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Synthesis and Structure of *N*-(4-Dialkylaminophenyl)hexafluoro-1,4-naphthoquinone 4-Imines

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Abstract—The reaction of heptafluoro-1-naphthol with *N*,*N*-dialkyl-*p*-nitrosoanilines or *N*,*N*-dialkyl-*p*-phenylenediamines in the presence of HIO_3 gave the corresponding polyfluorinated *N*-aryl-1,4-naphthoquinone 4-imine derivatives which exist in solution as equilibrium mixtures of *Z* and *E* isomers. 2,3,5,6,7,8-Hexafluoro-*N*-(4-dimethylaminophenyl)-1,4-naphthoquinone 4-imine in crystal has exclusively the *Z*-isomer structure.

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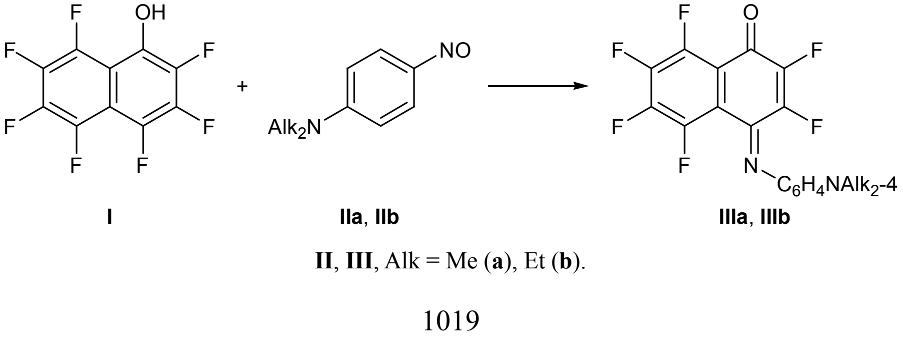
N-(4-Dialkylaminophenyl)-1,4-naphthoquinone 4-imines are used in color photography [1]. Introduction of electron-withdrawing substituents into the quinoid fragment gives rise to a strong charge-transfer band in the near-IR region of the electronic spectrum, which makes these compounds sensitive to semiconductor laser irradiation [2]. The resulting IR dyes are used in laser filters and printers [3] and were also proposed as materials for optical data recording [4, 5].

Among halogen-containing derivatives of *N*-(4-dialkylaminophenyl)-1,4-naphthoquinone 4-imines, 2-chloro- and 2-bromo-substituted analogs of Naphthol Blue [6] and 2,6-dibromo-4-(dialkylaminophenyl)-5-hydroxy-1,4-naphthoquinone imine [7] have been reported. Naphthoquinone imines having fluorine atoms in the naphthoquinone fragment were not described previously.

