

Ab-initio and NMR Studies on the Rotational Barrier for Thioacetamide and Acetamide

Yoong-Kee Choe, Gun-Il Song, Young-Sang Choi, and Chang-Ju Yoon*

Department of Chemistry, College of Science, Korea University, Anam-Dong 5-1, Songbuk-Ku, Seoul 136-701, Korea

*Department of Chemistry, College of Science & Technology, The Catholic University of Korea, Yokkok-Dong, Pucheon 420-743, Korea

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The rotational barriers of thioacetamide (TA) and acetamide (AA) were studied using the ab-initio molecular orbital theory and NMR spectroscopy. The calculated rotational barriers using MP2/6-31G**//MP2/6-31G** for TA was 72.26 kJ/mol and 58.19 kJ/mol for AA, respectively. These results are in good agreement with the experimental data. The tendency for the change of structural parameters is consistent with the result of formamide. In both amides, the rotational barrier arises from the pyramidalization of nitrogen. The chemical shifts of both amides are shifted upfield when temperature is raised, which confirms pyramidalization of nitrogen. The lineshape of ¹H-NMR spectra of TA shows quintet which is contributed from two triplet spectra. This means that the distribution of electrons around the nitrogen is rather symmetric. Ab-initio calculations of electric field gradient for both amides confirm the above results. The above experimental results are well understood by Keith's view on thioamides, which excludes the contribution of resonance structure and considers the origin of rotational barrier to be the same in both thioamides and in corresponding amides.

Introduction

The amide is one of the most important functional groups in chemistry. Its chemical properties are of importance in understanding the structure and dynamics of proteins. Recently, the progress in computer simulation of biomolecules requires an accurate rotational potential function of amides.¹ Hence, many ab-initio molecular orbital calculations on rotational barriers of amides have been reported.²⁻⁷

To understand the rotational behavior of amides, we must know the properties of their rotational ground and transition states. As in Figure 1, it is well known that there are two possible transition states on the potential energy curve for the rotation in amides, TS(1) and TS(2), respectively.² These two transition states are characterized by the relative position of the lone pair electrons on the nitrogen with respect to the C=X bond and they show an imaginary frequency. These two transition states resulted by rotation have been confirmed by several papers published previously.² The amide nitrogen in the rotational transition state has a sp³ hybridization, since its lone pair electrons are so placed to give nitrogen a typical pyramidal structure.

The ground state properties of amides upon rotation are readily understood by assuming the amide resonance type.⁸ One can understand many chemical properties of amide with connection to the resonance structure. Because of the double bond character on C-N bond, which is confirmed by postulating the resonance description of amide, the energy change along the rotation upon C-N bond shows higher rotational barrier. The barrier heights obtained by many theoretical and experimental studies are about 60-90 kJ/mol.^{1-5,9} The other chemical properties explained by the amide resonance is an increase in the rotational barrier of amide in polar solvents.^{9,10} Since the charge-separated structure of the ro-

tational ground state is stabilized by polar solvents, the barrier heights are increased. However, the published results on the rotation of formamide by Wiberg *et al.* reported inconsistent results with the resonance model.⁵ It arises from the two theoretical findings that do not accord with the expectation given by the resonance structure of amide. The resonance structure suggests that upon rotation about the C-N bond the C=O bond should contract and the C-N bond should lengthen in going from the planar ground state to the rotated transition state conformer. An ab-initio calculation carried out by Wiberg *et al.* showed that the C-N bond is elongated as expected by the resonance structure, but the C=O bond is almost unaltered upon rotation.⁵ Also, the calculated topological charge density based on Bader's theory of *Atoms in Molecule*^{11,12} showed that the electron population of nitrogen in the ground state conformer is greater than that in the rotated transition state form.⁵ This kind of charge distribution also is not predicted by the resonance description of amide, since the double-bonded form gives a positive charge on the nitrogen, while the transition state has no resonance contribution. This concept was supported experimentally by Brown *et al.* who found the correlation between the rate of amide hydrolysis and the hybridization on nitrogen.¹³ Other examples to confute the consequence

