New ionochromic azomethinimine chemosensors*

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A reaction of 5-phenylpyrazolidin-3-one with hydroxy-substituted aromatic aldehydes led to azomethinimines, the representatives of a new class of chemosensors exhibiting ionochromic properties. Electron spectroscopy was used to identify efficient chemosensors toward Cu^{2+} cations and F^- anions.

Key words: azomethinimines, pyrazolidone, chemosensors, aldehydes, cations, anions.

Azomethines containing a bipolar structural fragment $-\overset{-}{N}-\underset{|}{\overset{+}{N}}=$ are useful polyfunctional precursors in combinatoric chemistry of various heterocyclic systems.[1—6] Such systems also exhibit photochromic properties resulting from a reversible process of intramolecular cyclization.[7—9]

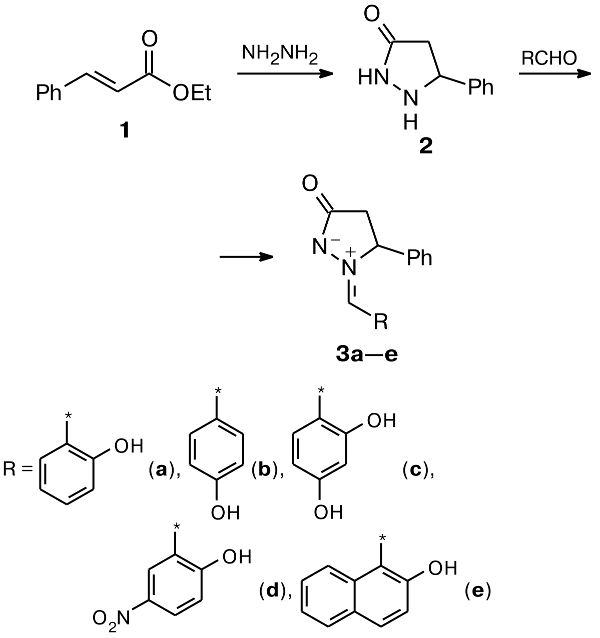
Another not yet studied area of application of these compounds can be chemosensorics. In the last years, a persistent attention is paid to the development of new sensitive and selective chemosensors, *i.e.*, compounds capable of discriminating cations or anions and playing a significant role in biological processes, medicine, ecology, *etc.*[10—14] Heterocyclic chemosensors for the studies of different ions by electron spectroscopy is a well known class of ionochromic compounds.[15—17]

The presence of a charged fragment and additional chelating centers in the structure of azomethinimines makes it possible to use them as reagents for different ions. The present work is devoted to the synthesis of a number of new hydroxyaldehyde-derived azomethinimines and studies of their chemosensory properties toward some cations and anions.

Results and Discussion

Ethyl cinnamate **1** and hydrazine hydrate were used to synthesize 5-phenylpyrazolidin-3-one (**2**)[18,19] as a basic compound for development of bipolar chemosensors. The product obtained was condensed[6] with hydroxy-substituted aromatic aldehydes to furnish a series of new 1-R-ylidene-substituted 3-oxo-5-phenylpyrazolidin-1,2-ylides **3a—e** (Scheme 1). The IR spectra of compounds **3a—e** exhibit an absorption band characteristic of the stretching vibrations of the OH group in the 3033—3111 cm^{-1} region. The ^{1}H NMR spectra exhibit signals for the diastereotopic protons of the cyclic CH_2 groups (two doublets of doublets in the regions δ 2.40—3.01 and 3.14—3.41) and the CH groups (a doublet of doublets in the region δ 5.52—6.02), as well as a signal for the proton of the hydroxy group at δ 10.36—12.82.

Scheme 1



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* Dedicated to Academician of the Russian Academy of Sciences V. I. Minkin on the occasion of his 80th birthday.

† Deceased.

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The studies of chemosensory properties of azomethinimines **3a—e** toward Zn^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Hg^{2+} cations and F^-, $H_2PO_4^-$, CN^-, AcO^- anions were carried out by electron spectroscopy. The absorption spectra of compounds **3a—e** (MeCN) exhibit several bands in the 250—500 nm region, the most strong of them have the maximum at 361 (**3a**), 361 (**3b**), 366 (**3c**), 468 (**3d**), and 377 nm (**3e**).

