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Tautomeric crown-containing chemosensors for alkali-earth metal cations

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Abstract

Crown-containing arylimines of 5-hydroxy- and 5-hydroxy-6-nitro-2,3-diphenylbenzo[*b*]furan-4-carbaldehydes were synthesized and their structure, spectral, luminescent, and complexing properties were studied by means of ^{1}H and ^{13}C NMR, IR, UV, and mass-spectrometry. In solution, these compounds exist as equilibrium mixtures of benzenoid and quinoid tautomers. The relative concentration of the quinoid form increases in the order of solvents: toluene, acetonitrile, 2-propanol, chloroform. The presence in the benzo[*b*]furan moiety of a strong withdrawing 6-NO_2 group favors stabilization of the quinoid tautomer. This finding is in accord with the results of the DFT B3LYP/6-311++g(d,p) calculations. Complexation of 5-hydroxy-6-nitro-2,3-diphenyl-1-benzofuran-4-carbaldehyde crown-containing imines with alkali and alkali-earth metal ions shifts the tautomeric equilibrium to the quinoid forms and is accompanied by blue shifts of the emission spectra. The Schiff bases obtained represent a new type of fluorescent tautomeric chemosensor for Mg^{2+}, Ca^{2+} (benzo-15-crown-5 derivative), and Ba^{2+} (benzo-18-crown-6 derivative) displaying diagnostic changes in both absorption and emission spectra.

Keywords: Schiff bases; Crown-ethers; Tautomerism; Quantum chemical calculations; Chemosensors; Alkali-earth metal ions

1. Introduction

The tautomerism of the Schiff bases derived from aromatic *o*-hydroxyaldehydes has been studied in much detail.[1–7] The rearrangement of these compounds due to the intramolecular proton transfer occurring in the ground or electron excited states was found to be interesting for implementation in various devices and fluorescent chemosensors for metal ions.[8–10] In the latter case, a crown-ether moiety must be attached to the arylimine fragment of the Schiff base. Two main types of fluorogenic chemosensors are based on the PET (Photo-induced Electron Transfer) and ICT (Internal Charge Transfer) mechanisms.[11,12] The former mechanism involves electron transfer from the highest occupied molecular orbital (HOMO) of a receptor to the HOMO of a signaling moiety in the electronic excited state thus almost completely suppressing fluorescent properties of the system. Coordination of a cation to the donor center of the receptor reduces the HOMO energy level of the PET sensor so that it becomes lower than that of the HOMO energy level of the signaling (fluorophore) moiety. As a result, the fluorescence intensity considerably increases while the position of the emission band remains virtually unchanged. ICT systems are usually of donor–acceptor type with a receptor moiety playing the role of either a donor or an acceptor component. By contrast with PET systems, those susceptible of ICT behavior after coordination of a cation undergo essential electron density redistribution, leading to pronounced shifts of absorption and emission bands accompanied with a slight change in the emission intensity.

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In the present work, we report on the synthesis of a novel type of tautomeric chemosensors (crown-containing Schiff bases of 5-hydroxy- and 5-hydroxy-6-nitro-2,3-diphenylbenzo[*b*]furan-4-carbaldehydes) and investigation into their structure, spectral, luminescent, and complexing properties as manifested by simultaneous changes in the absorption and emission spectra.

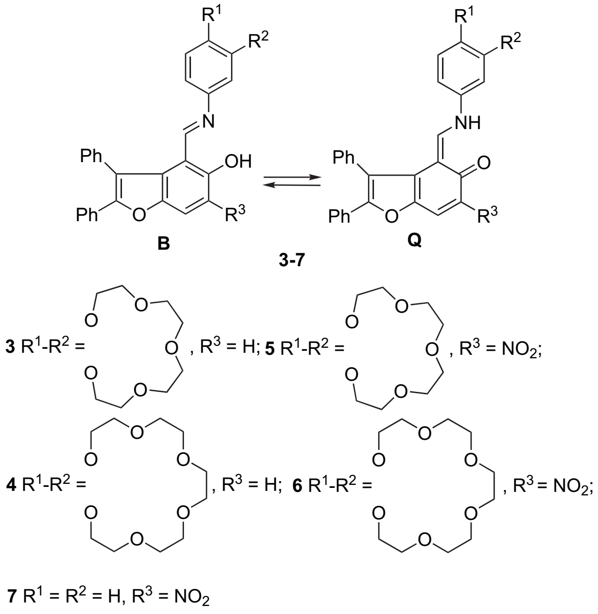
2. Results and discussion

2.1. Synthesis

5-Hydroxy-2,3-diphenylbenzo[*b*]furan-4-carbaldehyde **1** was prepared by coupling 5-hydroxy-2,3-diphenylbenzo[*b*]furan[13] with ethyl *N*-phenylformimidate and subsequent treatment of the reaction mixture with dilute hydrochloric acid. 5-Hydroxy-6-nitro-2,3-diphenylbenzo[*b*]furan-4-carbaldehyde **2** was synthesized by nitration of **1** with concentrated nitric acid. Condensation of compounds **1** and **2** with the corresponding amines afforded Schiff bases **3–7** (Scheme 1).

