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Ab initio study of 4-azidobutine

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Abstract

The geometry optimization of all five distinct conformations of 4-azidobutine (with labelling GG, GA, GG', AA and AG) has been carried out on the ab initio TZ + P SCF level. MP2 calculations have been performed for all molecules at the SCF geometry. Our theoretical and experimental results indicate that the conformers can be divided into two groups: the first group with low-energy conformers (GG, AG and AA) and the second one with high-energy conformers (GG' and GA). A decrease of the possible interation of π-systems of the C≡C bond with the azide group in comparison with the allylazide molecule was observed.

1. Introduction

The present study is devoted to the ab initio investigations of 4-azidobutine which can exist in five distinct conformations designated GG, GA, GG', AA and AG. These conformers of 4-azidobutine are depicted in Fig. 1. The numbering of atoms is shown in Fig. 2. All five conformers arise by rotation around both the C_3–C_4 bond (gauche or anti) and the C_4–N_5 bond (gauche or anti). 4-Azidobutine is the next molecule in the series of investigations of organic azides [1–9] that has been under theoretical and experimental study.

2. Methods and calculations

Ab initio molecular orbital calculations were performed using the standard HONDO-type [10] computer program. All calculations were carried out within the Huzinaga TZ + P [11] basis sets on an IBM RS 6000 (Model 365) RISC computer. The geometry optimization was realized on the SCF level, where all internal coordinates were taken into account and no assumptions on the symmetry were applied. For the optimization of geometry the norm of gradients was required to be less than 10^{-3} Da and the difference between energies in two subsequent optimization cycles to be less than 10^{-6} Da. To obtain a better energetic description, the MP2 calculations were performed for all molecules at the SCF optimized geometry.

In order to determine whether the optimized structure represents the true minimum or the saddle point, the vibrational analysis for optimized molecular structures has been done. The enthalpies at zero absolute temperature (ΔH^0) have been calculated as the sum of SCF + MP2 energies and zero point energy. Mullikean population analysis [12] was used to discuss the electronic distribution. This is adequate for the present purposes since

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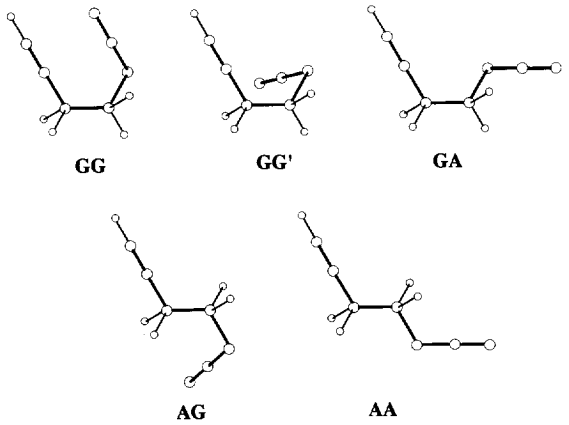

Fig. 1. The five possible conformations of 4-azidobutine: GA tC–C=60, tC–N=180; GG′ tC–C=60, tC–N=60; GG tC–C=60, tC–N= −60; AA tC–C=180, tC–N=180; AG tC–C=180, tC–N=60.

it is the trends in populations and charges which are important rather than their actual values.

3. Results and discussion

The final optimized geometries of all five conformers are listed in Table 1. The values of E_{SCF}, $E_{SCF+MP2}$ and $E_{0,SCF+MP2} \equiv \Delta H^{\circ}$ are given in Table 2. The charges on individual atoms have been calculated by the Mulliken population analysis [12] and are shown in Table 2 for atoms C_4, N_5, N_6 and N_7 together with dipole moments for all conformers.

It is clear from the Table 2, that the most stable conformers (having the lowest energy) on the SCF level are the AA and AG conformers. The conformer GG lies approximately 1 kJ mol^{-1} higher, but the GA and GG′ conformers have significantly higher SCF energies. Including the MP2 correction the order of energies changes completely.

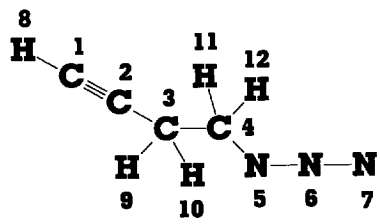

Fig. 2. Atom numbering in 4-azidobutine.

The energy differences become lower, the GG conformer now being the most stable one. The order of GA and GG′ conformers is exchanged. Thus, it is clear that the inclusion of MP2 correction is of great importance for achieving appropriate results. Finally, including the zero point energy we obtain the enthalpy at zero absolute temperature (ΔH^0). The order of conformer energies is changed again with the second most stable GG conformer together with the change of the GA and GG′ conformer order.

