

# Benzoid–Quinoid Tautomerism of Schiff Bases and Their Structural Analogs: LIII.\* Schiff Bases Derived from 5-Hydroxy- and 5-Hydroxy-6-nitro-2,3-diphenyl-1-benzofuran-4-carbaldehydes

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**Abstract**—4-Aryl(alkyl)iminomethyl-5-hydroxy- and 4-aryl(alkyl)iminomethyl-5-hydroxy-6-nitro-2,3-diphenyl-1-benzofurans were synthesized and were shown to exist in solution as equilibrium mixtures of benzoid and quinoid tautomers. The fraction of the quinoid form increases with rise in the solvent polarity and in going from *N*-aryl to *N*-alkyl derivatives; introduction of an electron-acceptor substituent (nitro group) into the 6-position of the benzofuran system also favors formation of the quinoid tautomer. Complex formation of alkali and alkaline-earth metal cations with the 5-hydroxy-6-nitro-2,3-diphenyl-1-benzofuran-4-carbaldehyde imine having a benzo-15-crown-5 fragment on the nitrogen atom is accompanied by specific changes in the luminescence spectrum and in the state of tautomeric equilibrium, so that this system may be regarded as tautomeric fluorogenic chemosensor for metal cations.

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The main types of fluorogenic chemosensors are PET and ICT systems [2, 3]. The first of these (PET) involve photoinduced electron transfer from the highest occupied molecular orbital (HOMO) of a receptor fragment to the HOMO of a signaling moiety; as a result, fluorescent properties of the latter are suppressed almost completely. Addition of a cation to the receptor of a PET sensor reduces its HOMO energy, so that it becomes lower than the HOMO energy of the signaling (fluorophore) moiety, and fluorescence intensity considerably increases, the position of the emission band remaining unchanged. Internal charge transfer (ICT) systems undergo essential electron density redistribution upon photoexcitation; this leads to a shift (as a rule, blue) of the emission band and a slight change of its intensity. We previously showed that complex formation of alkali metal cations with 5-hydroxy-6-nitro-2,3-tetramethylene-1-benzofuran-4-carbaldehyde imine containing a crown ether moiety is accompanied

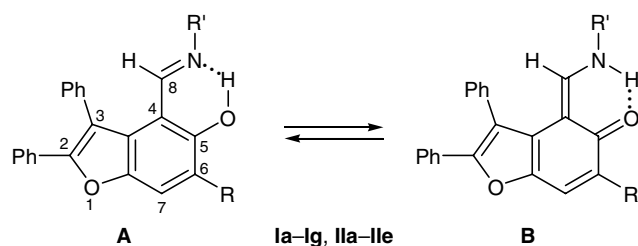
by a blue shift of the fluorescence maximum without appreciable change in its intensity [4]; therefore, this chemosensor may be classed with ICT systems.

With the goal of obtaining new ICT chemosensors capable of undergoing benzoid–quinoid tautomerism we synthesized *N*-aryl- and *N*-alkyl-substituted 5-hydroxy-2,3-diphenyl-1-benzofuran-4-carbaldehyde and 5-hydroxy-6-nitro-2,3-diphenyl-1-benzofuran-4-carbaldehyde imines **Ia–Ig** and **IIa–IIe** and examined their absorption and luminescence spectra. Compounds **Ia–Ig** and **IIa–IIe** were obtained by condensation of the corresponding amines with 5-hydroxy-2,3-diphenyl-1-benzofuran-4-carbaldehyde (**III**) and 5-hydroxy-6-nitro-2,3-diphenyl-1-benzofuran-4-carbaldehyde (**IV**), respectively. Aldehyde **III** was prepared by hydrolysis of 4-(4-methoxyphenyliminomethyl)-5-hydroxy-2,3-diphenyl-1-benzofuran (**Ia**) [5], and the subsequent nitration of **III** gave 6-nitro-substituted aldehyde **IV**.

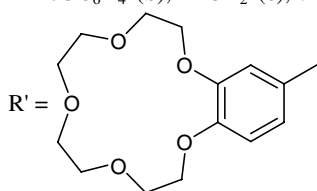
The electronic absorption spectra of *N*-aryl-substituted Schiff bases **Ia–Ie** contain a broad band with its

\* For communication LII, see [1].

Scheme 1.