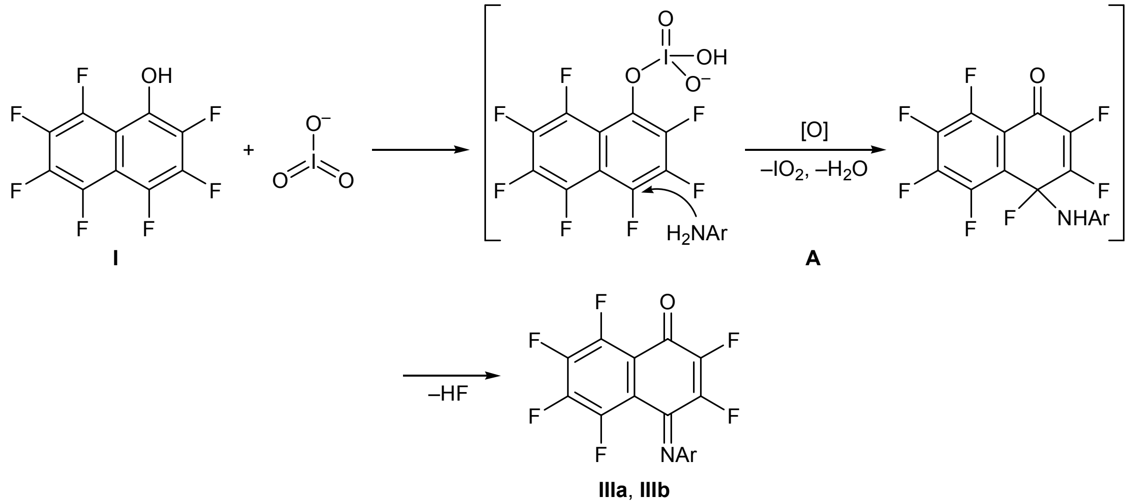
The goal of the present work was to synthesize polyfluorinated *N*-aryl-1,4-naphthoquinone 4-imines starting from heptafluoro-1-naphthol. *N*-Aryl-1,4-naphthoquinone 4-imines are generally obtained by reaction of α-naphthols with nitrosoarenes and by oxidative amination of α-naphthols [8]. Heptafluoro-1-naphthol (**I**) reacted with *N*,*N*-dialkyl-*p*-nitrosoanilines **IIa** and **IIb** in ethanol at room temperature to give in 2 h 2,3,5,6,7,8-hexafluoro-*N*-(4-dialkylaminophenyl)-1,4-naphthoquinone 4-imines **IIIa** and **IIIb** in ~30% yield (Scheme 1). We failed to improve the yield of **IIIa** and **IIIb** by raising the reaction temperature or increasing the reaction time. We succeeded in obtaining compounds **IIIa** and **IIIb** in 73 and 61% yield, respectively, by oxidative arylamination of fluorinated naphthol **I** with *N*,*N*-dialkyl-*p*-phenylenediamines in the presence of HIO_3 according to the procedure proposed by us previously for the synthesis of *N*-aryl-5-hydroxy-1,4-naphthoquinone imines [9]. This reaction is likely to follow ionic mechanism involving electrophilic attack by HIO_3 on the hydroxy group of heptafluoro-1-naphthol to give complex **A** [10] which reacts with aromatic amine to produce compound **IIIa** or **IIIb** (Scheme 2).

Scheme 1.



II, **III**, Alk = Me (**a**), Et (**b**).

Scheme 2.



The structure of **IIIa** and **IIIb** was determined by spectral methods. Their high-resolution mass spectra contained strong peaks from the molecular ions with *m*/*z* values corresponding to the calculated ones. In the IR spectra of **IIIa** and **IIIb** we observed absorption bands in the region 1550–1700 cm^{-1} due to stretching vibrations of the C=O and C=N groups. Compounds **IIIa** and **IIIb** in chloroform solution displayed in the electronic absorption spectra strong absorption bands at λ_{max} 662 (**IIIa**) and 680 nm (**IIIb**), which were displaced toward long-wave region by 67 and 63 nm, respectively, relative to those of their fluorine-free analogs [11]; on the other hand, the electronic spectra of **IIIa** and **IIIb** resemble those of 2,3-dicyano-*N*-(4-methoxyphenyl)- and 2,3-dicyano-*N*-(2,4-dimethoxyphenyl)-1,4-naphthoquinone 4-imines [2]. Obviously, the observed red shift is related to the electron-acceptor character of the fluorinated fragment.

