LITERATURE CITED

1. N. S. Kozlov, I. G. Shcherbak, and O. D. Zhikhareva, Izv. Akad. Nauk Belorussk. SSR, Ser. Khim. Nauk, No. 1, 74 (1982).
2. N. S. Kozlov, V. A. Serzhanina, and M. N. Shashikhina, Izv. Akad. Nauk Belorussk. SSR, Ser. Khim. Nauk, No. 1, 70 (1978).
3. N. S. Kozlov, V. V. Misenzhnikov, and M. S. Gaisinovich, Khim. Geterotsikl. Soedin., No. 3, 467 (1965).
4. K. Nakanishi, Infrared Spectra and Structures of Organic Compounds [Russian translation], Mir, Moscow (1965).
5. N. S. Kozlov, S. V. Mikhalevskaya, V. A. Serzhanina, and R. D. Sauts, Khim. Geterotsikl. Soedin., No. 4, 516 (1983).
6. N. S. Kozlov, S. V. Mikhalevskaya, V. A. Serzhanina, and R. D. Sauts, Dokl. Akad. Nauk Belorussk. SSR, 28, 810 (1984).
7. G. F. Bol'shakov, V. F. Vatago, and F. B. Agrest, Ultraviolet Spectra of Heterocyclic Compounds [in Russian], Khimiya, Leningrad (1969).
8. N. S. Kozlov, L. F. Gladchenko, R. D. Sauts, and V. A. Serzhanina, Khim. Geterotsikl. Soedin., No. 12, 1646 (1978).

ADDITIVE CHARACTER OF THE RESONANCE CONSTANTS OF AZINYL GROUPS

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The increments for the endocyclic nitrogen atoms in various positions of the azine ring, which make it possible to calculate the resonance constants of azinyl groups via an additive scheme, were found. A correlation between the resonance constants and the π-electron charges in the corresponding ipso positions of the azine ring was noted. Correlated constants of the Hammett type, which quantitatively describe the CH acidities of methyl azines and the NH acidities of amino azines were derived.

The concept [1] of the dependence of the π-acceptor character of the azine ring on the number of endocyclic nitrogen atoms is generally accepted in the chemistry of heterocycles. A qualitative dependence was established on the basis of numerous data on the reactivities of functional derivatives of azines and their physical characteristics. However, a quantitative form of this dependence has not yet been found.

For a systematic study of the electronic effects of azinyl groups (Az) as substituents we compared the resonance constants of pyridyl (Py) [2], pyridazinyl (Pyd) [3], pyrimidyl (Pym) [4, 5], and triazinyl groups (s-Tr [6], as-Tr [7]) with the constants of the phenyl group (Ph); the phenyl group was regarded as the zero member of the series of azinyl substituents presented. The averaged values of the σ_R^0 and σ_R^- resonance constants that were previously found by NMR spectroscopy for suitable model structures are presented in Table 1. The data pertaining to the phenyl group and regarded by us as reference points are discussed in greater detail below.

The σ_R^0 constants of the azinyl groups, which characterize only their mesomeric effect, were determined from the ^{13}C NMR spectra of phenylazines and the ^{19}F NMR spectra of fluorophenylazines in DMSO. A value of -0.11, which was derived as a result of statistical treatment of data for several correlation series [8], is usually adopted for the phenyl group. However, the sampling of the values of the constants that is used in this case primarily

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*Deceased.

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TABLE 1. Resonance Constants of the Phenyl and Azinyl Groups

No.	Group	σ_R^0		σ_R^-		σ_p^-
		found	calc. from Eq. (4)	found	calc. from Eq. (4)	calc.
1	Ph	−0,08	−0,08	0,04	0,04	0,17
2	2-Py	0,01	0,01	0,27	0,26	0,37
3	3-Py	−0,04	−0,05	0,06*	0,12	0,25
4	4-Py	−0,01	0,00	0,26	0,29	0,46
5	3-Pyd	0,04	0,04	0,30	0,34	0,48
6	4-Pyd	0,02	0,03	0,35	0,37	0,59
7	2-Pym	0,09	0,10	0,45	0,48	0,55
8	4-Pym	0,09	0,09	0,49	0,51	0,67
9	5-Pym	−0,04	−0,02	0,18	0,20	0,40
10	2-Pyz	—	0,04	—	0,34	0,50
11	3-*as*-Tr	0,12	0,13	0,55	0,56	0,72
12	5-*as*-Tr	0,13	0,12	0,69	0,59	0,93
13	6-*as*-Tr	0,07	0,07	0,50	0,42	0,72
14	2-*s*-Tr	0,19	0,18	0,74	0,73	0,88

