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From the Nonplanarity of the Amino Group to the Structural Nonrigidity of the Molecule: A Post-Hartree–Fock Ab Initio Study of 2-Aminoimidazole

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ABSTRACT: The results of an ab initio post-Hartree–Fock study of the details of the molecular structure and the pathways of the interconversion of the 2-aminoimidazole molecule enantiomers are reported. The geometry of the local minimum and the transition states were optimized by the gradient procedure at the MP2 and DFT/B3LYP levels of theory and were verified by energy second derivative calculations. The medium and large size basis sets [(6-31 + G(d, p), 6-311 + +G(df, pd), D95 + +(df, pd), and correlation consistent aug-cc-pVDZ)] have been used. Based on an analysis of the equilibrium geometry and the pathways of interconversion, we reveal that the phenomenon of a nonplanar geometry of the amino group in the amines has a more complex nature than previously expected. Our calculations show that this molecule is structurally nonrigid at least with respect to the torsion and umbrella vibration of the amino group. It results in a very complex picture of the amino group motion which includes tunneling of the barrier and an above barrier large amplitude motion. We have found that in contrast to

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the situation of aniline, the most probable pathway of the AIM interconversion is the cis-rotation of the amino group around the CN exocyclic bond. Int J Quant Chem 75: 245–253, 1999

Introduction

The experimental data [1–5] and the results of quantum-chemical calculations [6–12] reveal that the equilibrium geometry of the aromatic and heteroaromatic amines is nonplanar. These molecules have two different sources of nonplanarity. First, one is the internal nonplanarity of the amino group that originate from the partial sp^2 hybridization of a lone electron pair in the amines [9, 13]. The following structural features are accompanied by these phenomena: (i) the position of the amino hydrogen atoms is not in the plane of a carbon or heterocarbon backbone; (ii) the amino hydrogens are able to occupy a nonsymmetric position due to the interaction with the rest of the molecule.

The second source of nonplanarity was predicted first in [9] and was discovered recently [14, 15]. It originates from internal flexibility of the molecules with respect to the out-of-plane vibrations of the carbo- or heterocyclic ring. It could result in a nonplanar geometry of the ring during some specific intermolecular interactions. This feature has been initially addressed in [16].

There is at least one important conclusion which follows from the above discussion: the amines could be much more flexible than previously expected because of the low value of the inversion and rotation barriers of the amino group. In addition, it creates the possibility of one more source of conformational flexibility for the molecules having C_1-symmetry. In this case, rotation and inversion of the amino group would lead to the interconversion of the stereoisomers. These phenomena have not yet been addressed in the literature in the general form (for a discussion of some aspects of this problem, see [17]), and they are the subject of our article.

Although the above discussion is related to any aromatic and heteroaromatic molecules containing an amino group, there is a class of amines in which we expect that these effects will play an extremely important role due to its involvement in the proceeding of biological processes. It consists of the DNA and RNA bases and other amines having biological importance. The model molecule 2-aminoimidazole (AIM) has been chosen for this post-Hartree–Fock ab initio study of the structural nonrigidity of the amines. The structure of AIM contains all of the necessary components to investigate the most significant properties of the nonrigidity phenomena. We expect that this molecule has no symmetry; it has two different types of nitrogens in the heterocyclic ring which could yield a nonsymmetrical orientation of the amino group and a system of double bonds to conjugate with the lone electron pair of the amino nitrogen. It also has a relatively small number of atoms which permits the use of high level post-Hartree–Fock methods up to the QCISD(t) level. In addition, this molecule is important due to its biological properties as a growth inhibitor in plants [18], and incontrovertible proof of the existence of GABA receptors [19]. Finally, the backbone of the AIM is a model for the structural isomers of the DNA bases [17].