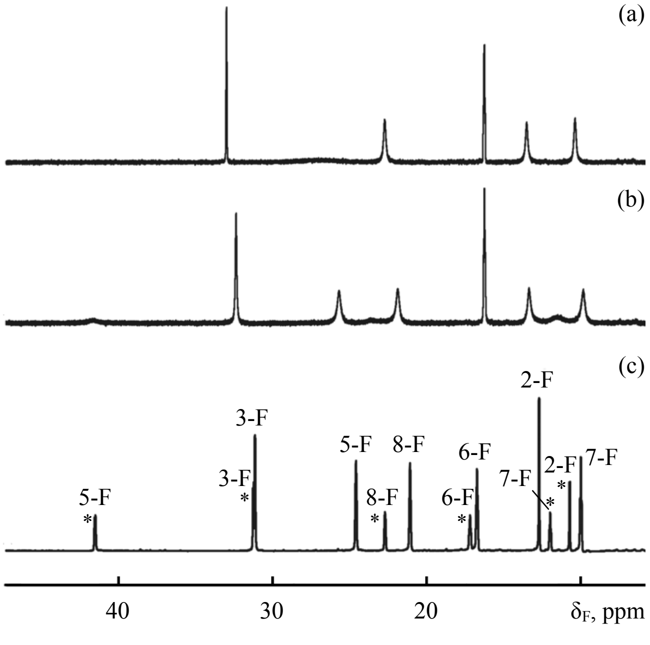
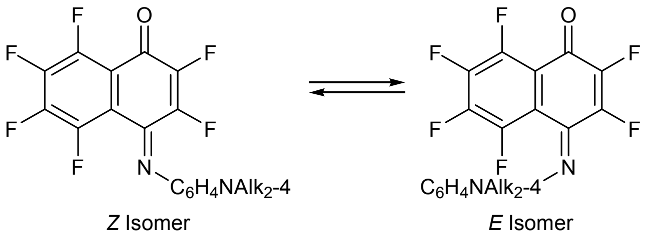


Fig. 1. ^{19}F NMR spectra of 2,3,5,6,7,8-hexafluoro-*N*-(4-dimethylaminophenyl)-1,4-naphthoquinone 4-imine (**IIIa**) in $CDCl_3$ recorded at (a) 55, (b) 25, and (c) –50°C. Signals from the minor *E* isomer in the bottom spectrum are marked with an asterisk.

The ^{19}F and ^{1}H chemical shifts in the NMR spectra of quinone imines **IIIa** and **IIIb** are generally consistent with the proposed structures. Nevertheless, the spectra recorded at room temperature contained two sets of signals with different intensities. In particular, in the ^{19}F NMR spectrum of **IIIa** (Fig. 1, Table 1) at room temperature we observed six diffuse signals together with less intense broadened signals at δ_{F} ~12–13, ~23–25, and ~42 ppm. These findings suggest the existence of two structures occurring in dynamic equilibrium with each other. By analogy with published data on the isomerization of *N*-aryl-1,4-benzoquinone imines [8], it was reasonable to presume that these structures are *Z* and *E* isomers with respect to the exocyclic C=N bond (Scheme 3). With a view to verify this assumption, we examined the temperature dependence of the ^{19}F NMR spectra of **IIIa**.

The spectrum recorded at –50°C contained two sets of signals with an intensity ratio of ~73 : 27. Each set included 6 signals whose resolution was sufficient to analyze their fine structure. Raising the temperature to 55°C lead to disappearance of the minor signals, the signal at δ_{F} 25.9 ppm belonging to the major isomer becomes strongly broadened (up to complete disappearance, while the other signals remain almost un-

Scheme 3.



changed. The subsequent cooling to room temperature restores the initial spectrum.

