Chemistry of Heterocyclic Compounds, Vol. 39, No. 1, 2003

COMPARATIVE CHARACTERISTICS OF SOME PHYSICOCHEMICAL PROPERTIES OF AZOLES

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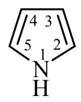
We have carried out a correlation analysis of some physicochemical characteristics of pyrrole, pyrazole, imidazole, triazole, and tetrazole, calculated by the semiempirical quantum-chemical AM1 method. We have found the linear dependences of the ionization potential, the dipole moment, and the acidity on the π-electron excess, and also the dependence of the ionization potential on the enthalpy of formation of the studied azoles.

Keywords: azoles, dipole moment, quantum-chemical calculations, correlation analysis, ionization potential, enthalpy.

Five-membered nitrogen-containing heterocyclic compounds (pyrrole (**1**), pyrazole (**2**), imidazole (**3**), 1,2,3-triazole (**4**), 1,2,4-triazole (**5**), and tetrazole (**6**)) have many useful properties [1], and so it is of interest to carry out a comparative analysis of some of their physicochemical properties.



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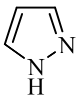

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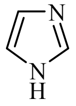

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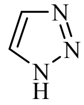

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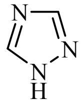

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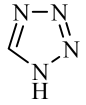

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With this aim, the AM1 quantum-chemical semiempirical method [2] was used to calculate the values of the enthalpy of formation (ΔH), the ionization potential (I), the dipole moment (μ), and the π-electron excess (π) [3] of the studied azoles. The calculations were performed with full optimization of the geometric parameters. The results obtained agree well with recent data [4, 5]. The correlation curves were plotted using these calculations (Figs. 1-3).

The physical meaning (Fig. 1*a*) of the dependence of the ionization potential of the studied azoles on their enthalpy of formation is not quite clear, but the high correlation coefficient according to Jaffe [6] ($r = 0.98$) allows us to draw the trivial conclusion that the ionization energy increases with an increase in the number of heterocyclic nitrogen atoms and consequently with an increase in the value of the enthalpy. At the same time, the ionization potential decreases linearly with an increase in the π-electron excess (Fig. 1*b*). This means that protonation centers can be not only the heterocyclic nitrogen atoms but also the carbon atoms on the five-membered ring, and that the π-electron excess facilitates the ionization process.

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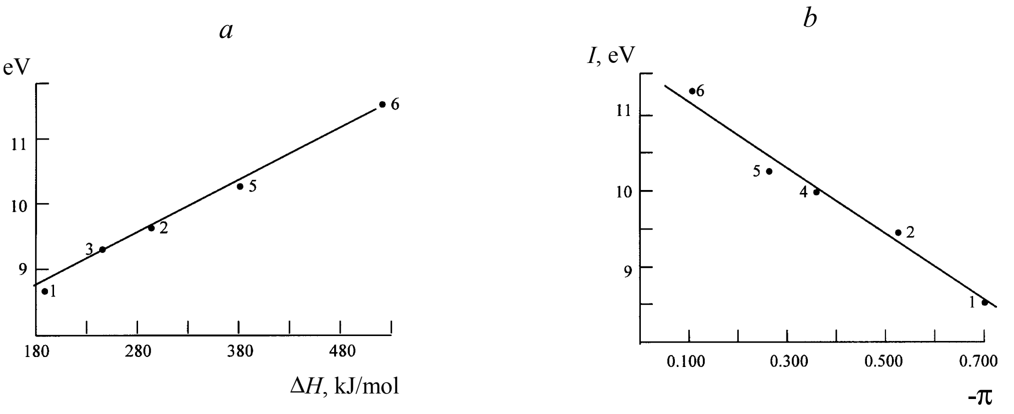

Fig. 1. Ionization potential I vs. the formation enthalpy ΔH (*a*) and the π-electron excess (π) for azoles (*b*).

Of course, for pyrrole **1**, as the progenitor of the azoles, the highest value of the π-electron excess and the lowest values of I are characteristic, while for tetrazole **6** we see the opposite. The correlation coefficient for this $r = 0.96$. Consequently, electrophilic substitution is the most typical for pyrrole [7], and such reactivity decreases in the series: **1** > **2** > **3** > **4** > **5** > **6**. An analogous correlation is also observed for the dipole moment (Fig. 2, $r = 0.95$). According to this dependence, with a decrease in the π-electron charge on the ring carbon atoms, the dipole moment of the molecule increases as a result of the increase in the charge on the ring nitrogen atoms and consequently the polarity of the molecule increases in the series **6** > **4** > **3** > **2** > **1**.