Computational Methods

The geometry of AIM has been optimized separately by the gradient procedure [20] at the second-order Møller-Plesset (MP2) level [21] and by the density functional theory (DFT) with Beckes' nonlocal exchange functional [22] in conjunction with the correlation functional of Lee–Yang–Parr (B3LYP) [23]. The 6-31 + G(d, p), 6-311 + G(dp, pd), D95 + +(df, pd), and correlation consistent aug-cc-pVDZ basis sets of the Gaussian 94 program [24] have been applied. The geometries of the local minima and the corresponding transition states were verified by establishing that the matrices of the energy second derivatives [Hessians calculated at the MP2/6-31G(d, p) and DFT/6-31 + G(d, p) levels] have zero and one negative eigenvalues, respectively. In addition, the single point calculations have been carried out at the QCISD(T), QCISD, MP4(SDTQ), and MP4(SDQ) levels of theory. The vibrational frequencies have been evaluated at the MP2/6-31 + G(d, p) and the DFT/ 6-31 + G(d, p) levels. The populations of the vibrational levels have been calculated by the Boltzmann expression.

The localized orbitals have been obtained by the Boyd procedure [25] at the HF/6-31 + G(d, p) level for the geometry optimized at the MP2/6-31 + G(d, p) level using the GAMESS-USA program [26]. They have been depicted by the program MOLDEN [27].

Results and Discussion

Beginning with the discovery of the nonplanarity of DNA bases [6, 8], an analysis of this phenomenon was limited by the observation of an equilibrium pyramidal configuration of the amino group including its nonsymmetrical orientation with respect to the plane of the heterocyclic ring [6–12]. In our opinion, a considerably deeper understanding of this phenomenon might be achieved if one took into account all possible pathways of interconversion (the anisotropic internal rotation of the amino group around the exocyclic C–N bond and the plane inversion of the CNH_2- fragment) of CNH_2- fragment in amines. To our knowledge, there are only two articles in which this question has been partially investigated regarding the aniline molecule [28, 29]. The inversion dynamics of the amino group have been investigated in [28], and the barriers for inversion and the internal rotation of the amino group in a quasi-classical approximation have been calculated [29].

Herein, we present more general analysis of the CNH_2 fragment interconversion (its plane inversion and anisotropic internal rotation of the amino group) and its influence on the structural relaxation of the rest of the molecule. The vibrational dynamics will be introduced in this approach by a comparison of the values of interconversion barriers (zero point energy uncorrected) with the energy of the fundamental vibration which is initiating a corresponding pathway of interconversion. Such a consideration is more complex and could have even more important physico-chemical and biochemical consequences in the case of DNA bases.

The labeling of the AIM atoms used throughout the article is shown in Figure 1. Because a search through the literature for the experimental values of the AIM structural parameters was not successful, for further reference a full set of equilibrium geometrical parameters which correspond to the