The major set of signals was assigned to the *Z* isomer taking into account the observed spin–spin coupling of 3-F with the *ortho*-protons (2′-H, 6′-H) in the 4-dimethylaminophenyl group: ${}^6J_{3\text{-F},2'\text{-H}} = {}^6J_{3\text{-F},6'\text{-H}} =$ 5.3 Hz. This coupling was identified by the ^{19}F–{^{1}H} and ^{1}H–{^{19}F} double-resonance techniques. We previously [9] revealed the coupling constant ${}^6J_{3\text{-H},2'\text{-F}} = {}^6J_{3\text{-H},6'\text{-F}} = 2.5$ Hz for 5-hydroxy-*N*-pentafluorophenyl-1,4-naphthoquinone 4-imine, where the *N*-aryl fragment is oriented *syn* with respect to the quinoid protons owing to strong intramolecular hydrogen bond between the *peri*-hydroxy group and nitrogen atom of the C=N bond. It is also known that the long-range coupling constant ${}^6J_{\text{FH}}$ may reach 11.9 Hz if the interacting nuclei appear spatially close to each other [12]. The minor set of signals in the spectrum of **IIIa** does not contradict the *E*-isomer structure. We observed no long-range coupling between 5-F and 2′(6′)-H in the 4-dimethylaminophenyl group (${}^7J_{5\text{-F},2'(6')\text{-H}}$), which could unambiguously indicate the isomer structure. On the other hand, change of the magnetic environment of 5-F in going from the *Z* to *E* isomer follows from the variation of chemical shifts. The largest difference in the fluorine chemical shifts between the *Z* and *E* isomers in the spectrum recorded at –50°C is observed for 5-F ($\Delta\delta_\text{F}$ ~17 ppm), while the chemical shifts of 2-F, 7-F, and 8-F in the two isomers differ by no more than 2 ppm, and the $\Delta\delta_\text{F}$ value for 3-F and 6-F amounts to a few tenth ppm. Compound **IIIa** displayed no signals from the *E* isomer in the ^{1}H NMR spectrum recorded at room or higher temperature, and the corresponding signals became visible only at –50°C at the same intensity ratio as in the ^{19}F NMR spectrum.

The ^{19}F and ^{1}H NMR spectra of **IIIb** showed analogous patterns (Table 1). The isomer ratio for **IIIb** was 77 : 23 at –50°C.

The difference in the Gibbs energies of the *Z* and *E* isomers of **IIIa** and **IIIb** was estimated by the equation $\Delta G^0 = -RT\ln K_\text{eq}$ at 0.44 and 0.53 kcal/mol, respectively, from the equilibrium isomer ratio K_eq at –50°C, which was determined from the signal intensities in the ^{19}F NMR spectrum. Processing of the ^{19}F NMR spectrum recorded at 25°C with the use of TOPSPIN 2.1 allowed us to estimate the $Z \rightarrow E$ isomerization rate constants: 240 and 290 s^{-1} for **IIIa** and **IIIb**, respectively. On the basis of these values we calculated by the Eyring equation the Gibbs energies of activation for the transformation of the *Z* isomer into *E* isomer: ΔG = 14.2 (**IIIa**), 14.1 kcal/mol (**IIIb**).

The temperature dependence of the ^{1}H NMR spectra was reported previously for *N*-aryl-2,3-bis(methoxycarbonyl)-1,4-naphthoquinone 4-imines [2]. However, no signal broadening was observed at room temperature in the ^{1}H NMR spectra of *N*-aryl-1,4-naphthoquinone 4-imines containing no fluorine atoms

Table 1. Chemical shifts in the ^{19}F and ^{1}H NMR spectra of 2,3,5,6,7,8-hexafluoro-*N*-(4-dialkylaminophenyl)-1,4-naphthoquinone 4-imines **IIIa** and **IIIb**

Temperature, °C	Comp. no.	Chemical shifts δ_F, δ, ppm								
		2-F	3-F	5-F	6-F	7-F	8-F	2′-H, 6′-H	3′-H, 5′-H	CH_3, CH_2
25	*Z*-**IIIa**	13.5	32.6	25.9	16.3	10.0	22.1	7.03	6.68	3.08 (3H)
	E-**IIIa**	10.7–12.7	32.6	41.1–42.6	16.3	10.7–12.7	23.0–24.4			
	Z-**IIIb**	12.5	32.1	25.4	15.9	9.3	21.6	7.03	6.66	1.22 (3H), 3.44 (2H)
	E-**IIIb**	9.9–11.9	32.1	40.9–42.9	15.9	9.9–11.9	22.1–24.1			
–50	*Z*-**IIIa**	12.7	31.2	24.6	16.6	9.9	21.1	7.07	6.69	3.12 (3H)
	E-**IIIa**	10.7	31.3	41.5	17.0	11.9	22.7	6.93	6.61	3.10 (3H)
	Z-**IIIb**	11.8	31.0	24.4	16.1	9.1	20.8	7.07	6.67	1.22 (3H), 3.45 (2H)
	E-**IIIb**	10.0	31.3	41.9	16.4	11.1	22.5	6.80–7.05	6.59	1.20 (3H), 3.43 (2H)
55	*E*,*Z*-**IIIa**	13.5	33.0	25.0–29.5	16.2	10.3	22.7	7.02	6.71	3.07 (3H)
	E,*Z*-**IIIb**	12.6	32.5	24.0–28.5	15.8	9.6	22.3	7.03	6.68	1.23 (3H), 3.44 (2H)

