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Reaction of Hexafluoro-*N*-(4-*N*,*N*-Dialkylaminophenyl)-1,4-naphthoquinon-4-imines with Primary Amines

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Abstract—Amination of 2,3,5,6,7,8-hexafluoro-*N*-(4-*N*,*N*-dialkylaminophenyl)-1,4-naphthoquinon-4-imines with primary amines led to the formation of 3-amino derivatives, which further underwent cyclization into 7-alkyl(aryl)-1,2,3,4,6-pentafluoro-5*H*-benzo[*a*]phenazin-5-ones. The spectral properties of compounds obtained were examined.

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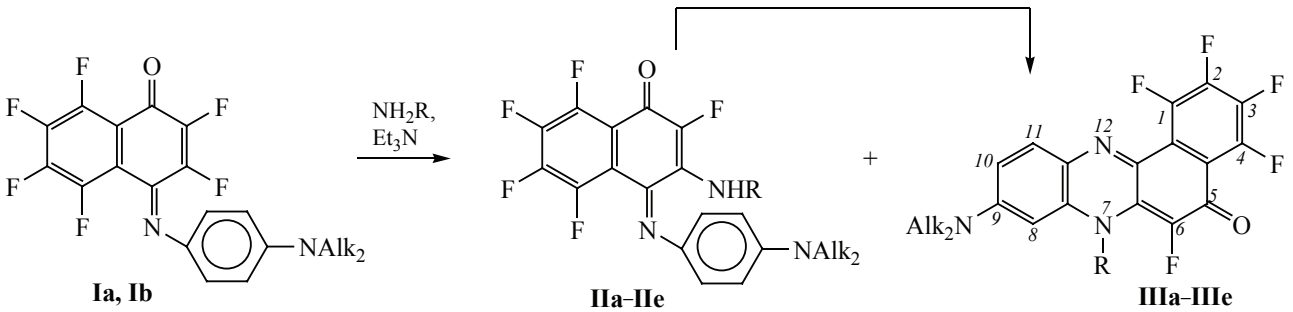
The oxidative amination of *N*-aryl-1,4-naphthoquinon-4-imine is known to proceed [1, 2] with the introduction of the amino group into the position *2*. The arising 2-aryl(alkyl)amino derivatives of naphthoquinonimines exhibits a high tuberculocidal activity [2]. It was also shown [3] that 2,5-diarylamino-*N*-aryl-1,4-benzoquinonimines enter into the reaction of oxidative heterocyclization, and therewith the arylamino group located in the *ortho*-position to the carbonyl group undergoes the cyclization into a phenoxazinonimine derivative, and the arylamino group in the *ortho*-position to the C=N group is involved in the formation of phenazinone derivative. The derivatives of phenazinones and phenoxazinononones possess a strong fluorescence [4].

We formerly [5] synthesized polyfluorinated derivatives of *N*-aryl-1,4-naphthoquinon-4-imines **Ia, Ib**. Taking into account the high nucleophilic lability of fluorine atoms in quinone derivatives (see, e.g., [6]), it was expectable that the reactions of compounds **Ia, Ib** provide a possibility of their further functionalization. In this study we investigated the products of reactions of naphthoquinonimines 2,3,5,6,7,8-hexafluoro derivatives **Ia, Ib** with primary aromatic and aliphatic amines.

In contrast to the nonfluorinated analogs quinonimines **Ia, Ib** react with the 4-substituted aniline derivatives and also with *n*-butylamine at maintaining for a short time (3–5 h) in organic solvent (ethanol, DMF) at room temperature with the formation of two substances. One among them is the product of a replacement of a fluorine atom in the position *3* of the quinone fragment of the



Ia, Ib **IIa–IIe** **IIIa–IIIe**

I, Alk = Me (**a**), Et (**b**); **II, III**, Alk = Me, R = 4-$Me_2NC_6H_4$ (**a**), 4-$CH_3OC_6H_4$ (**b**), C_4H_9 (**c**); Alk = Et, R = 4-$Et_2NC_6H_4$ (**d**), C_4H_9 (**e**).

molecule for the amino group (compounds **IIa–IIe**), the second one, the corresponding 1,2,3,4,6-pentafluoro-7-R-5*H*-benzo[*a*]phenazin-5-one **IIIa–IIIe**. It was shown by a special experiment that compound **IIe** under the reaction conditions is transformed into benzophenazine **IIIe**. Therefore the benzophenazines are the cyclization products of *N*-arylnaphthoquinonimines **IIa–IIe**.

