

Benzoid-Quinoid Tautomerism of Azomethines and Their Structural Analogs: LIV.* Dibenzo(benzo)-18-crown-6-containing Imines of 5-Hydroxy-2,3-tetramethylene- and 5-Hydroxy-2,3-diphenylbenzo[*b*]furan-4-carbaldehydes

A. D. Dubonosov^a, A. V. Tsukanov^a, E. N. Shepelenko^a, Yu. V. Revinskii^b,
V. A. Bren'^b, and V. I. Minkin^b

^a*Southern Scientific Center, Russian Academy of Sciences, Rostov-on-Don, 344090, Russia
e-mail: aled@ipoc.rsu.ru*

^b*Research Institute of Physical and Organic Chemistry at Southern Federal University,
Rostov-on-Don*

Received April 30, 2008

Abstract—Dibenzo(benzo)-18-crown-6-containing *N*-arylimines of 5-hydroxy-2,3-tetramethylene- and 5-hydroxy-2,3-diphenylbenzo[*b*]furan-4-carbaldehydes were synthesized and their spectral luminescence properties were investigated. In solutions of 6-bromo- and 6-nitro-substituted compounds a tautomeric equilibrium exists between the benzoid and quinoid forms. In the course of complexing of crown-ether-imines of 5-hydroxy-6-nitro-2,3-diphenylbenzo[*b*]furan-4-carbaldehyde and 5-hydroxy-6-nitro-2,3-tetramethylenebenzo[*b*]furan-4-carbaldehyde with cations of alkali and alkaline earth metals the content of the quinoid form was found to decrease. This phenomenon was accompanied by essential changes in the absorption and fluorescence spectra characteristic of chemosensor systems with an intramolecular charge transfer (ICT).

DOI: 10.1134/S1070428009020079

The selectivity of crown-ether receptors with respect to certain metal ions depends on the geometric parameters of the macrocycle, the energy of orbital interaction heteroatom–cation, and on solvation [2–4]. Results of our quantum-chemical calculations indicate the governing influence of the orbital effects on the stability of alkali metal cations complexes with 4-aminobenzo-15-crown-5-ether receptor and suggest the preferable complexing with [(benzo-15-crown-5)-4'-yl]imine of 5-hydroxy-6-nitro-2,3-tetramethylenebenzo[*b*]furan-4-carbaldehyde for lithium ion. The latter was proved experimentally [2].

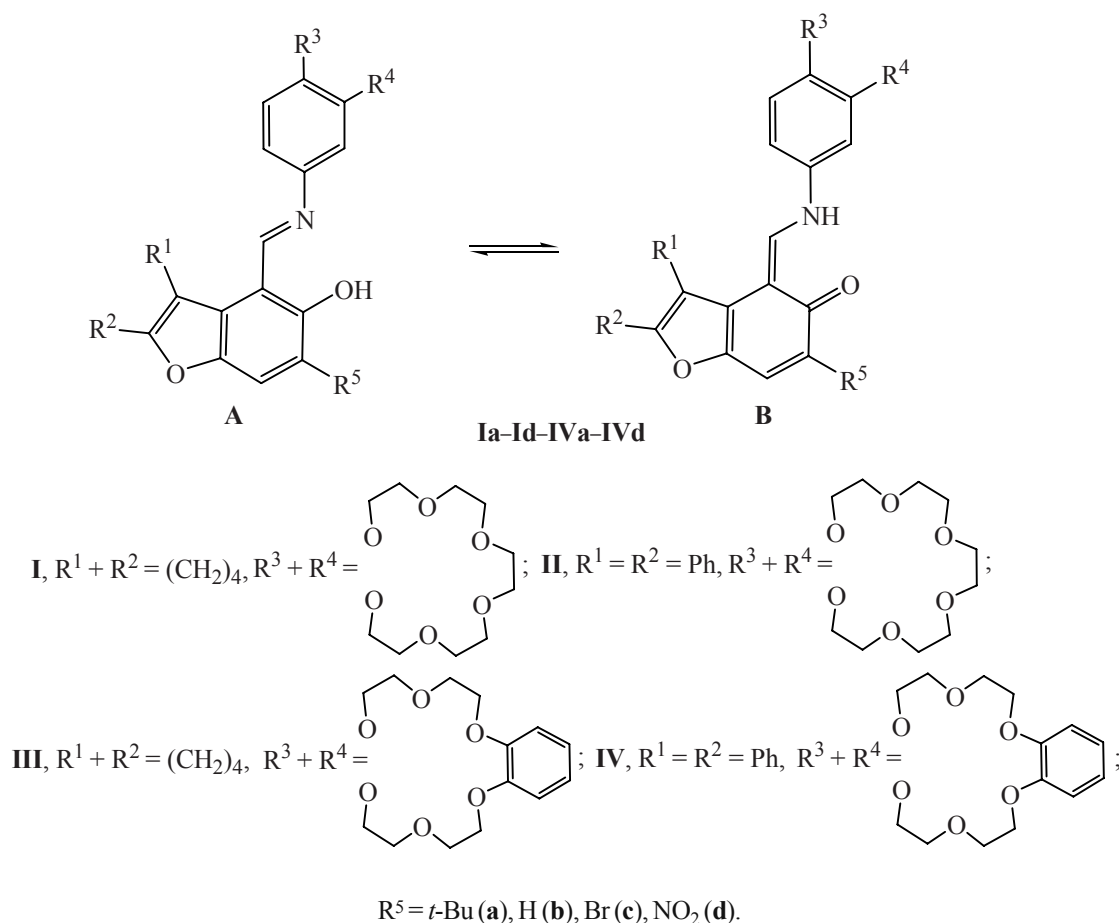
Aiming at the preparation new crown-containing tautomeric chemosensors sensitive to cations of *s*-metals possessing larger ionic radii (K⁺, Ba²⁺) we synthesized imines **I–IV** proceeding from 5-hydroxy-2,3-diphenylbenzo[*b*]furan-4-carbaldehyde and 5-hydroxy-2,3-tetramethylenebenzo[*b*]furan-4-carbaldehyde with benzo-18-crown-6- and dibenzo-18-crown-6-ether receptors (Scheme 1). Compounds **I–IV** were prepared by the condensation of