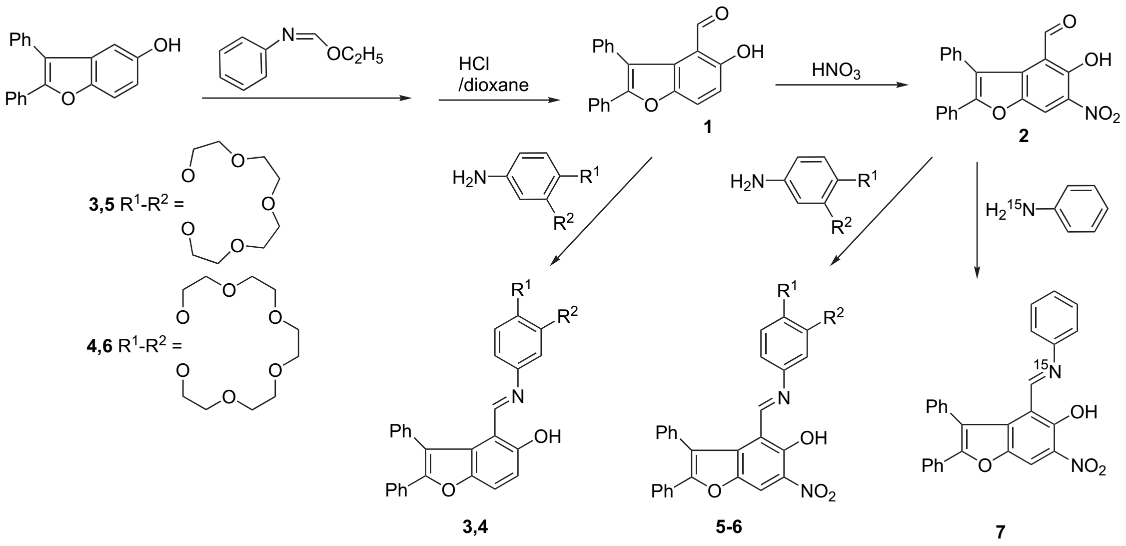
The electronic absorption spectra of **3** and **4** in solvents of different polarity (chloroform, toluene, acetonitrile, DMSO) reveal a broad absorption band at 370–375 nm. In CDCl$_3$, protons of the methine and hydroxy groups of these compounds in the ^{1}H NMR spectra appear as sharp singlets at 8.4 and 14.3 ppm, respectively. According to the earlier findings[14,15] these data indicate that compounds **3** and **4** exist in the solution in their benzenoid tautomeric form **B** (Scheme 2). By contrast, the absorption spectra of compounds **5–7** with an electron-withdrawing NO$_2$ group *o*-positioned to the hydroxyl-group display a long-wavelength band with a maximum centered around 500 nm (Fig. 1).

In the ^{1}H NMR spectra of **5–7**, the proton O···H···N signal is shifted downfield to ~16.9 ppm and split into a doublet (^3J=5.5 Hz for compounds **5** and **6**) due to coupling with the methine group protons. These observations point to the presence of the quinoid tautomers **Q** of **5–7** in chloroform solution (Scheme 2).[14]



Scheme 2. Benzenoid–quinoid tautomeric equilibria of Schiff bases **3–7**.

The value of the NH–CH coupling constant is proportional to the percentage of tautomer **Q** in the equilibrium mixture, which was estimated as ~44% (by using the value ^3J~12.5 Hz corresponding to the 100% content of the quinoid tautomers[14]). Based on the calculated concentration of the form **Q** in chloroform solution the molar extinction coefficient (ε_{500}) of the quinoid tautomers of **5** and **6** was evaluated as ε_{500}~2.2×10^4 L mol^{-1} cm^{-1}. These findings are in accord with the results obtained on the basis of ^{1}H NMR spectra of a model crown-free ^{15}N-isotopomeric compound **7**. In CDCl$_3$, the signal of the ^{15}NH proton is split into a quartet characterized by spin–spin coupling constants $^1J_{NH}$=41.3 Hz and $^2J_{HCN}$=5.7 Hz, respectively. Considering that the $^1J_{NH}$ coupling constant for the Schiff bases existing in solution exclusively in the quinoid tautomeric form is equal to



Scheme 1. Synthesis of Schiff bases **3–7**.

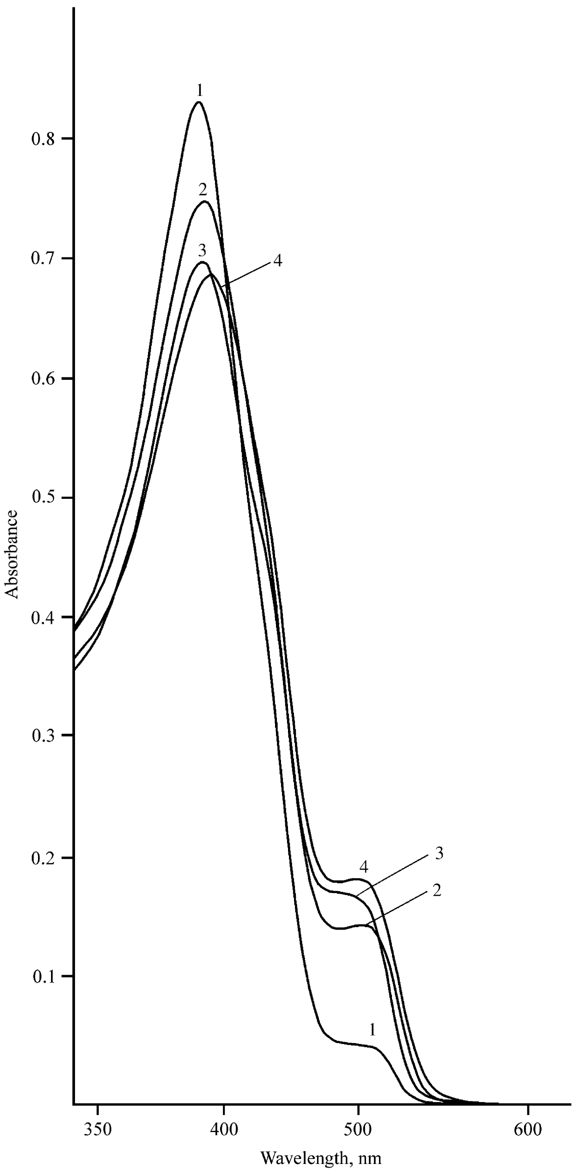


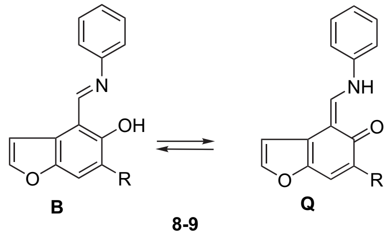
Figure 1. Absorption spectra of **5** (c=2.5×10^{-5} M) in toluene (1), acetonitrile (2), isopropanol (3), DMSO (4).