Table 2. Coupling constants in the ^{19}F and ^{1}H NMR spectra of 2,3,5,6,7,8-hexafluoro-*N*-(4-dialkylaminophenyl)-1,4-naphthoquinone 4-imines **IIIa** and **IIIb**, recorded at –50°C

Compound no.	Coupling constant *J*, Hz								
	2-F/3-F	3-F/2′(6′)-H	5-F/6-F	5-F/7-F	5-F/8-F	6-F/7-F	6-F/8-F	7-F/8-F	2-H/3-H
Z-**IIIa**	13.4	5.3	20.5	7.5	12.8	21.0	10.4	21.0	–
E-**IIIa**	15.0	–	24.0	9.0	11.0	21.0	9.5	20.8	–
Z-**IIIb**	14.2	5.7	20.6	7.0	12.7	21.5	10.0	21.0	7.0
E-**IIIb**	15.5	–	24.0	8.6	12.0	21.0	9.2	21.0	7.0

or other strong electron-withdrawing substituents, which may be interpreted as the absence of *Z*/*E* isomerization under the given conditions [7, 13]. According to the X-ray diffraction data, the substituent on the imino nitrogen atom in *N*-(4-methoxyphenyl)-2-(4-methoxyphenylamino)-1,4-naphthoquinone 4-imine in crystal is oriented opposite to the aromatic ring [14]; analogous configuration was observed for some other N-substituted 1,4-naphthoquinone 4-imines [15]. In order to rationalize the observed differences, we performed DFT calculations of the relative stabilities of the *Z* and *E* isomers of **IIIa** and its fluorine-free analog, as well as of the energy barriers to mutual isomer transformations. The calculations were carried out with the PBE/3*z* functional using Priroda software [16]. The *Z* isomer of **IIIa** turned out to be more stable than the *E* isomer by 1.3 kcal/mol, and the energy barrier to the transformation of *Z*-**IIIa** into *E*-**IIIa** was estimated at 12.6 kcal/mol. The corresponding isomer of the fluorine-free analog, in which the substituent on the imino nitrogen atom is oriented opposite to the aromatic ring, is more stable than the other isomer by 4.7 kcal/mol, and the energy of activation for the isomerization is 14.4 kcal/mol. Thus, in going from the fluorine-free to fluorinated compound the energies of formation of the isomers become closer, and the barrier to their interconversion decreases. This favors increased fraction of the *E* isomer and makes it possible to observe that isomer experimentally by NMR spectroscopy at reduced temperature.