*For communication LIII see [1].

the appropriate aldehydes [1, 5, 6] with 4-amino-benzo-18-crown-6- and 4-aminodibenzo-18-crown-6.

In the electron absorption spectra of crown-ether-imines **Ia**, **Ib–IVa**, **IVb** lacking substituents in the position 6 or containing *t*-Bu in this position a wide band is observed at 360–390 nm whose intensity weakly depended on the polarity of the solvent (Table 1). In the ¹H NMR spectra of these compounds the hydroxy group signal appeared as a narrow singlet in the region 13–14 ppm. In the electron absorption spectra of imines **Ic**, **Id–IVc**, **IVd** containing in the position 6 of the benzene ring electron-withdrawing groups Br and NO₂ new maxima appeared at 480–510 nm (Table 1), and in the ¹H NMR spectra of the nitro derivatives the signal of OH group was shifted downfield (16–17 ppm) and simultaneously split into a doublet (same as the signal of the methylene proton). The comparison of these data with the spectra of previously studied imines of 5-hydroxy-2,3-tetramethylenebenzo[*b*]furan-4-carbaldehyde and 5-hydroxy-2,3-diphenylbenzo[*b*]furan-4-carbaldehyde [1, 5, 6] indicates

Scheme.



that imines **Ia**, **Ib–IVa**, **IVb** are present in the solution predominantly in one benzoid form **A** whereas the 6-bromo and 6-nitro derivatives exist in the benzoid-quinoid equilibrium **A** \rightleftharpoons **B** (Scheme 1).

The content of quinoid **B** grows in the solvent series toluene, acetonitrile, 2-propanol, DMSO as seen from the increased intensity of the long-wave absorption maximum (Table 1).

By comparison of the data of electronic and ^1H NMR spectroscopy we formerly calculated the molar extinction coefficients of quinoid tautomers of ^{15}N -butylimine of 5-hydroxy-2,3-tetramethylenebenzo[*b*]furan-4-carbaldehyde [5] and ^{15}N -phenylimine of 5-hydroxy-6-nitro-2,3-diphenylbenzo[*b*]furan-4-carbaldehyde [1]. Assuming [1, 5, 7] that these coefficients are weakly sensitive to the polarity of solvent and the character of substituents R^3 , R^4 , and R^5 we estimated the content of tautomer **B** for crown-containing imines **Ic**, **Id–IVc**, **IVd** (Table 1).