89 Hz,[15,16] the content of **7Q** in chloroform is estimated as ∼46%. This value agrees well with that (45%) determined by the method of Brown and Nonhebel.[14] By comparison of ^{1}H NMR and absorption spectroscopy data, the molar extinction coefficient (ε_{505}) of **7Q** in chloroform was evaluated as 2.0×10^4 L mol^{-1} cm^{-1}.

The content of the quinoid tautomers **Q** of Schiff bases **5**−**7** decreases in the order of solvents: chloroform, 2-propanol, acetonitrile, toluene, in compliance with the decrease in the intensity of the long-wavelength absorption band (Fig. 1).

2.2. Quantum chemical calculations

In order to analyze the influence of 6-NO$_2$ group on the structure and relative stability of the benzenoid and quinoid forms of **3**−**6** in solvents of different polarity, quantum chemical calculations using the DFT (B3LYP/6-311++g(d,p)) method were carried out.[17] The solvent effect was taken into account in the framework of the IEFPCM model.[18] Schiff bases **8** and **9** were selected as model compounds (Scheme 3). All structures were calculated with full optimization of their geometry in the gas phase and in solution. The stationary points (local minima and transition state structures) of the potential energy surfaces (PES) were identified on the basis of the force constant matrices. The calculated structures of the tautomers **8Q** and **8B** are shown in Figure 2. Both tautomeric forms are characterized by strong chelate type intramolecular H-bonds with short O···N distances, 2.592 and 2.626 Å, respectively. Proton transfer along the H-bond bridges occurs with very low energy barriers (2.1−2.9 kcal mol^{-1}) through the transition state structure **8T**. Benzenoid tautomer **8B** is the most stable form of **8** in the gas phase and in toluene or acetonitrile. Solvation reduces the energy gap between the tautomers **8B** and **8Q** from 3.1 to 1.5 kcal mol^{-1} (Table 1).



8-9

8 R = H; **9** R = NO$_2$

Scheme 3. Model compounds for quantum chemical calculations.

As stems from the calculations, a strong electron-withdrawing 6-NO$_2$ group greatly affects the position of the benzenoid−quinoid equilibrium. In toluene, the tautomeric forms **9B** and **9Q** (Fig. 2) are close in energy, but in acetonitrile solution, the quinoid form **9Q** is 1.0 kcal mol^{-1} preferable with respect to the benzenoid structure. These trends, revealed by quantum chemical calculations are in accord with the experimental data in Section 2.1.

2.3. Metal ion recognition

The intensity of the longest wavelength absorption band at 510 nm inherent in the quinoid forms of **5** and **6** is sharply decreased on addition of alkali and alkaline-earth metal ions to their solutions (Fig. 3), with signals shifting from the quinoid to the benzenoid form (Scheme 4).

The cation-induced changes in the absorption spectra are notably stronger for alkali-earth metal ions as compared with those initiated by alkali metal ions. Compounds **5** and **6** are particularly responsive to Mg^{2+} and Ba^{2+} ions, respectively. No significant spectral changes were observed for the case of crown-free analogue **7**.

That the complexation of cations occurs within the crown-ether cavity stems from the analysis of the NMR spectra of the solutions of **5** and **6** in the presence of metal ions. In