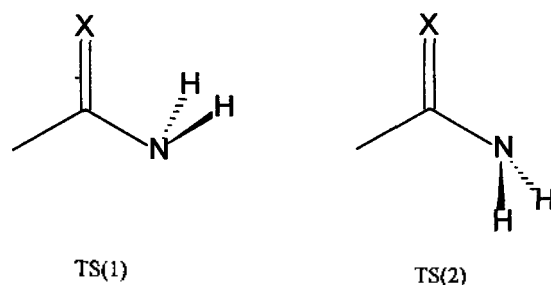


Figure 1. Two rotational transition states of amides.

*To whom correspondence should be addressed.

of resonance structure in some molecules have been reported.¹⁴⁻¹⁷ We were interested in this new concept on amide rotation, so we re-examined this theory to establish if it can be applicable to other amides including thioamide. We choose acetamide (AA) and thioacetamide (TA) as a model amide compound. These compounds have not been studied theoretically rather than formamide and thioformamide. One reason to use those as a model compound is that our laboratory has performed NMR experiments on these compounds so a lot of experimental data are available for us.¹⁸ Recently, thioamide has been investigated theoretically, since its higher rotational barrier than in corresponding amides can not be understood easily by the simple amide resonance.¹⁹⁻²¹ According to the resonance model of amide, it may be inferred that oxygen, which is more electronegative than sulfur, can pull more electrons *via* π system, leading the contribution of double-bond on C-N bond stronger.

We categorized this study into three sections. First, we apply the *ab-initio* molecular orbital method to TA and AA, and determine their equilibrium geometries and energetics. Our focuses will be placed on the role of resonance structure in amide chemistry. Second, we present the NMR experimental results to support the view deduced by theoretical calculations. Third, discussions on these results will be given, mainly focused on the rotational barrier difference of both amides and correlation between the theory and experiment.

Computational Methods

All the geometries were calculated using the optimization routines in *Gaussian 94*²² and *GAMESS*²³ programs on the pentium II PC and SGI Indy workstation respectively. We used 6-31G split valence basis sets with augmentation by d polarization function on heavy atoms, and p polarization function on hydrogen atoms for geometry optimizations.²⁴ The *C_s* symmetry was imposed on both ground and transition state amides. Each geometries obtained by HF calculations was reoptimized using Müller-Plesset second order (MP2) perturbation to consider an electron correlation.²⁵⁻²⁹ The optimized structures for all transition state conformer were confirmed by the imaginary frequency calculated by analytic second derivatives. Natural Population Analysis³⁰⁻³² was performed using MP2/6-31G** and B3LYP/6-31G**³³⁻³⁶ level of theory. In all calculations, we considered only the conformer of which dihedral angle between methyl hydrogen and oxygen or sulfur is zero. To investigate the energetic and structural changes along the C-N internal rotation, we used the intrinsic reaction coordinate (IRC) technique.^{37,38} We also used 6-31G** basis sets to generate the structures and energetics at each IRC points.

Experimental

TA (Riedel-deHan, 99%), AA (Aldrich, 99%) was used without further purification. Deuterated nitromethane (CD₃-NO₂, 99%) were obtained from Aldrich. The concentration of both solutions was 0.1 M.

The NMR spectra were obtained by FT-NMR Varian Unity Plus 600 Hz Spectroscopy equipped with variable temperature unit. The spectra were obtained by varying the tem-

perature from 280.1 K to 365.1 K separated by 5 K intervals. We used tetramethylsilane as an internal reference to obtain the chemical shifts of both amides.

Results and Discussions

Geometry. The two rotational transition states of TA are shown in Figure 2. The calculated rotational barrier height for TS(1) is of lower energy by 10 kJ/mol. We can think of two reasons for this energy difference. First, the structure of TS(1) is stabilized by the intramolecular sulfur-hydrogen interaction, the other is that in the TS(2) structure the electron repulsion between the lone pair electrons of nitrogen and that of C=S bond may increase the energy of molecule.⁷ In this paper, we will only consider the TS(1) which is the conformer of lower energy.

