EVALUATION OF THE CONTRIBUTION OF INTRAMOLECULAR INTERACTIONS TO PROTON AFFINITY OF AMINOFURAZANS BY THE SCF-MO METHOD IN THE MINDO/3 APPROXIMATION

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The study of the chemical properties of furazans showed that the amino group bound to the furazan ring has low nucleophilic activity [1]. For example, aminofurazans do not form salts with mineral acids and do not undergo alkylation [2]. The ability of a base to be protonated is characterized by the value of its proton affinity (PA). By definition, PA is equal to, but opposite in sign, to the enthalpy of the gaseous reaction:

$$X{-}NH_2 + H^+ \longrightarrow X{-}NH_3^+$$

The influence of substituent X on the PA of an amine can be characterized by its resonance and inductive effects. To find the qualitative dependence of the PA of an amine on the above effects of the substituent of the amino group, we must determine how the value of PA changes with change in the values of these effects. Therefore, in the present work, we compared the results of calculation for aminofurazan and aniline. To simplify the analysis, without losing any general considerations, we consider the simplest representative of the aminofurazan series, 3-aminofurazan.

The calculation is carried out by the MINDO/3 semiempirical SCF-MO method developed by M. Dewar and his co-workers [3]. The program by which all the computations were carried out makes it possible to find the geometry of the molecule, corresponding to the minimum of its total energy, with variation in the corresponding geometrical parameters (bond length, valence, and torsion angles). By the above minimization procedure, we found that the amino group in the two molecules has a planar structure and is coplanar with the ring of the substituent. In the protonated form of the molecules, the ammonium group has a tetrahedral structure.

The results of the analysis of the electron density distribution for the basic and protonated forms of the molecules are given in Fig. 1. For the basic form of the molecules, we can isolate MO with a π-orbitals symmetry. They are composed of the contributions of the $2p_z$ AO of the amino group nitrogen atom containing an unshared pair of electrons, and $2p_z$ AO of ring atoms of the substituent. The total number of electrons on the π-MO of unsubstituted furazane and benzene is six. When an amino group is introduced into these rings, according to the results of our calculation, the number of electrons on the $2p_z$ AO of furazanyl increases to 6.101, and in phenyl to 6.145, i.e., phenyl has a greater -R-resonance effect than furazanyl. From the data on the charges of the amino group atoms, listed in Fig. 1, and taking into account the above shift of part of the charge from its $2p_z$ AO as the result of the p–π conjugation with the substituent, we can evaluate the inductive effect of the substituent on the amino group. It was found that phenyl has a stronger +I-inductive effect than furazanyl.

In the protonated form of the two molecules, the ammonium group has no unshared pair of electrons, and also has a tetrahedral structure. Hence, when speaking of the influence of the substituent on the distribution of electrons in the protonated form, we can consider only its inductive effect. The overall charge of the ammonium group for the furazane ring is greater than for the benzene ring. This means that with respect to the ammonium group,

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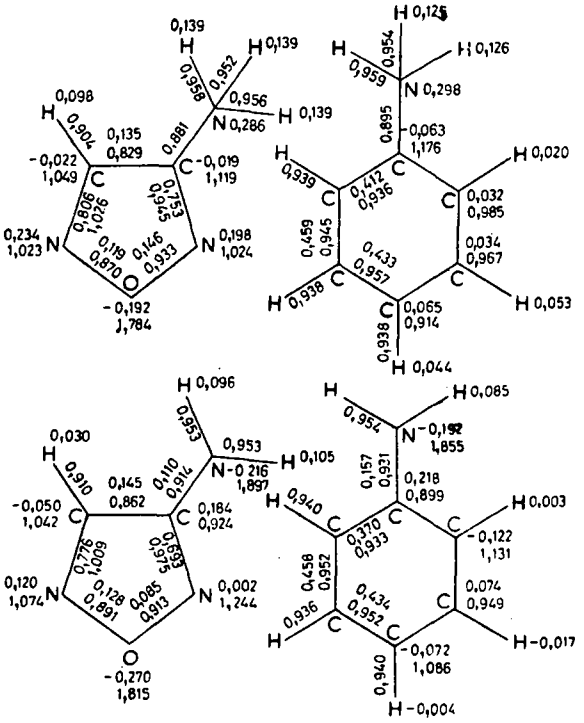

Fig. 1. Given: π-bond (upper value), σ-bond order (lower value); charges on atoms (upper value), number of electrons on p_z-orbital (lower value).

furazanyl has a weaker +I-effect than phenyl, i.e., the same tendency is retained for the +I-effect as in the case of the phenyl group. However, since the ammonium group is a stronger electron acceptor than the amino group, the value of the +I-effect of the two substituents is greater in the protonated form of the molecules.

