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Internal rotation about the C–N bond of amides

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Abstract

The internal rotation about the C–N bond of formamide (FA), acetamide (AA), *N*-methylformamide (NMF), *N*-methylacetamide (NMA), *N,N*-dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMA) in the gas phase, chloroform and water has been investigated at the HF level of theory with 6-31G(d), 6-31G(d,p) and 6-31+G(d) basis sets in order to figure out the appropriate level of theory in describing the *cis–trans* isomerization of the X-non-Pro and X-Pro peptide bonds. The conductor-like polarizable continuum model (CPCM) was used to calculate solvation free energies. The conformational electronic energies calculated at three levels predicted satisfactorily the experimental rotational barriers $\Delta G^{\ddagger}$ of FA, DMF and DMA, and the observed relative enthalpy changes $\Delta H_{cis/trans}$ of *cis* conformers for NMF and NMA to *trans* ones in the gas phase. The CPCM method at the HF/6-31+G(d) level predicted well experimental solvation free energies of acetamide derivatives. The $\Delta G^{\ddagger}$ for FA, NMF, DMF, NMA and DMA, and $\Delta H_{cis/trans}$ for NMF and NMA in chloroform and water were satisfactorily described by the CPCM method at HF/6-31G(d) and HF/6-31+G(d) levels. These results may indicate that the HF/6-31+G(d) level with the CPCM method appears to be the appropriate method in describing the *cis–trans* isomerization of the X-non-Pro and X-Pro peptide bonds in solutions.

Keywords: Ab initio and SCRF calculations; Internal rotation of amides; Rotational barriers; Solvation effects

1. Introduction

The internal rotation about the C–N bond in amides provides information in understanding conformational characteristics of the backbone of peptides and proteins. The barrier to rotation varies in the range of 15–23 kcal/mol in the gas phase and in solutions [1], which is attributed to the partial double bond based on the resonance model [2]. The barrier of amide bond increases as the polarity or hydrogen-bond ability of the solvent increases [3–7]. This observation was described in terms of the larger dipole moment of the ground state than that of the transition state from ab initio calculations on dimethylformamide and dimethylacetamide with the reaction field theory [6]. However, the *cis* population of secondary amides such as *N*-methylacetamide and *N*-methylformamide decreases to some extent by transferring from apolar to polar solvents, but remains nearly constant [8,9].

Secondary and tertiary amides play a role in constructing the backbone conformation of peptides and proteins. In a non-redundant set of 571 X-ray protein structures, the frequency of occurring the *cis* peptide bond for secondary amides (i.e. the X-non-Pro peptide bond) is 0.03%, whereas the value for tertiary amides (i.e. the X-Pro peptide bond) is 5.2% [10]. It has been shown that the *cis–trans* isomerization of the X-Pro bond is often involved in the rate-determining steps for folding and refolding of various proteins [11–14]. Several enzymes so-called peptidyl prolyl *cis–trans* isomerases (PPIases) have been identified, which significantly accelerate the isomerization of peptides and denatured proteins [11,12]. In particular, it has been reported that PPIases are involved in cell signalling and replication, and implicated in several diseases such as cancer, AIDS, and Alzheimer's disease [14].

The ab initio self-consistent reaction field (SCRF) method is known to be effective and useful in describing the solvation of molecules, in which the solute is placed in a cavity surrounded by a polarizable continuum solvent [15]. The SCRF methods such as the isodensity polarizable continuum model (IPCM) and the self-consistent isodensity

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polarizable continuum model (SCIPCM) [15] derived from the polarizable continuum model (PCM) [16] were applied to figure out the solvation effects on the rotational barrier and *cis/trans* population of amides [6,7,9,17–20]. In particular, IPCM and SCIPCM methods reasonably predicted the rotational barrier and *cis* population of the Ac-Pro peptide bond, respectively, for *N*-acetyl-*N*′-methylamides of proline [21,22], 5-methylated prolines [23], and pseudoprolines [24] in chloroform and water. However, neither the IPCM nor the SCIPCM described properly solvent effects on both of these two properties [21]. The conductor-like PCM (CPCM) was recently proposed [25] and gave a reasonable description of the conformational behavior of proline and hydroxyproline in aqueous solution [26]. The rotational barriers and populations of backbone as well as *cis* conformer for the proline dipeptide in chloroform and water were calculated using the CPCM method at the HF/6-31+G(d) level, which are consistent with the results from NMR experiments [27].