Enthalpy values (ΔH^0) of the conformers of 4-azidobutine fall into two groups: in the first group there are the most stable conformer AA and the conformers GG and AG, with very close enthalpy values of 0.68 and 0.80 kJ mol^{-1} higher than that of AA; in the second group there are the conformers GA and GG′ with enthalpies 2.56 and 2.59 kJ mol^{-1} higher than the AA conformer.

Earlier experimental and theoretical investigations [1–9,13,14] have shown that if there are in the organic azide molecule multiple C=C or C≡C (C≡N) bonds, the most stable conformers are those having the azide group oriented towards the π-system of the C=C or C≡C (C≡N) bond, an arrangement that enables optimal overlap between orbitals of the π-system of the C=C or C≡C (C≡N) bond and the π-system of the azide group. This behaviour has been shown experimentally for the molecules N≡C–CH_2N_3 [3], HC≡C–CH_2N_3 [4] and CH_3–C≡C–CH_2N_3 [5] which occur only in the gauche form. The preferable orientation of vinylazide is the syn orientation, a fact that has been confirmed both theoretically [6] and experimentally by means of microwave spectroscopy [15]. The preferable form of ethylazide is the gauche form, confirmed both experimentally [7] and theoretically [13].

In the most favourable conformation the allylazide molecule assumes the gauche orientation of the C–N bond, as shown by the order of the individual conformer stability: GG, SG, GG′, SA and GA, which has been confirmed experimentally and theoretically [1]. The conformers in which there is overlap of the π-systems of the C=C bond and the N_3 group possess the lowest energies. Thus in the case of ethylazide [13], allylazide [1] and 4-azidobutine, if we are to obtain the true order of conformer

Table 1
Optimized geometry parameters of the computed molecules (the internal coordinates defined according to the numbering of atoms in Fig. 1[a]; bond lengths in Da and all angles in degrees)

		GA	GG′	GG	AA	AG
stre	1, 2	2.233	2.233	2.234	2.234	2.234
stre	2, 3	2.774	2.773	2.775	2.774	2.773
stre	3, 4	2.881	2.896	2.893	2.879	2.897
stre	4, 5	2.772	2.770	2.770	2.775	2.772
stre	5, 6	2.307	2.312	2.312	2.312	2.312
stre	6, 7	2.066	2.065	2.064	2.064	2.065
stre	3, 9	2.050	2.051	2.051	2.047	2.051
stre	3, 10	2.048	2.052	2.047	2.047	2.046
stre	4, 11	2.052	2.055	2.043	2.052	2.039
stre	4, 12	2.051	2.038	2.051	2.052	2.052
stre	1, 8	1.992	1.992	1.992	1.992	1.992
bend	1, 3, 2	179.22	179.57	179.22	179.38	179.03
bend	2, 4, 3	113.30	113.73	112.98	111.74	111.64
bend	3, 5, 4	109.04	114.32	112.15	107.19	111.64
bend	4, 6, 5	114.10	113.80	114.76	113.47	114.04
bend	5, 7, 6	175.70	175.45	174.93	175.83	175.37
bend	8, 2, 1	179.55	179.67	179.75	179.68	179.63
bend	2, 9, 3	108.72	108.97	108.82	109.44	108.93
bend	2, 10, 3	109.26	108.92	109.23	109.48	109.66
bend	5, 11, 4	109.55	110.72	106.16	110.93	106.09
bend	5, 12, 4	111.29	105.26	111.56	110.90	111.56
tors	2, 3, 4, 5	67.75	61.19	69.81	180.96	176.87
tors	3, 4, 5, 6	206.78	72.17	259.39	180.30	87.49
tors	4, 5, 6, 7	177.58	175.20	189.52	179.90	173.64
tors	9, 3, 4, 5	188.73	182.44	190.85	−57.73	−62.02
tors	10, 3, 4, 5	−54.27	−61.37	−51.91	59.55	55.43
tors	2, 3, 4, 11	187.11	185.29	186.75	60.32	59.66
tors	2, 3, 4, 12	−54.54	−56.85	−55.06	−58.46	−58.70
lc	1, 3, 2, 4	−0.10	−0.18	0.74	0.62	0.97
lc	8, 3, 2, 4	−0.10	−0.08	0.67	0.47	0.80
lp	1, 3, 2, 4	−0.77	−0.39	−0.22	0.00	−0.09
lp	8, 3, 2, 4	−0.56	−0.27	−0.14	−0.01	−0.04

[a] Internal coordinates designed in a generally used manner; lc and lp mean the bending coordinates of near linear system, lc 1 2 3 4 means collinear bending of 1 2 3 bending angle in the plane of 2 3 4; lp 1 2 3 4 means the bending of 1 2 3 perpendicular to the plane 2 3 4. Stre = stretch, tors = torsion.

energies we have to take into account the correlation energy corrections at least on the MP2 level.

