reflux cold finger condenser connected to a cooled trap (–78°C), a gas-inlet tube, and a magnetic stirrer was charged 1.52 g (14 mmol) of *O*-phenylenediamine, 3.52 g of $NaHCO_3$ (42 mmol), 35 ml of ethyl ether and at stirring was passed through 3.2 g (14.8 mmol) of oxirane **I**. The reaction mixture was stirred at room temperature for 3 h, then 15 ml of acetone was added, insoluble residue was filtered off. After removal of solvents from the filtrate 3.2 g of yellow-brown residue was obtained containing according to ^{19}F NMR spectrum quinoxalinone **IV** and benzimidazole **VI** in a ratio 93 : 7. The product was dissolved in methanol, diluted with water, the precipitate was filtered off, dried in air, and recrystallized from aqueous methanol. Yield 2.88 g (78%). Colorless crystals, mp 181–182°C. IR spectrum, ν, cm^{-1}: 3340 (NH), 1687 (C=O). ^1H NMR spectrum (acetone-d_6), δ, ppm: 11.83 br.s (1H, NH), 7.91 d.d (1H, H^5, *J* 8.2, *J* 1.4 Hz), 7.74 d.d.d (1H, H^7, *J* 8.4, *J* 7.1, *J* 1.4 Hz), 7.51 d.d (1H, H^8, *J* 8.4, *J* 1.2 Hz), 7.44 d.d.d (1H, H^6, *J* 8.2, *J* 7.1, *J* 1.2 Hz). ^{13}C NMR spectrum (acetone-d_6), δ, ppm: 152.52 s (C^2), 145.72 t (C^3, $^2J_{CF}$ 24.9 Hz), 134.56 s (C^{4a}), 134.53 s (C^5), 131.38 s (C^{8a}), 131.13 s ($C^{6/7}$), 125.14 s ($C^{7/6}$), 119.91 q.t (C^{10}, $^1J_{CF}$ 286.5, $^2J_{CF}$ 35.5 Hz), 116.61 s (C^8), 112.28 t.q (C^9, $^1J_{CF}$ 256.2, $^2J_{CF}$ 37.3 Hz). ^{19}F NMR spectrum (acetone-d_6), δ, ppm: 81.26 t (3F, F^{10}, ^3J 1.2 Hz), 116.36 q (2F, F^9, ^3J 1.2 Hz). Found, %: C 45.48; H 1.63; F 35.94; N 10.63. $C_{10}H_5F_5N_2O$. Calculated, %: C 45.46; H 1.90; F 35.99; N 10.61.

XRD analysis of compound **IV** was carried out on a crystal fragment (colorless prism) of the size 0.49 × 0.21 × 0.18 mm. $C_{10}H_5F_5N_2O$. M 264.16, crystal system triclinic, space group P-1, unit cell parameters: *a* 5.3300(9), *b* 8.6012(18), *c* 11.324(3) Å, α 86.349(18), β 83.892(16), γ 85.230(15) deg, V 513.63(18) Å^3, Z 2, d_{calc} 1.708, μ 0.174 mm^{-1}. Region of scanning 3.07 ≤ θ ≤ 28.27, overall reflections number 2402 (R_{int} 0.0174), reflections number with $I > 2\sigma(I)$ 1377, the number of refined parameters 183. Final parameters of refinement: R_1 0.0345, wR_2 0.0766 [for reflections with $I > 2\sigma(I)$], R_1 0.0755, wR_2 0.0839 (for all reflections), quality factor *S* 1.000. The residual peaks of maximum and minimum electron density 0.190 and –0.195 e/Å^3.

2-Heptafluoropropylbenzimidazole (**IV**). ^{19}F NMR spectrum coincides with the data in [17]. ^1H NMR spectrum (acetone-d_6), δ, ppm: 6.35 m (2H), 6.28 m (2H) ($C^{4–7}$), AA'BB', Ar.

3-(Pentafluoroethyl)benzo[g]-2(1H)-quinoxalinone (V). Under similar conditions through the mixture of 1.44 g (9 mmol) of 2,3-diaminonaphthalene and 2.18 g (26 mmol) of $NaHCO_3$ in 35 ml of ethyl ether was bubbled 2.1 g (9.7 mmol) of oxirane **I**, the mixture was stirred at room temperature for 6 h, then 10 ml of acetone was added, the insoluble precipitate was filtered off. The precipitate and the filtrate were separately worked up.

The precipitate was treated with water, insoluble part was filtered off and dried in air, then recrystallized from a mixture of ethyl acetate and hexane, 2:1, to obtain 0.78 g of benzoquinoxalinone **V**, yellow needle crystals, mp 273–274°C (subl.).

The residue obtained from the filtrate on removing the solvents was dissolved in methanol, diluted with water, the separated precipitate was filtered off, dried in air, and recrystallized from aqueous methanol. We obtained 1.32 g of compound **V**.