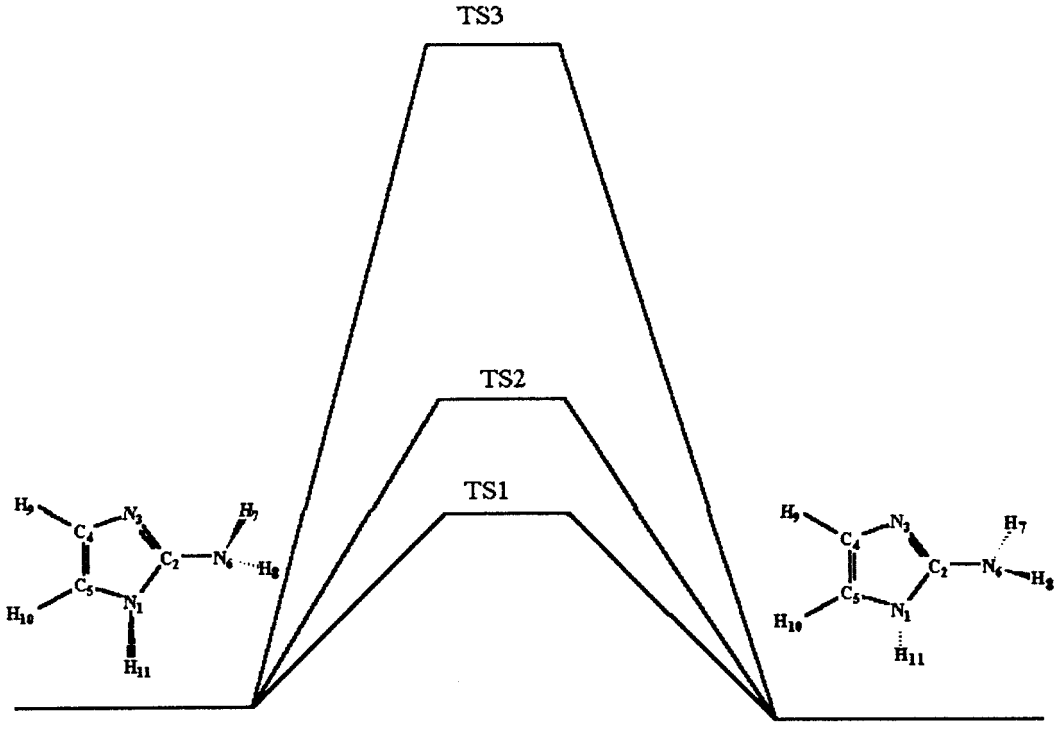

FIGURE 1. The numeration of atoms and the pathways of the interconversion of the AIM molecule. TS1, the transition state that corresponds to cis-rotation; TS2, the transition state that coresponds to plane inversion; and TS3, the transition state that corresponds to anti-rotation.

ground states of AIM calculated at the MP2 and DFT levels of theory have been presented in Table I.

The analysis of the predicted molecular parameters ensues the following outcome:

1. The AIM molecule has C_1 symmetry in the ground state. Thus, there are two mirror symmetrical stereoisomers (enantiomers) having exactly the same value of energy and differ from each other only in the sign of the torsion angles.
2. As was expected, the CNH_2- fragment is nonplanar (pyramidal) with the asymmetric positions of the hydrogen atoms H7 and H8. They lie on different sides of the imidazole ring plane being in the syn-orientation with respect to the C2N3 double bond. The amine nitrogen atom (N6) is out of the plane of the heterocyclic ring. The sum of all valence an-

TABLE I

Equilibrium geometrical parameters (bond lengths in Å, bond angles and torsional angles in degrees) of AIM molecule calculated at the MP2 and DFT level of the theory.

	6-31+G(d, p)		6-311++G(df, pd)		D95++(df, pd)		aug-cc-pVDZ	
Parameter	MP2	DFT	MP2	DFT	MP2	DFT	MP2	DFT
Bond length								
N_1C_2	1.367	1.368	1.362	1.365	1.364	1.369	1.372	1.368
C_2N_3	1.325	1.316	1.317	1.310	1.322	1.317	1.331	1.317
N_3C_4	1.383	1.385	1.379	1.382	1.381	1.382	1.389	1.386
C_4C_5	1.377	1.369	1.373	1.362	1.377	1.369	1.389	1.370
N_1C_5	1.382	1.393	1.379	1.390	1.380	1.393	1.387	1.393
C_2N_6	1.404	1.396	1.398	1.390	1.403	1.395	1.410	1.398
N_6H_7	1.013	1.014	1.013	1.011	1.011	1.011	1.019	1.015
N_6H_8	1.014	1.015	1.013	1.012	1.011	1.012	1.020	1.016
C_4H_9	1.077	1.080	1.079	1.077	1.075	1.077	1.088	1.085
C_5H_{10}	1.076	1.079	1.078	1.076	1.074	1.075	1.087	1.083
N_1H_{11}	1.008	1.009	1.008	1.006	1.005	1.006	1.013	1.009
Bond angle								
$N_1C_2N_3$	111.7	111.8	112.0	111.8	111.8	111.8	111.6	111.8
$C_2N_3C_4$	105.0	105.3	104.9	105.4	104.9	105.2	105.1	105.3
$N_3C_4C_5$	110.9	110.9	110.9	110.8	110.9	110.8	110.8	110.8
$N_1C_5C_4$	104.9	105.0	104.9	105.1	104.9	105.0	104.8	105.0
$C_2N_6H_7$	108.9	110.0	108.9	110.8	108.4	110.7	108.3	113.9
$C_2N_6H_8$	112.5	114.3	112.7	114.9	112.2	115.0	111.8	113.9
$H_7N_6H_8$	108.8	110.2	109.2	111.0	108.6	111.2	107.8	109.8
$N_3C_2N_6$	127.3	126.2	126.7	126.0	127.0	126.0	127.2	126.1
$N_1C_2N_6$	120.9	121.9	121.2	122.1	121.0	122.1	121.0	122.0
$N_3C_4H_9$	121.3	121.1	121.4	121.2	121.2	121.1	121.5	121.3
$N_1C_5H_{10}$	122.4	122.1	122.4	122.2	122.3	122.0	122.5	122.2
$C_5N_1H_{11}$	126.9	126.5	126.6	126.4	126.8	126.5	126.9	126.6
Torsion angle								
$N_1C_2N_3C_4$	0.4	0.6	0.8	0.6	0.3	0.4	0.1	0.5
$C_2N_3C_4C_5$	−0.7	−0.6	−0.6	−0.6	−0.5	−0.6	−0.6	−.06
$N_3C_4C_5N_1$	0.7	0.4	0.1	0.4	0.4	0.5	0.7	0.5
$C_4C_5N_1C_2$	−0.4	0.0	0.3	−0.1	−0.2	−0.3	−0.6	−0.2
$C_2N_3C_4H_9$	−179.8	−179.8	−179.5	−179.8	−179.2	−179.8	−179.9	−179.9
$N_3C_4C_5H_{10}$	−178.6	−178.6	−177.9	−178.5	−177.8	−178.7	−178.8	−178.7
$C_4C_5N_1H_{11}$	172.1	171.7	169.7	172.4	171.9	173.6	174.1	173.3
$N_3C_2N_6H_7$	11.4	−1.3	3.7	−3.9	7.1	−2.9	9.1	−2.8
$N_1C_2N_6H_8$	74.6	58.1	66.7	53.3	72.1	54.2	74.4	57.6
$C_5N_1C_2N_6$	176.6	176.2	175.6	176.2	175.7	176.3	177.0	176.3

