ELECTRONIC STRUCTURE OF THE THIABENZENE ANION

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2,4,6-Triphenyl-4H-thiapyran has considerably higher acidity than its oxygen analog (the pK_a values are estimated to be 19.5 and 37, respectively) [1]. In the opinion of Schmidt, Burkert, and Prewo [1], the substantial difference in the acidities of these compounds is due to the relatively high stability of the thiabenzene anion, which presumably has a six-electron π system similar to the thiapyrylium cation but in which the two additional electrons occupy the vacant 3d orbital of the sulfur atom.

To verify the adequacy of the proposed model we calculated the electronic structure of the thiabenzene anion by the standard CNDO/2 (complete neglect of differential overlap) method. This method gives a somewhat too high electron density on the vacant d orbitals [2] but, nevertheless, makes it possible to obtain the upper limit of their population.

Only a third of the total charge is concentrated on the heteroatom in the thiabenzene anion. The population of the vacant AO of the sulfur atom in the anion indicates that its state is close to the $s^2p_xp_yp_z^2$ valence state. The migration of a portion of the charge to the heteroatom is due entirely to the acceptor properties of its vacant $3d_\pi$ orbitals. Judging from the magnitude of the bond orders, the degree of localization of the double bonds in the system under consideration is higher than in the thiapyrylium cation. In terms of the theory of valence schemes this result can be interpreted as an increase in the relative weight of dienic resonance structures in the anion. Thus a resonance structure with three localized double bonds and two unshared pairs of electrons on the sulfur atom, one of which occupies the d orbital, cannot serve as a model of the thiabenzene anion.

The population of all of the 3d AO of sulfur constitutes only 0.683 of the elevated estimated value. Whereas the total population of these orbitals exceeds the corresponding value for the thiapyrylium cation by only 20%, the electron density on the $3d_\pi$ AO of sulfur is almost doubled in the anion (0.354 and 0.201, respectively). Moreover, the interaction of the latter with the π system of ring carbon atoms is due entirely to the effective charge on the heteroatom.

The results of the calculations provide evidence that the thiabenzene anion has a six-electron π system formed by the $2p_\pi$ AO of the carbon atoms and the $3d_\pi$ AO of the sulfur atom; however, $p_\pi-d_\pi$ conjugation does not lead to a significant decrease in the energy of the heteroring. According to Dewar [3], this sort of π system undergoes cleavage at the heteroatom and does not ensure aromatic stabilization of the molecule. The thiabenzene anion, like its oxygen analog, therefore could not be isolated from the reaction mixture. Thus the presence of d orbitals in the valence shell of sulfur does not explain the increased acidity of the thiapyran ring as compared with the pyran ring. It is apparently due to the relatively small change in the energy of the sulfur-containing ring when a proton is detached.

LITERATURE CITED

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