Overall yield 2.1 g (76%). IR spectrum, ν, cm^{-1}: 3106, 3332 (NH), 1672 (C=O), 1630 (C=N). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 12.91 br.s (1H, NH), 8.64 s (1H, H^5), 8.14 d (1H, H^6, *J* 8.3 Hz), 8.02 d (1H, H^9,

J 8.4 Hz), 7.74 s (1H, H^{10}), 7.66 d.d.d (1H, H^8, J 8.4, 6.8, 1.4 Hz), 7.53 d.d.d (1H, H^7, *J* 8.3, 6.8, 1.3 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 151.49 s (C^2), 145.18 m (C^3, $^2J_{CF}$ 24.5 Hz), 134.95 s (C^{9a}), 130.50 s (C^{10a}), 130.41 s (C^5), 129.52 s (C^{4a}), 129.47 s (C^{5a}), 129.21 s (C^8), 129.16 s (C^6), 126.88 s (C^9), 125.28 s, (C^7), 118.55 q.t (C^{12}, $^1J_{CF}$ 287.8, $^2J_{CF}$ 35.5 Hz), 111.06 c (C^{10}), 110.98 t.q (C^{11}, $^1J_{CF}$ 257.1, $^2J_{CF}$ 37.2 Hz). ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: 81.53 t (3F, F^{12}, *J* 1.4 Hz), 116.48 br.s (2F, F^{11}). Found, %: C 53.54; H 2.17; F 30.40; N 8.98. $C_{14}H_7F_5N_2O$. Found, %: C 53.50; H 2.23; F 30.25; N 8.92.

XRD analysis of compound **V** was performed on an orange needle crystal of the size 0.51 × 0.23 × 0.09 mm. $C_{14}H_7F_5N_2O$. M 314.22, crystal system monoclinic, space group $P2_1/n$, unit cell parameters: *a* 13.1743(15), *b* 5.1686(12), *c* 18.305(3) Å, α 90, β 92.736(14), γ 90 deg, V 1245.0(5) $Å^3$, Z 4, d_{calc} 1.676, μ 0.159 mm^{-1}. Region of scanning $3.10 \le \theta \le 26.37$, overall reflections number 2527 (R_{int} 0.0461), reflections number with $I > 2\sigma(I)$ 1080, the number of refined parameters 221. Final parameters of refinement: R_1 0.0463, wR_2 0.0923 [for reflections with $I > 2\sigma(I)$], R_1 0.1202, wR_2 0.1017 (for all reflections), quality factor S 1.002. The residual peaks of maximum and minimum electron density 0.229 and –0.202 e/$Å^3$.

REFERENCES

1. Tarrant, P., Allison, C.G., and Barthold, K.P., *Fluor. Chem. Rev*., 1971, vol. 5, p. 77.
2. Millauer, H., Schwertfeger, and W., Siegemund, G., *Angev. Chem.,* 1985, vol. 97, p. 164.
3. Eleuterio, H.S., *J. Macromol. Sci.-Chem.,* 1972, vol. A6, no. 6, p. 1027.
4. Ponomarenko, V.A., Krukovskii, S.P., and Alybina, A.Yu., *Ftorsoderzhashchie geterotsepnye polimery* (Fluorine-containing Heterochain Polymers), Moscow: Nauka, 1973.
5. *Novoe v tekhnologii soedinenii ftora* (New in the Technology of Fluorine Compounds), Isikava, N., Moscow: Mir, 1984.
6. Furin, G.G., *Ftorsoderzhashchie geterotsiklicheskie soedineniya. Sintez i primenenie* (Fluorine-Containing Heterocyclic Compounds. Synthesis and Application), Novosibirsk: Nauka, 2001, p. 183.
7. Knunyants, I.L., Shokhina, V.V., and Galakhov, I.V., *Khim. Geterotsikl. Soedin.,* 1966, vol. 6, p. 873.
8. Ishikava, N. and Sasaki, S., *Bull. Chem. Soc. Jpn.,* 1977, vol. 50, no. 8, p. 2164.
9. Cushman, M., Patel, H.P., Scheuring, J., and Bacher, A., *J. Org. Chem.,* 1992, vol. 57, p. 5630.
10. Nottke, J.E., US Patent 3928350, 1975; *Ref. Zh. Khim*., 1976, 16N248P.
11. Kvicala, J., Hovorkova, P., and Paleta, O., *J. Fluor. Chem.,* 2001, vol. 108, p. 1.
12. du Pont de Nemours, E.I. Co., UK Patent 904877, 1962; *Chem. Abstr*., 1963, vol. 58, 12513b.
13. Filyakova, T.I., Zapevalov, A.Ya., and Kolenko, I.P., Inventor's Certificate 666176; *USSR Byull. Izobr*., 1979, no. 21.
14. Saloutin, V.I., Piterskikh, I.A., Pashkevich, K.I., and Kodess, M.I., *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1983, p. 2586.
15. Mamedov, V.A., Valeeva, V.N., Antokhina, L.A., Nuretdinov, I.A., *Izv. Akad. Naul SSSR, Ser. Khim.,* 1991, p. 1422.
16. Sheldrick, G.M., *Acta Cryst*., 2008, vol. A64, p. 112.
17. Saloutina, L.V., Zapevalov, A.Ya., Saloutin, V.I., Kodess, M.I., Kirichenko, V.E., Pervova, M.G., and Chupakhin, O.N., *Zh. Org. Khim.,* 2006, vol. 42, p. 577.