

LITERATURE CITED

1. A. I. Gren', V. A. Bacherikov, and K. S. Zakharov, Zh. Obshch. Khim., 57, 2016 (1987).
2. C. A. G. Haasnoot, F. A. A. M. de Leew, and C. Altona, Tetrahedron, 36, 2783 (1980).
3. A. V. Bogatskii, A. I. Gren', S. G. Soboleva, and Yu. Yu. Samitov, Khim. Geterotsikl. Soedin., No. 7, 893 (1971).
4. P. Pasanen, Suom. Kem., B45, 363 (1972).
5. V. V. Kuznetsov and A. I. Gren', Zh. Obshch. Khim., 54, 2263 (1984).
6. K. Pihlaja, P. Pasanen, and J. Wähäsilta, Org. Magn. Reson., 12, 331 (1979).
7. V. A. Bacherikov and A. I. Gren', VINITI, No. 8373-B86; Deponir. Nauch. Raboty, No. 4, 88 (1987).
8. A. M. Turyanskaya, A. I. Gren', and V. A. Bacherikov, VINITI, No. 792-85; Ref. Zh. Khim, 12Zh, 114 Dep. (1985).
9. B. M. Mikhailov and T. A. Shchegoleva, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1080 (1957).

EFFECT OF STRUCTURAL FACTORS ON THE BASICITIES AND ELECTRONIC SPECTRA OF BETAINE ALDEHYDES OF AZOLES AND YLIDS OF MALONIC ESTER AND DIMEDONE

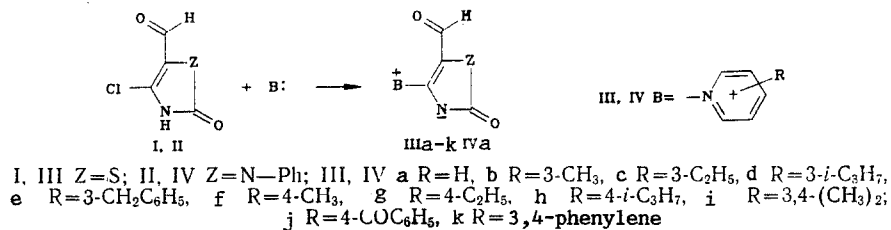
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Betaine aldehydes of thiazole and imidazole containing substituted pyridinium and isoquinolinium cations were synthesized and their basicities were determined. The effect of the type of charge separation (betaine and ylid) and the nature of the heteroatoms and substituents in the onium and anionoid parts of the molecules on their electronic spectra and basicities was studied; the principles established are presented in the form of linear dependences.

Important data regarding the electron interactions in compounds with structures of the inner organic salt type [1] are obtained by a study of their basicities; of the two modifications of structures with separated charges - betaines and ylids [2, 3] - the basicities of the former have been studied to a considerably smaller extent.

To fill this gap and to compare the properties of ylids and betaines we, in addition to the already described betaines IIIa, k and IVa [4, 5], accomplished the synthesis and determined the basicities of new betaine aldehydes IIIb-j of thiazole and thoroughly analyzed the literature data on the basicities and electronic spectra of ylids V and VI of malonic ester [6] and dimedone [2, 7, 8]. Betaines IIIa-k were obtained by previously developed methods [4, 5] starting from the corresponding chloroformylazolinones I and II [9] and substituted pyridines and isoquinolines.



