SHORT PAPER

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Theoritical *ab initio* study of internal rotation barriers, structures stabilities and population of formamide†

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The internal rotational barriers for formamide are calculated in gas and solution phases (acetonitrile) at the HF/6-31G* (16.64 and 16.18 kcal/mol, respectively) and MP2/6-31G* (16.86 and 16.71 kcal/ mol, respectively) level of theory. Calculated parameters are compared with experimental data and there is a good agreement between them. Orbital populations are obtained by MPA (mulliken population analysis) and NPA (natural population analysis) methods and bond energies are calculated by the NBO method (natural bond orbitals). The distribution of atomic charges are also given. These calculation indicate that the internal rotational barrier is produced because of change in the distribution of orbital populations of $2p_y$, $2p_z$, d_{yz}, d_y^2 and d_z^2 orbitals of the nitrogen atom.

Keywords: internal rotation, orbital population, atomic charge

The rates of processes which involve chemical change are determined in part by an energetic barrier. In reacting systems, the barrier is associated with energy required to reach the transition state in the reaction pathway. In the case of intramolecular conversions, such as rotation, there is also an activation energy, E_a, associated with the internal exchange process. The existence of these barriers in a chemical bond is fundamental to the structural properties of molecules and conformational analysis.[1] These energetic barriers can be mapped as a function of one molecular coordinate. In the case of rotation this is the dihedral angle across the reacting bond.

Here we describe an *ab initio* study on the rotational barrier in a simple amide, formamide. Amides are a major functional group in organic chemistry.[2] Because of the C=O group they are polar molecules and they have high boiling points because of their ability to be involved in strong intramolecular hydrogen bonding.

Calculation of molecular geometries were performed using the Gaussian 98 software package,[3] at the HF/6-31G* and MP2/6-31G* level of theory in both gasous and solution phases. We have used a PCM (Polarized Continuum Model) to perform our solvent calculations, whose results were used for comparison with the data obtained from gas calculations. Vibrational frequencies of the structures were done at 298.15 K and 1 atm. to verify the minimum energy configurations.

Results and discussions

Because of the variable effects of solvent interaction, gas phase studies are much better to show the intrinsic properties of molecules and to investigate kinetic and thermodynamic effects of substituents.

Here we report on the energetic barrier of formamide in the gas and solution phases at the HF/6-31G* and MP2/6-31G* levels of theory (Table 1). The maximum value for this barrier is at 100° (the degree of rotation of the dihedral angle around the C–N amide bond). Comparing the gas and solution phases, we see that at 100° there is not much difference between the calculated energies by HF gas-solution and MP2 gas-solution, but at –100° there is a difference between these values of the calculated gas phase energies (dotted curves in Fig.1). Figure 1 shows that the calculated gas phase energy by the MP2 method has a smaller value than in solution, while calculation of these values by the HF method shows a greater value than in solution. This indicates that the MP2 method, because it has a more integral type calculation and includes a perturbed Hamiltonian, in comparison with the HF method, can not show the solvent effect in a satisfactory way, and therefore this method has to make some correction to allow for the energy difference between gas and solution phases. Orbital populations have been calculated in two ways:

Table 1 Calculated internal rotation barrier (kcal/mol) of formamide in gas phase and solution (ε = 36.64)

	Calculated		
Medium	HF	MP2	Experimental
Gas	16.64	16.86	**Note**: Experimental Internal rotation barrier is 17.8–18.0 kcal/mol (ref. 6)
Acetonitrile	16.18	16.71	

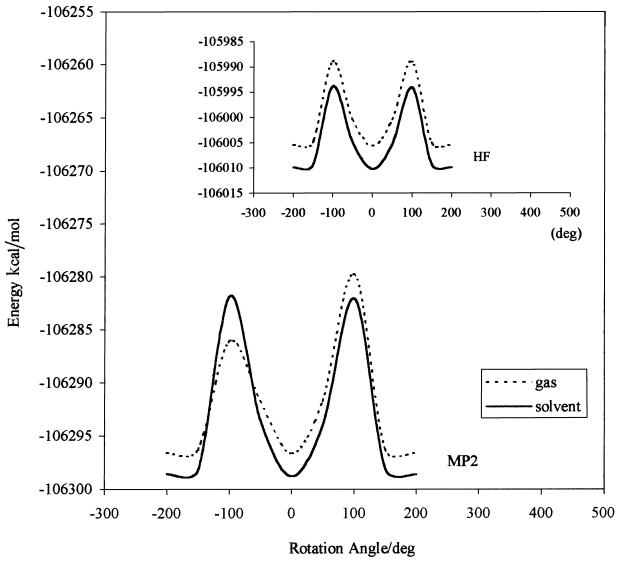

Fig. 1 Potential energy curve for internal rotation of formamide by HF and MP2 methods in gas phase and solution.

