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LETTERS TO THE EDITOR

ELECTRONIC STRUCTURE OF DIOXOPOLYHYDROACRIDINES

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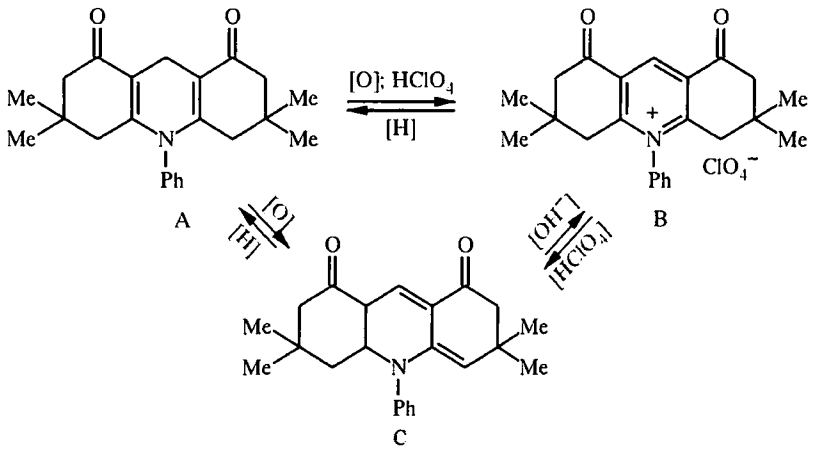
Reaction of primary aromatic amines, formaldehyde, and dimedone in the presence of mineral acid produces a mixture of 1,8-dioxodecahydroacridines (A) and 1,8-dioxooctahydroacridinium quaternary salts (B) [1]. Symmetric decahydroacridinediones without a substituent at the nitrogen atom have also been prepared by reacting the imine of dimedone with aldehydes in acetic acid [2]. Additional investigations revealed compound A as reaction intermediate which transform into salt B upon longer heating.

Quaternary salt B reacts with bases to produce bright red anhydrobase C, which is also produced from A via oxidation of its alcohol solutions. The transformation occurred according to the following scheme:



The structures of the prepared compounds were studied using IR, UV, and PMR spectra [1]. Therefore, it seemed interesting to investigate the geometry and electronic structures of A, B, and C using quantum-chemical calculations. The effective charges were calculated using the CNDO/2 method. The geometry of compounds was calculated using the AM1 method from the Hyperchem program set [3]. Models without the N-phenyl substituent (1,2,3) and with N-phenyl substituents (4, 5, 6) were calculated in order to reveal the effect of the N-phenyl substituent on the structure. As seen from the diagrams provided, compounds 1, 2, 4, and 5, in contrast with 3 and 6, have symmetric structures.

Effective Charges. The nitrogen atom is characterized by a high negative charge, that is decreased by the N-phenyl substituent. The greatest effect is seen for the compounds of B group. Only for group B does the N-phenyl group affect the charge on the carbon atoms of the pyridine ring. It reduces the negative charges (electron-withdrawing effect). The N-phenyl substituent decreases also the effective charge on the oxygen atom of the carbonyl group (in group B, the N-phenyl substituent has no effect in the other groups).

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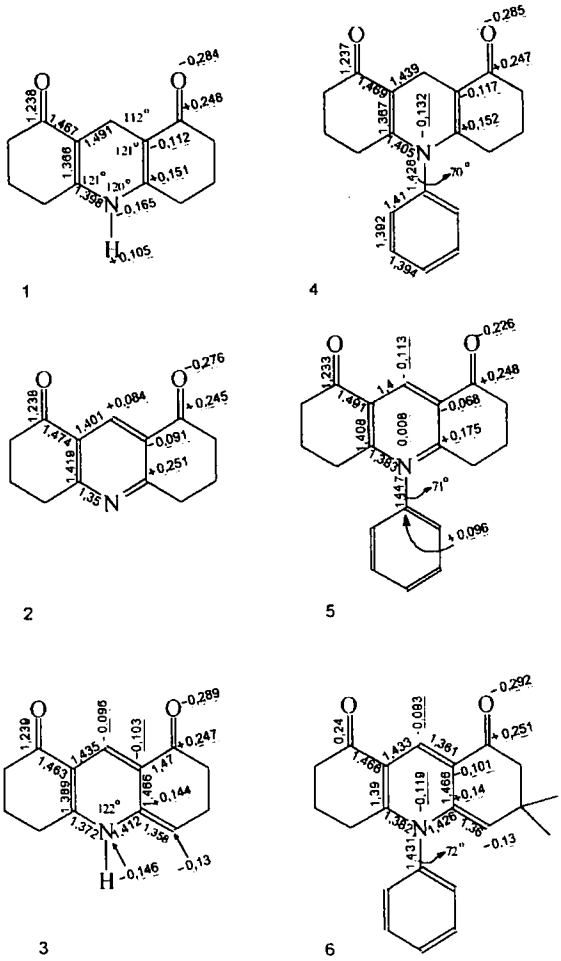

Calculated electron charges and geomety.

Optimized Geometry. Calculations confirm the dihydropyridine structure of compounds A. The bonds N–C_α and C_β–C_γ are lengthened; C_α–C_β is shortened. The N-phenyl substituent has practically no effect. For compound B, the bonds are aromatic with the exception of the N–C_α bond. The N-phenyl substituent evens out the bonds lengths of the pyridine ring.

The structure of the pyridine ring is more complicated for compounds of the C group. These compounds have a C_α=CH group bonded with the pyridine ring. In this instance the shortened and lengthened bonds alternate according to the structure of the anhydrobase C. The N-phenyl substituent has no effect on the bond orders in this system.

The dihydropyridine ring of compounds A is characterized by decreased C_β–C_γ–$C_{\beta'}$ bond angles (112°) compared with the normal angle for sp^2-hybridization. Some of the other angles are increased slightly. The pyridine ring of compounds B is planar.

The angle C_α–N–$C_{\alpha'}$ of anhydrobases C is slightly increased (122°). This suggests that the ring is internally strained. The plane of the N-phenyl substituent for all groups of compounds (A, B, and C) is twisted relative to the pyridine ring by 70-72°.

In general, the calculated effective charges and geometry of compounds studied are consistent with the structures previously assigned to them.

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