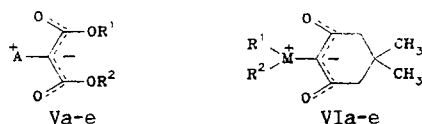
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TABLE 1. Characteristics of Betaines IIIb-j

Com- pound	Empirical formula	mp, °C	¹ H NMR spectrum,** δ, ppm					Yield, %
			CHO	2-H, δ-H	3-H, δ-H	4-H	other signals	
IIIb	C ₁₀ H ₈ N ₂ O ₂ S	248...249	9.56	9.08	8.28	9.05	2.75 (s, 3H, CH ₃)	95
IIIc	C ₁₁ H ₁₀ N ₂ O ₂ S	240...242	9.53	9.07	8.30	8.80	3.05 (q, 2H, CH ₂ CH ₃); 1.44 (t, 3H, CH ₂ CH ₃)	95
III d	C ₁₂ H ₁₂ N ₂ O ₂ S	225...227	9.54	9.05	8.30	8.30	3.35 (m, 1H, CH(CH ₃) ₂); 1.46 (d, 6H, CH(CH ₃) ₂)	30
IIIe	C ₁₆ H ₁₂ N ₂ O ₂ S	209...211	9.48	8.96	8.26	8.74	7.33 (m, 5H, C ₆ H ₅); 4.35 (s, 2H, CH ₂)	30
III f	C ₁₀ H ₈ N ₂ O ₂ S	265...267	—	—	—	—	—	95
III g	C ₁₁ H ₁₀ N ₂ O ₂ S	222...224	9.55	9.03	8.18	—	3.20 (q, 2H, CH ₂ CH ₃); 1.50 (t, 3H, CH ₂ CH ₃)	95
III h	C ₁₂ H ₁₂ N ₂ O ₂ S	248...250	9.55	9.03	8.23	—	3.93 (m, 1H, CH(CH ₃) ₂); 1.55 (d, 6H, CH(CH ₃) ₂)	80
III i	C ₁₁ H ₁₀ N ₂ O ₂ S	261...263	—	—	—	—	—	91
III j	C ₁₆ H ₁₀ N ₂ O ₂ S	253...256	9.68	9.50	8.63	—	7.83 (m, 5H, C ₆ H ₅)	62

*Crystallization solvents: dimethylformamide for IIIb-e, h, j, water for IIIf-g, and acetic acid for IIIi.

**The internal standard was hexamethyldisiloxane (HMDS) for IIIe.



V a A=S(CH₃)₂; b A=PPh₃; c A=quinolinium; d A=pyridinium; e A=isoquinolinium;
R¹=R²=CH₃; VI a R¹=R²=Ph, M=Se; b R¹=R²=CH₃, M=S; c R¹=R²=Ph, M=Te;
d R¹=C₆H₅, R²=CH₃, M=Te; e R¹=R²=CH₃, M=Te

The characteristics of betaines IIIb-j and ylids Va-e and VIa-e are presented in Tables 1-3.

A band that is absent in the spectra of the starting compounds - 4-chloro-5-formylthiazolin-2-one (I) and the azines - appears in the electronic absorption spectra of thiazole betaine aldehydes IIIa-k in the visible region of the spectrum. This band undergoes a regular shift as a function of the acceptor properties of the cation [10] (Table 2) and is characterized by negative solvatochromism in the series of solvents water-methanol-ethanol (95%)-acetonitrile-DMSO-acetone (for betaine IIIa λ_{\max} 375, 382, 393, 411, 412, and 430 nm, respectively) and vanishes on protonation. From this, and proceeding from the Bouguer-Lambert-Beer law, one can assign the described band to intramolecular charge transfer (ICT) from the anionoid to the onium part of the betaine; the energy of excitation of ICT E (in kilocalories per mole) correlates linearly with the empirical characteristics of the enumerated solvents (the Z parameter) [11]:

$$E_{\text{ICT}} = (45.1 \pm 3.2) + 0.3Z \quad (1)$$

(n=6; S_{tot} = 1.0; r=0.97).