Adding of salts of alkali and alkaline earth metals to acetonitrile solutions of crown-containing 6-nitro-sub-

stituted imines **Id–IVd** results in the decreased content of the quinoid tautomer with the simultaneous growth of the content of the benzoid form in the series $\text{Ba}^{2+} > \text{Ca}^{2+} > \text{K}^+ > \text{Na}^+ > \text{Mg}^{2+} > \text{Cs}^+ > \text{Li}^+$ (see the figure). The involvement of the crown-ether in the complex formation is accompanied by a decrease in the content of the quinoid form calculated from the change in the extinction coefficient of the band in the region 470–510 nm (Table 2).

The reaction of crown-containing imines **Id–IVd** with metal ions is accompanied with significant changes in their emission spectra, characteristic of ICT-chemosensor [8]. The excitation of compounds **Id–IVd** in acetonitrile solutions at the absorption band of the benzoid form [λ_{exc} 390 nm (**Id**, **IVd**) and 370 nm (**Id**, **IIIId**)] results in fluorescence appearance in the region 555–585 nm with an abnormal Stokes shift due to the intramolecular proton transfer in the excited state [9]. In the presence of cations of alkali and alkaline earth metals a notable blue shift of the fluorescence band is observed without visible changes in its intensity. The strongest effect on the luminescence

Table 1. Spectral characteristics of imines **I–IV** and parameters of equilibrium $A \rightleftharpoons B$

Compd. no.	Solvent	Electron absorption spectra, λ_{\max} , nm ($\epsilon \times 10^{-4}$, l mol ⁻¹ cm ⁻¹)	Content of B form, %	$K^{\circ} = [B]/[A]$	ΔG°_{293} , kJ mol ⁻¹
Ia	Toluene	372 (2.06)	0	–	–
	CH ₃ CN	367 (2.30)	0	–	–
	2-Propanol	365 (2.15)	0	–	–
	DMSO	371 (2.22)	0	–	–
Ib	Toluene	367 (2.34)	0	–	–
	CH ₃ CN	364 (2.52)	0	–	–
	2-Propanol	364 (2.43)	0	–	–
	DMSO	367 (2.35)	0	–	–
Ic	Toluene	375 (2.14)	0	–	–
	CH ₃ CN	376 (2.61), 490 (0.06)	5.8	0.062	6.8
	2-Propanol	373 (2.52), 490 (0.08)	7.7	0.083	6.0
	DMSO	372 (2.55), 490 (0.10)	9.6	0.106	5.5
Id	Toluene	375 (2.11), 490 (0.05)	4.8	0.050	7.3
	CH ₃ CN	375 (2.35), 490 (0.41)	39.4	0.650	1.0
	2-Propanol	374 (1.99), 485 (0.42)	40.4	0.678	0.9
	DMSO	378 (2.00), 490 (0.71)	68.3	2.155	-1.9
Iib	Toluene	375 (3.29)	0	–	–
	CH ₃ CN2-	373 (3.27)	0	–	–
	PropanolDMSO	289 (1.64), 374 (3.33)	0	–	–
		374 (3.32)	0	–	–
Iic	Toluene	388 (3.24), 500 (0.06)	2.9	0.030	8.5
	CH ₃ CN	382 (3.10), 500 (0.14)	6.9	0.074	6.3
	2-Propanol	288 (1.70), 390 (3.36), 500 (0.22)	10.8	0.121	5.1
	DMSO	388 (3.59), 500 (0.20)	9.8	0.109	5.4
Iid	Toluene	398 (3.37), 500 (0.20)	9.8	0.109	5.4
	CH ₃ CN2-	402 (3.02), 500 (0.56)	27.6	0.381	2.3
	PropanolDMSO	399 (2.99), 500 (0.74)	36.4	0.572	1.4
		403 (2.52), 500 (0.80)	39.4	0.650	1.0
IIIa	Toluene	367 (1.86)	0	–	–
	CH ₃ CN	369 (1.70)	0	–	–
	DMSO	370 (1.76)	0	–	–
IIIb	Toluene	368 (2.16)	0	–	–
	CH ₃ CN	363 (1.64)	0	–	–
	DMSO	368 (0.28)	0	–	–
IIIc	Toluene	372 (2.59)	0	–	-7.94.8
	CH ₃ CN	370 (2.74), 495 (0.04)	3.8	0.040	
	DMSO	373 (2.42), 495 (0.10)	9.6	0.106	
IIIId	Toluene	375 (1.84), 500 (0.06)	5.8	0.062	6.81.8
	CH ₃ CN	375 (1.92), 497 (0.34)	32.7	0.486	
IVb	Toluene	376 (3.12)	0	–	–
	CH ₃ CN	283 (1.66), 371 (3.10)	0	–	–
	DMSO	377 (3.18)	0	–	–
IVc	Toluene	388 (2.98), 500 (0.06)	2.9	0.030	8.5
	CH ₃ CN	282 (1.74), 383 (3.06), 500 (0.10)390	4.9	0.051	7.2
	DMSO	(2.98), 500 (0.16)	7.9	0.086	6.0
IVd	Toluene	396 (3.26), 510 (0.19)	9.3	0.102	5.5
	CH ₃ CNDMSO	267 (1.86), 396 (3.01), 505 (0.60)	29.5	0.418	2.1
		400 (2.42), 500 (0.80)	39.4	0.650	1.0