The optimized geometries of the ground and transition state molecules at MP2/6-31G** level are shown in Figure 3. The intramolecular C-N-H angles of the ground state molecule show typical *sp*² hybridization of nitrogen. We summarized the above results in Table 1. X-ray diffraction data for TA are 1.731 Å for C=S bond, 1.324 Å for C-N bond, and 120.7° for C1-C2=S angle.³⁹ From experimental data of AA, we can see that calculated results are more close to gas phase data than that of solid state. Ou *et al.* reported that geometry data of amides obtained by *ab-initio* calculations including MP4 level of electron correlation are very close to microwave data.⁴² The calculated geometrical data by our group are in good agreement with the experimental values even though the level of our calculations are MP2, but slightly different from the crystal data in case of TA. The difference of geometrical data for TA maybe arises from the low level of electron correlation used since TA contains a heavy atom. It can be seen that

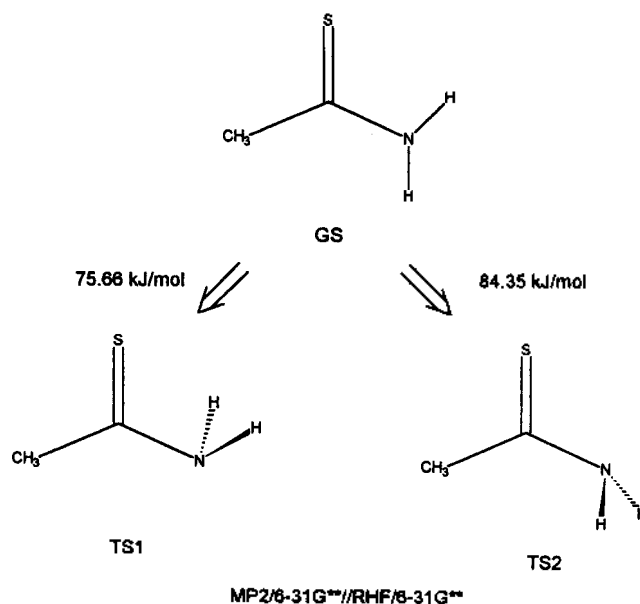


Figure 2. Rotational barrier of two rotated transition states of thioacetamide. The geometries were obtained at RHF/6-31G** level calculation and MP2/6-31G** single point energy calculation was carried out based on geometries obtained by RHF calculation.

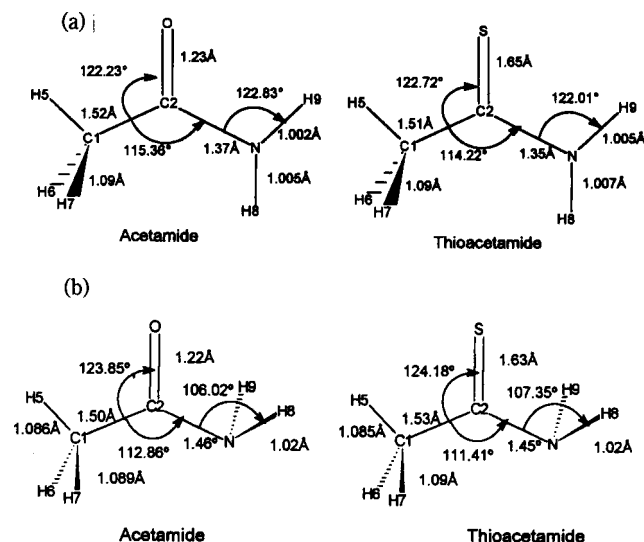


Figure 3. The optimized geometries of (a) ground state and (b) transition state of acetamide and thioacetamide obtained at MP2/6-31G** level calculation.