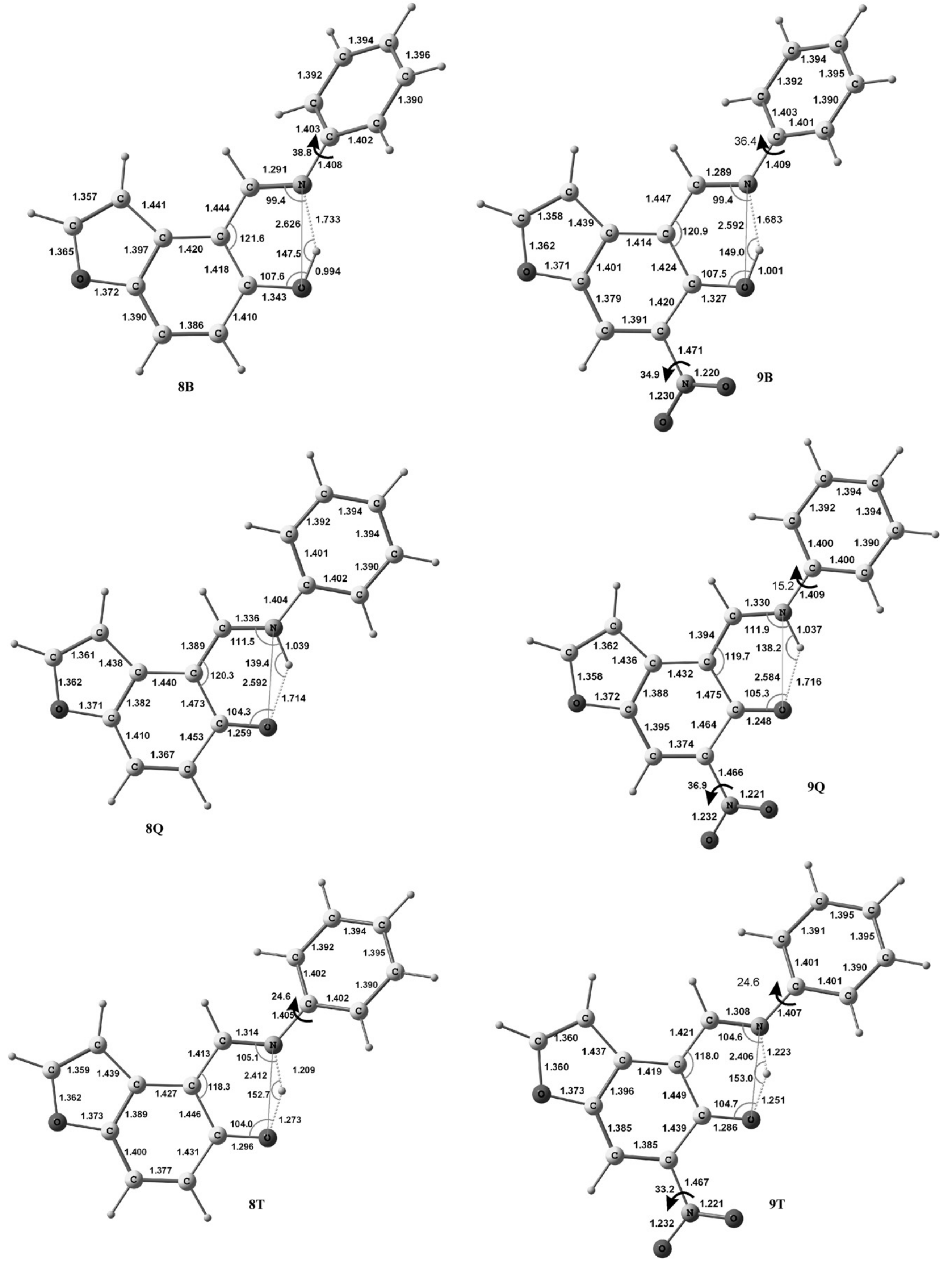


Figure 2. The gas phase geometries of **8B**, **9B**, **8Q**, **9Q**, **8T**, and **9T** calculated by the DFT B3LYP/6-311++g(d,p) method. Bond lengths are given in angstrom units, angles—in degrees.

Table 1
The DFT B3LYP/6-311++g(d,p) calculated total energies ($\Delta E_{\mathrm{tot\ ZPE}}$) with the account for zero harmonic vibration energies, relative energies (ΔE_{ZPE}), ω^1—lowest vibration frequencies of the structures **8** and **9**

Structure	Solvent	$E_{\mathrm{tot\ ZPE}}$ (a.e.)	ΔE_{ZPE} (kcal mol^{-1})	ω^1 (cm^{-1})
8Q	Gas	−783.386602	3.1	14
8B		−783.391465		35
8T		−783.386773	2.9	−1174
8Q	Toluene	−783.390459	2.4	12
8B		−783.394323		33
8T		−783.390154	2.6	−1189
8Q	Acetonitrile	−783.395602	1.5	15
8B		−783.398051		29
8T		−783.394647	2.1	−1208
9Q	Gas	−987.939335	1.3	18
9B		−987.941474		32
9T		−987.939104	1.5	−1173
9Q	Toluene	−987.946514	0.4	21
9B		−987.947098		31
9T		−987.945596	0.9	−1182
9Q	Acetonitrile	−987.955567		20
9B		−987.954024	1.0	30
9T		−987.953619	1.2	−1179

CD_3CN–nitrobenzene-d_6 (1:1 v/v) solution the NH and methylene doublets (^3J=3.5 Hz) of **6** collapse to a broad singlet upon addition of a twofold molar excess of $Ba(ClO_4)_2$ thus signaling the decrease of the equilibrium content of the quinoid tautomer. Complexation leads to downfield shift of signals of crown-ether protons ($\Delta\delta\sim$0.35–0.40 ppm), protons of the benzene ring ($\Delta\delta\sim$0.15–0.20 ppm), and methine proton ($\Delta\delta\sim$0.10 ppm) (Fig. 4). This observation serves as a supportive evidence for insertion of the cation into the crown-ether cavity.[19,20]

The results obtained indicate that binding of cations with a crown-ether moiety is an important factor affecting the position of the benzenoid–quinoid equilibrium.

Illumination of acetonitrile solutions of **5** and **6** by the 390 nm light excites the fluorescence at 580 nm with large Stokes shifts ($\Delta\nu$=7814 and 7734 cm^{-1}, respectively), which are due to intramolecular photo-induced proton transfer.[10] Addition of Mg^{2+} and Ca^{2+} ions to a solution of **5** in acetonitrile brings about a blue shift of the emission spectra ($\Delta\nu$=6887 cm^{-1}) whereas the presence of other alkali and alkali-earth metal ions does not have any pronounced effects on the fluorescence spectra of this Schiff base (Fig. 5).

Compound **6**, with a larger crown ring, shows in acetonitrile solution, selective fluorescence Stokes shift only for the case of complexation with Ba^{2+} ions ($\Delta\nu$=7122 cm^{-1}). No significant changes in intensity of fluorescence were observed for **5** and **6** with these metal ions. These data allow Schiff bases **5** and **6** to be considered as a novel type of fluorescent tautomeric chemosensors distinct from PET systems (in which increasing fluorescence intensity occurs without changes in the wavelength) and from ICT systems (characterized by simultaneous shifts in the position of emission and absorption bands).