**I**, R = H, R' = 4-MeOC<sub>6</sub>H<sub>4</sub> (**a**), 4-MeC<sub>6</sub>H<sub>4</sub> (**b**), 4-EtOCO-C<sub>6</sub>H<sub>4</sub> (**c**), 4-BrC<sub>6</sub>H<sub>4</sub> (**e**), PhCH<sub>2</sub> (**f**), *i*-Pr (**g**); **II**, R = O<sub>2</sub>N, R' = Ph (**a**), 4-MeOC<sub>6</sub>H<sub>4</sub> (**b**), PhCH<sub>2</sub> (**c**), *i*-Pr (**d**); **Ig**, **Ile**,



maximum in the region  $\lambda$  360–370 nm, whose intensity weakly depends on the solvent polarity (see table). Only in the spectra of compounds **Ia** and **Ib** in proton-donor isopropyl alcohol we observed a weak absorption band at longer wavelengths. Comparison of these data with those obtained previously for Schiff bases derived from 5-hydroxy-2,3-tetramethylene-1-benzofuran-4-carbaldehyde [6] indicates the existence of benzoid tautomer **A** in solution (Scheme 1).

In going from *N*-aryl to *N*-alkyl derivatives (Schiff bases **Ie** and **If**) and to 6-nitro-substituted analogs **II**, new long-wave maxima appear in the electronic absorption spectra at  $\lambda$  435–437 (**Ie**, **If**) and 472–514 nm (**II**) (see table). The intensity of these maxima increases as the solvent polarity (and especially proton-donor power) rises. By analogy with our previous results [6, 7], we presumed the existence of tautomeric equilibrium between the benzoid (**A**) and quinoid (**B**) forms (see table).

The parameters of tautomeric equilibrium were determined from the <sup>1</sup>H NMR and electronic absorption spectra for [<sup>15</sup>N]-labeled *N*-phenylimine **IIa**. In the <sup>1</sup>H NMR spectrum of this compound in dimethyl sulfoxide, the signal from the labile proton was split due to coupling with <sup>15</sup>N with a constant  $J_{\text{HN}}$  of 25.6 Hz, which corresponds to 26.7% of the quinoid tautomer [8]. Assuming that the molar absorption coefficient of the quinoid form ( $\epsilon_{\text{B}} = 2.62 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ ) weakly depends on the solvent polarity and the nature of R and R' substituents [6, 7], we calculated the fraction of tautomer **B** for the other Schiff bases **I** and **II** (see table).

Schiff bases **Ig** and **Ile** having a crown ether fragment are potential dynamic tautomeric fluorogenic chemosensors for metal cations [4]. Addition of alkali and alkaline-earth metal salts to solutions of **Ig** in various solvents insignificantly affected the electronic absorption and emission spectra. By contrast, 6-nitro-4-[3,4-(1,4,7,10,13-pentaoxatridecane-1,13-diyl)-phenyliminomethyl]-2,3-diphenyl-1-benzofuran-5-ol (**Ile**) showed a high sensitivity to alkali and alkaline-earth metal cations: the concentration of the quinoid tautomer of **Ile** decreased in the series  $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Li}^+ > \text{Na}^+ \approx \text{K}^+ > \text{Cs}^+$ ; simultaneously, the fraction of the benzoid tautomer increased. Thus binding of cations with a crown ether moiety provides one more factor determining the position of the benzoid–quinoid equilibrium. Complex formation is accompanied by variation of the fluorescence spectra of Schiff base **Ile**, which is typical of ICT chemosensors. Excitation of **Ile** in a solution in acetonitrile at the wavelength corresponding to absorption of the benzoid tautomer ( $\lambda_{\text{excit}}$  390 nm) gives rise to a strong fluorescence band at  $\lambda$  584 nm with an anomalous Stokes shift ( $\Delta\nu = 7814 \text{ cm}^{-1}$ ) due to intramolecular proton transfer in the excited state [9]. Complex formation with alkali and alkaline-earth metal cations at the crown ether moiety leads to a considerable blue shift of the fluorescence maximum, especially for  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions, with no appreciable change of the fluorescence intensity.

Specific changes in the absorption and fluorescence spectra upon complex formation with metal cations make compound **Ile** an effective tautomeric fluorogenic ICT chemosensor for magnesium and calcium cations.