We report here the results on the rotational barriers, solvation free energies, and relative energies (or free energies) of *cis* conformers of primary, secondary and tertiary amides calculated in the gas phase, chloroform and water using the ab initio computations with the CPCM method at the HF levels of theory to figure out which level of theory is appropriate in describing the *cis–trans* isomerization of X-non-Pro and X-Pro peptide bonds in solutions.

2. Computational methods

All ab initio calculations were carried out using the GAUSSIAN 98 [28] packages. Amides studied here are primary amides such as formamide (FA) and acetamide (AA), secondary amides such as *N*-methylformamide (NMF) and *N*-methylacetamide (NMA), and tertiary amides such as *N,N*-dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMA). The experimental structures of amides in the gas phase [1] were used as initial (*trans* and *cis*) conformations for optimization at the HF/6-31G(d) level. Two transition structures were examined for each amide, where ts1 has the nitrogen lone pair *anti* to the carbonyl oxygen and ts2 has the nitrogen lone pair *syn* to the carbonyl

Table 1
Relative electronic energies (ΔE_e) in the gas phase and free energies (ΔG_{tot}) in chloroform and water at the HF/6-31G(d) level (ΔG_{tot} for transition states ts1 and ts2 correspond to rotational barriers for the C–N amide bond). Energies are in kcal/mol and gs stands for ground state

Amides		Gas phase		$CHCl_3$		Water	
		ΔE_e	Exptl	ΔG_{tot}	Exptl	ΔG_{tot}	Exptl
Formamide	gs	0.00		0.00		0.00	
	ts1	15.69	16.0[a]	17.38		18.59	
	ts2	18.55		18.29		18.26	18.2[b]
N-Methylformamide	*trans*	0.00		0.00		0.00	
	cis	1.09	1.3[c]	1.23	1.25[d]	1.31	1.42[d]
	ts1	18.18		19.93	19.0[e]	21.25	
	ts2	20.17		20.35		20.38	
N,N-Dimethylformamide	gs	0.00		0.00		0.00	
	ts1	18.73	19.4[f]	19.94		20.75	
	ts2	19.72		19.70	20.0[g]	19.63	22.0[g]
Acetamide	gs	0.00		0.00		0.00	
	ts1	14.01		15.44		16.61	
	ts2	18.26		17.62		17.27	
N-Methylacetamide	*trans*	0.00		0.00		0.00	
	cis	2.50	2.3[c]	2.56	2.10[d]	2.78	2.48[d]
	ts1	16.26		17.93	18.0[e]	19.26	18.8[e]
	ts2	20.82		20.69		20.54	
N,N-Dimethylacetamide	gs	0.00		0.00		0.00	
	ts1	13.29	15.3[h]	14.55	16.7[g]	15.21	19.1[g]
	ts2	17.72		17.66		17.34	

[a] Taken from Ref. [30].
[b] Taken from Ref. [7].
[c] Taken from Ref. [33].
[d] Taken from Ref. [8].
[e] In $C_2H_4Cl_2$ and water, taken from Ref. [4].
[f] Taken from Ref. [31].
[g] In butyl ether and water, taken from Ref. [6].
[h] Taken from Ref. [32].

oxygen [6]. Initially, the torsion angles for the X–C–N–Y sequence (X, Y=H or CH_3) were assigned as ±120° and ±60° for ts1 and ts2 structures, respectively. Optimized structures at the HF/6-31G(d) level were used as starting points for optimization at HF/6-31G(d,p) and HF/6-31+G(d) levels.

We have employed the CPCM method [25] implemented in the GAUSSIAN 98 to calculate solvation free energies of amides in chloroform and water, whose dielectric constants (ϵ) used are 4.7 and 78.4 at 25 °C [29]. Optimized structures at HF/6-31G(d), HF/6-31G(d,p) and HF/6-31+G(d) levels in the gas phase were used as starting structures for optimization in chloroform and water at the same level.