of these tautomeric systems was produced by ions Ba^{2+} , Ca^{2+} , and K^{+} .

Thus the obtained dibenzo(benzo)-18-crown-6-ether-imines of 5-hydroxy-2,3-diphenylbenzo-*[b]*furan-4-carbaldehyde and 5-hydroxy-2,3-tetramethylenebenzo-*[b]*furan-4-carbaldehyde are chemosensor tautomeric systems whose action originates from the shift in the benzoid-quinoid equilibrium resulting in the changes in the absorption and fluorescence spectra at their complexing with cations of alkali and alkaline earth metals.

EXPERIMENTAL

^1H NMR spectra were registered on a spectrometer Varian Unity-300 (300 MHz). As internal reference served residual signals of CHCl_3 (δ 7.25 ppm). Electronic absorption spectra were taken on a spectrophotometer Specord M-40, fluorescence spectra, on a spectrofluorimeter Hitachi 650-60. IR spectra were obtained on a spectrophotometer Specord 75IR (from mulls in mineral oil). Mass spectra were measured on MKh-1321A instrument.

Compounds **Ia–Id**, **Ic**, **IIIa–IIIc**, **IVb–IVd** were obtained by procedure [1].

6-tert-Butyl-5-hydroxy-2,3-tetramethylenebenzo-*[b]*furan-4-carbaldehyde [(benzo-18-crown-6)-4'-yl]imine (Ia) was prepared from 1 mmol of 6-tert-butyl-5-hydroxy-2,3-tetramethylenebenzo-*[b]*furan-4-carbaldehyde and 1 mmol of 4-aminobenzo-18-crown-6. Yield 57%, mp 125–126°C. IR spectrum, ν , cm^{-1} : 3500, 1610, 1580, 1500. ^1H NMR spectrum (CDCl_3), δ , ppm: 1.48 s (9H, 3CH_3), 1.82–1.98 m (4H, $2\text{CH}_2^{2,3}$), 2.71–2.87 m (4H, $2\text{CH}_2^{4,5}$), 3.68–4.25 m (20H, $10\text{CH}_2\text{O}$), 6.83–7.27 m (7H, H_{arom}), 7.45 s (1H, H7), 9.11 s (1H, =CH), 14.38 s (1H, OH). Found, %: C 68.26; H 7.43; N 2.35. $\text{C}_{33}\text{H}_{43}\text{NO}_8$. Calculated, %: C 68.14; H 7.45; N 2.41.