## EXPERIMENTAL

The <sup>1</sup>H NMR spectra were obtained on a Varian Unity-300 instrument (300 MHz) relative to the residual proton signals of the deuterated solvents (CHCl<sub>3</sub>,  $\delta$  7.25 ppm; Me<sub>2</sub>SO,  $\delta$  2.50 ppm). The electronic absorption spectra were recorded on a Specord M-40 spectrophotometer, and the luminescence spectra were measured on a Hitachi 650-60 spectrofluorimeter. The IR spectra were recorded on a Specord 75IR spectrometer from samples dispersed in mineral oil.

**4-(4-Methoxyphenyliminomethyl)-2,3-diphenyl-1-benzofuran-5-ol (Ia)** was synthesized according to the procedure described in [5]. Yield 87%, mp 149–150°C. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 3420, 1610, 1580, 1550. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 3.79 s (3H, CH<sub>3</sub>),

Spectral parameters of Schiff bases **Ia–Ig** and **IIa–IIe** and parameters of the benzoid–quinoid equilibrium ( $A \rightleftharpoons B$ )

Compound no.	Solvent	Electronic absorption spectrum, $\lambda_{\max}$ , nm ( $\epsilon \times 10^{-4}$ , $l \text{ mol}^{-1} \text{ cm}^{-1}$ )	Concentration of tautomer <b>B</b> , %	$K^0 = [B]/[A]$	$\Delta G_{293}^0$ , kJ/mol
<b>Ia</b>	Toluene	370 (3.23)	0	–	–
	CH <sub>3</sub> CN	364 (3.36)	0	–	–
	Propan-2-ol	368 (3.34), 482 (0.08)	3.1	0.032	8.4
	DMSO	371 (3.19)	0	–	–
<b>Ib</b>	Toluene	363 (3.18)	0	–	–
	CH <sub>3</sub> CN	358 (3.28)	0	–	–
	Propan-2-ol	361 (2.98), 440 (0.06)	2.3	0.023	9.1
	DMSO	364 (3.30)	0	–	–
<b>Ic</b>	Toluene	372 (3.11)	0	–	–
	CH <sub>3</sub> CN	366 (3.17)	0	–	–
	Propan-2-ol	370 (3.12)	0	–	–
	DMSO	371 (3.05)	0	–	–
<b>Id</b>	Toluene	369 (2.99)	0	–	–
	CH <sub>3</sub> CN	361 (3.24)	0	–	–
	Propan-2-ol	363 (3.28)	0	–	–
	DMSO	367 (3.19)	0	–	–
<b>Ie</b>	Toluene	326 (2.51)	0	–	–
	CH <sub>3</sub> CN	323 (2.54), 437 (0.12)	4.6	0.048	7.4
	Propan-2-ol	325 (2.58), 437 (0.20)	7.6	0.082	6.1
	DMSO	326 (2.48), 437 (0.08)	3.1	0.032	8.4
<b>If</b>	Toluene	325 (2.50), 435 (0.04)	1.5	0.015	10.2
	CH <sub>3</sub> CN	322 (2.58), 435 (0.10)	3.8	0.039	7.9
	Propan-2-ol	325 (2.80), 437 (0.36)	13.7	0.159	4.5
	DMSO	325 (2.20), 435 (0.12)	4.6	0.048	7.4
<b>Ig</b>	Toluene	296 (1.41), 375 (3.13)	0	–	–
	CH <sub>3</sub> CN	288 (1.55), 372 (3.28)	0	–	–
	Propan-2-ol	290 (1.57), 373 (3.25), 500 (0.06)	2.3	0.023	9.1
	DMSO	292 (1.52), 377 (3.18)	0	–	–
<b>IIa</b>	Toluene	385 (3.12), 495 (0.16)	6.1	0.065	6.6
	CH <sub>3</sub> CN	387 (2.80), 494 (0.56)	21.4	0.272	3.2
	Propan-2-ol	389 (2.60), 494 (0.62)	23.7	0.311	2.8
	DMSO	392 (2.52), 496 (0.70)	26.7	0.364	2.5
<b>IIb</b>	Toluene	389 (3.55), 500 (0.14)	5.3	0.056	7.0
	CH <sub>3</sub> CN	389 (3.26), 500 (0.56)	21.4	0.272	3.2
	Propan-2-ol	392 (3.10), 500 (0.68)	26.0	0.351	2.5
	DMSO	402 (2.73), 500 (0.65)	24.8	0.330	2.7
<b>IIc</b>	Toluene	370 (2.23), 473 (0.32)	12.2	0.139	4.8
	CH <sub>3</sub> CN	293 (1.63), 380 (2.13), 475 (1.23)	46.9	0.883	0.3
	Propan-2-ol	290 (1.72), 383 (2.20), 472 (1.32)	50.4	1.016	0.0
	DMSO	296 (1.56), 383 (1.98), 479 (1.29)	49.2	0.968	0.1
<b>IId</b>	Toluene	370 (2.11), 472 (0.53)	20.2	0.253	3.3
	CH <sub>3</sub> CN	292 (1.54), 378 (2.00), 472 (1.39)	53.0	1.128	–0.3
	Propan-2-ol	291 (1.70), 381 (2.14), 468 (1.48)	56.5	1.299	–0.6
	DMSO	295 (1.48), 382 (1.87), 476 (1.35)	51.5	1.062	–0.1
<b>IIe</b>	Toluene	394 (3.39), 514 (0.23)	8.8	0.096	5.7
	CH <sub>3</sub> CN	401 (2.99), 514 (0.60)	22.9	0.297	2.9
	Propan-2-ol	401 (2.81), 516 (0.64)	24.4	0.323	2.7
	DMSO	402 (2.83), 514 (0.77)	29.4	0.416	2.1