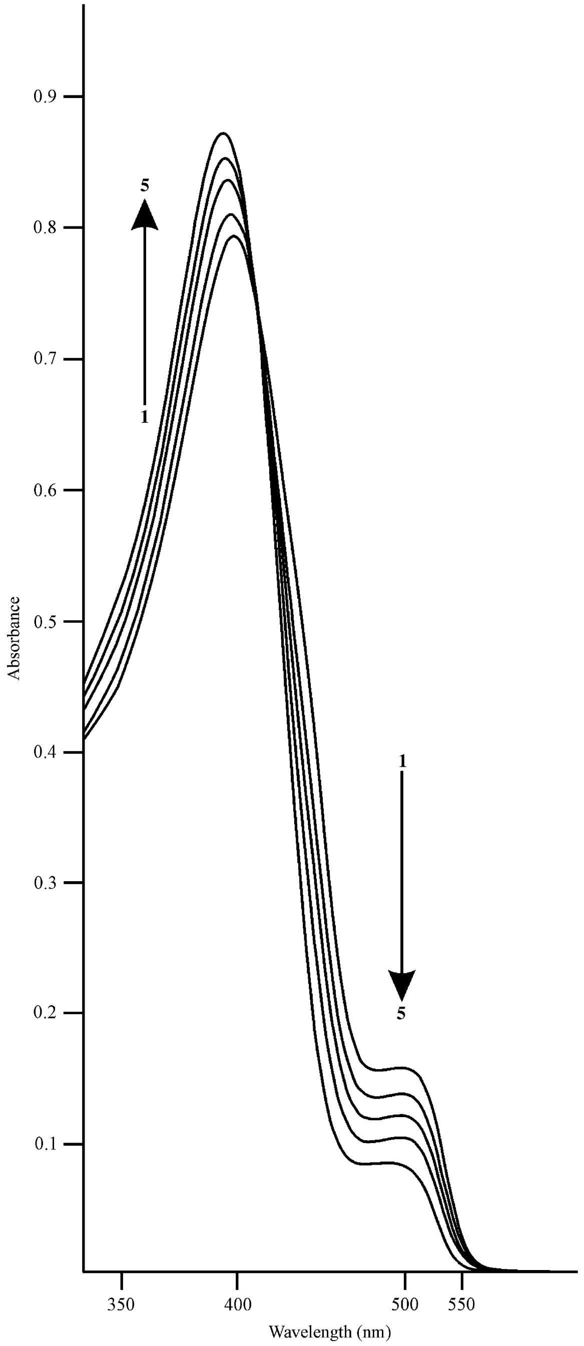
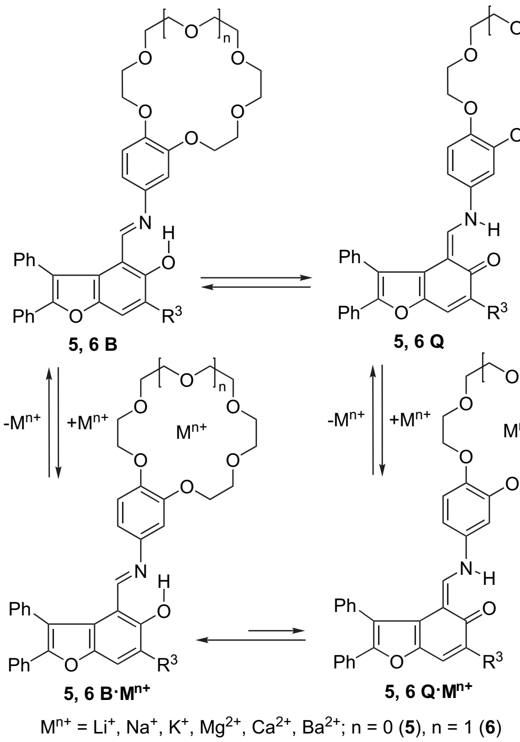


Figure 3. Effect of $Mg(ClO_4)_2$ on the absorption spectrum of **5** (c=2.5×10^{-5} M) in acetonitrile: (1) 0 μM, (2) 25 μM, (3) 50 μM, (4) 100 μM, (5) 250 μM of $Mg(ClO_4)_2$.

3. Conclusions

In solutions of chloroform, 2-propanol, acetonitrile, toluene crown-containing imines of 5-hydroxy- and 5-hydroxy-6-nitro-2,3-diphenylbenzo[*b*]furan-4-carbaldehydes exist as equilibrium mixtures of benzenoid and quinoid tautomers. Introduction of a strong electron-withdrawing nitro group into benzo[*b*]furan moiety increases the equilibrium content of the quinoid form. By contrast, binding of alkali and alkali-earth cations with a crown-ether moiety shifts the benzenoid–quinoid equilibrium



Scheme 4. Complexation of **5** and **6** with metal ions.

to the benzenoid form and is accompanied by blue shifts of the emission spectra. Schiff bases **5** and **6** represent a new type of tautomeric fluorescent chemosensors for Mg^{2+}, Ca^{2+} (**5**), and Ba^{2+} (**6**) ions as manifested by substantial lowering of long-wavelength ('quinoid') maxima intensity (without shifting their location) with simultaneous blue shifts of the emission spectra.

4. Experimental

4.1. General

The ^1H and ^{13}C NMR spectra were recorded on a Varian Unity 300 spectrometer. IR spectra in Nujol were measured using a Specord 75IR spectrometer. UV–vis absorption spectra in CH_3CN were obtained with a Specord M-40 spectrophotometer. Alkali metal ions were added to solutions as iodides and alkali-earth metal ions—as perchlorates. Fluorescence emission and excitation spectra were recorded on a Hitachi 650-60 spectrofluorimeter. Mass spectra were measured with a MX-1321A spectrometer.