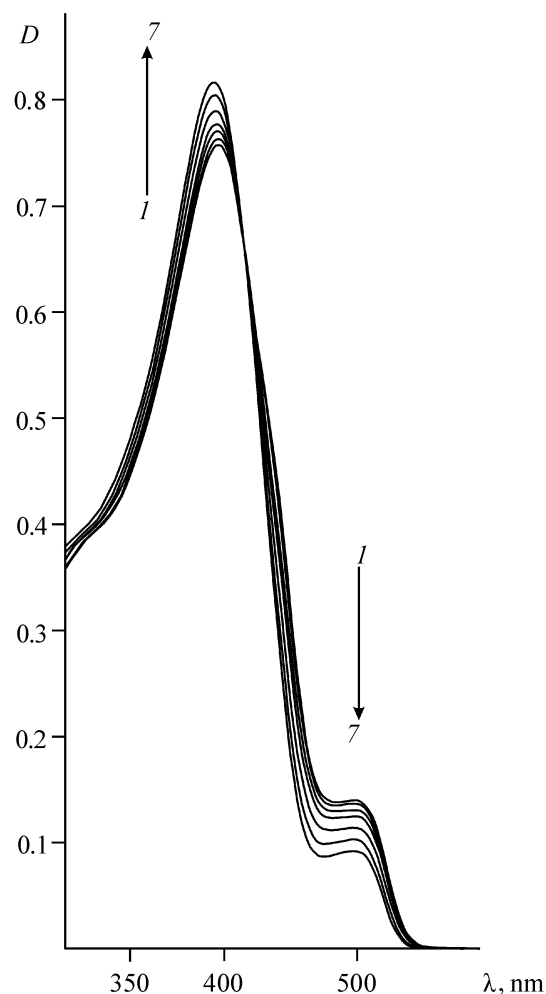
5-Hydroxy-2,3-tetramethylenebenzo-*[b]*furan-4-carbaldehyde[(benzo-18-crown-6)-4'-yl]imine (Ib) was prepared from 1 mmol of 5-hydroxy-2,3-tetramethylenebenzo-*[b]*furan-4-carbaldehyde and 1 mmol of 4-aminobenzo-18-crown-6. Yield 65%, mp 87–88°C. IR spectrum, ν , cm^{-1} : 3500, 1600, 1580, 1550, 1500. ^1H NMR spectrum (CDCl_3), δ , ppm: 1.86–1.99 m (4H, $2\text{CH}_2^{2,3}$), 2.74–2.90 m (4H, $2\text{CH}_2^{4,5}$), 4.66–4.25 m (20H, $10\text{CH}_2\text{O}$), 6.80–7.40 m (5H, H_{arom}), 9.10 s (1H, =CH), 13.67 s (1H, OH). Found, %: C 66.20; H 6.59; N 2.53. $\text{C}_{29}\text{H}_{35}\text{NO}_8$. Calculated, %: C 66.27; H 6.71; N 2.66.

6-Bromo-5-hydroxy-2,3-tetramethylenebenzo-*[b]*furan-4-carbaldehyde [(benzo-18-crown-6)-

Table 2. The decrease in content of quinoid tautomer (Δv_{B} , %) on addition to acetonitrile solutions of imines **Id–IVd** of cations of alkali and alkaline earth metals

Imine	Δv_{B} , %						
	Li^{+}	Na^{+}	K^{+}	Cs^{+}	Mg^{2+}	Ca^{2+}	Ba^{2+}
Id	0.0	9.1	18.2	12.5	7.3	29.0	29.2
IId	0.0	8.8	11.8	5.7	5.9	17.6	31.6
IIId	0.0	15.6	18.2	~6.0	0.0	18.8	25.0
IVd	0.0	15.5	19.0	~3.0	0.0	20.7	34.5

4'-yl]imine (Ic) was prepared from 1 mmol of 6-bromo-5-hydroxy-2,3-tetramethylenebenzo-*[b]*furan-4-carbaldehyde and 1 mmol of 4-aminobenzo-18-crown-6. Yield 70%, mp 108–109°C. IR spectrum, ν , cm^{-1} : 3400, 1610, 1510. ^1H NMR spectrum (CDCl_3), δ , ppm: 1.83–2.00 m



Electron absorption spectra of compound **IVd** in acetonitrile (c $2.5 \times 10^{-5} \text{ mol l}^{-1}$) before (**I**) and after addition of $\text{Ba}(\text{ClO}_4)_2$: 0.5×10^{-5} (**2**), 1×10^{-5} (**3**), 1.5×10^{-5} (**4**), 2×10^{-5} (**5**), 2.5×10^{-5} (**6**), 5×10^{-5} (**7**) mol l^{-1} .

(4H, $2\text{CH}_2^{2,3}$), 2.70–2.89 m (4H, $2\text{CH}_2^{1,4}$), 3.62–4.23 m (20H, $10\text{CH}_2\text{O}$), 6.82–6.98 m (3H, H_{arom}), 7.68 s (1H, H^7), 9.02 s (1H, =CH), 15.08 s (1H, OH). Found, %: C 57.58; H 5.60; N 2.40. $\text{C}_{29}\text{H}_{34}\text{BrNO}_8$. Calculated, %: C 57.62; H 5.67; N 2.32.