In most cases, the addition of metal salts to the solutions of azomethinimines causes just insignificant changes in the absorption spectra (Table 1). However, in the case of compound **3c** the reaction with the Hg^{2+} ions leads to the appearance of an absorption band in the visible region of the spectrum (410 nm). It should be also noted that the addition of the Cu^{2+} cations to the solution of compound **3d** in MeCN leads to the change of the entire absorption spectrum and the appearance of a strong band in the 250 nm region (see Table 1, Fig. 1). This effect, apparently, is related to the oxidation properties of the copper(II) ions. Azomethinimine **3d** will be studied as a chemodosimeter.[20]

The compounds obtained were also studied on the chemosensory properties toward F^-, CN^-, $H_2PO_4^-$, and AcO^- anions. The introduction of the corresponding tetrabutylammonium salts into solutions of compounds **3a—e** causes different effects, which lead to the change in the position of absorption bands and their intensities. 1-(2-Hydroxybenzylidene)-3-oxo-5-phenylpyrazolidinium-1,2-ylide (**3a**) is the most efficient chemosensor for the anions among the studied compounds, which exhibits the ion-active properties while detecting the F^- anions, that is indicated by the appearance of a strong band at 464 nm and a yellowish green color of the solution (see Table 1, Fig. 2).

In conclusion, the studies of a number of azomethinimines **3** as potential chemosensors for different cations and anions resulted in the identification of efficient sensors for F^- anions (compound **3a**) and Cu^{2+} cations (compound **3d**).

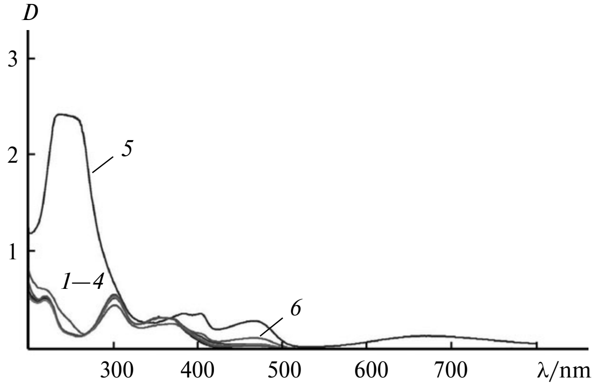

Fig. 1. Absorption spectra of solutions ($5 \cdot 10^{-5}$ mol L^{-1}) of compound **3d** (*1*) upon addition of cations ($2.5 \cdot 10^{-4}$ mol L^{-1}): Zn^{2+} (*2*), Ni^{2+} (*3*), Co^{2+} (*4*), Cu^{2+} (*5*), and Hg^{2+} (*6*).

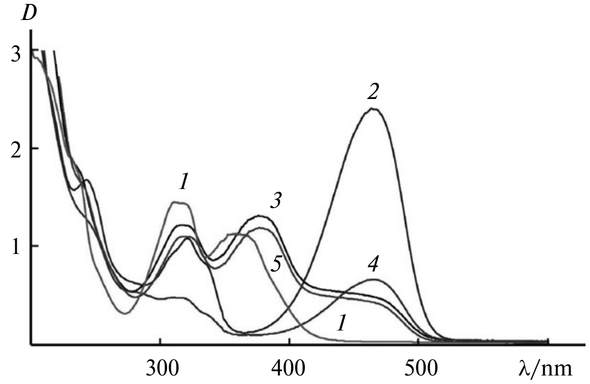

Fig. 2. Absorption spectra of solutions ($5 \cdot 10^{-5}$ mol L^{-1}) of compound **3a** (*1*) upon addition of anions ($2.5 \cdot 10^{-4}$ mol L^{-1}): F^- (*2*), AcO^- (*3*), CN^- (*4*), and $H_2PO_4^-$ (*5*) ($2.5 \cdot 10^{-5}$ mol L^{-1}).

Experimental

Acetonitrile purchased from Kriokhrom (quality 0, high purity grade.) was used in the work. IR spectra were obtained on

Table 1. Optical density values (*D*) of solutions of compounds **3a—e** ($5 \cdot 10^{-5}$ mol L^{-1}) in MeCN in the absorption maximum region (λ_{max}/nm) upon addition of cations (salts of $HClO_4$, $2.5 \cdot 10^{-4}$ mol L^{-1}) and anions (salts of NBu_4^+, $2.5 \cdot 10^{-4}$ mol L^{-1})

Compound	D (λ_{max})								
	Zn^{2+}	Ni^{2+}	Co^{2+}	Cu^{2+}	Hg^{2+}	F^-	$H_2PO_4^-$	CN^-	AcO^-
3a	1.14 (361)	1.15 (361)	1.14 (361)	1.18 (361)	1.16 (361)	2.40 (463)	0.45 (463)	0.67 (465)	0.51 (463)
3b	0.35 (361)	0.34 (361)	0.35 (361)	0.37 (361)	0.36 (361)	0.73 (413)	0.39 (414)	0.71 (413)	0.17 (413)
3c	0.56 (365)	0.57 (365)	0.56 (365)	0.58 (365)	0.45 (411)	1.70 (411)	1.08 (389)	1.70 (411)	0.92 (391)
3d	0.05 (469)	0.10 (468)	0.08 (467)	2.50 (250)	0.22 (469)	1.15 (468)	1.14 (468)	1.12 (468)	1.15 (468)
3e	0.55 (377)	0.54 (377)	0.54 (377)	0.58 (377)	0.57 (377)	0.70 (457)	0.31 (450)	0.32 (457)	0.10 (458)

