ASYMMETRIC NITROGEN.

76.* QUANTUM CHEMICAL STUDY OF GEOMETRY AND CONFIGURATIONAL STABILITY OF KETENIMINES

G. V. Shustov, A. V. Kachanov, S. N. Denisenko, and R. G. Kostyanovskii

MNDO calculations were carried out of the ground and transitional states of the planar inversion of the N atom for ketenimines containing σ (Me, NH₂, OH, OMe, and F) and π(CH=O) acceptor N substituents as well as for C-amino- and C-formylketenimines. Configurationally stable N-amino-, N-alkoxy-, and N-fluoroketenimines (inversion barriers ~27-45 kcal/mole) are of interest for further experimental stereochemical studies. The geometry of the ketenimine fragment is determined in general by nN-Trcc* conjugation. Other orbital and Coulombic interactions affect C- and N-substituent orientation relative to this fragment.

Keywords: ketenimine geometry, nitrogen atom inversion.

C,C-Asymmetrically substituted ketenimines possess allene asymmetry (axial chirality) and owing to high reactivity [2] can be used in the optically active form as reagents for asymmetric synthesis. However, in the case of ordinary N-alkyl- and N-arylketenimines this is inhibited by the low barrier to planar inversion (BPI) of the N atom, 8.9-14.7 kcal/mole [3, 4] (at 20°C the period of half racemization is less than 1 sec).

From the example of imines it is known that introduction of a σ acceptor substituent of the amino, alkoxy group, or halogen type on an sp² hybridized N atom significantly lowers the BPI of the latter [5, 6]. However, up to now N-alkoxy- and N-halogen-substituted ketenimines have not been described and the configurational stability of the known N-amino derivatives has not been studied [7]. The most reliable quantitative estimates of the energetic and structural parameters of N-heteroketenimines can be obtained by using nonempirical quantum chemical calculations as was shown previously with the simple ketenimine 1a [8, 10]. Nonetheless, we have found that the BPI and geometric parameters of this compound, obtained by the semiempirical MNDO method [11], are closer to the experimental values than the data of several ab initio calculations (Table 1). The BPI calculated by us for N-methylketenimine (1b) (Table 2) using this method also corresponds well to the experimental values for N-alkylketenimines [3, 4]. Therefore, the geometry and configurational stability of the N-hetero-substituted ketenimines 1e-f and 2 were studied by the MNDO method. For a more complete explanation of the dependence of the properties that interest us on the nature of the substituent we also studied the ketenimine 1g with a π-accepting formyl N substituent and the 3a, b ketenimines containing an amino group (π donor) and a formal group (π acceptor), respectively, on the C¹ atom.

For previous communication, see [1].

The main factor determining the geometry of the ketenimine fragment \( \text{C} = \text{C} = \text{N} \) is probably the \( \pi_{\text{N}} - \pi_{\text{CC}}^* \) conjugation. The latter can be observed from a drawing obtained using the MINDO/3-PERVAL program [12] of the highest occupied molecular orbital (MO) of the \( 1\alpha \) ketenimine (Fig. 1), the geometry of which was optimized with the MNDO method (Tables 1 and 2).

As is seen from scheme (3) in terms of the valence bonds realization of the above conjugation should lead to an increase in the multiplicity of the CN bond and a decrease in that of the CC. Correspondingly, the CN bond should be shortened and that of the CC lengthened.

As the electronegativity of X decreases the capacity of the nonbonding orbital of the N atom for conjugation increases owing to an increase in the contribution of the \( \rho \) function. In fact, shortening of the CN bond and lengthening of the CC bond as the electronegativity of the N substituent decreases in the series Me < H < NH\(_2\) < OH(OMe) < F is observed (Table 2). The electron density (negative charge) on the C\(_1\) atom is also increased (Table 2).

The shortest CN bond and longest CC, as well as the largest negative charge on the C are characteristic for the \( 3\beta \) ketenimine and depend on the \( \pi \) acceptor C formyl group which shifts the \( \pi \) electron density to C\(_1\) and strengthens the \( \pi_{\text{N}} - \pi_{\text{CC}}^* \) conjugation.

The significant lengthening of the CC bond for a relatively short CN bond in the C-amino-substituted ketenimine \( 3\alpha \) is explained by the preferred realization of "reverse" \( \pi_{\text{NH}_2} - \pi_{\text{CC}}^* \) conjugation because the amine N is a stronger \( \pi \) donor than the imine.

"Reverse" conjugation also facilitates stabilization of the rotamer around the C\(_1\)-N bond with maximum overlap of \( \pi_{\text{NH}_2} \) and \( \pi_{\text{CC}}^* \) orbitals.

In general, stabilizing \( \pi_{\text{X}} - \pi_{\text{CN}}^* \) and destabilizing \( \pi_{\text{N}} - \pi_{\text{X}} \) interactions have an effect on the configuration around the N-N and N-O bonds in ketenimines \( 1\alpha-\epsilon \) and 2. The tendency to maximize the first and to minimize the second leads to the following most stable rotamers around the N-X bond:

\[
\text{(1a-}\varepsilon, 2) \quad \text{(1c)}
\]