5-Hydroxy-6-nitro-2,3-tetramethylenebenzo[b]furan-4-carbaldehyde [(benzo-18-crown-6)-4'-yl]imine (Id) was prepared from 1 mmol of 5-hydroxy-6-nitro-2,3-tetramethylenebenzo[b]furan-4-carbaldehyde and 1 mmol of 4-aminobenzo-18-crown-6. Yield 80%, mp 107–108°C. IR spectrum, ν , cm^{-1} : 3450, 1600, 1500. ^1H NMR spectrum (CDCl_3), δ , ppm: 1.91–2.03 m (4H, $2\text{CH}_2^{2,3}$), 2.78–2.89 m (4H, $2\text{CH}_2^{1,4}$), 3.64–4.24 m (20H, $10\text{CH}_2\text{O}$), 6.86–6.98 m (3H, H_{arom}), 8.22 s (1H, H^7), 9.01 d (1H, =CH, J 2.8 Hz), 16.47 d (1H, OH + NH, J 2.8 Hz). Found, %: C 61.11; H 5.92; N 4.92. $\text{C}_{29}\text{H}_{34}\text{N}_2\text{O}_{10}$. Calculated, %: C 61.04; H 6.01; N 4.91.

[(Benzo-18-crown-6)-4'-yl]imines of 5-hydroxy- and 5-hydroxy-6-nitro-2,3-diphenylbenzo[b]furan-4-carbaldehydes **Ib** and **IId** were obtained by procedure [10].

6-Bromo-5-hydroxy-2,3-diphenylbenzo[b]furan-4-carbaldehyde (benzo-18-crown-6)-4'-yl]imine (IIc) was prepared from 1 mmol of 6-bromo-5-hydroxy-2,3-diphenylbenzo[b]furan-4-carbaldehyde and 1 mmol of 4-aminobenzo-18-crown-6. Yield 67%, mp 172°C. IR spectrum, ν , cm^{-1} : 3500, 1600, 1580, 1500. ^1H NMR spectrum (CDCl_3), δ , ppm: 3.65–4.20 m (20H, $10\text{CH}_2\text{O}$), 6.36–7.63 m (13H, H_{arom}), 7.87 s (1H, H^7), 8.30 s (1H, =CH), 15.78 s (1H, OH). Found, %: C 63.11; H 5.25; N 1.96. $\text{C}_{37}\text{H}_{36}\text{BrNO}_8$. Calculated, %: C 63.25; H 5.16; N 1.99.

5-Hydroxy-6-tert-butyl-2,3-tetramethylenebenzo[b]furan-4-carbaldehyde [(dibenzo-18-crown-6)-4'-yl]imine (IIIa) was prepared from 1 mmol of 5-hydroxy-6-tert-butyl-2,3-tetramethylenebenzo[b]furan-4-carbaldehyde and 1 mmol of 4-aminodibenzo-18-crown-6. Yield 62%, mp 108–109°C. IR spectrum, ν , cm^{-1} : 3450, 1620, 1570. ^1H NMR spectrum (CDCl_3), δ , ppm: 1.48 s (9H, 3CH_3), 1.84–1.96 m (4H, $2\text{CH}_2^{2,3}$), 2.70–2.84 m (4H, $2\text{CH}_2^{1,4}$), 4.02–4.25 m (16H, $8\text{CH}_2\text{O}$), 6.83–6.95 m (7H, H_{arom}), 7.44 s (1H, H^7), 9.10 s (1H, =CH), 14.39 s (1H, OH). Mass spectrum: m/z 629 $[M]^+$. Found, %: C 70.45; H 6.90; N 2.33. $\text{C}_{37}\text{H}_{43}\text{NO}_8$. Calculated, %: C 70.57; H 6.88; N 2.22.

5-Hydroxy-2,3-tetramethylenebenzo[b]furan-4-carbaldehyde [(dibenzo-18-crown-6)-4'-yl]imine (IIIb) was prepared from 1 mmol of 5-hydroxy-2,3-tetra-

methylenebenzo[b]furan-4-carbaldehyde and 1 mmol of 4-aminodibenzo-18-crown-6. Yield 73%, mp 183–184°C. IR spectrum, ν , cm^{-1} : 3400, 1680, 1610, 1590, 1570, 1510. ^1H NMR spectrum (CDCl_3), δ , ppm: 1.84–1.98 m (4H, $2\text{CH}_2^{2,3}$), 2.71–2.87 m (4H, $2\text{CH}_2^{1,4}$), 4.03–4.24 m (16H, $8\text{CH}_2\text{O}$), 6.80–7.39 m (9H, H_{arom}), 9.09 s (1H, =CH), 13.70 s (1H, OH). Mass spectrum: m/z 573 $[M]^+$. Found, %: C 69.09; H 6.10; N 2.53. $\text{C}_{33}\text{H}_{35}\text{NO}_8$. Calculated, %: C 69.10; H 6.15; N 2.44.