the C-N bond is elongated for both TA and AA, but the C=S(O) bond is almost unaffected by rotation. The C-N bond length of transition state increased 7.63% for TA and 6.53% for AA. The associated decrease of C=S(O) bond is 3.29% for TA and 0.97% for AA. As in the case of formamide, the geometrical alteration of C=O bond of AA is negligible in comparison with that of C-N bond. These are coincident

Table 1. Structural parameters of thioacetamide and acetamide (MP2/6-31G**//MP2/6-31G**)

Parameter	Thioacetamide		Acetamide			
	GS	Experimental ^a	GS	Experimental		
C=S(O)	1.6464	1.731	1.2283	1.28 ^b	1.21 ^c	
C-N	1.3495	1.324	1.3666	1.38	1.36	
C-C	1.5102		1.5153	1.51	1.53	
C-H	1.0901		1.0878			
C-H	1.0872		1.0875			
C-H	1.0872		1.0875			
N-H8	1.0071		1.0053			
N-H9	1.0053		1.0023			
C1-C2-S(O)	122.72	120.7	122.23			
C1-C2-N	114.22		115.36	129	122	
C2-C1-H5	112.69		113.54			
C2-C1-H6	109.27		108.46			
C2-C1-H7	109.27		108.46			
C2-N-H8	119.03		117.94			
C2-N-H9	122.01		122.83			
H5-C-C-S(O)	180.0		180.0			
H6-C-C-N	121.34		121.61			
H7-C-C-N	-121.24		-121.61			
S(O)-C-N-H8	180.0		180.0			
S(O)-C-N-H9	0.0		0.0			

^a X-ray diffraction data.³⁹ ^b Crystal data⁴⁰ ^c Gas phase data⁴¹

Table 1. (Continued)

Parameter	Thioacetamide	Acetamide
	TS	TS
C=S(O)	1.6264	1.2204
C-N	1.4498	1.4558
C-C	1.4971	1.5025
C-H	1.0854	1.0893
C-H	1.0911	1.0855
C-H	1.0911	1.0855
N-H8	1.0177	1.0188
N-H9	1.0177	1.0188
C1-C2-S(O)	124.18	123.85
C1-C2-N	111.41	112.86
C2-C1-H5	112.14	109.18
C2-C1-H6	108.81	110.46
C2-C1-H7	108.81	110.46
C2-N-H8	107.35	106.02
C2-N-H9	107.35	106.02
H5-C-C-S(O)	180.0	180.0
H6-C-C-N	57.74	121.84
H7-C-C-N	-57.54	-121.84
S(O)-C-N-H8	-55.49	-54.73
S(O)-C-N-H9	55.49	54.73

Abbreviations: GS means Ground State, TS means Transition State

with the results on formamide. Figure 4 shows the geometrical variations of C-N bond length and C=S bond length of TA along the reaction path. The reaction path was searched as described in the paper by Wiberg *et al.*⁵ Figure 4. shows different curvature for the change of structural parameters

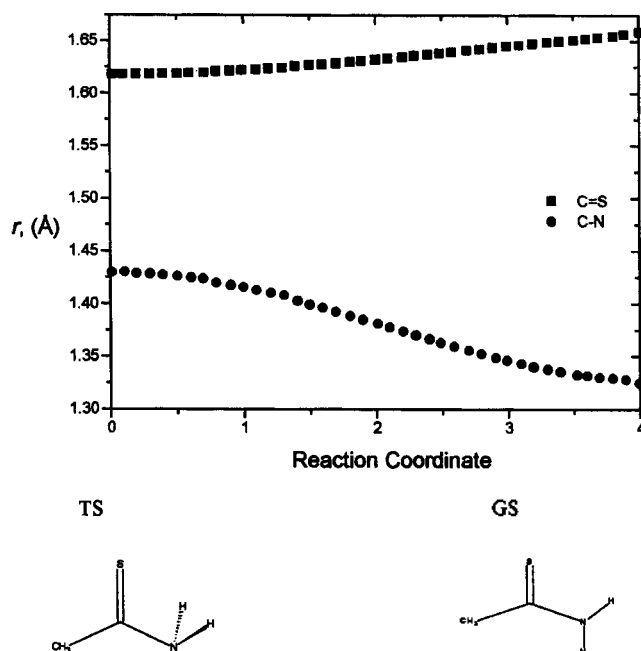


Figure 4. Bond length changes for thioacetamide on rotation about C-N bond.