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

MPA method (Fig. 2); the NPA method (Figs 3 and 4) which confirm the MPA calculation that we have done. As can be seen the orbital population of the $2p_x$ orbital of the C (carbon) and N (nitrogen) atoms and the $2p_z$ orbital population of O (oxygen) atom show little change. These orbitals, also have the most energy.

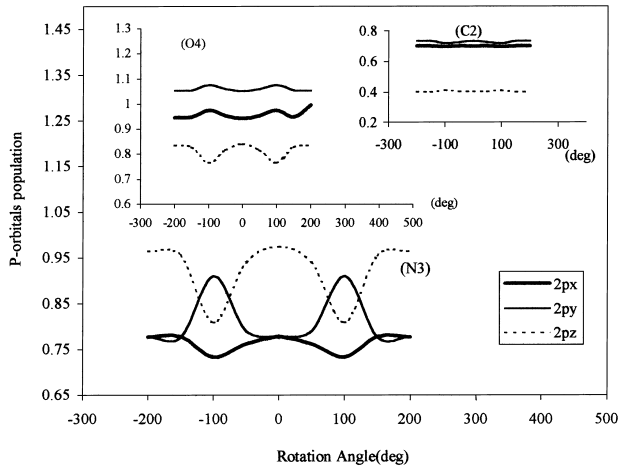

Fig. 2 Calculated *p*-orbitals population of formamide by MPA method in gas phase.

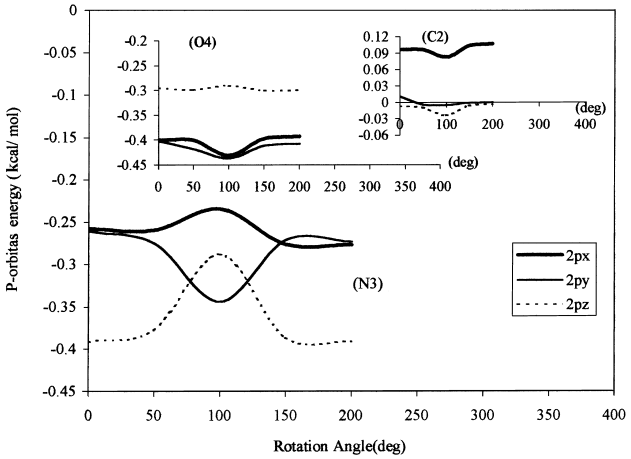

Fig. 3 Calculated orbitals energy of N, O, C, atoms of formamide by NPA method in gas phase.

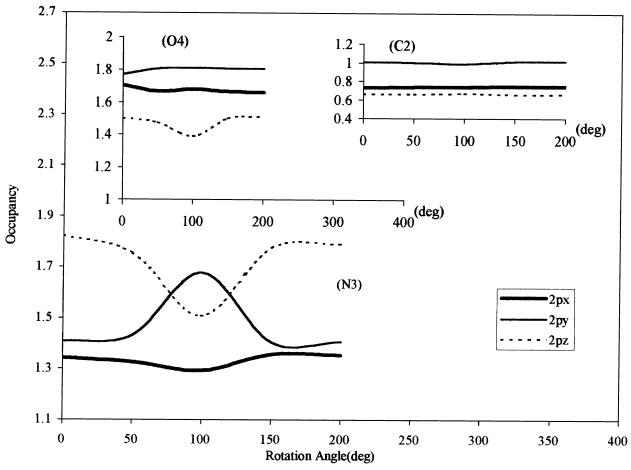

Fig. 4 Calculated *p*-orbitals occupancy of N, O,C atoms of formamide by NPA method in gas phase.

Table 2 NBO Hybridisation coefficient for CN bond

	Orbital coefficient	
Orbital	C	N
2s	0.5616	0.6112
$2p_x$	–0.7395	0.7081
$2p_y$	–0.3630	0.3510
$2p_z$	0.0000	0.0000
$3d_{xy}$	0.0359	0.0274
$3d_{xz}$	0.0000	0.0000
$3d_{yz}$	0.0000	0.0000
$3d_{x^2-y^2}$	0.0313	0.0187
$3d_{z^2}$	–0.0230	–0.0192