6-Bromo-5-hydroxy-2,3-tetramethylenebenzo[b]furan-4-carbaldehyde [(dibenzo-18-crown-6)-4'-yl]imine (IIIc) was prepared from 1 mmol of 6-bromo-5-hydroxy-2,3-tetramethylenebenzo[b]furan-4-carbaldehyde and 1 mmol of 4-aminodibenzo-18-crown-6. Yield 85%, mp 205–206°C. IR spectrum, ν , cm^{-1} : 3400, 1610, 1590, 1560, 1510. ^1H NMR spectrum (CDCl_3), δ , ppm: 1.84–1.99 m (4H, $2\text{CH}_2^{2,3}$), 2.70–2.86 m (4H, $2\text{CH}_2^{1,4}$), 4.01–4.23 m (16H, $8\text{CH}_2\text{O}$), 6.83–6.94 m (7H, H_{arom}), 7.67 s (1H, H^7), 9.02 s (1H, =CH), 15.11 s (1H, OH). Mass spectrum: m/z 651 $[M]^+$. Found, %: C 60.80; H 5.36; N 2.02. $\text{C}_{33}\text{H}_{34}\text{NO}_8$. Calculated, %: C 60.74; H 5.25; N 2.15.

5-Hydroxy-6-nitro-2,3-tetramethylenebenzo[b]furan-4-carbaldehyde [(dibenzo-18-crown-6)-4'-yl]imine (IIIId) was prepared from 1 mmol of 5-hydroxy-6-nitro-2,3-tetramethylenebenzo[b]furan-4-carbaldehyde and 1 mmol of 4-aminodibenzo-18-crown-6. Yield 78%, mp 222°C. IR spectrum, ν , cm^{-1} : 3400, 1590, 1500. ^1H NMR spectrum (CDCl_3), δ , ppm: 1.87–2.01 m (4H, $2\text{CH}_2^{2,3}$), 2.77–2.85 m (4H, $2\text{CH}_2^{1,4}$), 4.00–4.23 m (16H, $8\text{CH}_2\text{O}$), 6.82–6.96 m (7H, H_{arom}), 8.24 s (1H, H^7), 9.02 d (1H, =CH, J 2.4 Hz), 16.49 d (1H, OH+NH, J 2.4 Hz). Mass spectrum: m/z 618 $[M]^+$. Found, %: C 64.21; H 5.44; N 4.50. $\text{C}_{33}\text{H}_{34}\text{N}_2\text{O}_{10}$. Calculated, %: C 64.07; H 5.54; N 4.53.

5-Hydroxy-2,3-diphenylbenzo[b]furan-4-carbaldehyde [(dibenzo-18-crown-6)-4'-yl]imine (IVb) was prepared from 1 mmol of 5-hydroxy-2,3-diphenylbenzo[b]furan-4-carbaldehyde and 1 mmol of 4-aminodibenzo-18-crown-6. Yield 66%, mp 159–160°C. IR spectrum, ν , cm^{-1} : 3400, 1630, 1610, 1520, 1510. ^1H NMR spectrum (CDCl_3), δ , ppm: 4.00–4.24 m (16H, $8\text{CH}_2\text{O}$), 6.36–7.59 m (19H, H_{arom}), 8.39 s (1H, =CH), 14.32 s (1H, OH). Mass spectrum: m/z 671 $[M]^+$. Found, %: C 73.25; H 5.53; N 2.13. $\text{C}_{41}\text{H}_{37}\text{NO}_8$. Calculated, %: C 73.31; H 5.55; N 2.09.