gles (C2N6H7, C2N6H8, H7N6H8), which determine the pyramidality of the N6 atom, is considerably less than 360° (it is in between 331–337° depending on the methods of the calculation).

3. The equilibrium geometry of the heterocyclic backbone is rather planar. The only exception is the position of imine hydrogen atom H11 which definitely lies out of the plane ring probably because of its interaction with the lone electron pair of the N6 atom.
4. The interconversion of the AIM molecule could be realized through three topologically and energetically nonequivalent pathways (see Fig. 1). Among them there are two highly nonequivalent (syn- and anti-) amino group rotations and one plane inversion of the CNH_2 fragment. All three transition states are characterized by C_s point group molecular symmetry. All pathways of the interconversion are accompanied by mutual structural relaxation of the CNH_2 fragment and the rest of the molecule. For example, for the transition states that correspond to syn-rotation, an increase in the pyramidality of the amino group is by 3–7°. The C2N6 bond length is decreased (0.02–0.03 Å) in the transition state which corresponds to plane inversion and is increased (0.01–0.02 Å) in the transition states which correspond to internal rotation of the amino group. The bond lengths and bond angles of the rest of the molecule are not changed by more than 0.015 Å and 3°, respectively.
5. All trends discussed above do not depend on the level of theory and the basis set chosen.

The values of the interconversion barriers (ΔE) are collected in Tables II–IV. Although the DFT results are noticeably different for the syn-rotation

TABLE II
The values of the barrier (kcal mol^{-1}) for the syn-rotation of the amino group in AIM molecule.

Basis set	MP2	DFT	MP4 (SDTQ)	MP4 (SDQ)	QCISD	QCISD(T)
6-31+G(d, p)	0.27	1.17	0.44	0.64	0.65	0.52
aug-cc-pVDZ	0.42	1.46	0.61	0.84	0.85	
D95++df, pd	0.31	1.39	0.52	0.74		
6-311++G(df, pd)	0.48	1.52				

TABLE III
The values of the barrier (kcal mol^{-1}) for the plane inversion of the CNH_2 fragment in AIM molecule.

Basis set	MP2	DFT	MP4 (SDTQ)	MP4 (SDQ)	QCISD	QCISD(T)
6-31+G(d, p)	3.80	2.04	4.14	3.43	3.42	3.98
aug-cc-pVDZ	3.46	1.96	3.48	3.07	3.06	
D95++df, pd	4.33	1.58	4.61	4.48		
6-311++G(df, pd)	3.70	1.65				

TABLE IV
The values of the barrier (kcal mol^{-1}) for the anti-rotation of the amino group AIM molecule.