Table 2. Rotational barrier heights calculated by various methods

	Energies ^c	ref.
Acetamide		
RHF/3-21G//RHF/3-21G	73.04	^b
RHF/6-31G//MP2/6-31G*	89.20	^a
MP3/6-31G//MP2/6-31G*	75.91	^a
MP2/6-311G(2d,2p)//MP2/6-	58.65	^a
CISD/6-31G**//MP2/6-31G*	58.44	^a
MP2/6-31G**//MP2/6-31G**	58.19	this work
Thioacetamide		
RHF/3-21G**//RHF/3-21G*	106.07	^b
MP2/6-31G**//MP2/6-31G**	72.26	this work

^a ref. 6. ^b ref. 2 (a). ^c Barrier heights in kJ/mol

of TA. This means the changes of both C-N and C=S are affected differently by the rotation.

Energetics. The calculated rotational barrier heights at the MP2/6-31G**//MP2/6-31G** level are 72.26 kJ/mol for TA and 58.19 kJ/mol for AA. It has been reported that an *ab-initio* calculation depends upon the chosen basis set. Hence, for comparison, we summarized the calculated rotational barrier heights using several methods by other researchers in Table 2. Chan *et al.* have reported that the rotational barrier height of AA in polystyrene matrix is 55.6 kJ/mol.⁹ Our calculations agree well with the experimentally obtained barrier. Wiberg said that the lone pair electrons in nitrogen play a major role in determining the rotational barrier of formamide.⁵ He said that in the transition state, the nitrogen is hybridized to place the lone pair electrons in an orbital to maximize its *s* character and upon rotation to the ground state, the nitrogen is rehybridized to *sp*², allowing the lone pair electrons to be donated to the vacant *p* orbital of the carbon, which stabilized the lone pair electrons of nitrogen, hence making the ground state energy lower. This means that the energy of the transition state is increased in proportion to the amount of *p* character that lone pair electrons in the nitrogen of amide have. From the point of nitrogen, its energy is raised if its hybridization became more *sp*² like in transition state. Following the above reasoning, the lone pair electrons in the nitrogen of transition state conformer of TA is expected to have more *p* character than AA, since rotational barrier of TA is larger than that of AA. To investigate the nature of hybridization of nitrogen, we carried out a NBO population analysis. Table 3 shows the results of NBO population analysis about the lone pair electrons of nitrogen. In both MP2, B3LYP cases, the lone pair electrons of AA has more *s* character than that of TA in transition state. This shows that relatively large *s* character

Table 3. Hybridization of nitrogen. Results are obtained by NBO populations analysis

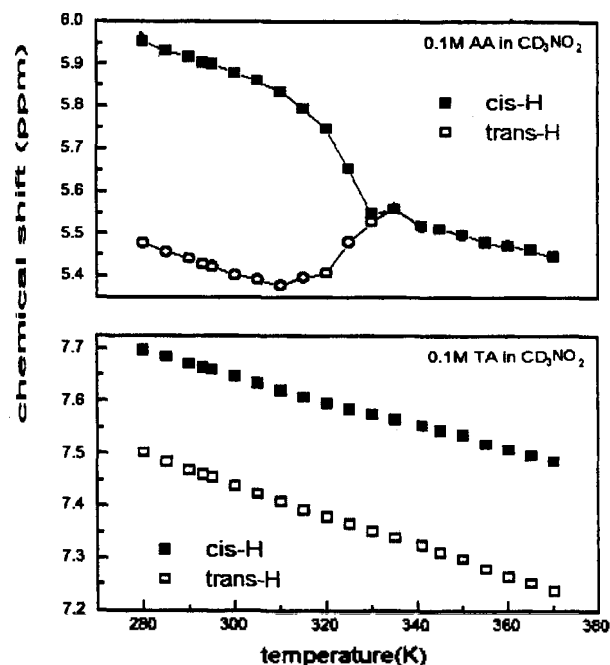
	MP2/6-31G**//MP2/6-31G**	B3LYP/6-31G**//MP2/6-31G**
AA-GS	sp1.57	sp1.55
AA-TS	sp2.4	sp2.40
TA-GS	sp1.49	sp1.48
TA-TS	sp2.28	sp2.28