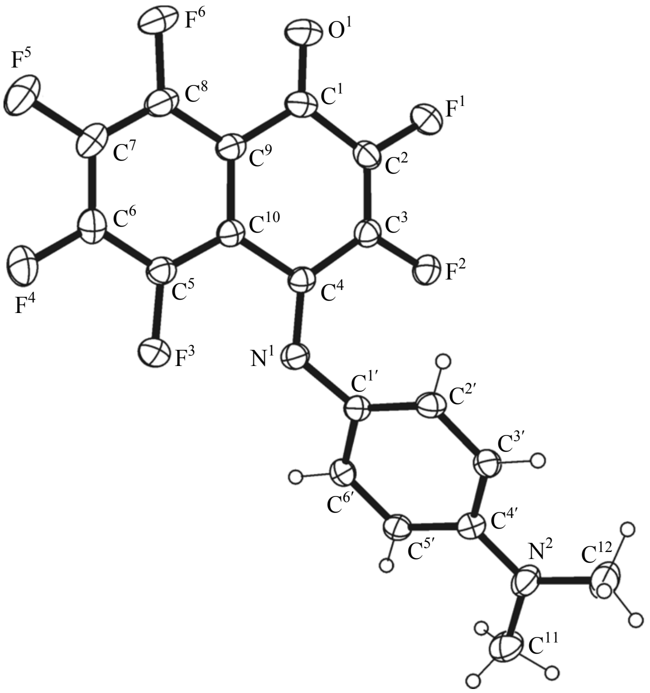


Fig. 2. Structure of the molecule of 2,3,5,6,7,8-hexafluoro-*N*-(4-dimethylaminophenyl)-1,4-naphthoquinone 4-imine (**IIIa**) according to the X-ray diffraction data.

The crystalline structure of compound **IIIa** was determined by X-ray analysis; suitable single crystals were obtained by crystallization from benzene–hexane (Fig. 2). According to the X-ray diffraction data, molecule **IIIa** in crystal has *Z* configuration, the naphthoquinone fragment is planar, and the deviations of atoms from the mean-square plane including all atoms of that fragment do not exceed 0.030 Å. The phenyl ring is turned through a dihedral angle of 55.90° with respect to the naphthoquinone plane. The dimethylamino group is also planar; the mean-square deviation from the $N^2C^{4'}C^{11}C^{12}$ plane is 0.024 Å. No shortened non-valence contacts (as compared to the sum of the corresponding van der Waals radii) were observed in the crystal packing of **IIIa**. Molecules **IIIa** are linked to dimers via π-stacking interaction between the perfluorinated naphthoquinoid fragment (C^1–C^{10}) and nonfluorinated $C^{1'}$–$C^{6'}$ ring [intercentroid distance 3.546(1) Å, interplane angle 3.54(8)°]. The experimental X-ray powder pattern of **IIIa** confirmed the presence of only one isomer in the crystalline state.

Thus *N*-(4-dialkylaminophenyl)hexafluoro-1,4-naphthoquinone 4-imines in chloroform solution exist as a dynamic equilibrium mixture of the *Z* and *E* isomers, the former prevailing. Dimethylamino derivative **IIIa** in the crystalline state exists exclusively as the *Z* isomer.

EXPERIMENTAL

The spectral studies were carried out at the Shared Chemical Service Center, Siberian Branch, Russian Academy of Sciences. The IR spectra were recorded in KBr on a Bruker Vector 22 spectrometer. The electronic absorption spectra were measured from solutions in chloroform on a Hewlett Packard 4853 spectrophotometer. The NMR spectra were obtained on Bruker Avance 300 (300.13 MHz for ^{1}H and 282.4 MHz for ^{19}F) and Avance 400 spectrometers (400.13 MHz for ^{1}H and 376.5 MHz for ^{19}F) from solutions in $CDCl_3$ using the residual proton signal of the solvent ($CHCl_3$, δ 7.24 ppm) as reference (for ^{1}H). The ^{19}F chemical shifts were determined relative to C_6F_6 as external reference. The mass spectra were recorded on DFS and Finnigan MAT-8200 instruments; the molecular weights and elemental compositions were determined from the precise *m*/*z* values of the molecular ions. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using chloroform as eluent.