Basis set	MP2	DFT	MP4 (SDTQ)	MP4 (SDQ)	QCISD	QCISD(T)
6-31+G(d, p)	5.40	5.98	5.77	5.80	5.83	5.81
aug-cc-pVDZ	4.82	5.64	4.94	5.23	5.23	
D95++df, pd	5.51	6.02	5.65	5.92		
6-311++G(df, pd)	5.40	6.01				

of the amino group and the plane inversion of the CNH_2 fragment, the qualitative results are the same for all approximations considered in this article and are as follows:

$$\Delta E(\text{syn-rotation}) < \Delta E(\text{plane inversion}) < \Delta E(\text{anti-rotation}).$$

Therefore, unlike the case of the aniline molecule [28, 29], the most probable pathway of the AIM interconversion is the rotation of the amino group around the C2N6 bond resulting in the transition state having the syn-orientation of the amino hydrogens. The possible explanation of this phenomenon is the difference in the orientation of the amino hydrogens (H7 and H8) in the AIM and aniline. As was mentioned previously, in the AIM two hydrogens are positioned on different sides of the heterocyclic ring plane. This is the reason for the decrease in the barrier for the rotation in the syn-direction. Such effect is not possible in the case of aniline where the amino hydrogens are on the same side of the aromatic ring plane.

The heights of the barriers presented in Table II–IV are governed by the balance of at least four factors: the interaction of the N3 lone electron pair with the H7 and H8 atoms; the interaction of the H11 atom with the N6 lone electron pair; the conjugation of the N6 lone electron pair with the π-system of the heterocyclic ring; and the repulsion between the N6 and the N3 lone electron pairs. Qualitatively, the magnitudes of the barriers can be explained as follows (Fig. 2). In the case of the syn-rotation of the amino group (the lowest value of the barrier), the corresponding transition state (TS1 in Fig. 2) is stabilized by the attractive interaction of the H11 atom with the lone electron pair of N6 and by the attractive interaction of the H7 and H8 atom with the lone electron pair of the N3 atom. The repulsion of the lone electron pairs is minimal for this transition state. The opposite situation takes place in the case of the transition