The cyclization apparently proceeds through an intramolecular attack of the *ortho*-position of the hydrocarbon aromatic ring of *N*-arylnaphthoquinonimines **IIa–IIe** with the spatially close amine residue followed by the oxidation of the air oxygen. A similar mechanism was formerly suggested for the formation of 2-arylamino-5-arylphenazin-3-ones at the oxidation of *N*-phenyl-2,5-diarylamino-1,4-benzoquinonimines [7].

The structure of compounds obtained was established using the combination of the spectral data. In the high resolution mass spectra the intensive peaks of molecular ions were registered, whose *m*/*z* values corresponded to calculated ones. IR spectra of compounds **IIa–IIe, IIIa–IIIe** contained in the region 1550–1650 cm^{-1} the absorption bands of the stretching vibrations of the C=O and C=N groups, and in the spectra of compounds **IIa–IIe** an absorption band characteristic of the NH group was additionally present.

Chemical shifts and spin-spin coupling constants in the ^{1}H and ^{19}F NMR spectra of compounds **IIa–IIe, IIIa–IIIe** are in agreement with the assumed structures. In the ^{19}F NMR spectra of 1,2,3,4,6-pentafluorobenzo phenazinones **IIIc, IIIe** the chemical shifts of the F of the polyfluorinated benzene ring and of F^{6} are close in values to those in the spectrum of 1,2,3,4,6-pentafluoro-9-diethylamino-5*H*-benzo[*a*]phenoxazin-5-one [8]. The assignment of the signals in the ^{19}F NMR spectra was performed based on the analysis of coupling constants typical for polyfluorinated benzenes and analogous to those observed in the spectra of unsubstituted imines **Ia, Ib** [5]. The location of the amine substituent in the position *3* of compounds **IIa–IIe**, which follows from the conversion of **IIa–IIe** into **IIIa–IIIe**, was confirmed by an example of compound **IIe** using ^{13}C NMR spectroscopy. For instance, in the ^{13}C NMR spectrum of compound **IIe** the signal of the atom C^{1} appears as a doublet with the constant $^{2}J_{C^{1}F^{2}}$ 18 Hz characteristic of $^{2}J_{CF}$ [9]. The identification of this constant was proved by an experiment with its selective decoupling.

Unlike initial compounds **Ia, Ib** whose ^{19}F NMR spectra at room temperature and especially at cooling contain two sets of signals indicating the existence of a dynamic equilibrium between *Z*- and *E*-isomers [5], the ^{19}F NMR spectra of all 3-amino substituted pentafluoro-4-(4-*N,N*-dialkylaminophenyl)-1,4-naphthoquinon-4-imines **IIa–IIe** contain only the signals of a single spatial isomer. Therewith the signal of F^{2} atom is observed as a broadened singlet in the range 13–16 ppm for 3-arylamino derivatives **IIa, IIb, IId** and at –1.6 and –1.8 ppm for 3-butylamino derivatives **IIc, IIe**. The signals of fluorine atoms of the tetrafluororbenzene ring are multiplets at 22 ppm for F^{8} and 11–12 ppm for the atoms F^{6} and F^{7}. The chemical shift of the atom F^{5} in the ^{19}F NMR spectra of these compounds is shifted downfield to 39 ppm and it is located in the same region as the shift of the corresponding atom in the *E*-isomers of initial compounds **Ia, Ib** suggesting that in compounds **IIa, IIb** the substituent at the imine nitrogen atom is directed to the tetrafluorobenzene ring. Same as in the spectra of compounds **Ia, Ib** no coupling was observed here between the atom F^{5} and H$^{2'}$, H$^{6'}$ of the 4-dialkylaminophenyl group. Therefore we examined compound **IIc** for the presence of the nuclear Overhauser effect in the ^{1}H NMR spectrum at the selective irradiarion of the fluorine atoms. Weak positive effects were found for atoms H$^{2'}$, H$^{6'}$ of the 4-dimethylaminophenyl group at the irradiation of the atom F^{5}, for the atom H^{1} of the butyl group, at the irradiation of the atom F^{2}. This result confirms the spatial proximity of these nuclei.