As expected, the introduction of electron-acceptor substituents into the pyridinium ring (vis-a-vis the same anionoid part) leads to a bathochromic shift of the ICT band, while the introduction of electron-donor substituents leads to a hypsochromic shift of the ICT band; the effect of the σ constants of the substituents on the energy of excitation of ICT and the basicity of the betaines is described by, respectively, Eqs. (2) and (3):

$$E = (76.83 \pm 0.70) + (-16.36 \pm 2.37)\sigma \quad (2)$$

(n=5; S_{tot} = 1.56; r=0.97).

$$\begin{aligned} pK_{\text{BH}^+} &= pK_{\text{BH}^+} + \rho\sigma; \\ pK &= (0.80 \pm 0.01) - (0.69 \pm 0.07)\sigma \quad (3) \\ &(n=9; S_{\text{tot}} = 0.04; r=0.97). \end{aligned}$$

TABLE 2. Basicity Constants and Wave and Energy Parameters of Intramolecular Charge Transfer (ICT) of Betaines IIIa-j

Compound	pK_{BH^+}		λ_{max} , (ICT) nm	$\lg \epsilon$	E_{ICT} , kcal/ mole
	betaine	pyridine			
IIIj	0.50	3.35	422	3.20	67.75
IIIa	0.72	5.20	375	—	76.24
IIIe	0.84	—	373	3.60	76.65
IIIb	0.84	5.65	—	—	—
IIId	0.88	5.72	371	3.62	77.07
IIIc	0.90	5.70	370	3.63	77.27
IIIh	0.91	6.02	364	3.38	78.55
IIIg	0.91	6.02	—	—	—
IIIf	0.91	6.02	364	—	78.55
IIIi	0.99	6.46	345	3.59	82.87

TABLE 3. Basicity Constants (pK_{BH^+}) and Long-Wave Maxima of the Absorption Bands in the Electronic Spectra of Ylids Va-e [6] and VIa-e [2, 7, 8]

Compound	A*	M	λ_{max} , nm	pK_{BH^+}
Va	(CH ₃) ₂	—	239	1.81
Vb	PPh ₃	—	228	1.96
Vc	Quinoline	—	396	4.62
Vd	Pyridine	—	366	5.12
Ve	Isoquinoline	—	382	5.20
VIa	—	Se	267	9.59
VIb	—	S	261	9.67
VIc	—	Te	262	10.59
VIe	—	Te	268	11.22
VIe	—	Te	270	12.07

In simpler form the efficiency of transmission of the electronic effects of substituents in the pyridinium cation on the basicities of betaines IIIa-j can be represented by relationships between the basicities of the betaines and pyridines that form the corresponding betaines [Eq. (4)] and between the basicity constants of the betaines and the position of the ICT band [Eq. (5)]:

$$pK_{BH^+ \text{ bet}} = (20.06 \pm 0.06) + pK_{BH^+ \text{ pyrid}}(0.16 \pm 0.01) \quad (4)$$

$(n=9; S_{tot}=0.03; r=0.98).$

$$pK_{BH^+ \text{ bet}} = (3.34 \pm 0.32) - 0.01\lambda \quad (5)$$

$(n=8; S_{tot}=0.05; r=0.95).$

The establishment of the enumerated regularities evidently may prove to be useful for the specific synthesis of betaines with a predesignated color (as well as the energy of excitation of ICT) and basicity. For example, the relationship between the position of the charge-transfer (CT) band and the basicity of the pyridine necessary for the synthesis has the following form:

$$\lambda_{max \text{ ICT}} = (500 \pm 10) + pK_{BH^+ \text{ pyrid}}(-23 \pm 2) \quad (6)$$

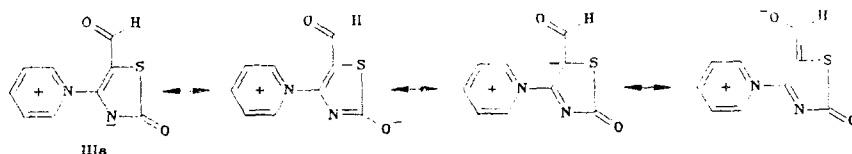
$(n=5; S_{tot}=5; n=0.99).$

On passing from pyridinium betaine IIIa to isoquinolinium betaine IIIk, as in the case of ylids Vd, e [6], one observes an increase in the basicity (the pK_{BH^+} values of betaines IIIa and IIIk are, respectively, 0.72 and 0.86).

