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INVERSION OF THE NITROGEN ATOM IN THE AZIRIDINE RING.

CALCULATION OF 1-ETHYLIDENEAMINOAZIRIDINE BY THE CNDO/2 METHOD

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It is shown that in the ground state of the 1-ethylideneaminoaziridine molecule there is virtually no conjugation of its unshared pair of electrons with the π electrons of the N═C bond in the case of a pyramidal structure of the inversion center. A potential surface map was constructed for the conformational transitions due to the possibility of inversion of the nitrogen atom of the heteroring and rotation about the N—N bond. The equivalence of the vicinal protons of the heteroring that is observed in the PMR spectra of the hydrazone derivatives of 1-aminoaziridine is explained.

In the present research we analyzed the conformational transitions in the 1-ethylideneaminoaziridine (I) molecule. A number of compounds with analogous structure have been investigated by PMR spectroscopy [1]. A characteristic feature of their PMR spectra is the anisochronicity of the protons of the aziridine ring, the resonance signal of which is a complex multiplet of the AA'BB' type. It is shown that this form of the spectrum is due to the nonequivalence of the geminal protons of the heteroring [2]. The equivalence of the vicinal protons of the ring with retention of the pyramidal configuration of the inversion center can be explained in two ways: 1) Rapid rotation of the N═CH—CH$_3$ group about the N—N bond leads to averaging of their signals; 2) rotation about the N—N bond is inhibited; the stable conformation is the conformation in which the N═CH—CH$_3$ fragment is situated in a plane perpendicular to the heteroring.

It is obvious that one cannot answer the question of the rate of rotation about the N—N bond only on the basis of the results of PMR experiments. In our study of the inversion of the heteroring nitrogen atom we therefore also took into account the possibility of rotation about the nitrogen—nitrogen bond. The calculation was performed by the semiempirical MO self-consistent-field (SCF) method within the CNDO/2 (complete neglect of differential overlap) approximation [3] with parameters specially adjusted for the calculation of the barriers to inversion [4]. In our study of the dynamics of the process we varied only two internal coordinates of the molecule: the angle of inversion (φ) and the angle of rotation (θ) of the N═CH—CH$_3$ fragment relative to the heteroring about the N—N bond (Fig. 1; $\varphi = 0$ when N$_8$ lies in the plane of the heteroring, and $\theta = 0$ when the N$_8$—C$_9$ bond lies in the plane perpendicular to the plane of the heteroring). The geometry of the aziridine ring used in the calculations is in agreement with the data in [5], and the standard values of the bond lengths and valence angles [6] were selected for the remainder of the molecule. The nitrogen—nitrogen bond length was optimized, since the calculated values of the conformational barriers depend substantially on this. Its length was varied in tetrahedral ($\varphi = 65°$, $\theta = 0°$) and trigonal ($\varphi = 0°$, $\theta = 90°$) configurations of the inversion center, and the variation was found to be almost identical in each case (1.31 Å). This also made it possible to dispense with the introduction of

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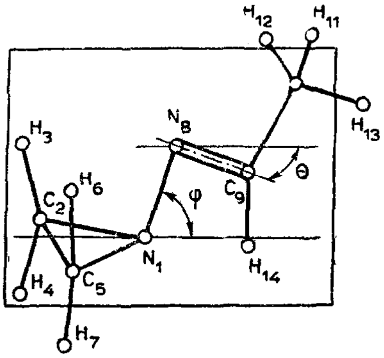

Fig. 1. Three-dimensional structure of 1-ethylideneaminoaziridine.

a third variable — the nitrogen–nitrogen bond length — in the calculations, and this reduced the computational volume to a great degree.

The total energies of the I molecule were calculated for φ values of 0, 15, 35, 55, 65, and 75°, for each of which angle θ was varied over the 0-180° range at 10° intervals. As a result, we found the absolute minimum value of the energy when $\varphi = 65°$ and $\theta = 0°$. From these results we determined the relative potential energy of the molecule [V(φ, θ)] from the expression

$$V(\varphi,\theta) = E_{\text{tot}}\,(\varphi,\theta) - E_{\text{tot}}\,(65.0),$$

where $E_{\text{tot}}(\varphi, \theta)$ is the total energy of the I molecule for given φ and θ values.

On the basis of the calculated V(φ, θ) values, by means of graphical interpolation we constructed the two-dimensional map of the potential energy levels with 10.5 kJ/mole (2.5 kcal/mole) intervals between the levels (Fig. 2). Because of the symmetry of the I molecule, the V(φ, θ) map has a center of symmetry with coordinates $\varphi = 0°$ and $\theta = 90°$.