From the interrelationship between the +I- and -R-effects of the substituent and the distribution of the electron density in the basic and protonated forms of the amines examined by us, it is easy to assess the influence of these effects on the proton affinity.

The higher the −R-resonance effect of the substituent, exhibited only in the basic form of the amine molecule, the more stable is this form. This is because the −R-effect of the substituent indicates an increase in the order of the N-C π-bond between the amino group and the substituent, and also an increase in the π-electron density on the AO of the substituent itself. Hence, the higher −R-effect of the substituent, the lower is the proton affinity of the amine.

The inductive effect of the substituent is manifested in both the basic and the protonated forms of the amine molecules. However, as we have already noted, in the case of the ammonium group its value is higher, since this group, being positively charged, has electron-acceptor properties which are considerably stronger than those of the amino group. The +I-effect of the substituent leads to strengthening of the σ-bonds in the functional group, while their number in the ammonium group is greater by one than in the amino group. This shows that the +I-effect of the substituent affects the stabilization of the protonated form of the molecule more strongly than the stabilization of the basic form. Therefore, the proton affinity of the amine is higher the greater the +I-effect of the substituent.

According to our calculations, the proton affinity of aminofurazan is equal to 7.772 eV, which is less than 8.301 eV for aniline. Moreover, as we have already noted, the +I- and −R-effects in furazanyl are less pronounced than in phenyl. By considering these results, and the above analysis of only the qualitative influence of the +I- and −R-effects of the substituent on the proton affinity of amines, we can explain the experimentally established fact that the nucleophilic activity of the amino group in aminofurazans is appreciably lower than in aniline. In fact, the −R-effect in furazanyl is much less pronounced than in

phenyl, but the proton affinity is higher in aniline than in aminofurazan. Hence, the reason why the nucleophilic activity of aminofurazan is appreciably lower than for aniline is that the +I-effect of furazanyl is lower than that of phenyl.

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THERMOLYSIS OF QUATERNARY SALTS OF 2,3,3-TRIMETHYLINDOLENINE AND INDOCARBOCYANINES

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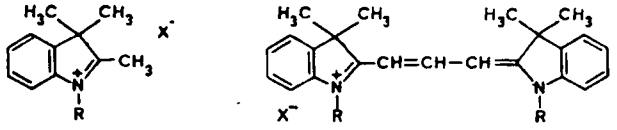
The rearrangement of alkyl- and aryl-substituted indoles, indolenines, and quaternary salts of the latter, which involves the migration of the hydrocarbon substituents between the 2 and 3 positions, has been the subject of many studies (e.g., [1,2]). The conversion of 2-ethyl- and 2-isopropyl-3,3-dimethylindolenine methiodides to 3-ethyl- and 3-isopropyl-2,3-dimethylindolenine methiodides has been reported [1]. The authors assumed that any 2,3,3-trialkylindolenine alkiodide undergoes decomposition at a certain temperature to a 1,2,3-trialkylindole and an alkyl iodide as a result of elimination of the alkyl group from the 2 position and migration of the 3-alkyl group to the 2 position. The resulting alkyl iodide subsequently enters the 3 position of the indole. However, no evidence of this rearrangement pathway was presented.

In the present research we investigated the pathways of the thermal transformations of quaternary 2,3,3-trimethylindolenine salts (Ia-d) and indocarbocyanine salts (IIa-d) with the aid of pyrolytic gas chromatography.



Ia-d IIa-d

I,II a-c R=CH_3; d R=C_2H_5; a,d X=I; b X=Br, c X=Cl

The investigated compounds were heated to 300°C in the vaporization chamber of a gas chromatograph with a flame-ionization detector. The pyrolysis products were identified from the chromatographic characteristics of the individual compounds, the presence of which was assumed in the pyrolyzate, and also from the UV spectra of the isolated fractions of the pyrolyzate. Data on the compositions and structures of the chromatographically identified compounds with an indication of the relative retention times (α_{rel}) and the relative percentages of each of them in the mixture are presented in Table 1.

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