The effect of changes in the anionoid part of the betaine molecules is similar. Thus, replacement of the sulfur atom by the less electronegative nitrogen atom in the 1 position of theazole ring leads to an increase in the electron density in the anion (and to an in-

crease in its donor capacity); this is accompanied by a bathochromic shift of the ICT band (from 375 nm for betaine IIIa to 401 nm for betaine IVa) and an increase in the basicity from 0.72 to 2.43. The basicity also changes similarly on passing from unsubstituted thiazole (pK_{BH^+} 2.53) to imidazole (pK_{BH^+} 6.95). An increase in the basicity is also observed on passing from sulfonium and phosphonium ylids to ammonium ylids, for which this value is approximately four orders of magnitude greater. A number of authors [12, 13] explain this fact by the possibility of delocalization of the negative charge using the vacant d orbitals of the sulfur and phosphorus atoms (which is excluded for nitrogen); the greater the delocalization, the lower the basicity. Thus, the effect of the heteroatom (S, N) on the basicity is manifested monotypically and does not depend on the character of the charge separation (betaine, ylid) and the charge of the ion.

In the discussion of the protonation center of betaines III one must take into account the contribution of the following mesomeric structures:



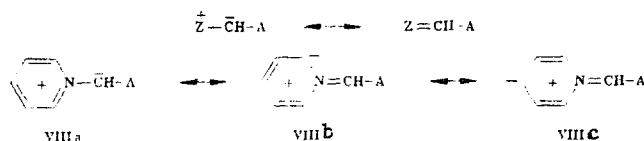
A comparison of the IR spectra of I and IIIk and salt VII (the hydrochloride of betaine IIIk) indicates protonation at the nitrogen atom of the amide fragment. Thus, in the spectrum of salt VII, in contrast to betaine IIIk, one observes the appearance of a new band at 1555 cm^{-1} , which is present in the spectrum of starting I and is assignable to in-plane deformation vibrations of the NH groups of cyclic amides (an amide II band) [14], as well as a band of NH stretching vibrations at $3055\text{--}3100\text{ cm}^{-1}$. Thus, the data on the direction of nitration and alkylation [15] of betaines of azoles coincide.

Convenient objects for comparison of the properties with betaines IIIa-k are malonic ester ylids Vc-e, which contain azinium cations and display, like betaines III and IV, the properties of intramolecular charge-transfer complexes (CTC). Using the literature data [6] we established, as in the case of betaines III and IV, the possibility of a linear correlation between the basicities of ylids Va-e and the position of the long-wave maximum of the absorption band in their electronic spectra (Table 3):

$$pK_{BH^+} = (-2.78 \pm 1.01) + 0.02\lambda \quad (7)$$

$(n=5, S_{\text{tot}}=0.50, r=0.97).$

However, ylids Va, b with sulfonium and phosphonium cations also enter into this correlation series, although, as was previously demonstrated on the basis of experimental data and Hückel MO calculations for them [16] and a number of other ylids [17], the long-wave maxima of the absorption bands in their electronic spectra cannot be ascribed to CTC. Nevertheless, the difference in the origin of the bands in the spectra of ylids Vc-e and Va, b does not serve as an obstacle to making a correlation, and, consequently, the long-wave maxima characterize something general that is peculiar to two different groups of ylids. This common factor, which affects both the basicity and the position of the long-wave maximum, is evidently the degree of double-bond character of the carbanion-heteroatom onium center; a lower energy of excitation of the electron transitions of the interannular bond (a greater wavelength) and a greater basicity of the ylid correspond to a lower degree of double-bond character (Table 3). In the case of cyclammonium ylids, in contrast to ammonium ylids and in analogy with sulfur and phosphorus ylids, an increase in the degree of double-bond character of the interannular bond can be achieved through delocalization of the negative charge of the anion with the participation of the π system of the heteroring, which, in general form, can be represented by the following formalized schemes:



Z=S, P; A — electron-acceptor group

Considering the complex character of the long-wave bands in the electronic absorption spectra of cyclammonium ylids [17], the formation of CTC in the case of ylids Vc-e can be regarded as one of the pathways of stabilization of the carbanion (structures VIIIb, c). Data from the PMR spectroscopy of a number of ylids of β -dicarbonyl compounds [18], particularly ylid Va, for which the resonance of the α and γ protons of the pyridine ring shows up at much stronger field as compared with compounds for which 1,2-separation of the charges is excluded by virtue of the shielding caused by migration of the electron density from the carbanion to the pyridine ring (for example, betaines of azoles), constitute evidence for the informal contribution of structures VIIIa-c.

The character of the correlation between the basicity and the position of the long-wave maximum in the electronic absorption spectra of ylids for dimedone ylids VIa-e also constitutes evidence that this maximum may characterize the degree of double-bond character of the interannular bond:

$$pK_{BH^+} = (-38.32 \pm 8.89) + (0.19 \pm 0.03)\lambda \quad (8)$$

($n=5$; $S_{tot} = 0.36$; $r=0.95$).

On the whole, taking into account the data on the complex character of the long-wave bands in the electronic absorption spectra of cyclammonium ylids [17], the formation of CTC can be regarded as one of the possible pathways of stabilization of the carbanions. Additional stabilization (the initial condition for flattening of the structure, which makes charge transfer along the system of conjugated π bonds possible) may be achieved in accordance with the Mulliken principle [19] also due to charge transfer in the formation of intramolecular hydrogen bonds. The formation of such bonds can be assumed, combining data on the hydrogen bonds in pyridinium ylids [18] and data on the presence of unidentified bands in their electronic absorption spectra. One should expect that the research that has been commenced in this direction [20] will help to verify the validity of the indicated assumption.

Thus, the observed differences in the character of the dependence of the basicity on the position of the long-wave maximum for ylids V and VI (a symbatic dependence) and betaines III [21] (an antibatic dependence) are associated with different origins of the corresponding bands and are determined by the type of charge separation, reflecting for ylids the effect of the degree of double-bond character and the length of the carbanion-onium center bond and, for betaines, the efficiency of the transmission of the electronic effects of the substituents in the anion on the basicity and the position of the long-wave maximum (ICT).

Unfortunately, the disconnected character and the incompleteness of the data from IR spectroscopy (the frequencies of the C=O vibrations), ^{13}C NMR spectroscopy (the chemical shifts of the ylid atoms), x-ray diffraction analysis, and investigations of the dipole moments of ylids do not make it possible to expand the sphere of such correlations in order to verify the correctness of the conclusions set forth in our paper. The establishment of such principles evidently may prove to be useful in evaluating the contribution of ylid and betaine types of charge separation to the structures of inner organic salts for the specific creation (establishment) of reaction centers.

EXPERIMENTAL

The electronic absorption spectra of the synthesized compounds were recorded with a Specord UV-vis spectrophotometer. The ^1H NMR spectra of solutions in trifluoroacetic acid were obtained with a Tesla BS-487 spectrometer (60 MHz) with tetramethylsilane (TMS) as the internal standard.

The basicity constants of betaines IIIa-k and IV in aqueous solutions at 25°C were determined by spectrophotometry. The spectra of the limiting forms were recorded in 20% H_2SO_4 , while the spectra of the equilibrium forms were recorded in hydrochloric acid solutions with different concentrations.

The starting 3- and 4-isopropylpyridines were obtained by the method in [22].

The results of elementary analysis for C, H, N, and S of betaines IIIb-j and salt VII were in agreement with the calculated values.

5-Formyl-4-(3-R¹-4-R²-1-pyridinia)thiazol-2-olates IIIa-k were obtained by the methods in [4, 5].