a Varian Excalibur 3100 FT-IR spectrometer by the frustrated total internal reflection using a ZnSe crystal. ^{1}H NMR spectra were recorded on a Varian Unity 300 spectrometer (300 MHz) in $CDCl_3$ or DMSO-d$_6$, using residual signals of the solvent as a reference (δ 7.25 and 2.50). Electron absorption spectra were recorded on a Varian Cary 100 spectrophotometer. Mass spectra were recorded on a Shimadzu GCMS-QP2010 SE mass-spectrometer, using method of electron ionization with direct injection of the sample into the source of ions (70 eV). Elemental analysis was performed on a EuroVector EA-3000 elemental analyzer. Melting points were determined in glass capillaries on a PTP(M) apparatus. Reaction progress and purity of compounds obtained were monitored by TLC (Silufol U-254 plates, eluent chloroform—methanol, 5 : 1; visualization by iodine vapors in a moist chamber).

5-Phenylpyrazolidin-3-one (2) was synthesized according to the procedure described earlier.[19] M.p. 101—102 °C (ethyl acetate); *cf.* Ref. 19: m.p. 95—97 °C (toluene); *cf.* Ref. 21: m.p. 101—102 °C (propan-2-ol). Found (%): C, 66.58; H, 6.15; N, 17.35. $C_9H_{10}N_2O$. Calculated (%): C, 66.65; H, 6.21; N, 17.27.

Synthesis of azomethinimines (general procedure). Trifluoroacetic acid (0.1 mL) was added to a mixture of 5-phenylpyrazolidin-3-one (**2**) (10 mmol) and the corresponding substituted benzaldehyde (10 mmol) in propan-2-ol (25 mL). The reaction mixture was refluxed for 3 h. The reaction completion was determined by TLC. Then, the reaction mixture was cooled to ~20 °C, a precipitate formed was filtered off, crystallized from *n*-butanol, and dried in air.

1-(2-Hydroxybenzylidene)-3-oxo-5-phenylpyrazolidinium-1,2-ylide (3a) was obtained from pyrazolidone **2** and 2-hydroxybenzaldehyde. The yield was 45%. A light yellow powder, m.p. 234—235 °C (decomp.). Found (%): C, 72.24; H, 5.25; N, 10.60. $C_{16}H_{14}N_2O_2$. Calculated (%): C, 72.17; H, 5.30; N, 10.52. MS (EI, 70 eV), m/z (I_{rel} (%)): 266 $[M]^+$ (46). ^{1}H NMR ($CDCl_3$), δ: 2.91 (dd, 1 H, CH, ^3J = 6.0 Hz, ^2J = 16.8 Hz); 3.33 (dd, 1 H, CH, ^3J = 10.0 Hz, ^2J = 17.1 Hz); 5.52 (dd, 1 H, CH, ^3J = 6.3 Hz, ^2J = 9.9 Hz); 6.72—6.96 (m, 4 H, C_{Ar}H); 7.22—7.45 (m, 6 H, C_{Ar}H, CH=N); 12.82 (s, 1 H, OH). IR, ν/cm^{-1}: 3078 (OH); 1629 (C=O); 1600 (N—C(O)); 1558 (C=N); 1459 (N—N); 1260, 1246 (C—O); 1069 (C—N).

1-(4-Hydroxybenzylidene)-3-oxo-5-phenylpyrazolidinium-1,2-ylide (3b) was obtained from pyrazolidone **2** and 4-hydroxybenzaldehyde. The yield was 49%. A colorless powder, m.p. > 250 °C (decomp.). Found (%): C, 72.26; H, 5.22; N, 10.58. $C_{16}H_{14}N_2O_2$. Calculated (%): C, 72.17; H, 5.30; N, 10.52. MS (EI, 70 eV), m/z (I_{rel} (%)): 266 $[M]^+$ (42). ^{1}H NMR (DMSO-d$_6$), δ: 2.35—2.53 (m, 1 H, CH); 3.07—3.21 (m, 1 H, CH); 5.71—5.82 (m, 1 H, CH); 6.87 (d, 2 H, C_{Ar}H, ^3J = 7.5 Hz); 7.26 (s, 1 H, CH=N); 7.28—7.45 (m, 5 H, C_{Ar}H); 8.17 (d, 2 H, C_{Ar}H, ^3J = 7.5 Hz); 11.14 (s, 1 H, OH). IR, ν/cm^{-1}: 3033 (OH), 1639 (C=O), 1610 (N—C(O)), 1577 (C=N), 1444 (N—N), 1296 (C—O), 1076 (C—N).