The present investigation of 4-azidobutine enables us to conclude, that owing to the presence of a methylene group separator between the C≡C and C≡N bonds, the system has lower possible overlap of the pertinent π-systems with the consequence that the C_3–C_4 bond has optimal energy in the anti orientation. Thus the AA conformer has the lowest energy with two anti orientations. The exception is the second conformer in the energy order (GG), which is energetically stabilized by π-interaction of the C≡C bond and the azido group. The third one in the energy order is the AG conformer with favourable anti orientation with respect to the C_3–C_4 bond. The conformers GA and GG′ have higher energies due to the less favourable gauche orientation. In contrast to allylazide [1] the energy differences between the two neighbouring conformers are lower by a factor of two.

From the experimental investigations by means of IR and Raman spectroscopy [14] it follows that the five conformers of 4-azidobutine form two

Table 2
Calculated SCF, SCF + MP2 and SCF + MP2 + E_0 energies[a], gross atomic charges on individual atoms of the computed molecules and dipole moments[b] of the computed molecules

	GA	GG′	GG	AA	AG
E_{SCF}	−317.651904	−317.650681	−317.652655	−317.654038	−317.653057
$E_{SCF+MP2}$	−318.854758	−318.854761	−318.855677	−318.855650	−318.855553
$E_{0.SCF+MP2}$	−318.759574	−318.759424	−318.760290	−318.760549	−318.760244
ΔE_{SCF}	5.60	8.81	3.63	0.00	2.58
$\Delta E_{SCR+MP2}$	2.42	2.41	0.00	0.08	0.33
$\Delta E_{0.SCF+MP2}$	2.56	2.95	0.68	0.00	0.80
C_4	−0.006	−0.026	−0.028	0.002	−0.023
N_5	−0.334	−0.333	−0.343	−0.340	−0.337
N_6	0.270	0.278	0.283	0.270	0.270
N_7	−0.115	−0.117	−0.115	−0.109	−0.114
μ	2.06	2.12	2.00	1.27	1.38

[a] Energies are in Da, differences of energies are in kJ mol^{-1}.
[b] Dipole moments are in Debye.

groups. The first group consists of low-energy GG, AG and AA conformers; the second one is composed of Gg′ and GA conformers. From the recent measurements it was not possible to determine energy differences between individual conformers. According to the interpretation of the IR and Raman spectra by means of the scaled ab initio force field one can show that the order of conformers in decreasing stability is as follows: GG, AG, AA and two high-energy conformers GG′ and GA. Our ab initio results are in good agreement with these experimental observations.

The computed geometry of the azide group is slightly bent with an N–N–N angle of approximately 175°. This is in agreement with experimental and theoretical studies [1–9,13] as well. The calculated charges on atoms C_4, N_5, N_6 and N_7 are shown in Table 2. Listed values confirm the assumption about the charge distribution in the azide group

$$R-\overset{\delta-}{N}=\overset{\delta+}{N}\equiv\overset{\delta-}{N}$$

which is in agreement with previous investigations [4].

The standard bond lengths are 2.36 Da [16] and 2.08 Da [16] for N(2)=N(2) (where the numbers in parentheses indicate the number of neighbouring bond partners) and N(1)≡N(1) bonds, respectively. It is clear from the Table 1 that the calculated bond lengths of the azide group are in good agreement with standard bond lengths. This confirm again the assumptions concerning the structure of the azide group

$$R-\overset{\delta-}{N}=\overset{\delta+}{N}\equiv\overset{\delta-}{N}$$

4. Conclusions

Present ab initio calculations of 4-azidobutine have shown, in agreement with experimental results [14], that its conformers can be divided into two groups: the first one populated with low-energy conformers (GG, AG and AA) and the second group with high-energy conformers (GG′ and GA). We observed the decrease of the possible interaction of the π-systems of the C≡C bond and the azide group as a consequence of the shift of the triple C≡C bond in the direction from the azide group by one CH_2 group. This phenomenon is manifested in the energy preference of the AA and AG conformers. The exception is the GG conformer, because of the space orientation; the enhanced interaction of both π-systems energetically stabilizes the molecular system. Due to the decrease of the possible interaction of the π-systems of the triple C≡C bond and azide group, we observed that the decrease of the energy difference

between the most stable and the most unstable conformers is roughly one half of that of allylazide [1].

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