3. Results and discussion

Although considerable ab initio or density functional calculations have been reported for amides, we do not compare our results with them and instead compare with experimental values, because the main object of this work is to figure out which level of theory is appropriate in describing the *cis–trans* isomerization of X-non-Pro and X-Pro peptide bonds in solutions.

3.1. In the gas phase

Overall calculated bond lengths and bond angles of amides are consistent with available experiments with mean absolute deviations (MAD) of about 0.02 Å and 3.0°, respectively, as seen in NMA [20] They are not compared each other in detail. Tables 1–3 include relative electronic energies (ΔE_e) of amides at the HF level with 6-31G(d), 6-31G(d,p) and 6-31+G(d) basis sets. The values of ΔE_e for transition states ts1 and ts2 correspond to rotational barriers ($\Delta G^{\ddagger}$) for the C–N amide bond. All ts1 transition states are calculated to be more stable than ts2 structures at three levels in the gas phase.

Experimental rotational barriers ($\Delta G^{\ddagger}$) for FA, DMF and DMA in the gas phase are known to be 16.0 [30], 19.4 [31] and 15.3 kcal/mol [32], respectively. The values of MAD for these three amides are calculated to be 1.0, 0.8 and 0.9 kcal/mol with 6-31G(d), 6-31G(d,p) and 6-31+G(d) basis sets, respectively, which do not show any significant difference.

Table 2

Relative electronic energies (ΔE_e) in the gas phase and free energies (ΔG_{tot}) in chloroform and water at the HF/6-31G(d,p) level (ΔG_{tot} for transition states ts1 and ts2 correspond to rotational barriers for the C–N amide bond). Energies are in kcal/mol and gs stands for ground state

Amides		Gas phase		$CHCl_3$		Water	
		ΔE_e	Exptl	ΔG_{tot}	Exptl	ΔG_{tot}	Exptl
Formamide	gs	0.00		0.00		0.00	
	ts1	15.98	16.0[a]	17.68		18.92	
	ts2	18.68		18.48		18.52	18.2[b]
N-Methylformamide	*trans*	0.00		0.00		0.00	
	cis	1.07	1.3[c]	1.19	1.25[d]	1.24	1.42[d]
	ts1	18.32		20.06	19.0[e]	21.42	
	ts2	20.23		20.43		20.49	
N,*N*-Dimethylformamide	gs	0.00		0.00		0.00	
	ts1	18.93	19.4[f]	20.14		20.96	
	ts2	19.91		19.93	20.0[g]	19.81	22.0g
Acetamide	gs	0.00		0.00		0.00	
	ts1	14.26		15.70		16.89	
	ts2	18.37		17.79		17.49	
N-Methylacetamide	*trans*	0.00		0.00		0.00	
	cis	2.53	2.3[c]	2.57	2.10[d]	2.78	2.48[d]
	ts1	16.34		18.02	18.0[e]	19.40	18.8[e]
	ts2	20.83		15.41		20.61	
N,*N*-Dimethylacetamide	gs	0.00		0.00		0.00	
	ts1	13.40	15.3[h]	14.69	16.7[g]	15.33	19.1[g]
	ts2	17.86		17.80		17.51	

[a] Taken from Ref. [30].

[b] Taken from Ref. [7].

[c] Taken from Ref. [33].

[d] Taken from Ref. [8].

[e] In $C_2H_4Cl_2$ and water, taken from Ref. [4].

[f] Taken from Ref. [31].

[g] In butyl ether and water, taken from Ref. [6].

[h] Taken from Ref. [32].