6.78–7.60 m (16H,  $H_{\text{arom}}$ ), 8.35 s (1H, 8-H), 14.19 s (1H, OH). Found, %: C 80.00; H 5.18; N 3.40.  $C_{28}H_{21}NO_3$ . Calculated, %: C 80.19; H 5.01; N 3.34.

**5-Hydroxy-2,3-diphenyl-1-benzofuran-4-carbaldehyde (III)** was synthesized by hydrolysis of Schiff base **Ia** as described in [6]; the product was recrystallized from butan-1-ol. Yield 68%, mp 186–187°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3420, 1630, 1605, 1580.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 6.93–7.71 m (12H,  $H_{\text{arom}}$ ), 9.58 s (1H, CHO), 12.02 s (1H, OH). Found, %: C 80.12; H 4.47.  $C_{21}H_{14}O_3$ . Calculated, %: C 80.25; H 4.46.

**5-Hydroxy-6-nitro-2,3-diphenyl-1-benzofuran-4-carbaldehyde (IV)** was obtained by nitration of aldehyde **III** according to the procedure reported in [4]; the product was recrystallized from butan-1-ol. Yield 34%, mp 218–219°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3400, 1630, 1610, 1510.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 7.28–7.60 m (10H,  $H_{\text{arom}}$ ), 8.53 s (1H, 7-H), 9.62 s (1H, CHO), 13.21 s (1H, OH). Found, %: C 70.34; H 3.57; N 3.85.  $C_{21}H_{13}NO_5$ . Calculated, %: C 70.19; H 3.62; N 3.90.

**Schiff bases Ib–Ig and IIa–IIe** (*general procedure*). Aldehyde **III** or **IV**, 1 mmol, was dissolved in a minimal amount of butan-1-ol, and 1 mmol of the corresponding amine was added. The mixture was heated for 1–5 h under reflux and cooled, and the precipitate was filtered off and recrystallized from butan-1-ol–toluene (1:1).

**4-(4-Methylphenyliminomethyl)-2,3-diphenyl-1-benzofuran-5-ol (Ib)**. Yield 86%, mp 174°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3450, 1600, 1570, 1550.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 2.35 s (3H,  $\text{CH}_3$ ), 6.76–7.62 m (16H,  $H_{\text{arom}}$ ), 8.41 s (1H, 8-H), 14.22 s (1H, OH). Found, %: C 83.51; H 5.19; N 3.30.  $C_{28}H_{21}NO_2$ . Calculated, %: C 83.37; H 5.21; N 3.47.