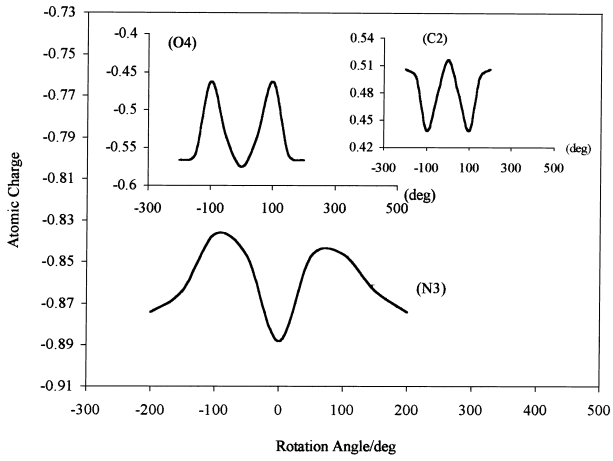

Fig. 5 Calculated atomic charges curve of N,C,O atoms of formamide by MPA method in gas phase.

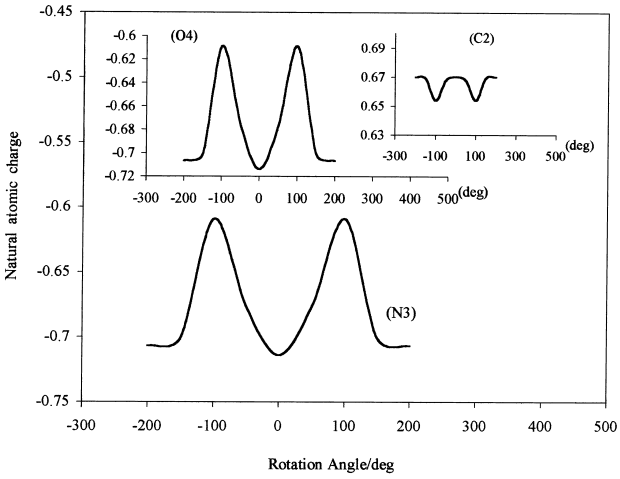

Fig. 6 calculated natural atomic charge curve of N,O,C atoms of formamide by NPA method in gas phase.

The first result is that these orbitals have enough energy to make bonds (CN and CO bonds), this fact is proven by the hibridisation coefficient for CN and CO bonds. It means that the highest hibridisation coefficient in CN is related to the 2s and $2p_x$ orbitals and the highest hibridisation coefficient in CO is related to the 2s and $2p_z$ orbitals.

For example, the hibridisation coefficient for the CN orbitals are given in Table2.

This can be followed by another result: when the C–N amide bond is placed on the *x*-axis, so upon rotating the dihedral around the C–N bond, in some points where there is the maximum repulsion between the orbitals (100° and –100°) an internal rotational barrier is produced.

Table 3 Calculated properties of formamaide in gas phase and solution (ε = 36.64)

	Gas phase		Solution	
Parameter	HF	MP2	HF(PC-Model)	Experimental[a]
r(C-N)	1.348	1.362	1.343	1.360
r(C=O)	1.193	1.225	1.196	1.219
r(C-$H_{1)}$	1.091	1.105	1.100	1.098
r(N-$H_{5)}$	0.996	1.010	0.996	1.002
r(N- H_6)	0.993	1.008	0.993	1.002
∠NCO	124.9	124.7	125.1	125.0
∠H_1CO	122.3	122.9	122.1	122.4
∠H_5CN	119.3	118.9	119.6	118.5
∠H_6CN	121.8	121.9	121.7	119.4
∠H_5NH_6	118.9	119.2	118.7	121.6
∠NCH_1	112.7	112.4	112.8	112.7
E	–168.931	–169.394	–168.936	–
μ	4.10	4.28	4.40	3.85

HF/6-31G* and MP2/6-31G* values. Bond lengths are given in angstrom and bond angles in degree Energy in hartree and dipole moment in debye.
[a]Taken from refs 4,5,6

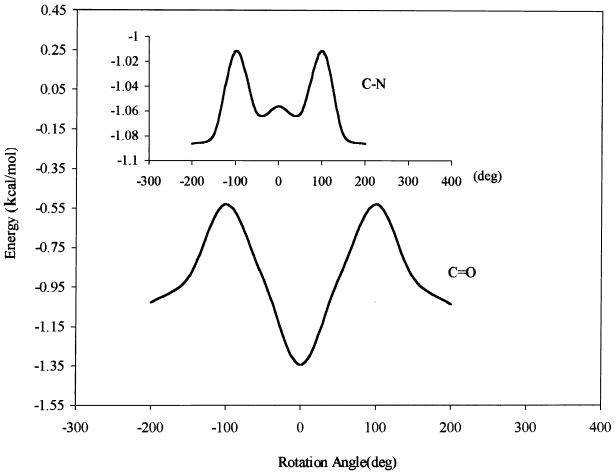

Fig. 7 Calculated energies for C–N and C=O bond of formamide by NBO method in gas phase.