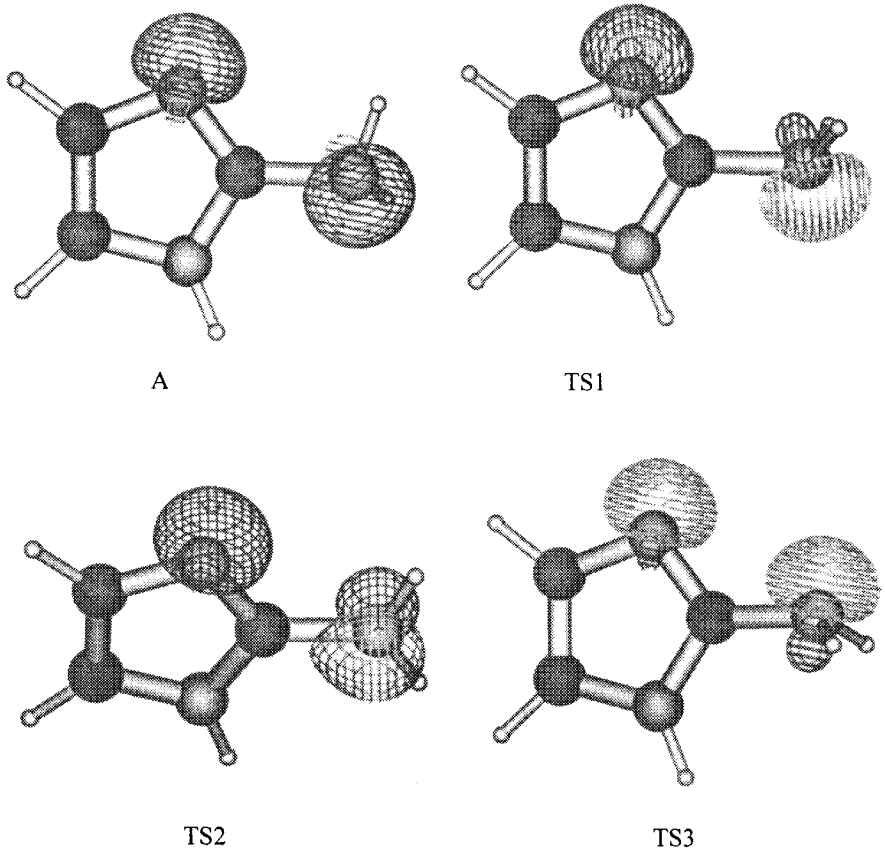

FIGURE 2. Mutual orientation of the N3 and N6 lone electron pairs in AIM molecule. A, in ground state; TS1, in transition state that coresponds to syn-rotation; TS2, in transition state that corresponds to plane inversion; and TS3, in transition state that corresponds to anti-rotation.

state that corresponds to anti-rotation of the amino group (TS3 in Fig. 2). There is maximum repulsion of the lone electron pairs with the amine (H7, H8) and imine (H11) hydrogen atoms. The n, π-conjugation is lacking in both of these cases. The intermediate tendencies are observed in the case of the inversion.

A comparison of the calculated values of the barriers of interconversion with the energy of the vibrations that initiate the corresponding transformation is a necessary step in the investigation of structural nonrigid molecules [30]. In the considered case, the internal rotation of the amino group is initiated by torsional vibration around the C2N6 bond with a frequency of 145 cm^{-1} (MP2/6-31 + G(d, p) level and is equal to 216 cm^{-1} [DFT/6-31 + G(d, p) level]. The plane inversion of CNH_2 fragment is initiated by umbrella vibration of the amino group having a frequency of 858 cm^{-1} and 784 cm^{-1} [MP2/6-31 + G(d, p) and the DFT/6-31