of lone pair electrons of AA nitrogen in its transition state reduced the orbital energy, leading to the lower rotational barrier. The transition state of TA has more *sp*² character than that of AA, which is related to the higher *p* character of lone pair electrons in nitrogen.

Discussion

TA shows a higher rotational barrier than AA by 10 kJ/mol. Recently, there have been some arguments about this energy difference. Wiberg and Rablen calculated the rotational barrier of thioformamide and compared the calculated results with that of formamide.¹⁹ They explained the higher rotational barrier of thioformamide by introducing the resonance structure of amide. They said that the contribution of resonance structure is trivial in case of formamide, but not so in case of thioformamide. Therefore, the rotational barrier of thioformamide is larger than that of formamide by the contribution of double bond character in the planar conformation.¹⁹ Ou *et al.* also calculated the rotational barrier of thioformamide.²¹ They showed by the aid of natural population analysis that a charge is more transferred from nitrogen to sulfur in thioformamide than in formamide, which is the same conclusion that is led by Wiberg *et al.* However, the above conclusion is opposite to the anticipation that the more electronegative oxygen would pull more charge from nitrogen than sulfur. Keith *et al.* showed by using Fermi hole that the amount of charge transfer from nitrogen to sulfur is little.²⁰ They introduced new viewpoint that thioamides behave as thioformylamine, which regards thioamide as a amine connected by thioformyl group.

Figure 5. is the NMR spectra of AA and TA in nitromethane solution along the temperature changes. Since what we want to know from NMR spectra is the intrinsic

**Figure 5.** ¹H NMR spectra of thioacetamide and acetamide in nitromethane solution at various temperatures.

nature of amide, we have to minimize the effect of solvent on a lineshape of NMR spectra. Hence, the reason that we have chosen nitromethane as a solvent is to prevent the proton exchange of solvent with amides. The existence of exchangeable proton in solvent make the interpretation of spectra be more complicated. Works in other solvents are in progress now and will be published upcoming next article. The ^1H NMR spectra of amide proton of AA show that there is a difference between two proton chemical shifts at low temperature. Two peaks collapse into one broad line when temperature is raised, but this tendency is not so strong in case of TA. At 360 K, it is clear that the difference between two chemical shifts of amide proton in AA are hard to discriminate. This means qualitatively that TA has a higher rotational barrier than AA because at high temperature the rotation on C-N bond become more feasible. From Figure 5, we can see that with the raise of temperature, the proton resonance of amides is shifted upfield. In Figure 6, we can see more quantitatively the change of chemical shift along the temperature. This result seems to be correlated to the fact that both amides change their hybridization from sp^2 to sp^3 when temperature is raised. The NMR spectra of TA appeared as a merged triplet, actually quintet, at every temperature. The nitrogen has a quadruple moment so the proton spectra of hydrogen attached to it show very broad lineshape. It is rare to observe a triplet spectrum except highly symmetric molecules, e.g. NH_3 , NH_4^+ , because of a rapid relaxation of ^{14}N .⁴³ The triplet spectra of TA arise from the fact that the electric environments around the nitrogen are symmetric. We have observed triplet spectra of TA in various solutions including acetone, methanol at room temperature.¹⁶ The triplet spectra means that the three substituents attached to the nitrogen provide similar elec-