*Obtained by averaging the values 0.03 (^{1}H NMR $H_2NC_6H_4$Py-3 in DMSO [2]) and 0.08 (^{1}H NMR HOC_6H_4Py-3 in DMSO, δ_{OH-p} 9.58 ppm); see [4] for the calculation.

encompasses reactions and equilibria with the participation of charged particles, for which solvation effects are significant − acid-base equilibria in series of acids and the hydrolysis of their esters in hydroxy-containing solvents. The inclusion in the statistical sampling of values obtained from IR and PMR spectra data, together with data on the reactivities (Table 2), gives −0.08 ± 0.03 for σ_R, which is in good agreement with the theoretically calculated value. Let us note that the value −0.11 presented above and the other known value of −0.06 [20] lie within this range. In conformity with the statistical-mean values of the σ_I [9] and σ_R^0 constants for the phenyl group one can derive the constant $\sigma_p^0 = 0.05$, which is confirmed by the data in [21].

The resonance constants of the azinyl groups calculated on the basis of the chemical shifts of the protons of p-amino and p-hydroxy groups in the ^{1}H NMR spectra of aminophenyl- and hydroxyphenylazines in DMSO [2-4, 6, 7] are also presented in Table 1. These constants characterize the effect of direct polar conjugation through the benzene ring of electron-acceptor azinyl substituents with electron-donor amino and hydroxy groups and are essentially nucleophilic σ_R^- constants. The value of the constant for the phenyl group was taken from a review [8]; it was calculated from data on the acidic dissociation of p-hydroxybiphenyl and the conjugate acid of p-aminobiphenyl in water and is in good agreement with the data from the ^{1}H NMR spectrum of p-aminobiphenyl in DMSO [9]. The correlated σ_p^- constant presented in Table 1 for the phenyl group is also fully substantiated proceeding from the available values of 0.179 [22] and 0.156 [23].

We found that the values of the resonance constants of both types correlate satisfactorily with one another for the entire series of azinyl substituents:

$$\sigma_R^- = 2{,}76\sigma_R^0 + 0{,}25 \quad (r = 0{,}970;\ s = 0{,}04). \tag{1}$$

Let us note that, in addition to the indicated resonance constants, one can calculate the σ_R constants of azinyl groups using data from the ^{1}H NMR spectra of m-aminophenyl azines in DMSO [2-4, 6, 7]. For this, in Eq. (2) [4] one must substitute the corresponding values of the σ_I constants and the relative chemical shifts of m-NH_2 with corrections for the magnetic anisotropy of the azine rings.

$$\sigma_R = \frac{0{,}008 - \Delta\delta_{NH_2-m} - 1.138\sigma_I}{0{,}43}. \tag{2}$$

In Eq. (2) the values of the $\Delta\delta_{NH_2}$ chemical shifts relative to the signal of aniline in DMSO (4.90 ppm) are taken with a negative sign and, after subtraction of the inductive component in the numerator, remain very small. The accuracy of this calculation of σ_R is

TABLE 2. Values of the σ_R^0 Constants of the Phenyl Groups

Solvent	Method of determination and model compound	σ_R^0
CCl_4	IR spectrum $A^{1/2}$ (ν_8)Ph—Ph [10]	−0.10
CCl_4	IR spectrum $A^{1/2}$ ($\nu_{C=C}$)$PhCH=CH_2$ [11]	−0.10
CCl_4	IR spectrum $A^{1/2}$ ($\nu_{C\equiv C}$)$PhC\equiv CH$ [12]	−0.06
Acetone	^{13}C NMR Ph—Ph [13]	−0.07
Acetone-D_6	^{13}C NMR Ph—Ph [13]	−0.07
Aprotic solvents methanol	^{19}F NMR PhC_6H_4F [14]	−0.09*
Benzene	pK PhC_6H_4COOH, 25 °C [15]	−0.11
Water	pK_a PhC_6H_4COOH, 25 °C [15]	−0.11
—	log k_1, thermal decomposition of p-$PhC_6H_4OCOOC_2H_5$, 363,4 °C [16]	−0.02**
60% acetone	log k_2, alkaline hydrolysis of p-$PhC_6H_4CH_2COOC_2H_5$, 25 °C [17]	−0.11**
Benzene	log k_2, piperidino-dechlorination of-2-$NO_2C_6H_3Cl$, 45 °C [18]	−0.05
—	Calculation ab initio in the 4-31G basis. $PhCH=CH_2$ [19]	−0,07

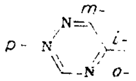
*Average value.

