APPLICATION OF AM1 METHOD IN STUDYING TAUTOMERIC CONVERSIONS OF 1,3-DIIMINOISOINDOLINE AND ITS NITRO AND AMINO DERIVATIVES

A. V. Lyubimtsev, A. Baran'ski, M. K. Islyaikin, and R. P. Smirnov

The semiempirical method AM1 was used to calculate transition states corresponding to conformational and tautomeric conversions of 1,3-diiminoisoindoline, and also its nitro and amino derivatives. Tautomeric conversions through an intermolecular mechanism involving a protic solvent have a lower energy barrier than in the case of intramolecular proton transfer. Substitution in the benzene ring of 1,3-diiminoisoindoline does not have any significant effect on the energy barriers of the conformational transitions and tautomeric conversions. Calculated IR and electronic spectra of 1,3-diiminoisoindoline are in satisfactory agreement with the experimental spectra.

1,3-Diiminoisoindoline and its derivatives are finding extensive applications in the synthesis of phthalocyanines and macroheterocyclic compounds [1-3]; however, many questions regarding the features of its structure (stereoisomerism, tautomerism, and the influence of substitution on these processes) have not been studied adequately. On the basis of electronic absorption spectra of solutions of isoindoline derivatives, it was concluded in [4, 5] that these compounds exist in isoindoline and isoindolenine forms; this conclusion was subsequently confirmed by means of IR spectroscopy [6].

Theoretical study of the stereoisomeric conversions of 1,3-diiminoisoindoline and its derivatives has been limited to calculations of the tautomers by the Hückel method (Zaitsev et al. [7]). In that work, on the basis of an examination of energy and electronic indexes, the investigators concluded that the isoindoline form is more stable than the isoindolenine.

Investigation of the stereochemistry of 1,3-diiminoisoindoline and its derivatives is an important task from the standpoint of examining the reactivities of these compounds. The work reported here was aimed at investigating conformational and tautomeric conversions of 1,3-diiminoisoindoline, and also the influence of substituents and the choice of solvent on the energetics of the isomer transitions.

Calculations of the stationary points on the potential energy surfaces were performed by the AM1 method, using the MOPAC-7 program package [8] with full optimization of geometric parameters. The saddle points corresponding to transition states were found by means of the SADDLE procedure with subsequent optimization (NLLSQ) and testing for correspondence to critical conditions [9]. The calculations were performed at the Krakow Computer Center on a CONVEX C3220 computer and at the Ivanovo State Chemical Technology Academy on a DX2 computer (Intel 486 processor).

1,3-Diiminoisoindoline can be represented in the form of three geometric isomers identified as I, II, and III in the following scheme. Calculated heats of formation of compounds I-III are listed under the structural formulas.

Structure I is the most favorable energetically. The transition I → II encounters a barrier higher than 600 kJ/mole, so that this transition is improbable. In contrast, the transition between the isomers I and III encounters only a relatively low potential barrier, 92.6 kJ/mole.

The structure of the transition state I → III is shown in Fig. 1. Characteristic for this structure is a decrease of the N10-H13 bond length to 0.96 Å (from 0.99 Å in the original structure I), and also a change of the C(1)-N(10)-H(13) angle from 117.13° to 173.46°.
The transition from the isoindoline structure to the isoindolenine structure (1-amino-3-iminoisoindolenine IV) can be represented as intramolecular transfer of a proton from the cyclic nitrogen atom to an exocyclic nitrogen atom, with the participation of the unshared pair of electrons of the exocyclic atom.

From the standpoint of conformance to stereoelectronic requirements, structure III is preferred over structure I. Calculations of transition states for the conversions I → IV and III → IV have shown that the activation energy of the first transition is greater than 600 kJ/mole; i.e., the transition is improbable. For the transition III → IV, the energy barrier is 303.9 kJ/mole, which is in good agreement with the results from ab initio calculations (4-31G basis) for formamidine, where a value of 248.0 kJ/mole was found for the barrier [10]. The structure of the transition state III → IV is shown in Fig. 2.

In the transition state, the H(12) migrating proton is in the field of the nitrogen atoms N(2) and N(10). The distances N(2)-H(12) and N(10)-H(12) are approximately equal (1.40 and 1.42 Å, respectively).

Thus, the most energetically favorable is the conversion of the indoline form I to the indolenine form IV through the structure III.

With the aim of evaluating the influence of substitution on transitions between isomers and tautomeric conversions, we calculated the isoindoline structures V-XVI and isoindolenine structures XVII-XXIV of 4-nitro, 5-nitro, and amino derivatives, and also transition states corresponding to possible interconversions. The structures under consideration and the values of the heat of formation and activation barrier are listed in Tables 1 and 2. From the data of Table 2, it follows that the introduction of the electron-accepting nitro group lowers the energy barrier of both the conformational and tautomeric conversions. The amino group has the opposite effect.