tronic effect to amide nitrogen. The electric field gradient (efg) is an important indicator for describing the distribution of electrons around an atom. For example, the efg of NH_4^+ , tetrahedral, is zero. Bagno *et al.* have reported the electric field gradient (efg) of thioformamide and formamide calculated by *ab-initio* molecular orbital method using triple- ζ basis set with all atom polarization functions.⁴⁴ The calculated q_{zz} for thioformamide is 0.808, formamide is 0.956. We also calculated the efg for both TA and AA using MP2/6-311+(d,p)//MP2/6-31G(d,p) level of theory. The results for TA is -0.4454 and -0.5180 for AA. Same trends were observed in both thioformamide-formamide and T-AA system. The absolute value of q_{zz} is smaller in case of TA, which confirms the above experimental results. We found that it is reasonable to interpret experimental results adopting Keith's view about thioformamide. As mentioned above, Keith said that higher rotational barrier of thioformamide is easily explained by regarding it as thioformylamine. According to his paper, an inversion barrier of amine is increased when it has electron donating substituent and decreased when substitute has the tendency to pull the electron, so thioformamide has a larger rotational barrier because the nature of a thioformyl substituent is more electron donating to NH_2 than is the polarized formyl group.²⁰ Our experimental results can be interpreted as follows: in case of TA, thioacetformyl group has a electron donating power similar to hydrogen allowing to form symmetric distribution of electronic cloud around the nitrogen and in case of AA, acetyl group withdraws the charge more than hydrogen making unsymmetric electronic distribution around the nitrogen.

Conclusions

We have investigated the structure and energetics of TA and AA both theoretically and experimentally. Our calculated results on both amides are in good agreement with the experimentally observed results. The rotational barrier of both amides arises from the pyramidalization of nitrogen. The higher p character of nitrogen in TA is the reason that TA has a higher rotational barrier than AA. The ^1H NMR spectra of both amides show indirectly that both amides alter its hybridization from sp^2 to sp^3 when they undergo rotation from planar conformer to rotated transition state. The ^1H NMR spectra of TA show triplet lineshape which indicates symmetric electronic distribution around the nitrogen. This was confirmed by the *ab-initio* calculations of efg for both amides. The experimental results are well understood by adopting Keith's view on thioformamide which regards the molecule as a thioformyl-amine.

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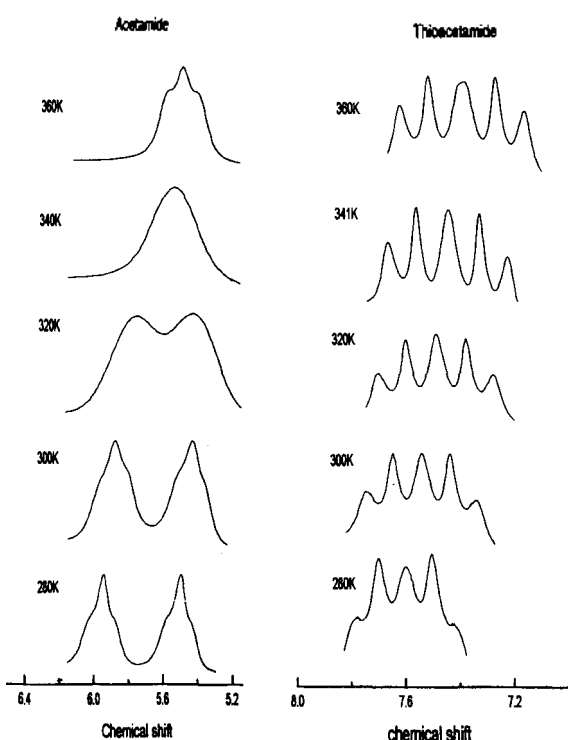


Figure 6. The variation of chemical shift along the temperature change (Left: AA, Right: TA).

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