In order to interpret the experimental results on the regioselectvity of the amination of compounds **Ia, Ib** we carried out quantum-chemical calculations by the density functional method. Assuming that the reaction proceeds through the intermediate formation of σ-complexes we considered the complexes formed by compound **Ia** with a model nucleophile, ammonia molecule. In the PBE/3z approximation that we had previously [5] applied to the calculation of this class compounds we failed to obtain σ-complexes corresponding to the addition at the position *2*. Therefore, we performed the calculations in the approximation CAMB3LYP/6-31G*. The total and relative (with respect to the most stable complex) energies of the localized σ-complexes are compiled in Table 1. The digit in the notations corresponds to the position of the substitution, and the letter corresponds to the position of the substituent at the C=N bond. The higher stability of the σ-complexes 3*E* and 3*Z* compared with 2*E* and 2*Z* may govern the proceeding of the reaction at the position *3* of compounds **Ia, Ib**. The higher stability of 3*E* than 3*Z* suggests that the prevailing conformation of the product

Table 1. Total E^{tot} (a.u.) and relative ΔE (kcal mol^{-1}) energies of σ-complexes of quinonimine **Ia** with NH_3

σ-complex	PBE/3z		CAMB3LYP/6-31G*	
	E^{tot}	ΔE	E^{tot}	ΔE
2*E*	–		–1531.49126	8.8
2*Z*	–		–1531.49719	5.1
3*E*	–1531.09061	0	–1531.50528	0
3*Z*	–1531.07847	7.6	–1531.49981	3.4

is determined already at the stage of the formation of the σ-complex.

However the occurrence of the cyclization reaction requires the presence of *Z*-isomers of compounds **IIa**, **IIb**. Therefore, we calculated the relative stability and the energy of the mutual transformations of the *Z*- and *E*-isomers of the model *N*-(4-*N,N*-dimethylaminophenyl)-3-methylaminopentafluoro-1,4-naphthoquinon-4-imine (**IIf**, Alk = Me, R = NHMe), a reaction product of compound **Ia** with NH_2Me. In the approximation PBE/3z its *E*-isomer is more stable than the *Z*-isomer by 4.5 kcal mol^{-1}, and the activation energy of the transformation of *E* into *Z* amounts to 15.1 kcal mol^{-1}. A close value of the relative stability of the isomers (4.3 kcal mol^{-1}) was also obtained on the calculation level CAMB3LYP/6-31G*.

The results obtained are in keeping with the presence in the NMR spectra of 3-amino-substituted 1,4-naphthoquinon-4-imines **IIa, IIb** exclusively of the signals of *E*-isomers; the possibility of the cyclization of **IIa–IIe** into **IIIa–IIIe** is apparently due to the rather low inversion barrier.

The electron absorption spectra of 3-amino derivatives of polyfluorinated naphthoquinonimines contain strong absorption bands in the region 560–580 nm for compounds **IIa–IIc** and 580–600 nm for **IId, IIe** that are subjected to a blue shift of 80–100 nm with respect to the longwave absorption maxima of initial compounds **Ia, Ib**. Note that in the nonfluorinated 2-aryl-amino-*N*-aryl-1,4-naphthoquinon-4-imines also a blue shift of the longwave absorption maxima of 20–30 nm was observed with respect to the λ_{max} of *N*-(4-*N,N*-dialkylaminophenyl)-1,4-naphthoquinon-4-imines [10].

In the electron absorption spectra of pentafluorobenzophenazinones **IIIa–IIIe** two absorption maxima are present in the visible region at 540–550 and 570–580 nm.

Compounds **IIIa–IIIe** are luminescent in the solutions of organic solvents, the luminescence maximum is in the region 598–603 nm, and the Stokes shift value is 20–28 nm (Table 2).

Thus the reaction of hexafluoro-4-(4-*N,N*-dialkylaminophenyl)-1,4-naphthoquinon-4-imines with primary amines results in the formation of 3-amino-substituted pentafluoronaphthoquinonimines which undergo cyclization into pentafluorobenzophenazinones.

EXPERIMENTAL

The spectral investigations were performed in the Chemical Service Center of the shared access of the Siberian Branch of the Russian Academy of Sciences.