5-Formyl-4-(2-isoquinolinia)thiazol-2-ate Hydrochloride (VII, $C_{13}H_8N_2O_2S \cdot HCl$). A 1.32-ml (15 mmole) sample of concentrated HCl was added with stirring to a heated (to 70°C) suspension of 2.56 g (10 mmole) of 5-formyl-4-(2-isoquinolinia)thiazol-2-olate (IIIk) in 10 ml of concentrated CH_3COOH . The precipitate that formed when the solution was cooled was separated and washed with 5 ml of acetic acid and 20 ml of ether to give 2.84 g (97%) of colorless crystals with mp 205-207°C.

LITERATURE CITED

1. A. Johnson, *The Chemistry of Ylids* [Russian translation], Mir, Moscow (1969).
2. I. D. Sadekov, V. I. Minkin, V. V. Semenov, and S. A. Shevelev, *Usp. Khim.*, 50, 813 (1981).
3. Yu. V. Belkin and N. A. Polezhaeva, *Usp. Khim.*, 50, 925 (1981).
4. R. O. Kochkanyan, A. N. Zaritovskii, G. I. Belova, and S. N. Baranov, *Khim. Geterotsikl. Soedin.*, No. 2, 278 (1975).
5. R. O. Kochkanyan, N. V. Spitsyn, and S. N. Baranov, *Khim. Geterotsikl. Soedin.*, No. 4, 505 (1983).
6. O. Ya. Neiland and S. V. Kalnin', *Zh. Org. Khim.*, 4, 140 (1976).
7. I. D. Sadekov, A. I. Usachev, A. A. Maksimenko, and V. I. Minkin, *Zh. Obshch. Khim.*, 45, 2563 (1975).
8. I. D. Sadekov, A. I. Usachev, V. A. Bren', M. S. Korobov, I. D. Tseimakh, and V. I. Minkin, *Zh. Obshch. Khim.*, 47, 2232 (1977).
9. S. N. Baranov, R. O. Kochkanyan, A. N. Zaritovskii, G. I. Belova, and S. S. Radkova, *Khim. Geterotsikl. Soedin.*, No. 1, 85 (1975).
10. L. Andrews and R. Kiefer, *Molecular Complexes in Organic Chemistry* [Russian translation], Mir, Moscow (1967), p. 208.
11. E. J. Kosower, *An Introduction to Physical Organic Chemistry, Part 2*, Wiley-Interscience, New York (1968).
12. H. Lumbroso, D. Lloid, and G. S. Harris, *Compt. Rend., C*, 378, 219 (1974).
13. K. L. Ratts, *J. Org. Chem.*, 37, 848 (1972).
14. L. Bellamy, *New Data on the IR Spectra of Complex Molecules* [Russian translation], Mir, Moscow (1971), p. 300.
15. S. N. Baranov, L. M. Zueva, A. N. Zaritovskii, and R. O. Kochkanyan, *Summaries of Papers Presented at the 14th Ukrainian Republican Conference on Organic Chemistry* [in Russian] (1982), p. 18.
16. O. Ya. Neiland, *Izv. Akad. Nauk Latv. SSR, Ser. Khim.*, No. 1, 64 (1971).
17. V. É. Kampar and O. Ya. Neiland, *Izv. Akad. Nauk Latv. SSR, Ser. Khim.*, No. 6, 727 (1975).
18. A. Ratajczak and V. G. Orville-Thomas (eds.), *Molecular Interactions* [Russian translation], Mir, Moscow (1984), p. 276.
19. O. Ya. Neiland, R. V. Kampare, D. É. Prikule, and É. É. Liepin'sh, *Khim. Geterotsikl. Soedin.*, No. 3, 379 (1979).
20. P. Huyskens, *J. Mol. Struct. Theor. Chem.*, 135, 67 (1986).
21. R. O. Kochkanyan, A. N. Zaritovskii, L. A. Klyuev, B. M. Zolotarev, and S. N. Baranov, *Khim. Geterotsikl. Soedin.*, No. 2, 255 (1978).
22. H. C. Brown and W. A. Murphey, *J. Am. Chem. Soc.*, 73, 3308 (1951).