The X-ray diffraction data and X-ray powder pattern for compound **IIIa** were obtained at room temperature on a Bruker Kappa Apex II diffractometer equipped with a two-coordinate CCD detector (MoK_α irradiation, graphite monochromator). A 0.06×0.35×0.90-mm single crystal of **IIIa** was analyzed by ω–φ scanning in the range $2\theta < 50°$. Monoclinic crystal system: $a = 12.9314(5)$, $b = 8.0283(3)$, $c = 15.7845(6)$ Å; $\beta = 106.190(2)°$; $V = 1573.7(1)$ Å^3; space group $P2_1/n$; $Z = 4$; $C_{18}H_{10}F_6N_2O$; $d_{calc} = 1.622$ g/cm^3; $\mu = 0.151$ mm^{-1}. Intensities of 2783 independent reflections were measured. A correction for absorption was applied using SADABS program [17] (transmission 0.81–0.86). The structure was solved by the direct method using SHELXS-97 and was refined by the least-squares procedure in full-matrix anisotropic approximation for all non-hydrogen atoms using SHELXL-97 [18]. The positions of hydrogen atoms were calculated in each iteration cycle from the coordinates of the corresponding carbon atoms. The final refinement against F^2 was carried out up to $wR_2 = 0.1278$; goodness of fit $S = 1.07$; 246 variables ($R = 0.0361$ for 2124 reflections with $F > 4\sigma$). The CIF file containing the complete set of crystallographic data for compound **IIIa** was deposited to the Cambridge Crystallographic Data Centre (entry no. CCDC 888443) and is available at *www.ccdc.cam.ac.uk/data_request/cif*. The bond lengths and bond angles in molecule **IIIa** are consistent with the corresponding standard values [19] within 3σ.

Compounds IIIa and IIIb (*general procedure*). *a*. A mixture of 0.27 g (1 mmol) of heptafluoro-1-naphthol (**I**) and 2 mmol of *N*,*N*-dimethyl- or *N*,*N*-diethyl-*p*-nitrosoaniline hydrochloride in 20 ml of ethanol was stirred for 2 h at 20°C. The mixture was poured into water, the precipitate was filtered off, washed with water, dried in air, and dissolved in chloroform, and the solution was subjected to column chromatography on silica gel (gradient elution with carbon tetrachloride–chloroform, 0 to 100 vol % of the latter). Compounds **IIIa** and **IIIb** were isolated from the main blue zone.

4-(4-Dimethylaminophenylimino)-2,3,5,6,7,8-hexafluoro-1,4-dihydronaphthalen-1-one (IIIa). Yield 32%, mp 190–192°C. IR spectrum, ν, cm^{-1}: 1650 (C=O), 1625 (C=N), 1606 (C=C). The ^{19}F and ^{1}H NMR spectra are given in Tables 1 and 2. Electronic absorption spectrum ($CHCl_3$): λ_{max} 662 nm (logε 4.34). Found: *m*/*z* 384.07044 $[M]^+$. $C_{18}H_{10}F_6N_2O$. Calculated: *M* 384.06972.

4-(4-Diethylaminophenylimino)-2,3,5,6,7,8-hexafluoro-1,4-dihydronaphthalen-1-one (IIIb). Yield 30%, mp 166–167°C. IR spectrum, ν, cm^{-1}: 1665 (C=O), 1629 (C=N), 1606 (C=C). The ^{19}F and ^{1}H NMR spectra are given in Tables 1 and 2. Electronic absorption spectrum ($CHCl_3$): λ_{max} 680 nm (logε 4.57). Found: *m*/*z* 412.10086 $[M]^+$. $C_{20}H_{14}F_6N_2O$. Calculated: *M* 412.10102.

b. A solution of 2 mmol of HIO_3 in 15 ml of water was added dropwise under stirring to a suspension of 0.27 g (1 mmol) of heptafluoro-1-naphthol (**I**) and 1.1 mmol of *N*,*N*-dimethyl-*p*-phenylenediamine hydrochloride or *N*,*N*-diethyl-*p*-phenylenediamine sulfate in 50 ml of ethanol, and the mixture was stirred for 2 h at 20°C and treated as described above in *a*. Yield 73% (**IIIa**), 61% (**IIIb**).

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