IR spectra of compounds obtained were recorded on a spectrophotometer Vector 22 from pellets with KBr, electron absorption spectra, on a spectrophotometer Hewlett Packard 4853 from solutions in $CHCl_3$. The fluorescence of the studied compounds in the chloroform solutions was measured on a spectrofluorimeter Cary Eclipse Varian equipped with a pulse xenon lamp and a scheme of the luminescence registration at an angle of 90° with the excitation and emission slits of 5 nm, quartz

Table 2. Spectral properties of 1,2,3,4,6-pentafluoro-7-R-5*H*-benzo[*a*]phenazin-5-ones **IIIa–IIIe** in chloroform solution

Compound no.	Absorption λ_{max}, nm (logε)	Excitation λ_{max}, nm	Emission λ_{max}, nm	$\lambda_{phl} - \lambda_{abs}$, nm	$I_{phl.}$, rel.units.[a]
IIIa	543 (4.16), 577 (4.11)	544, 576	602	25	194
IIIb	541 (4.53), 575 (4.50)	544, 578	603	28	700
IIIc	536 (4.50), 570 (4.50)	536, 573	598	28	541
IIId	546 (4.57), 579 (4.58)	544, 576	599	20	555
IIIe	539 (4.38), 573 (4.54)	544, 575	598	25	947

[a]At excitation on the longwave maximum.

cells 10 mm thick, at room temperature. The operating solution concentration at the registering the excitation and emission spectra was 2.5×10^{-6} mol l^{-1}. NMR spectra were registered from solutions of compounds in $CDCl_3$ on spectrometers Bruker AV-300 [operating frequencies 300.13 (^{1}H) and 282.36 MHz (^{19}F)], AV-600 [operating frequencies 600.30 (^{1}H), 564.84 (^{19}F), 150.94 MHz (^{13}C)], and AV-400 [(^{1}H) 400.13 MHz]. Before the NOE experiment the solution was flushed with argon. The residual signal of the solvent protons (δ_H 7.24, δ_C 77.0 ppm) served as internal reference, the chemical shifts of ^{19}F were measured with respect to external reference C_6F_6. The ^{13}C NMR spectra were registered with decoupling from protons. Mass spectra were recorded on instruments DFS and Finnigan MAT-8200 (the molecular mass and composition of compounds were determined from the precise value of the molecular ion mass).

Quantum-chemical calculations were carried out in approximations PBE/3z and CAMB3LYP/6-31G* using PRIRODA [11] and GAMESS [12] software, respectively. The complete optimization of the geometric parameters was carried out, the localization of the transition state of the *Z*-*E*-isomerization was confirmed by the calculation by the eigenvalues of the Hesse matrix and by the calculation of the intrinsic reaction coordinate (IRC).

The progress of reaction was monitored and the purity of compounds was checked by TLC on Silufol UV-254 plates (eluent chloroform), preparative chromatography was carried out on columns packed with silica gel KSK (L 50–100 μm).

All reactions were performed in air.

Reaction of 2,3,5,6,7,8-hexafluoro-*N*-(4-*N*,*N*-dimethylaminophenyl)-1,4-naphthoquinon-4-imine (Ia) with 4-*N*,*N*-dimethylaminoaniline. To a solution of 0.190 g (0.5 mmol) of compound **Ia** in 50 ml of ethanol was added 0.110 g (0.5 mmol) of 4-*N*,*N*-dimethylaminoaniline and 0.14 ml (0.5 mmol) of triethylamine, the reaction mixture was maintained for 3 h at 20°C, then it was poured in water, and 10 g of NaCl was added. The separated precipitate was filtered off, washed with water, and dried, then it was dissolved in $CHCl_3$ and subjected to column chromatography on silica gel, gradient elution with a mixture CCl_4–$CHCl_3$ ($CHCl_3$ gradient from 10 to 100 vol%). From the blue zone initial compound **Ia** was isolated, yield 0.010 g (5%).