We know that azoles exhibit both basic and acidic properties [1]. The basicity (pK_b) does not correlate with the π-electron excess, and in this series we do not observe any regular connection with other physicochemical characteristics. But the acidity (pK_a) increases linearly with a decrease in the π-electron excess (Fig. 3*a*, $r = 0.96$). A decrease in the π-electron charge on the ring carbon atoms causes an increase in the charge on the nitrogen atoms bonded to a hydrogen atom and consequently an increase in acidity.

The possibility of establishing a general rule describing the change in physicochemical properties of azoles is apparently unrealistic, but finding some correlations certainly helps us provide a comparative quantitative description for them.

The acidity of azoles may also be described quantitatively using the values of the bond order for the NH group (P_{NH}). In fact, as we see from Fig. 3*b*, the acidity of azoles decreases linearly with an increase in the value of P_{NH} ($r = 0.97$), which is explained by the increase in the mobility of the amine proton.

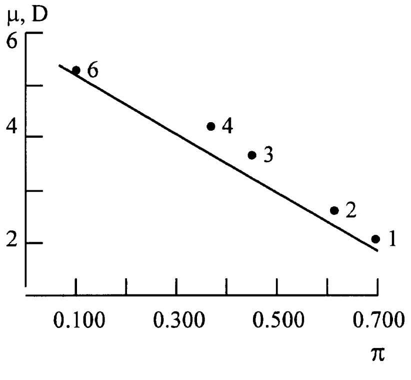

Fig. 2. Dipole moment μ vs. π-electron excess (π) for azoles.

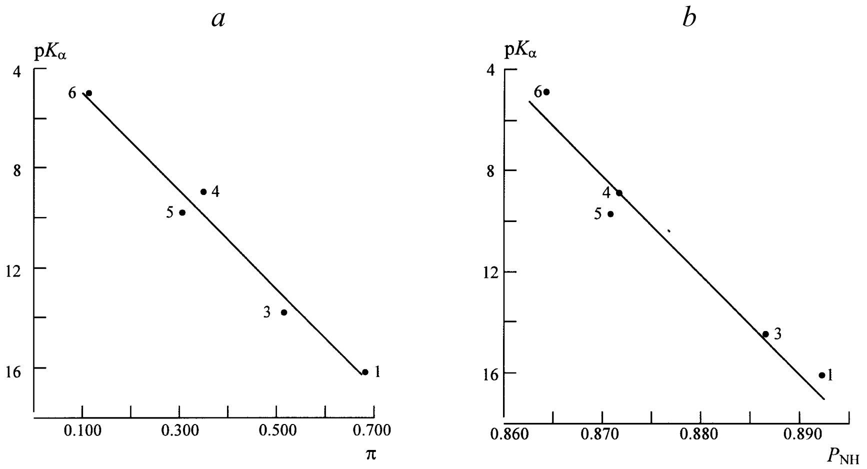

Fig. 3. Acidity (pK_a) vs. π-electron excess (π) for azoles (*a*) and bond order for the NH group (P_{NH}) (*b*).

This research was done with the financial support of the Department of Science and Technology of the Republic of Georgia.

REFERENCES

1. M. R. Grimmet, *General Organic Chemistry*, Khimiya, Moscow (1985), **8**, 429.
2. M. I. S. Dewar, E. G. Zeobish, E. F. Healy, and J. S. Stewart, *J. Am. Chem. Soc.*, **107**, 3902 (1985).
3. A. F. Pozharskii, *Khim. Geterotsikl. Soedin.*, 723 (1977).
4. C. Ogretir and S. Yarligan, *J. Mol. Struct. THEOCHEM,*, **425**, 249 (1998).
5. C. S. Gyeong, C. Y. Gu, and P. B. Sam, *J. Mol. Struct. THEOCHEM*, **432**, 41 (1998).
6. H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).
7. G. Marino, *Adv. Heterocycl. Chem.*, **13**, 235 (1971).