4.2. Synthesis

4.2.1. 5-Hydroxy-2,3-diphenylbenzo[b]furan-4-carbaldehyde (1)

A mixture of 5-hydroxy-2,3-diphenylbenzo[*b*]furan[13] (10 g, 35 mmol) and ethyl *N*-phenylformimidate (15 ml) was kept for 6 h at 170–180 °C. Dioxane (100 ml) was then added, diluted with 18% HCl (40 ml) and solution obtained was kept for 10–15 min at 60–70 °C. The reaction mixture was poured into water (100 ml). The crude product was filtered, dried, and purified by recrystallization from toluene. Yield 48%. Mp 186–187 °C. IR ν_{max} (Nujol): 3420, 1630, 1605, 1580. ^1H NMR (300 MHz, $CDCl_3$) δ 6.93–7.71 (m, 12H, Ar–H), 9.58 (s, 1H, CHO), 12.02 (s, 1H, OH). ^{13}C NMR (300 MHz, $CDCl_3$) δ 112.86,

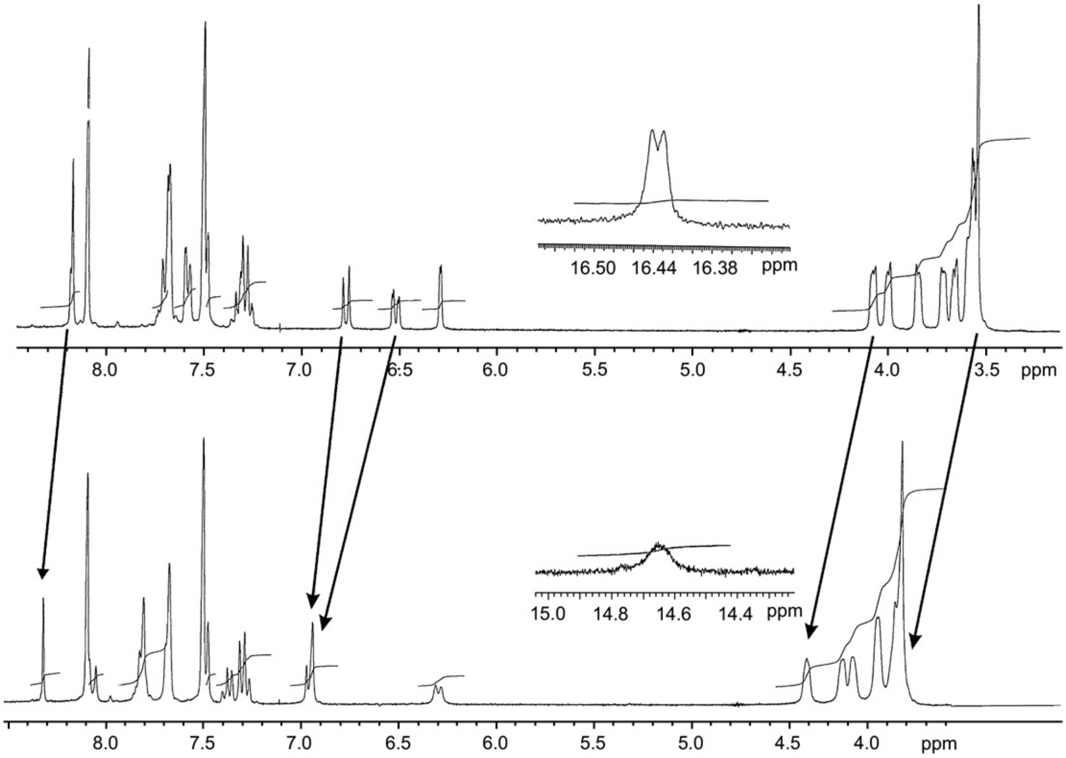


Figure 4. Changes in ^1H NMR spectra of **6** in CD_3CN–nitrobenzene-d_6 after addition of $Ba(ClO_4)_2$.

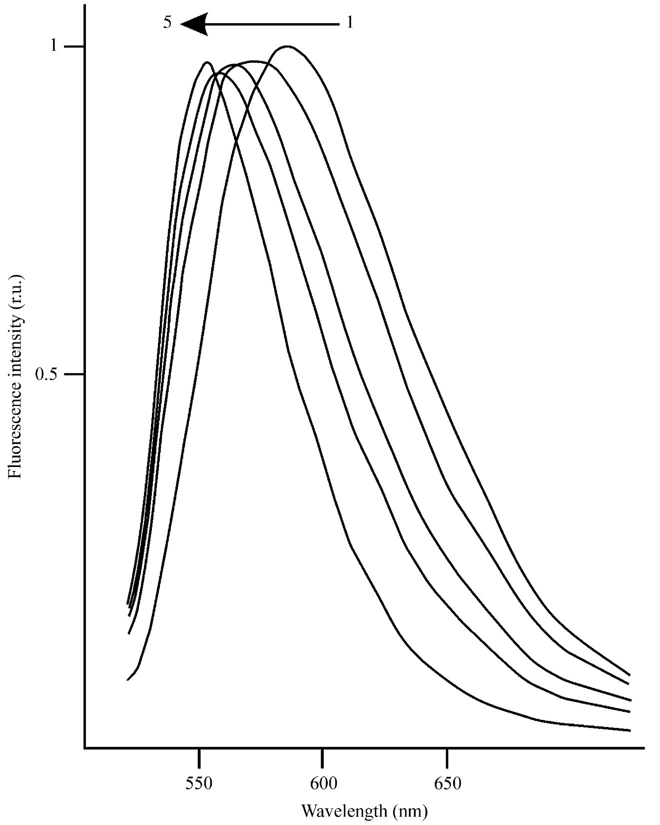


Figure 5. Changes in fluorescent spectra of **5** (c=2×10^{-5} M) during titration of its acetonitrile solution with $Mg(ClO_4)_2$: (1) 0 μM, (2) 14 μM, (3) 20 μM, (4) 40 μM, (5) 200 μM of $Mg(ClO_4)_2$.

114.57, 117.29, 120.25, 126.71, 128.49, 128.80, 128.83, 129.91, 129.98, 130.20, 130.80, 134.18, 147.46, 153.72, 160.92, 193.51. MS (EI): *m/z* 314 $[M]^+$. Anal. Calcd for $C_{21}H_{14}O_3$: C, 80.24; H, 4.49. Found: C, 80.12; H, 4.47.