From the violet zone **2,5,6,7,8-pentafluoro-3-(4-*N*,*N*-dimethylaminophenylamino)-*N*-(4-*N*,*N*-dimethylaminophenyl)-1,4-naphthoquinon-4-imine (IIa)** was isolated**.** Yield 0.100 g (40%), t.decomp. 330°C. IR spectrum, ν, cm^{-1}: 3350 (NH), 1646 (C=O), 1610 (C=N), 1579 (C=C). ^{1}H NMR spectrum, δ, ppm: 2.92 s (6H, $2CH_3$), 3.04 s (6H, $2CH_3$), 6.61 d ($2H_{arom}$, *J* 9 Hz), 6.67 d ($2H_{arom}$, *J* 9 Hz), 6.83 d ($2H_{arom}$, *J* 9 Hz), 7.05 m ($2H_{arom}$), 7.79 br.s (1H, NH). ^{19}F NMR spectrum, δ, ppm: 11.4 m (1F, F^7), 12.2 m (1F, F^6), 14.2 s (1F, F^2), 22.1 m (1F, F^8), 39.1 m (1F, F^5). EAS ($CHCl_3$), λ_{max}, nm (logε): 571 (4.20). Found $[M]^+$ 500.1635. $C_{26}H_{21}F_5N_4O$. Calculated *M* 500.1630.

From the red zone **1,2,3,4,6-pentafluoro-7-(4-*N*,*N*-dimethylaminophenyl)-9-dimethylamino-*5H*-benzo[*a*]phenazin-5-one (IIIa)** was isolated. Yield 0.099 g (40%), t.decomp. 350°C. IR spectrum, ν, cm^{-1}: 1620 (C=O), 1564 (C=N), 1523 (C=C). ^{1}H NMR spectrum, δ, ppm: 2.95 s (6H, $2CH_3$), 3.10 s (6H, $2CH_3$), 5.82 d (1H, H^8, *J* 2 Hz), 6.75 m (1H, H^{10}), 6.86 d ($2H_{arom}$, *J* 9 Hz), 7.21 d ($2H_{arom}$, *J* 9 Hz), 7.73 d (1H, H^{11}, *J* 9 Hz). ^{19}F NMR spectrum, δ, ppm: 7.8 m (1F, F^3), 8.0 s (1F, F^6), 9.7 m (1F, F^2), 18.4 m (1F, F^4), 25.7 m (1F, F^1). Found $[M]^+$ 498.1479. $C_{26}H_{19}F_5N_4O$. Calculated *M* 498.1474.

Reaction of 2,3,5,6,7,8-hexafluoro-*N*-(4-*N*,*N*-dimethylaminophenyl)-1,4-naphthoquinon-4-imine (Ia) with *p*-anisidine. To a slurry of 0.190 g (0.5 mmol) of compound **Ia** and 0.120 g (1 mmol) of *p*-anisidine in 30 ml of DMF was added 0.07 ml of triethylamine, and the mixture was stirred for 5 h at 20°C. The reaction mixture was poured in water, the separated precipitate was filtered off, washed with water, and dried, then it was dissolved in $CHCl_3$ and subjected to column chromatography on silica gel, gradient elution with a mixture CCl_4–$CHCl_3$ ($CHCl_3$ gradient from 10 to 100 vol%). From the blue zone initial compound **Ia** was isolated, yield 0.025 g (13%).

From the violet zone **2,5,6,7,8-pentafluoro-3-(4-methoxyphenylamino)-*N*-(4-*N*,*N*-dimethyl-aminophenyl)-1,4-naphthoquinon-4-imine (IIb)** was isolated**.** Yield 0.096 g (39%), mp 160–162°C. IR spectrum, ν, cm^{-1}: 3434 (NH), 1649 (C=O), 1622 (C=N), 1609 (C=C). ^{1}H NMR spectrum, δ, ppm: 3.02 s (6H, $2CH_3$), 3.80 s (3H, OCH_3), 6.62 d ($2H_{arom}$, *J* 8 Hz), 6.84 m ($4H_{arom}$), 7.08 m ($2H_{arom}$), 7.77 br.s (1H, NH). ^{19}F NMR spectrum, δ, ppm: 11.6 m (1F, F^7), 12.7 m (1F, F^6), 15.8 s (1F, F^2), 22.4 m (1F, F^8), 39.3 m (1F, F^5). EAS ($CHCl_3$), λ_{max}, nm (logε): 579 (4.69). Found $[M]^+$ 487.1301. $C_{25}H_{18}F_5N_3O_2$. Calculated *M* 487.1314.