**Ethyl 4-(5-hydroxy-2,3-diphenyl-1-benzofuran-4-ylmethylideneamino)benzoate (Ic)**. Yield 76%, mp 137–138°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3400, 1705, 1700.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 1.38 t (3H,  $\text{CH}_3$ ), 4.36 q (2H,  $\text{CH}_2$ ), 6.84–7.93 m (16H,  $H_{\text{arom}}$ ), 8.40 s (1H, 8-H), 13.77 s (1H, OH). Found, %: C 78.01; H 5.10; N 3.18.  $C_{30}H_{23}NO_4$ . Calculated, %: C 78.09; H 4.99; N 3.04.

**4-(4-Bromophenyliminomethyl)-2,3-diphenyl-1-benzofuran-5-ol (Id)**. Yield 82%, mp 227–229°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3450, 1600, 1560.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 6.67–7.60 m (16H,  $H_{\text{arom}}$ ),

8.38 s (1H, 8-H), 13.79 s (1H, OH). Found, %: C 69.12; H 3.78; N 3.11.  $C_{27}H_{18}BrNO_2$ . Calculated, %: C 69.23; H 3.85; N 2.99.

**4-Benzyliminomethyl-2,3-diphenyl-1-benzofuran-5-ol (Ie)**. Yield 72%, mp 137–138°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3500, 1610, 1600, 1580.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 4.38 s (2H,  $\text{CH}_2$ ), 6.85–7.57 m (17H,  $H_{\text{arom}}$ ), 8.02 s (1H, 8-H), 14.18 s (1H, OH). Found, %: C 83.19; H 5.41; N 3.41.  $C_{28}H_{21}NO_2$ . Calculated, %: C 83.37; H 5.21; N 3.47.

**4-Isopropyliminomethyl-2,3-diphenyl-1-benzofuran-5-ol (If)**. Yield 68%, mp 114°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3500, 1620, 1580.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 1.05 d (6H,  $\text{CH}_3$ ,  $J = 6.5$  Hz), 3.10 m (1H, CH), 6.87–7.56 m (12H,  $H_{\text{arom}}$ ), 7.88 s (1H, 8-H), 14.48 s (1H, OH). Found, %: C 80.96; H 5.91; N 4.05.  $C_{24}H_{21}NO_2$ . Calculated, %: C 81.13; H 5.92; N 3.94.

**2,3-Diphenyl-4-[3,4-(3,6,9-trioxaundecamethyleneedioxy)phenyliminomethyl]-1-benzofuran-5-ol (Ig)**. Yield 74%, mp 151–152°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3400, 1610, 1580, 1560.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 3.75–4.14 m (16H,  $\text{CH}_2\text{O}$ ), 6.37–7.60 m (15H,  $H_{\text{arom}}$ ), 8.41 s (1H, 8-H), 14.26 s (1H, OH). Found, %: C 72.73; H 5.60; N 2.41.  $C_{35}H_{33}NO_7$ . Calculated, %: C 72.54; H 5.70; N 2.42.

**6-Nitro-2,3-diphenyl-4-([ $^{15}\text{N}$ ]-phenyliminomethyl)-1-benzofuran-5-ol (IIa)**. Yield 70%, mp 194–195°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3500, 1620, 1580, 1550.  $^1\text{H}$  NMR spectrum ( $\text{DMSO}-d_6$ ),  $\delta$ , ppm: 6.85–7.70 m (15H,  $H_{\text{arom}}$ ), 8.30 s (1H, 8-H), 8.42 s (1H, 7-H), 15.74–15.83 d (1H, OH, NH,  $J_{\text{HN}} = 25.6$  Hz). Found, %: C 74.40; H 4.15; N 6.72.  $C_{27}H_{18}N^{15}NO_4$ . Calculated, %: C 74.48; H 4.13; N 6.66.

**4-(4-Methoxyphenyliminomethyl)-6-nitro-2,3-diphenyl-1-benzofuran-5-ol (IIb)**. Yield 84%, mp 234–235°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3400, 1610, 1600, 1580.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 3.82 s (3H,  $\text{CH}_3$ ), 6.81–7.68 m (14H,  $H_{\text{arom}}$ ), 8.24 d (1H, 8-H,  $J = 5.4$  Hz), 8.45 s (1H, 7-H), 16.68 d (1H, OH, NH,  $J = 5.4$  Hz). Found, %: C 72.25; H 4.38; N 6.05.  $C_{28}H_{20}N_2O_5$ . Calculated, %: C 72.41; H 4.31; N 6.03.