**Calculated from two-parameter correlation equations (see Table VIII in [8]); $\sigma_I = 0.13$ [9] was adopted for Ph.

TABLE 3. $\Delta\sigma_{R(N)}$ Increments

Position of the nitrogen atom in the ring*		$\Delta\sigma^0_{R(N)}$	$\Delta\sigma^-_{R(N)}$
ortho-	(2-N)	0,09	0,22
meta-	(3-N)	0,03	0,08
para-	(4-N)	0,08	0,25

*Relative to the ipso carbon atom. For the example, for the



(5-as-Tr) group

all three increments are taken into account.

therefore low. However, it was established that these constants for the azinyl groups can, when necessary, be estimated by a simple conversion starting from the corresponding σ_R^- constants:

$$\sigma_R = 0{,}88\sigma_R^- . \tag{3}$$

It follows from the data presented in Table 1 that both resonance constants depend on the number and position of the nitrogen atoms in the heteroaromatic ring. The relative contributions of endocyclic nitrogen atoms [increments $\Delta\sigma_{R(N)}{}^0$ and $\Delta\sigma_{R(N)}$] to the corresponding resonance constants of azinyl groups (Table 3) were determined by the method of least squares (MLS). The nitrogen atoms in the ortho and para positions of the heteroaromatic ring, which are in conjugation with the side bond, make the most substantial contribution to the constants. The increments found make it possible a priori to calculate the resonance constants of other azinyl groups also:

$$\sigma_R(Az) = \sigma_R(Ph) + \Sigma\Delta\sigma_{R(N)}. \tag{4}$$

It follows from Eq. (4) that the resonance constants of the 3-pyridazinyl and 2-pyrazinyl (2-Pyz) groups should be virtually equal (Table 1). The mean-square deviations of the values calculated via an additive scheme from the empirically found values amount to 0.01 for $\sigma_R{}^0$ and 0.05 for $\sigma_R{}^-$. The greatest deviations are noted for the 5- and

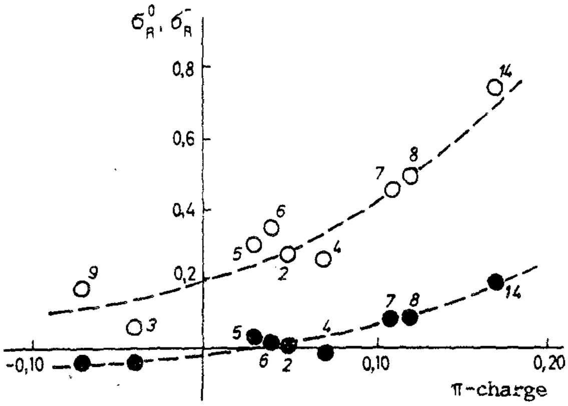


Fig. 1. Correlation of the resonance constants with the π-electron charges on the ipso atoms of the azinyl groups. The data from calculation by the ab initio method were taken from [1]. The numbering of the points corresponds to the numbering in Table 1: σ_R^0) •; σ_R^-) o.

TABLE 4. Equilibrium Acidities of Pyrazine Derivatives

Compound	Solvent, gegenion	Correlation equation	*n*	*r*	*s*	p*K*	
						calc.	found
2-CH_3Pyz	DME Cs+	$pK_{CH} = 44{,}3 - 25{,}3\sigma_p^-$ (Az)	10	0,970	1,4	31,6	31,7 [25]
2-NH_2Pyz	DMSO K+	$pK_{NH} = 32{,}6 - 13{,}1\sigma_p^-$ (Az)	10	0,975	0,7	26,1	25,8 [26]
2-CH_3COPyz	DMSO K+	$pK_{CH} = 26{,}8 - 14{,}8\sigma_p^-$ (Az)	9	0,928	1,0	19,4	18,7 [26]

6-unsym-triazinyl groups; this may be associated with the pronounced decrease in the accuracy of the values in the case of summing up several increments.

The different effects of nitrogen atoms from the ortho, meta, and para positions (2-N, 3-N, 4-N) relative to the ipso carbon atom of the ring on the resonance constants of the azinyl groups depend on the distribution of the π-electron density over the heteroring. In particular, distinct symbatic character of these constants and the π-electron charges in the corresponding positions of the ring is observed (Fig. 1).

The correlated constants of the Hammett type (Table 1) can be readily derived on the basis of the inductive and resonance constants found for the azinyl groups. For the 2-pyrazinyl group the σ_p^- constant had not been previously determined. Nevertheless, this constant can be estimated after prior calculation of its components σ_R^- (see above) and σ_I within the framework of the computational schemes developed. Assuming that the dipole moment of the 2-pyrazinyl group $\mu(Pyz) \approx 0$, we obtain, in accordance with [9], that $\sigma_I = 0.16$, whence $\sigma_p^-(Pyz) = 0.50$.