From the light red zone **1,2,3,4,6-pentafluoro-7-(4-methoxyphenyl)-9-dimethylamino-*5H*-benzo[*a*]phenazin-5-one (IIIb)** was isolated. Yield 0.077 g (32%),

t.decomp. >330°C. IR spectrum, ν, cm^{-1}: 1618 (C=O), 1552 (C=N). ^{1}H NMR spectrum, δ, ppm: 2.91 s (6H, $2CH_3$), 3.90 s (3H, OCH_3), 5.62 d (1H, H^{8}, *J* 2.5 Hz), 6.72 d.d (1H, H^{10}, *J* 9, 2.5 Hz), 7.08 m ($2H_{arom}$), 7.31 m ($2H_{arom}$), 7.67 d (1H, H$^{11'}$, *J* 9 Hz). ^{19}F NMR spectrum, δ, ppm: 8.0 m (1F, F^{3}), 8.2 s (1F, F^{6}), 10.0 m (1F, F^{2}), 19.0 m (1F, F^{4}), 25.9 m (1F, F^{1}). Found $[M]^+$ 485.1162. $C_{25}H_{16}F_5N_3O_2$. Calculated *M* 485.1157.

Reaction of 2,3,5,6,7,8-hexafluoro-*N*-(4-*N,N*-dimethylaminophenyl)-1,4-naphthoquinon-4-imine (Ia) with butylamine. To a solution of 0.192 g (0.5 mmol) of compound **Ia** in 100 ml of ethanol was added 0.1 ml (1 mmol) of butylamine, 0.14 ml of triethylamine, and the reaction mixture was maintained for 3 h at 20°C, then it was poured in water, and 10 g of NaCl was added. The separated precipitate was filtered off, washed with water, and dried, then it was dissolved in $CHCl_3$ and subjected to column chromatography on silica gel, gradient elution with a mixture CCl_4–$CHCl_3$ ($CHCl_3$ gradient from 10 to 100 vol%).

From the violet zone **2,5,6,7,8-pentafluoro-3-(butylamino*)*-*N*-(4-*N,N*-dimethylamino-phenyl)-1,4-naphthoquinon-4-imine (IIc)** was isolated. Yield 0.171 g (78%), mp 149–150°C. IR spectrum, ν, cm^{-1}: 3347 (NH), 1644 (C=O), 1607 (C=N), 1591 (C=C). ^{1}H NMR spectrum, δ, ppm: 0.94 t (3H, CH_3, *J* 7 Hz), 1.41 m (2H, CH_2), 1.61 m (2H, CH_2), 3.00 s (6H, $2CH_3$), 3.58 m (2H, CH_2), 6.12 br.s (1H, NH), 6.60 d ($2H_{arom}$, *J* 9 Hz), 6.78 d ($2H_{arom}$, *J* 9 Hz). ^{19}F NMR spectrum, δ, ppm: –1.6 s (1F, F^{2}), 11.4 m (1F, F^{7}), 11.9 m (1F, F^{6}), 22.2 m (1F, F^{8}), 38.6 m (1F, F^{5}). EAS ($CHCl_3$), λ_{max}, nm (logε): 564 (4.04). Found $[M]^+$ 437.15270. $C_{22}H_{20}F_5N_3O$. Calculated *M* 437.15264.

From the red zone **1,2,3,4,6-pentafluoro-7-butyl-9-dimethylamino-*5H*-benzo[*a*]phenazin-5-one** (**IIIc**) was isolated. Yield 0.010 g (5%), mp 241–243°C. IR spectrum, ν, cm^{-1}: 1618 (C=O), 1561 (C=N), 1517 (C=C). ^{1}H NMR spectrum, δ, ppm: 0.93 t (3H, CH_3, *J* 7 Hz), 1.56 m (2H, CH_2), 2.07 m (2H, CH_2), 3.17 s (6H, $2CH_3$), 4.28 m (2H, CH_2), 6.29 d (1H, H^{8}, *J* 2 Hz), 6.82 d.d (1H, H^{10}, *J* 9, 2 Hz), 7.65 d (1H, H^{11}, *J* 9 Hz). ^{19}F NMR spectrum, δ, m.d: 3.3 s (1F, (F^{6}), 8.0 m (1F, F^{3}), 10.1 m (1F, F^{2}), 19.0 m (1F, F^{4}), 25.8 m (1F, F^{1}). Found $[M]^+$ 435.1356. $C_{22}H_{20}F_5N_3O$. Calculated *M* 435.1365.