*4.2.2. 5-Hydroxy-6-nitro-2,3-diphenylbenzo[b]furan-4-carbaldehyde (**2**)*

A solution of 70% nitric acid (2 ml) in acetic acid (10 ml) was added over a period 30 min to 5-hydroxy-2,3-diphenylbenzo[*b*]-furan-4-carbaldehyde (4.4 g, 12.2 mmol) in a mixture of acetic anhydride–acetic acid (1:1 v/v) with stirring at 0 °C. The reaction mixture was kept at the same temperature for 2 h and poured into water. The residue was filtered, dried, and purified by recrystallization from 1-butanol–toluene mixture (1:1 v/v). Yield 34%. Mp 218–219 °C. IR ν_{max} (Nujol): 3400, 1630, 1610, 1510 (C═C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28–7.60 (m, 10H, Ar–H), 8.53 (s, 1H, H^7), 9.62 (s, 1H, CHO), 13.21 (s, 1H, OH). MS (EI): *m/z* 359 $[M]^+$. Anal. Calcd for $C_{21}H_{13}NO_5$: C, 70.19; H, 3.65; N, 3.90. Found: C, 70.34; H, 3.57; N, 3.85.

*4.2.3. 4-[(6,7,9,10,12,13,15,16-Octahydro-5,8,11,14,17-pentaoxabenzocyclopentadecen-2-ylimino)methyl]-2,3-diphenylbenzo[b]furan-5-ol (**3**)*

The 2-propanol solution (20 ml) of 4-aminobenzo-15-crown-5 (283 mg, 1 mmol) with 5-hydroxy-2,3-diphenylbenzo[*b*]furan-4-carbaldehyde **1** (314 g, 1 mmol) was heated under reflux for 0.5 h and cooled to room temperature. The precipitate obtained was filtered and then washed with 2-propanol. The crude product was purified by recrystallization from 2-propanol to afford 430 mg (74%) product as a yellow solid. Mp 151–152 °C. IR ν_{max} (Nujol): 3400, 1610, 1580, 1560 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.75–4.14 (m, 16H, $8CH_2O$), 6.37–7.60 (m, 15H, Ar–H), 8.41 (s, 1H, H^8); 14.26 (s, 1H, OH). ^{13}C NMR (300 MHz, $CDCl_3$) δ 69.41–69.23, 70.45, 71.13, 105.19, 111.00, 113.47, 114.19, 114.85, 117.28, 126.96, 128.64, 129.01, 129.11, 129.74, 130.21, 130.35, 133.52, 134.91, 135.70, 136.07, 143.31, 149.21, 150.00, 152.31, 157.38, 161.12. MS (EI): *m/z* 579 $[M]^+$. Anal. Calcd for $C_{35}H_{33}NO_7$: C, 72.52; H, 5.74; N, 2.42. Found: C, 72.63; H, 5.60; N, 2.41. UV ($CHCl_3$): λ_{max}=374 nm, ε=40,800 L mol^{-1} cm^{-1}.

*4.2.4. 6-Nitro-4-[(6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaoxabenzo-cyclopentadecen-2-ylimino)methyl]-2,3-diphenylbenzo[b]furan-5-ol (**5**)*

Compound **5** was synthesized in a similar way to **3**. Yield of a red powder 74%. Mp 229–230 °C. IR ν_{max} (Nujol): 3450, 1605, 1580 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.70–4.17 (m, 16H, $8CH_2O$), 6.35–7.64 (m, 13H, Ar–H), 8.24 (d, J=5.5 Hz, 1H, H^8), 8.46 (s, 1H, H^7), 16.89 (d, J=5.5 Hz, 1H, OH+NH). ^{13}C NMR (300 MHz, $CDCl_3$) δ 69.23–69.41, 70.46, 71.13, 105.19, 111.01, 113.47, 114.19, 114.85, 117.28, 126.96, 128.64, 129.01, 129.11, 129.74, 130.22, 130.35, 133.52, 134.91, 135.70, 136.07, 143.31, 149.21, 150.00, 152.32, 157.38, 161.12. MS (EI): *m/z* 624 $[M]^+$. Anal. Calcd for $C_{35}H_{32}N_2O_9$: C, 67.30; H, 5.16; N, 4.48. Found: C, 67.15; H, 5.10; N, 2.56. UV ($CHCl_3$): λ_{max}=402 nm, ε=29,800 L mol^{-1} cm^{-1}; λ_{max}=500 nm, ε=9800 L mol^{-1} cm^{-1}.

*4.2.5. 4-[(6,7,9,10,12,13,15,16,18,19-Decahydro-5,8,11,14,17,20-hexaoxabenzocyclooctadecen-2-ylimino)methyl]-2,3-diphenylbenzo[b]furan-5-ol (**4**)*

Compound **4** was synthesized in a similar way to **3**. Yield of a yellow powder 51%. Mp 89–90 °C. IR ν_{max} (Nujol): 3400, 1610, 1580 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.84–4.18 (m, 20H, $10CH_2O$), 6.34–7.60 (m, 15H, Ar–H), 8.40 (s, 1H, H^8), 14.28 (s, 1H, OH). ^{13}C NMR (300 MHz, $CDCl_3$) δ 69.22–69.60, 70.79, 70.84, 105.81, 110.90, 114.23, 114.71, 114.92, 117.49, 126.45, 128.38, 129.43, 129.72, 130.00, 130.40, 130.53, 133.76, 134.21, 135.07, 141.35, 147.46, 148.32, 149.69, 152.27, 155.77, 159.81. MS (EI): *m/z* 623 $[M]^+$. Anal. Calcd for $C_{37}H_{37}NO_8$: C, 71.25; H, 5.98; N, 2.25. Found: C, 71.23; H, 5.85; N, 2.38. UV ($CHCl_3$): λ_{max}=373 nm, ε=33,000 L mol^{-1} cm^{-1}.