The calculations showed that the molecule has two conformational minima, (65, 0) and (−65, 180), which are geometrically identical owing to its symmetry. Two different (with respect to height) saddle points (1 and 2) are situated on the potential energy surface (Fig. 2). The first saddle point corresponds to the transition state of the (65, 0) $\rightleftarrows$ (−65, 180) transformation, and the second corresponds to the (65, 0) $\rightleftarrows$ (65, 360) transformation. Both transformations are effected with a simultaneous change in angles φ and θ; i.e., compression of the pyramidal configuration of the nitrogen atom in the heteroring must be accompanied by rotation about the N–N bond. However, in the case of surmounting of barrier 1 this nitrogen atom undergoes inversion, while transition through barrier 2 is effected with retention of the pyramidal configuration.

The values of potential barriers 1 and 2 are 73.2 kJ/mole (17.5 kcal/mole) and 22.4 kJ/mole (5.4 kcal/mole), respectively. The magnitude of barrier 1 is in good agreement with the experimental free energy of activation $\Delta G^* = 83.7$ kJ/mole (20 kcal/mole) [1]. It is apparent from the magnitude of surmounting of barrier 2 that it takes place at a high rate and is not recorded by PMR spectroscopy.

Let us examine the ground and transition states of the I molecule for inversion of the heteroring nitrogen atom. The (65, 0) geometry in which the heteroring and the $N_8{=}C_9$ bonds are situated in mutually perpendicular planes (Fig. 3), corresponds to the ground state. The orbital of the unshared pair of electrons of the nitrogen atom of the heteroring is a hybrid of the 2s and 2p AO, the axis of which is oriented orthogonally to the 2p AO that form the π orbital. In the case of a pyramidal structure of the nitrogen atom of the heteroring participation of the unshared pair of electrons of this nitrogen atom in conjugation with the π electrons of the double bond is virtually excluded. The axes of the unshared pairs of both nitrogen atoms form a torsion angle of 180°.

In the inversion transition state the I molecule has (0, 90) geometry in which the heteroring and the double bond lie in one plane (Fig. 3); the optimum condition for conjugation of the unshared pair of electrons of the nitrogen atom of the heteroring, which is a 2p AO, with the π electrons of the double bond is ensured in this case. The unshared pairs of both nitrogen atoms are oriented in mutually perpendicular directions, which in this situation corresponds to their minimal interaction with one another.

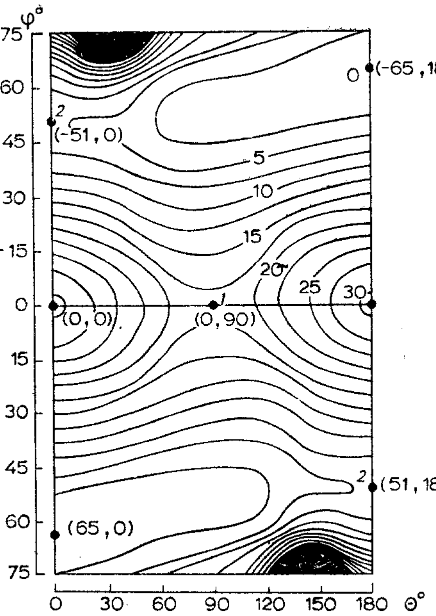

Fig. 2

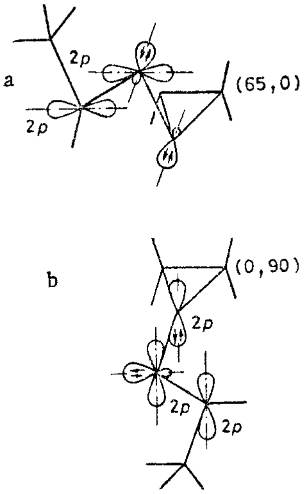

Fig. 3

Fig. 2. Potential energy surface V(φ, θ). The intervals between the equipotential levels are 2.5 kcal/mole.

Fig. 3. a) Ground state of the I molecule (65, 0), no conjugation between the unshared pair of electrons of the heteroring and the π electrons of the N = C bond; b) I molecule in the inversion transition state (0, 90), the conditions for conjugation are optimal.

The participation in π conjugation of the unshared pair of electrons of the nitrogen atom of the heteroring that occurs in the inversion transition state (0, 90) leads to a considerable decrease in the inversion barrier in aziridine I as compared with molecules in which the inversion center also is bonded to the heteroatom but conjugation is impossible [4].

In conclusion, we turn to the problem of the equivalence of the PMR signals of the vicinal protons of the heteroring. It follows from results of calculation of the I molecule that in its ground state (65, 0) the vicinal protons should be equivalent owing to their symmetry. However, the rapid rotation of the $N{=}CH{-}CH_3$ fragment about the N–N bond that occurs with surmounting of barrier 2 (Fig. 2) leads to averaging of the effect of this fragment on the signals of the vicinal protons and therefore does not affect their equivalence in the PMR spectra.

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