Reaction of 2,3,5,6,7,8-hexafluoro-*N*-(4-*N,N*-diethylaminophenyl)-1,4-naphthoquinon-4-imine (Ib) with 4-*N,N*-diethylaminoaniline. To a solution of 0.206 g (0.5 mmol) of compound **Ib** in 50 ml of ethanol was added 0.130 g (0.5 mmol) of 4-*N,N*-diethylaminoaniline sulfate and 0.14 ml of triethylamine, and the reaction mixture was maintained for 3 h at 20°C, then it was poured in water, and 10 g of NaCl was added. The separated precipitate was filtered off, washed with water, and dried, then it was dissolved in $CHCl_3$ and subjected to column chromatography on silica gel, gradient elution with a mixture CCl_4–$CHCl_3$ ($CHCl_3$ gradient from 10 to 100 vol%). From the blue zone initial compound **Ib** was isolated, yield 0.014 g (7%).

From the violet zone **2,5,6,7,8-pentafluoro-3-(4-*N,N*-diethylaminophenylamino)-*N*-(4-*N,N*-diethylaminophenyl)-1,4-naphthoquinon-4-imine (IId)** was isolated**.** Yield 0.061 g (22%), t.decomp. 169–171°C. IR spectrum, ν, cm^{-1}: 3294 (NH), 1644 (C=O), 1609 (C=N), 1574 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.16 t (6H, $2CH_3$, *J* 7 Hz), 1.21 t (6H, $2CH_3$, *J* 7 Hz), 3.35 q (4H, $2CH_2$, *J* 7 Hz), 3.41 q (4H, $2CH_2$, *J* 7 Hz), 6.61 m ($4H_{arom}$), 6.84 d ($2H_{arom}$, *J* 9 Hz), 7.03 m ($2H_{arom}$), 7.81 br.s (1H, NH). ^{19}F NMR spectrum, δ, ppm: 11.0 m (1F, F^{7}), 11.9 m (1F, F^{6}), 13.4 s (1F, F^{2}), 21.9 m (1F, F^{8}), 39.3 m (1F, F^{5}). EAS ($CHCl_3$), λ_{max}, nm (logε): 599 (4.16). Found $[M]^+$ 556.2250. $C_{30}H_{29}F_5N_4O$. Calculated *M* 556.2256.

From the red zone **1,2,3,4,6-pentafluoro-7-(4-*N,N*-diethylaminophenyl)-9-diethylamino-*5H*-benzo[*a*]phenazin-5-one** (**IIId**) was isolated. Yield 0.086 g (25%), t.decomp. 267–268°C. IR spectrum, ν, cm^{-1}: 1614 (C=O), 1560 (C=N), 1517 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.07 t (6H, $2CH_3$, *J* 7 Hz), 1.19 t (6H, $2CH_3$, *J* 7 Hz), 3.27 q (4H, $2CH_2$, *J* 7 Hz), 3.41 q (4H, $2CH_2$, *J* 7 Hz), 5.80 s (1H, H^{8}), 6.74 m (3H, $2H_{arom}$, H^{10}), 7.13 m ($2H_{arom}$), 7.69 d (1H, H^{11}, *J* 9 Hz). ^{19}F NMR spectrum, δ, ppm: 7.6 m (1F^{3}), 7.8 s (1F, F^{6}), 9.5 m (1F^{2}), 18.7 m (1F, F^{4}), 25.4 m (1F, F^{1}). Found $[M]^+$ 554.2097. $C_{30}H_{27}F_5N_4O$. Calculated *M* 554.2100.

Reaction of 2,3,4,5,6,7,8-hexafluoro-*N*-(4-*N,N*-diethylaminophenyl)-1,4-naphthoquinon-4-imine (Ib) with butylamine. To a solution of 0.206 g (0.5 mmol) of compound **Ib** in 50 ml of ethanola was added 0.1 ml (1 mmol) of butylamine, 0.14 ml triethylamine, and the reaction mixture was maintained for 3 h at 20°C, then it was poured in water, and 10 g of NaCl was added. The separated precipitate was filtered off, washed with water, and dried, then it was dissolved in $CHCl_3$ and subjected to column chromatography on silica gel, gradient elution with a mixture CCl_4–$CHCl_3$ ($CHCl_3$ gradient from 10 to 100 vol%).