*4.2.6. 6-Nitro-4-[(6,7,9,10,12,13,15,16,18,19-decahydro-5,8,11,14,17,20-hexaoxabenzocyclooctadecen-2-ylimino)methyl]-2,3-diphenylbenzo[b]furan-5-ol (**6**)*

Compound **6** was synthesized in a similar way to **3**. Yield of a red powder 65%. Mp 204–205 °C. IR ν_{max} (Nujol): 3400, 1610, 1580 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.64–4.19 (m, 20H, $10CH_2O$), 6.34–7.68 (m, 13H, Ar–H), 8.27 (d, J=5.5 Hz, 1H, H^8), 8.45 (s, 1H, H^7), 16.87 (d, J=5.5 Hz, 1H, OH+NH). ^{13}C NMR (300 MHz, $CDCl_3$) δ 69.28–69.47, 70.72, 70.74, 70.85, 105.03, 110.96, 113.45, 114.26, 114.76, 117.27, 126.91, 128.58, 129.06, 129.12 129.69, 130.19, 130.28, 133.42, 134.85, 135.64, 136.01, 143.22, 149.01, 149.84, 152.25, 157.32, 161.06. MS (EI): *m*/*z* 668 [M]$^+$. Anal. Calcd for $C_{37}H_{36}N_2O_{10}$: C, 66.46; H, 5.43; N, 4.19. Found: C, 66.61; H, 5.34; N, 4.10. UV (CHCl$_3$): λ_{max}=402 nm, ε=30,200 L mol^{-1} cm^{-1}; λ_{max}= 500 nm, ε=9800 L mol^{-1} cm^{-1}.

4.2.7. ^{15}N-4-(Phenyliminomethyl)-2,3-diphenylbenzo[b]-furan-5-ol (**7**)

Compound **7** was synthesized in a similar way to **3**. Yield of a red powder 70%. Mp 194–195 °C. IR ν_{max} (Nujol): 3500, 1620, 1580, 1550 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.81–7.68 (m, 15H, Ar–H), 8.30 (dd, J_{H15N}=1.9 Hz, J_{HH}=5.7 Hz, 1H, H^8), 8.46 (s, 1H, H^7), 16.46 (dd, J_{H15N}=41.3 Hz, J_{HH}=5.7 Hz, 1H, OH+NH). ^{13}C NMR (300 MHz, CDCl$_3$) δ 110.75, 115.71, 117.41, 119.81, 126.90, 127.67, 128.62, 129.00, 129.09, 129.58, 129.76, 130.15, 130.34, 133.25, 135.25, 135.76, 142.35, 143.09, 154.09, 157.43, 161.94. MS (EI): *m*/*z* 435 [M]$^+$. Anal. Calcd for $C_{27}H_{18}N^{15}NO_4$: C, 74.48; H, 4.13; N, 6.66. Found: C, 74.40; H, 4.15; N, 6.72. UV (CHCl$_3$): λ_{max}=400 nm, ε=28,000 L mol^{-1} cm^{-1}; λ_{max}=505 nm, ε=9400 L mol^{-1} cm^{-1}.

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References and notes

1. Alarcon, S. H.; Olivieri, A. C.; Saur, D.; Claramunt, R. M.; Elguero, J. *J. Mol. Struct.* **2004**, *705*, 1–9.
2. Antonov, L.; Fabian, W.; Nedeltcheva, D.; Kamounah, F. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1173–1179.
3. Rozwadowski, Z.; Majewski, E.; Dziembowska, T.; Hansen, P. E. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2809–2817.
4. Vargas, V.; Amigo, L. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1124–1129.
5. Alarcon, S.; Pagani, D.; Bacigalupo, J.; Olivieri, A. *J. Mol. Struct.* **1999**, *475*, 233–240.
6. Rybalkin, V. P.; Shepelenko, E. N.; Popova, L. L.; Dubonosov, A. D.; Bren, V. A.; Minkin, V. I. *Russ. J. Org. Chem.* **1996**, *32*, 90–94.
7. Rybalkin, V. P.; Dubonosov, A. D.; Shepelenko, E. N.; Popova, L. L.; Makarova, N. I.; Tsukanov, A. V.; Bren, V. A.; Minkin, V. I. *Russ. J. Org. Chem.* **2002**, *38*, 1326–1330.
8. Feringa, B.; Jager, W.; Lange, B. *Tetrahedron Lett.* **1992**, *33*, 2877–2890.
9. Przybylski, P.; Schroeder, G.; Brzezinski, B. *J. Mol. Struct.* **2004**, *699*, 65–77.
10. Bren, V. A.; Dubonosov, A. D.; Makarova, N. I.; Popova, L. L.; Rybalkin, V. P.; Shepelenko, E. N.; Tsukanov, A. V. *Russ. J. Org. Chem.* **2002**, *38*, 139–140.
11. Callan, J. F.; de Silva, A. P.; Magri, D. C. *Tetrahedron* **2005**, *61*, 8551–8588.
12. Bren, V. A. *Russ. Chem. Rev.* **2001**, *70*, 1017–1036.
13. Japp, F. R.; Meldrum, A. N. *J. Chem. Soc.* **1899**, *75*, 1035–1043.
14. Brown, N. M. D.; Nonhebel, D. C. *Tetrahedron* **1968**, *24*, 5655–5664.
15. Dudek, G. O.; Dudek, E. P. *J. Am. Chem. Soc.* **1964**, *86*, 4283–4287.
16. Dudek, G. O.; Dudek, E. P. *J. Am. Chem. Soc.* **1966**, *88*, 2407–2412.
17. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision D.01*; Gaussian: Wallingford, CT, 2004.
18. Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *106*, 5151–5158.
19. Gromov, S. P.; Ushakov, E. N.; Fedorova, O. A.; Baskin, I. I.; Buevich, A. V.; Andryukhina, E. N.; Alfimov, M. V.; Johnels, D.; Edlund, U. G.; Whitesell, J. K.; Fox, M. A. *J. Org. Chem.* **2003**, *68*, 6115–6125.
20. Kim, Y.-H.; Hong, J.-I. *Chem. Commun.* **2002**, 512–513.