1-(2,4-Dihydroxybenzylidene)-3-oxo-5-phenylpyrazolidinium-1,2-ylide (3c) was obtained from pyrazolidone **2** and 2,4-dihydroxybenzaldehyde. The yield was 42%. A light yellow powder, m.p. > 250 °C (decomp.). Found (%): C, 68.16; H, 4.92; N, 10.01. $C_{16}H_{14}N_2O_3$. Calculated (%): C, 68.08; H, 5.00; N, 9.92. MS (EI, 70 eV), m/z (I_{rel} (%)): 282 $[M]^+$ (29). ^{1}H NMR (DMSO-d$_6$), δ: 2.47 (dd, 1 H, CH, ^3J = 4.8 Hz, ^2J = 14.1 Hz); 3.15 (dd, 1 H, CH, ^3J = 9.9 Hz, ^2J = 16.5 Hz); 5.82 (dd, 1 H, CH, ^3J = 4.5 Hz, ^2J = 9.9 Hz); 6.27—6.38 (m, 2 H, C_{Ar}H); 7.31—7.47 (m, 6 H, C_{Ar}H, CH=N); 8.36 (d, 1 H, C_{Ar}H, ^3J = 9.0 Hz); 10.36 (s, 1 H, OH); 11.46 (s, 1 H, OH). IR, ν/cm^{-1}: 3509, 3033 (OH), 1610 (N—C(O)), 1563 (C=N), 1297 (C—O).

1-(2-Hydroxy-5-nitrobenzylidene)-3-oxo-5-phenylpyrazolidinium-1,2-ylide (3d) was obtained from pyrazolidone **2** and 2-hydroxy-5-nitrobenzaldehyde. The yield was 38%. A yellow powder, m.p. > 250 °C (decomp.). MS (EI, 70 eV), m/z (I_{rel} (%)): 311 $[M]^+$ (16). Found (%): C, 61.81; H, 4.15; N, 13.43. $C_{16}H_{13}N_3O_4$. Calculated (%): C, 61.73; H, 4.21; N, 13.50. ^{1}H NMR (DMSO-d$_6$), δ: 2.59 (dd, 1 H, CH, ^3J = 4.5 Hz, ^2J = 16.8 Hz); 3.22 (dd, 1 H, CH, ^3J = 9.8 Hz, ^2J = 16.8 Hz); 6.02 (dd, 1 H, CH, ^3J = 4.5 Hz, ^2J = 9.9 Hz); 7.05 (d, 1 H, C_{Ar}H, ^3J = 9.0 Hz); 7.37—7.48 (m, 4 H, C_{Ar}H, CH=N); 8.22 (dd, 1 H, C_{Ar}H, ^3J = 3.0 Hz, ^2J = 9.0 Hz); 9.82 (d, 1 H, C_{Ar}H, ^3J = 3.0 Hz); 12.40 (s, 1 H, OH). IR, ν/cm^{-1}: 3111 (OH); 1637 (C=O); 1613 (N—C(O)); 1546 (C=N); 1491 (N=O); 1293, 1279 (C—O); 1250 (N=O); 1085 (C—N).

1-[(2-Hydroxynaphthalen-1-yl)methylidene]-3-oxo-5-phenylpyrazolidinium-1,2-ylide (3e) was obtained from pyrazolidone **2** and 2-hydroxynaphthalene-1-carbaldehyde. The yield was 72%. A light yellow powder, m.p. 223—224 °C. Found (%): C, 76.01; H, 5.03; N, 8.92. $C_{20}H_{16}N_2O_2$. Calculated (%): C, 75.93; H, 5.10; N, 8.85. MS (EI, 70 eV), m/z (I_{rel} (%)): 316 $[M]^+$ (42). ^{1}H NMR ($CDCl_3$), δ: 3.01 (dd, 1 H, CH, ^3J = 6.3 Hz, ^2J =16.8 Hz); 3.41 (dd, 1 H, CH, ^3J = 9.9 Hz, ^2J =17.1 Hz); 5.70 (dd, 1 H, CH, ^3J = 6.3 Hz, ^2J = 9.6 Hz); 7.10—7.52 (m, 9 H, C_{Ar}H); 7.68 (s, 1 H, CH=N); 7.70—7.87 (m, 2 H, C_{Ar}H); 12.01 (s, 1 H, OH). IR, ν/cm^{-1}: 3058 (OH); 1661 (C=O); 1594 (C=N); 1247, 1238 (C—O); 1101 (C—N).

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