Table 3
Relative electronic energies (ΔE_e) in the gas phase and free energies (ΔG_{tot}) in chloroform and water at the HF/6-31+G(d) level (ΔG_{tot} for transition states ts1 and ts2 correspond to rotational barriers for the C–N amide bond). Energies are in kcal/mol and gs stands for ground state

Amides		Gas phase		$CHCl_3$		Water	
		ΔE_e	Exptl	ΔG_{tot}	Exptl	ΔG_{tot}	Exptl
Formamide	gs	0.00		0.00		0.00	
	ts1	16.13	16.0[a]	18.03		19.45	
	ts2	18.80		18.68		18.77	18.2[b]
N-Methylformamide	*trans*	0.00		0.00		0.00	
	cis	1.21	1.3[c]	1.20	1.25[d]	1.12	1.42[d]
	ts1	18.66		20.59	19.0[e]	22.07	
	ts2	20.48		20.68		20.71	
N,*N*-Dimethylformamide	gs	0.00		0.00		0.00	
	ts1	18.90	19.4[f]	20.40		21.45	
	ts2	19.63		19.72	20.0[g]	19.72	22.0[g]
Acetamide	gs	0.00		0.00		0.00	
	ts1	14.34		15.92		17.34	
	ts2	18.43		17.84		17.65	
N-Methylacetamide	*trans*	0.00		0.00		0.00	
	cis	2.62	2.3[c]	2.52	2.10[d]	2.64	2.48[d]
	ts1	16.72		18.52	18.0[e]	19.98	18.8[e]
	ts2	21.10		20.92		20.75	
N,*N*-Dimethylacetamide	gs	0.00		0.00		0.00	
	ts1	13.35	15.3[h]	14.87	16.7[g]	15.70	19.1[g]
	ts2	17.62		17.61		17.32	

[a] Taken from Ref. [30].
[b] Taken from Ref. [7].
[c] Taken from Ref. [33].
[d] Taken from Ref. [8].
[e] In $C_2H_4Cl_2$ and water, taken from Ref. [4].
[f] Taken from Ref. [31].
[g] In butyl ether and water, taken from Ref. [6].
[h] Taken from Ref. [32].

In N_2 matrix experiments, the enthalpy differences ($\Delta H_{cis/trans}$) between the *trans* and *cis* conformers of NMF and NMA were estimated to be 1.3 and 2.3 kcal/mol, respectively [33]. The values of 1.09 and 2.50 kcal/mol at the HF/6-31G(d) level, 1.07 and 2.53 kcal/mol at the HF/6-31G(d,p) level, and 1.21 and 2.62 kcal/mol at the HF/6-31+G(d) level are consistent with these experiments within 0.2 kcal/mol. Therefore, the values of ΔE_e at three levels appear to predict reasonably experimental values of $\Delta G^{\ddagger}$ and $\Delta H_{cis/trans}$ for the C–N bond of amides.

3.2. In solutions

The relative free energies of conformers for amides calculated at three levels in chloroform and water are summarized in Tables 1–3. In chloroform, all ts1 transition states are calculated to be more stable than ts2 structures at three levels, as seen in the gas phase, except for DMF. In particular, the ts2 conformer of NMA is more stabilized by 2.6 kcal/mol than the ts1 structure at the HF/6-31G(d,p) level, which seems to be a problem in the model employed for the solvation free energy calculation at the HF/6-31G(d,p) level.

Experimental rotational barriers ($\Delta G^{\ddagger}$) for NMF and NMA in chloroform ($\epsilon = 4.7$), and DMF and DMA in butyl ether ($\varepsilon = 3.1$) are reported to be 19.0 [4], 18.0 [4], 20.0 [6] and 16.7 kcal/mol [6], respectively. Our calculated values are consistent with these experimental values within 1 kcal/mol at all three levels. The values of $\Delta H_{cis/trans}$ between the *trans* and *cis* conformers of NMF and NMA in chloroform were calculated to be 1.23 and 2.56 kcal/mol at the HF/6-31G(d) level, and 1.20 and 2.52 kcal/mol at the HF/6-31+G(d) level, respectively, which are in agreement with experimental values of 1.25 and 2.10 kcal/mol [8], respectively.

In water, the ts2 transition states for formamide derivatives of FA, NMF and DMF are more stabilized than the ts1 structures at all three levels, whereas acetamide derivatives of AA, NMA and DMA have the opposite conformational preference. This is because the rotational barriers for the ts1 and ts2 transition states increase largely and decrease a little, respectively, as the increase of solvent polarity at all three levels.