From the violet zone **2,5,6,7,8-pentafluoro-3-(butylamino)-*N*-(4-*N*,*N*-diethylaminophenyl)-1,4-naphthoquinon-4-imine (IIe)** was isolated. Yield 0.173 g (74%), mp 130–132°C. IR spectrum, ν, cm^{-1}: 3345 (NH), 1649 (C=O), 1605 (C=N), 1585 (C=C). ^{1}H NMR spectrum, δ, ppm: 0.95 t (3H, CH_3, *J* 7 Hz), 1.172 t (6H, 2 CH_3, *J* 7 Hz), 1.40 m (2H, CH_2), 1.64 m (2H, CH_2), 3.37 q (4H, 2CH_2, *J* 7 Hz), 3.57 m (2H, CH_2), 6.1 br.s (1H, NH), 6.57 d (2H_{arom}, *J* 9 Hz), 6.77 d (2H_{arom}, *J* 9 Hz). ^{13}C NMR spectrum, δ, ppm: 12.8 (2C, CH_3), 14.0 (1C, CH_3), 20.1 (1C, CH_2), 33.0 (1C, CH_2), 44.7 (1C, CH_2), 44.8 (2C, CH_2), 111.9, 123.5 (C$^{2'}$, C$^{6'}$, C$^{3'}$, C$^{5'}$), 113.9, 116.0 (C^{4a}, C^{8a}), 137.6, 139.9, 140.6, 147.9 (C^{3}, C^{4}, C$^{1'}$, C$^{4'}$), 139.4 (C^{2}, $^1J_{CF}$ 238 Hz), 142.2 (C^{6}, $^1J_{CF}$ 259, $^2J_{CF}$ 17, 12 Hz), 142.6 (C^{7}, $^1J_{CF}$ 260, $^2J_{CF}$ 17, 12 Hz), 143.4 (C^{5}, $^1J_{CF}$ 263, $^2J_{CF}$ 12 Hz), 147.0 (C^{8}, $^1J_{CF}$ 267, $^2J_{C}$ 1 Hz), 170.7 (C^{1}, $^2J_{CF}$ 18 Hz). ^{19}F NMR spectrum, δ, ppm: –1.8 s (1F, F^{2}), 10.9 m (1F, F^{7}), 11.5 m (1F, F^{6}), 21.9 m (1F, F^{8}), 38.8 m (1F, F^{5}). EAS ($CHCl_3$), λ_{max}, nm (logε): 583 (4.10). Found $[M]^+$ 465.1828. $C_{24}H_{24}F_5N_3O$. Calculated M 465.1834.

From the red zone **1,2,3,4,6-pentafluoro-7-butyl-9-diethylamino-*5H*-benzo[*a*]phenazin-5-one (IIIe)** was isolated. Yield 0.021 g (9%), mp 224–225°C. IR spectrum, ν, cm^{-1}: 1614 (C=O), 1556 (C=N), 1499 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.05 t (3H, CH_3, *J* 7 Hz), 1.31 t (6H, 2CH_3, *J* 7 Hz), 1.56 m (2H, CH_2), 2.07 m (2H, CH_2), 3.53 m (4H, 2CH_2), 4.27 m (2H, CH_2), 6.37 d (1H, H^{8}, *J* 2 Hz), 6.83 d.d (1H, H^{10}, *J* 9, 2 Hz), 7.67 d (1H, H^{11}, *J* 9 Hz). ^{19}F NMR spectrum, δ, ppm: 6.1 s (1F, F^{6}), 10.9 m (1F, F^{3}), 13.0 m (1F, F^{2}), 21.9 m (1F, F^{4}), 28.5 m (1F, F^{1}). Found $[M]^+$ 463.1671. $C_{24}H_{22}F_5N_3O$. Calculated *M* 463.1678.

Cyclization of 2,5,6,7,8-pentafluoro-3-(butylamino)-*N*-(4-*N*,*N*-diethylaminophenyl)-1,4-naphtho-quinon-4-imine (IIe). A solution of 0.124 g of compound **IIe** in 50 ml of ethanol was heated at 60°C for 5 h, the solution was evaporated to dryness and chromatographed on a column packed with silica gel, gradient elution with a mixture CCl_4–$CHCl_3$ ($CHCl_3$ gradient from 10 to 100 vol%). From the red zone compound **IIIe** was isolated. Yield 0.083 g (68%), mp 224–225°C.

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