**4-Benzyliminomethyl-6-nitro-2,3-diphenyl-1-benzofuran-5-ol (IIc)**. Yield 66%, mp 170–173°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3450, 1630, 1590, 1570.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 4.35 d (2H,  $\text{CH}_2$ ,  $J = 3.7$  Hz), 7.08–7.57 m (15H,  $H_{\text{arom}}$ ), 7.76 d (1H, 8-H,  $J = 8.6$  Hz), 8.44 s (1H, 7-H), 15.57 m (1H, OH, NH). Found, %: C 74.96; H 4.57; N 6.20.  $C_{28}H_{20}N_2O_4$ . Calculated, %: C 75.00; H 4.46; N 6.25.

**4-Isopropyliminomethyl-6-nitro-2,3-diphenyl-1-benzofuran-5-ol (II<sub>d</sub>).** Yield 64%, mp 183°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3400, 1630, 1590, 1570, 1570.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 1.12 d (6H,  $\text{CH}_3$ ,  $J = 6.5$  Hz), 3.40 m (1H, CH), 7.26–7.64 m (10H,  $\text{H}_{\text{arom}}$ ), 8.48 d (1H, 8-H,  $J = 11.0$  Hz), 8.48 s (1H, 7-H), 15.11 m (1H, OH, NH). Found, %: C 71.83; H 5.11; N 7.08.  $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_4$ . Calculated, %: C 72.00; H 5.00; N 7.00.

**6-Nitro-2,3-diphenyl-4-[3,4-(3,6,9-trioxaundecamethylenedioxy)phenyliminomethyl]-1-benzofuran-5-ol (II<sub>e</sub>).** Yield 74%, mp 229–230°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3450, 1605, 1580.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 3.70–4.17 m (16H,  $\text{CH}_2\text{O}$ ), 6.35–7.64 m (13H,  $\text{H}_{\text{arom}}$ ), 8.46 d (1H, 8-H,  $J = 5.6$  Hz), 8.46 s (1H, 7-H), 16.89 d (1H, OH, NH,  $J = 5.6$  Hz). Found, %: C 67.15; H 5.10; N 4.56.  $\text{C}_{35}\text{H}_{32}\text{N}_2\text{O}_9$ . Calculated, %: C 67.31; H 5.13; N 4.49.

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## REFERENCES

- Rybalkin, V.P., Dubonosov, A.D., Shepelenko, E.N., Popova, L.L., Makarova, N.I., Tsukanov, A.V., Bren', V.A., and Minkin, V.I., *Russ. J. Org. Chem.*, 2002, vol. 38, p. 1321.
- Callan, J.F., Prasanna de Silva, A.P., and Magri, D.C., *Tetrahedron*, 2005, vol. 61, p. 8551.
- Bren', V.A., *Usp. Khim.*, 2001, vol. 70, p. 1152.
- Bren', V.A., Dubonosov, A.D., Makarova, N.I., Minkin, V.I., Popova, L.L., Rybalkin, V.P., Shepelenko, E.N., and Tsukanov, A.V., *Russ. J. Org. Chem.*, 2002, vol. 38, p. 139.
- Mezheritskii, V.V., Olekhovich, E.P., Luk'yanov, S.M., and Dorofeenko, G.N., *Ortoefiry v organicheskom sinteze* (Ortho Esters in Organic Synthesis), Rostov-on-Don: Rostov. Gos. Univ., 1976, p. 163.
- Rybalkin, V.P., Bushkov, A.Ya., Bren', V.A., and Minkin, V.I., *Zh. Org. Khim.*, 1986, vol. 22, p. 565.
- Rybalkin, V.P., Shepelenko, E.N., Popova, L.L., Dubonosov, A.D., Bren', V.A., and Minkin, V.I., *Russ. J. Org. Chem.*, 1996, vol. 32, p. 90.
- Dudek, G.O. and Volpp, G.P., *J. Am. Chem. Soc.*, 1963, vol. 85, p. 2694.
- Knyazhanskii, M.I. and Metelitsa A.V., *Fotoinitsirovanye protsessy v molekulakh azometinov i ikh strukturnykh analogov* (Photoinitiated Processes in Molecules of Schiff Bases and Their Structural Analogs), Rostov-on-Don: Rostov. Gos. Univ., 1992.