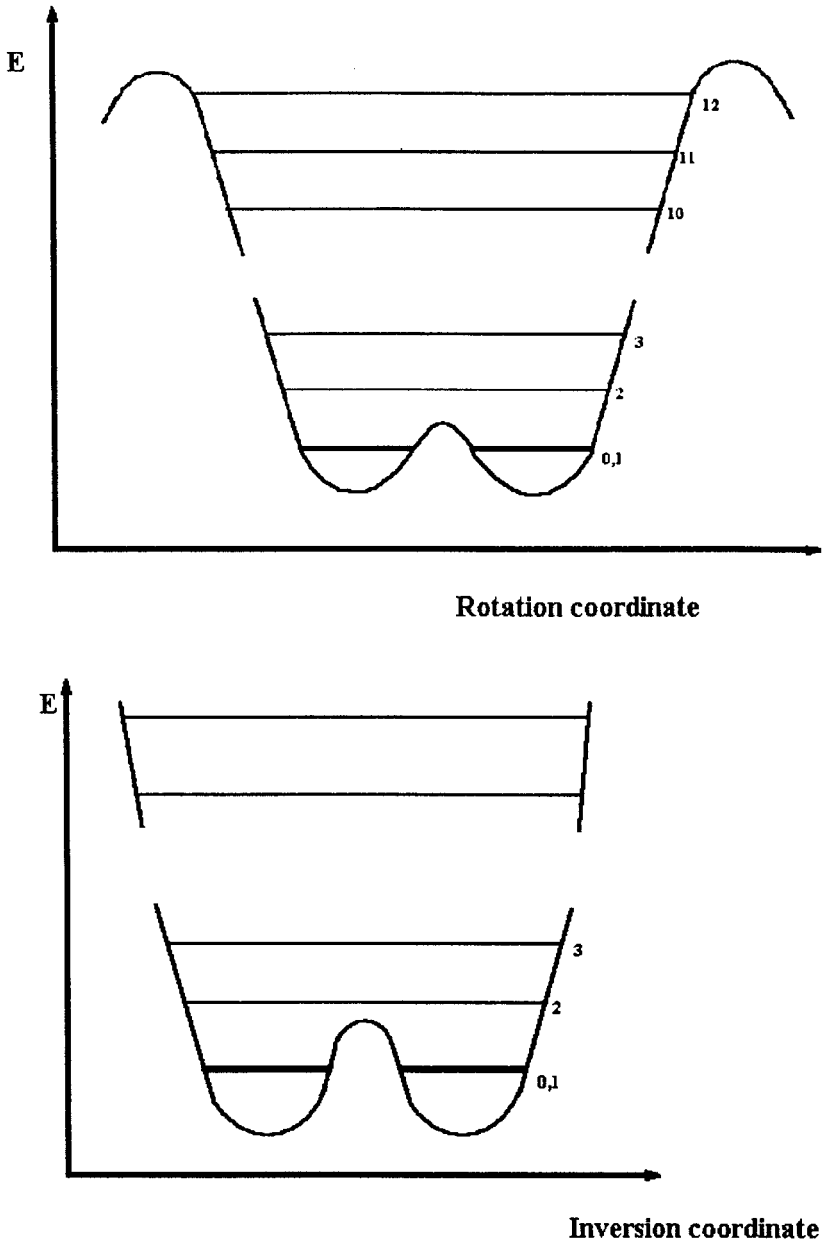

FIGURE 3. The arrangement of the torsion and umbrella vibrational levels in the AIM molecules. A: syn- and anti-rotation; B: plane inversion.

+G(d, p) levels, respectively]. Let us compare these values with the energy of the corresponding barriers (see Tables II–IV). One notices (see Fig. 3) that in the case of syn-rotation and plane inversion, the heights of the corresponding barriers allow for the existence of only one vibrational energy level below the barrier. Therefore, the AIM molecule should be considered as structurally nonrigid with respect to the syn-rotation of the amino group and to the plane inversion of the CNH_2 fragment [30]. In the case of anti-rotation, there are at least 12 vibrational energy levels lying below the barrier.

The mechanism of the syn-rotation and plane inversion at $T = 0$ K involves tunneling the barrier by the amino hydrogens (see Fig. 3). The tunneling frequencies amount to 27 and 30 cm^{-1} for syn-rotation and plane inversion, respectively. They were estimated by the formula [31]

$$\Delta\nu = \nu_0 \exp(-d\sqrt{2mE}/\hbar)$$

where ν_0 is the vibrational frequency that initiates interconversion; m is the tunneling mass; E is the interconversion barrier, $\hbar$ is the Planck constant; and d is the transparency of the barrier for tunneling. The value of the barrier transparency ($d = 0.35$ Å) has been estimated based on similar data on tunnel splitting at the zero vibrational level in aniline [28] where only one vibrational level exists below the barrier [29].

When the temperature increases, the next vibrational levels that lie above the barrier will be populated, and large amplitude torsion and umbrella vibrations in the amino group will take place. Nevertheless, there is a principal difference in the mechanism of the interconversion along the syn-rotation and plane inversion pathways at room temperature. In the first case, the population of the first vibrational level below the barrier is approximately 50%. Consequently, the same amount of the molecule (50%) will interconvert by the tunneling. In the case of plane inversion, the population of the first vibrational level below the barrier is only $\sim 2\%$. So, the predominant way of interconversion for this pathway should be the tunneling even at the room temperature. Therefore, the static definition of the molecular structure [29] is not valid in both cases. In the case of the amino group anti-rotation, we expect quasi-classical behavior of this torsional mode. The importance of this phenomenon for DNA bases will be revealed by the study currently performed in our laboratory.

Conclusion

In this paper we have reported the results of a comprehensive post-Hartree–Fock investigation of the equilibrium structure and the pathways of interconversion of the AIM molecule. Based on an analysis of the pathways of the interconversion of AIM molecule, we have come to following conclusions:

1. In contrast to the situation with the aniline molecule, the most probable pathway of AIM interconversion is the rotation of the amino group around the CN exocyclic bond of the molecule.
2. The phenomenon of the nonplanarity of amino group has a much more complex nature than it had been assumed by previous studies. Our investigation shows that AIM is structurally nonrigid at least with respect to the torsion and umbrella vibrations of the amino group. It results in a complex picture of the amino group motion which includes tunneling and large amplitude motion above barrier. We expect similar nonlinear dynamic behavior in the case of the DNA bases.

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