6-Bromo-5-hydroxy-2,3-diphenylbenzo[b]furan-4-carbaldehyde [(dibenzo-18-crown-6)-4'-yl]imine (IVc) was prepared from 1 mmol of 6-bromo-5-hydroxy-

2,3-diphenylbenzo[*b*]furan-4-carbaldehyde and 1 mmol of 4-aminodibenzo-18-crown-6. Yield 71%, mp 139°C. IR spectrum, ν , cm^{-1} : 3400, 1600, 1590, 1500. ^1H NMR spectrum (CDCl_3), δ , ppm: 3.98–4.24 m (16H, $8\text{CH}_2\text{O}$), 6.34–7.63 m (17H, H_{arom}), 7.88 s (1H, H^7), 8.27 s (1H, =CH), 15.81 s (1H, OH). Found, %: C 65.65; H 4.67; N 1.96. $\text{C}_{41}\text{H}_{36}\text{BrNO}_8$. Calculated, %: C 65.60; H 4.83; N 1.87.

5-Hydroxy-6-nitro-2,3-diphenylbenzo[*b*]furan-4-carbaldehyde [(dibenzo-18-crown-6)-4'-yl]imine (IVd) was prepared from 1 mmol of 5-hydroxy-6-nitro-2,3-diphenylbenzo[*b*]furan-4-carbaldehyde and 1 mmol of 4-aminodibenzo-18-crown-6. Yield 75%, mp 189–190°C. IR spectrum, ν , cm^{-1} : 3450, 1610, 1580, 1570, 1500. ^1H NMR spectrum (CDCl_3), δ , ppm: 3.98–4.23 m (16H, $8\text{CH}_2\text{O}$), 6.35–8.24 m (17H, H_{arom}), 8.24 d (1H, =CH, J 5.3 Hz), 8.42 C (1H, H^7), 16.87 d (1H, OH+NH, J 5.3 Hz). Found, %: C 68.59; H 5.10; N 4.03. $\text{C}_{41}\text{H}_{36}\text{N}_2\text{O}_{10}$. Calculated, %: C 68.71; H 5.06; N 3.91.

The study was carried out under a financial support of Ministry of Education and Science of the Russian Federation (RNP.5592 and RNP.2.2.1.1/2348), Foundation for support of domestic science, of a grant from Ministry of Education and Science of the Russian Federation/CRDF (RNP.2.2.2.3.16012; REC-004), and of a Council for grants of the President of the Russian Federation (program supporting the Leading scientific schools, grant 363.2008.3).

REFERENCES

1. Shepelenko, E.N., Tsukanov, A.V., Revinskii, Yu.V., Dubonosov, A.D., Bren', V.A., and Minkin, V.I., *Zh. Org. Khim.*, 2007, vol. 43, p. 561.
2. Minkin, V.I., Griбанова, T.N., Dubonosov, A.D., Bren', V.A., Minyaev, R.M., Shepelenko, E.N., Tsukanov, A.V., *Ros. Khim. Zh.*, 2004, vol. 48, p. 30.
3. Tsvadze, A.Yu., Varnek, A.A., and Khutorskii, V.E., *Koordinatsionnye soedineniya metallov s kraunligandami* (Coordination Compounds of Metals with Crown-Ethers), Moscow: Nauka, 1991, 397 p.
4. Islam, M.S., Pethrick, R.A., Pugh, D., and Wilson, M.J., *J. Chem. Soc., Faraday Trans.*, 1997, vol. 93, p. 387.
5. Rybalkin, V.P., Bushkov, A.Ya., Bren', V.A., and Minkin, V.I., *Zh. Org. Khim.*, 1986, vol. 22, p. 565.
6. Rybalkin, V.P., Shepelenko, E.N., Popova, L.L., Dubonosov, A.D., Bren', V.A., and Minkin, V.I., *Zh. Org. Khim.*, 1996, vol. 32, p. 101.
7. Brown, N.M.D. and Nonhebel, D.C., *Tetrahedron*, 1968, vol. 24, p. 5655.
8. Callan, J.F., de, Silva, A.P., and Magri, D.C., *Tetrahedron*, 2005, vol. 61, p. 8551.
9. Knyazhanskii, M.I. and Metelitsa, A.V., *Fotoinitsirovannye protsessy v molekulakh azometinov i ikh strukturykh analogov* (Photoinitiated Processes in Azomethine Molecules and in Their Structural Analogs), Rostov-na-Donu: Izd. RGU, 1992, 208 p.
10. Dubonosov, A.D., Minkin, V.I., Bren, V.A., Shepelenko, E.N., Tsukanov, A.V., Starikov, A.G., and Borodkin, G.S., *Tetrahedron*, 2008, vol. 64, p. 3160.