Experimental rotational barriers ($\Delta G^{\ddagger}$) for FA, DMF, NMA and DMA in water are reported to be 18.2 [7], 22.0 [6], 18.8 [4] and 19.1 kcal/mol [6], respectively.

Table 4
Solvation free energies (ΔG_s) in chloroform and water at the HF level with 6-31G(d), 6-31G(d,p) and 6-31+G(d) basis sets (ΔG_s is calculated by subtracting ΔE_e in the gas phase from ΔG_{tot} in solution). Energies are in kcal/mol and gs stands for ground state

Amides		6-31G(d)		6-31G(d,p)		6-31+G(d)		Exptl	
		$CHCl_3$	Water	$CHCl_3$	Water	$CHCl_3$	Water	$CHCl_3$	Water
Formamide	gs	−4.65	−10.24	−4.64	−10.32	−5.30	−11.71		
N-Methylformamide	*trans*	−4.50	−9.63	−4.51	−9.76	−5.08	−10.90		
N,N-Dimethylformamide	gs	−3.30	−6.48	−3.33	−3.27	−3.90	−7.71		
Acetamide	gs	−4.39	−9.81	−4.39	−9.88	−4.99	−11.26	−7.1[a]	−9.7[b]
N-Methylacetamide	*trans*	−4.25	−9.32	−4.26	−9.47	−4.78	−10.53		−10.1[b]
N,N-Dimethylacetamide	gs	−3.06	−5.98	−3.08	−6.11	−3.59	−7.14		−8.6[b]

[a] Taken from Ref. [34].
[b] Taken from Ref. [35].

The corresponding calculated values are 18.26, 19.63, 19.26 and 15.21 kcal/mol at the HF/6-31G(d) level, and 18.77, 19.72, 19.98 and 15.70 kcal/mol at the HF/6-31+G(d) level, respectively. There are the values of MAD to be 1.7 and 1.9 kcal/mol at HF/6-31G(d) and HF/6-31+G(d) levels, respectively. The values of $\Delta H_{cis/trans}$ between the *trans* and *cis* conformers of NMF and NMA in water were calculated to be 1.31 and 2.78 kcal/mol at the HF/6-31G(d) level, and 1.12 and 2.64 kcal/mol at the HF/6-31+G(d) level, respectively, and the corresponding experimental values are 1.42 and 2.48 kcal/mol [8], respectively.

Solvation free energies (ΔG_s) for amides in chloroform and water are listed in Table 4. Only experimental values are reported for AA in chloroform [34], and AA, NMA and DMA in water [35], and the CPCM method at the HF/6-31+G(d) level predicts better experimental values than other levels. By analyzing distribution coefficients for transfer of AA, NMA and DMA from dilute aqueous solution to the vapor phase, NMA was found to be more soluble than either AA or DMA in water [35]. However, the anomalous ΔG_s of NMA compared to that of AA cannot be explained by the CPCM method at all three levels. The rotational barriers and populations of backbone as well as *cis* conformer for the proline dipeptide in chloroform and water were calculated using the CPCM method at the HF/6-31+G(d) level, which are consistent with the results from NMR experiments [27].

4. Conclusions

The conformational electronic energies calculated at HF/6-31G(d), HF/6-31G(d,p) and HF/6-31+G(d) levels predicted satisfactorily the experimental rotational barriers $\Delta G^\ddagger$ of FA, DMF and DMA, and the observed relative enthalpy changes $\Delta H_{cis/trans}$ of *cis* conformers for NMF and NMA to *trans* ones in the gas phase. The CPCM method at the HF/6-31+G(d) level predicted well experimental solvation free energies of acetamide derivatives. The $\Delta G^\ddagger$ for FA, NMF, DMF, NMA and DMA, and $\Delta H_{cis/trans}$ for NMF and NMA in chloroform and water were satisfactorily described by the CPCM method at HF/6-31G(d) and HF/6-31+G(d) levels. These results may indicate that the HF/6-31+G(d) level with the CPCM method appears to be the appropriate method in describing the *cis–trans* isomerization of the X-non-Pro and X-Pro peptide bonds in solutions.

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