Also hibridisation of CN and CO bonds and the highest coefficient for each atom have been calculated as follows:

$$C2–N3: sp^{1.25}(68.9\%P)_C + sp^{1.67}(62.49\%P)_N$$

And by calculating the coefficients,

$$C2–N3: 0.6057\ (sp1.25)_C + 0.7957\ (sp1.67)_N$$

And the highest coefficient for each atom in the CN bond,

$$h_C = 0.5616(2s)_C - 0.7395\ (2p_x)_C$$
$$h_N = 0.6112(2s)_N + 0.7081\ (2p_x)_N$$

and for the CO bond,

$$C2–O4: sp^1(99.46\%P)_C + sp^1(99.63\%P)_O$$
$$C2–O4: 0.5191\ (sp^{1)})_C + 0.8547\ (sp^{1)})_O$$
$$h_C = 0.9956(2p_z)_C + 0.0594\ (3d_{xz})_C$$
$$h_O = 0.9981\ (2p_z)_O - 0.0488\ (3d_{xz})_O$$

Also the most strongest interactions in formamide, are as follows:

LP N(3) BD* C2–O4 → (76.73 kcal / mol): for a stable structure

LP O(4) BD* C2–N3 → (31.82 kcal / mol): for an unstable structure

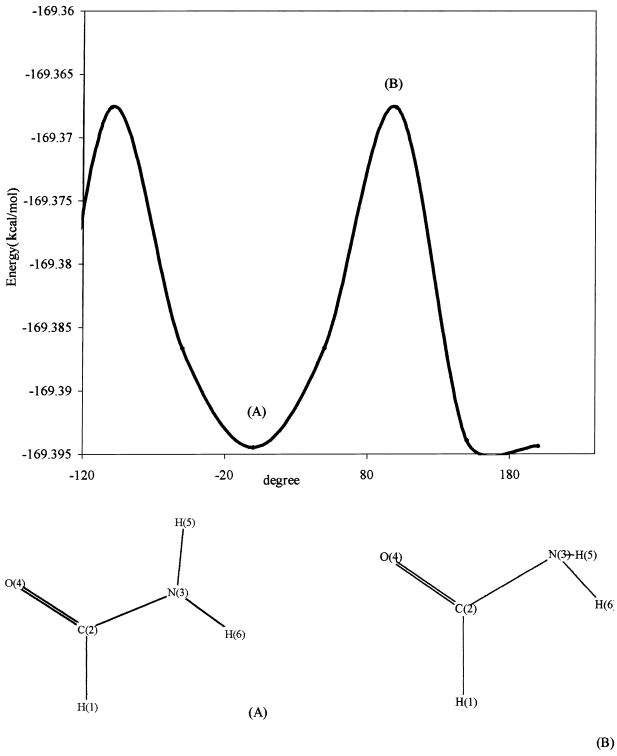

Fig. 8 Global minimum, local minimum and unstable structures of formamide.

In the range of the energy barrier, the reactivity of the molecule becomes greater. This means that the energy gap between the bonding molecular orbitals and antibonding molecular orbitals of the CN and CO bonds in the energy barrier of the rotated structure, with respect to the unrotated structure, becomes smaller (1.7623kcal/mol for unrotated structure decreasing to 1.64896 kcal/mol for the unstable rotated structure).

Studying atomic charges shows a symmetrical charge distribution for C(2) and O(4), which means there are no changes during the rotation for these atoms (Figs 5 and 6).

We also compared our calculated parameters with experimental data (Table 3) which shows good agreement. Also, the resonance model for amides can be seen clearly: there is a slight negative charge on the oxygen atom and a slight positive charge on the nitrogen atom at 100°. At this point, we also have an increase in the CN bond length (from 1.3618 Å at 0° to 1.4291 Å at 100°) and an increase in CN bond energy (from –1.09491 kcal /mol at 0° to –1.01137 kcal/mol at 100°), which both indicate the unstability of the CN bond. The other observation is the decrease in C=O bond length (from 1.2249 Å to 1.215 Å) and increase in C=O bond energy, (from –1.33447 kcal/mol at 0° to –0.52991 kcal /mol at 100°), which also show the unstability of the CO bond at 100°. Thus it can be inferred that we have an unstable structure at this point (100°). The CN and C=O bond energies are calculated by use of the NBO method and are shown in Fig.7. The result which we found above indicates that, the structure at 0° is the stable structure (or global minimum structure) and the two others (–200°, 200°) are local minimum structures (Fig.8). These structures has been verified by frequency calculations.

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