Since the σ_p^- constants of azinyl groups satisfactorily describe the equilibrium CH acidities of methyl azines and the NH acidities of amino azines [24], one could verify the correctness of the calculated $\sigma_p^-(Pyz)$ value. The pK values of 2-methylpyrazine and 2-aminopyrazine in aprotic solvents, found experimentally and predicted on the basis of the corresponding correlation equations and the above-established $\sigma_p^-(Pyz)$ value, are presented in Table 4. The result obtained serves as a confirmation of the usefulness of an additive scheme for evaluating the σ constants of azinyl groups. Let us note that calculation of the CH acidity of 2-acetylpyrazine gives a poorer result, since a cruder correlation relationship than in the preceding two examples is used in the calculation.

LITERATURE CITED

1. A. F. Pozharskii, Khim. Geterotsikl. Soedin., No. 9, 1155 (1979).
2. O. P. Shkurko, S. G. Baram, and V. P. Mamaev, Khim. Geterotsikl. Soedin., No. 1, 66 (1983).

3. O. P. Shkurko, S. A. Kuznetsov, A. Yu. Denisov, and V. P. Mamaev, Khim. Geterotsikl. Soedin., No. 7, 951 (1986).
4. O. P. Shkurko and V. P. Mamaev, Zh. Org. Khim., 15, 1737 (1979).
5. S. G. Baram, O. P. Shkurko, and V. P. Mamaev, Izv. Sibirsk. Otd. Akad. Nauk SSSR, Ser. Khim., No. 4, 135 (1982).
6. O. P. Shkurko, L. L. Gogin, S. G. Baram, and V. P. Mamaev, Izv. Akad. Nauk SSSR, Ser. Khim. Nauk, No. 2, 95 (1980).
7. O. P. Shkurko, L. L. Gogin, S. G. Baram, and V. P. Mamaev, Khim. Geterotsikl. Soedin., No. 2, 257 (1987).
8. S. Ehrenson, R. T. C. Bownlee, and R. W. Taft, Progress in Physical Organic Chemistry, Vol. 10, R. W. Taft, (ed.), Wiley-Interscience, New York (1973), p. 1.
9. O. P. Shkurko and V. P. Mamaev, Khim. Geterotsikl. Soedin., No. 5, 672 (1987).
10. R. T. C. Brownlee, R. E. J. Hutchinson, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, J. Am. Chem. Soc., 90, 1757 (1968).
11. A. R. Katritzky, R. F. Pinzelli, M. V. Sinnott, and R. D. Topsom, J. Am. Chem. Soc., 92, 6861 (1970).
12. T. B. Grindley, K. F. Johnson, A. R. Katritzky, H. J. Keogh, C. Thirkettle, R. T. C. Brownlee, J. A. Munday, and R. D. Topsom, J. Chem. Soc., Perkin 2, 276 (1974).
13. S. G. Baram, O. P. Shkurko, and V. P. Mamaev, Izv. Akad. Nauk SSSR, Ser. Khim., No. 2, 294 (1983).
14. R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, J. Am. Chem. Soc., 85, 3146 (1963).
15. R. W. Taft, S. Ehrenson, I. C. Lewis, and R. E. Glick, J. Am. Chem. Soc., 81, 5352 (1959).
16. G. G. Smith, D. A. K. Jones, and R. Taylor, J. Org. Chem., 28, 3547 (1963).
17. Y. Yukawa, Y. Tsuno, and M. Sawada, Bull. Chem. Soc. Jpn., 39, 2274 (1966).
18. W. Greizerstein, R. A. Bonelli, and J. A. Brieux, J. Am. Chem. Soc., 84, 1026 (1962).
19. S. Marriott and R. D. Topsom, J. Chem. Soc., Perkin 2, 1045 (1985).
20. O. Exner, Coll. Czech. Chem. Commun., 31, 65 (1966).
21. M. Sjöström and S. Wold, Chem. Scripta, 9, 200 (1976).
22. L. K. Dyall, Aust. J. Chem., 17, 419 (1964).
23. Y. Tsuno, L. Fujio, Y. Takai, and Y. Yukawa, Bull. Chem. Soc. Jpn., 45, 1519 (1972).
24. V. P. Mamaev, O. P. Shkurko, and S. G. Baram, Advances in Heterocyclic Chemistry, Vol. 42, A. R. Katritzky, (ed.), Academic Press, Orlando (1987), p. 20.
25. M. I. Terekhova, É. S. Petrov, O. P. Shkurko, M. A. Mikhaleva, V. P. Mamaev, and A. I. Shatenshtein, Zh. Org. Khim., 19, 465 (1983).
26. M. I. Terekhova, É. S. Petrov, M. A. Mikhaleva, O. P. Shkurko, V. P. Mamaev, and A. I. Shatenshtein, Zh. Org. Khim., 18, 9 (1982).