Basis Set and Electron Correlation Effects on the Internal Rotational Barrier Heights of Formamide and Acetamide

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The internal rotational barrier heights of formamide and acetamide were studied by *ab initio* molecular orbital calculations using several basis sets up to 6-311G(2d,2p) with electron correlation correction. The calculated barrier heights depended on the basis set used. The calculated barrier heights with the MP3 (Møller–Plesset 3rd order perburbation) electron correlation correction were decreased by the augmentation of polarized functions by as much as 5–6 kcal mol^{-1}.[†] Further augmentation of multiple polarized functions and diffuse functions had little effect on the calculated barrier heights. The calculated barrier heights using polarized basis sets were decreased by the incorporation of electron correlation by as much as 1–2 kcal mol^{-1} from the values obtained by HF method. The calculated barrier heights of formamide and acetamide using polarized basis sets with electron correlation correction were 14.5–15.4 and 12.5–13.2 kcal mol^{-1}, respectively. Whereas these barrier heights were 1–8 kcal mol^{-1} lower than the experimental values measured in the liquid phase, the calculated values were close to the barrier heights measured in a polystyrene matrix. Zero point and thermal vibrational energies of formamide were calculated at HF/6-31G* level. The calculated vibrational energy correction for the barrier height was only -0.75 kcal mol^{-1}.

The internal rotational potential of amide C–N bonds is important for the understanding of the conformation of proteins. Recently developed computer simultations of proteins, for example molecular dynamics, require accurate rotational potentials of amides. Hence many experimental[1–74] and theoretical[73–84] studies have been reported on the internal rotation of the amide bond. The internal rotational barrier heights of formamide **1** and acetamide **2** have not been measured in the gas phase. The barrier heights measured in the liquid phase are 17–21 kcal mol^{-1}.[1–5]

Several *ab initio* molecular orbital calculations of the internal rotational barrier heights of amides have been reported.[71,73,75–84] The calculated barrier heights of formamide and acetamide at the HF level using basis sets of double-zeta quality are 17–20 kcal mol^{-1},[76–79,81,82] which are close to the experimental values in the liquid phase. However, the calculated barrier heights using improved polarized basis sets are 13–16 kcal mol^{-1},[79–81] which are considerably smaller than the experimental barrier heights.

The cause of this disagreement is not certain. One possible explanation of this disagreement is that intermolecular interaction in the liquid phase increases the barrier heights. Experimental observations have revealed that the internal rotational barrier height of the amide bond is strongly affected by the solvent.[1–5,63–70] The trend of increasing rotational barrier height with increasing dielectric constant has been reproduced by molecular orbital calculations.[78] A significant increase in the internal rotational barrier height of amides in proton-donating solvents has been observed.[63,64] Cation bonding to the carbonyl oxygen of amide molecules also increases the barrier height.[71–74] Molecular orbital calculations have also supported the observation that cation bonding increases the barrier heights.[73,74] Another possible reason for the disagreement between experimental and calculated barrier heights is the insufficient accuracy of the calculations.

The importance of the use of a large basis set and electron correlation correction in conformational energy calculations has been claimed.[85–90] Recently conformational energy calculations of butane using a triple-zeta basis set with multiple polarized functions with the MP2 electron correlation correction have been reported.[87] The calculated *syn* barrier heights at this level are considerably lower than the calculated barrier height using the 6-31G** basis set.[85,86] The same tendency has been observed in the calculation on ethyl methyl ether.[90] Whereas the calculations on formamide using polarized basis sets with electron correlation correction[79,80] and HF level calculation of acetamide using a polarized basis set[79] have been reported, further improved calculations have not been reported. In this paper we describe the calculation of internal rotational barrier heights of formamide and acetamide using several basis sets, up to 6-311G(2d,2p) basis set with electron correlation correction, to evaluate basis set and electron correlation effects on the calculated barrier heights. Basis set and electron correlation effects on the optimized geometries are also discussed.

Computational Technique.—The GAUSSIAN82[91] and GAUSSIAN86 programs[92] were used for the *ab initio* calculations. All the geometries were optimized using the geometry optimization routines in these programs. Default convergence criteria for SCF and geometry optimization were used. The basis sets implemented in these programs were used for calculations.[93–101] 3-21G and 6-31G basis sets have double-zeta quality valence orbitals. Valence orbitals of these basis sets are separated into two parts, an inner and an outer. The coefficients of these two types of orbitals can be optimized independently in the SCF cycle. Thus the sizes of the atomic orbitals which constitute the molecular orbitals can be changed. The 6-311G basis set has triple-zeta quality valence orbitals. 6-31G* and 6-311G* basis sets have a set of d orbitals on heavy atoms as polarized functions, which allows a deformation of p orbitals. 6-31G** and 6-311G** basis sets have a set of d orbitals on heavy atoms and a set of p orbitals on hydrogen atoms. The 6-311++G** basis set has a set of diffuse sp orbitals on heavy atoms and a diffuse s orbital on hydrogen atoms. 6-311G(2d,p) basis set has two sets of d orbitals on heavy atoms and a set of p orbitals on hydrogen atoms. 6-311G(2d,2p) basis set has two sets of d orbitals on heavy atoms and two sets of p orbitals on hydrogen atoms. Electron correlation energies were calcu-

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[†] 1 cal = 4.184 J.

Table 1 Calculated geometrical parameters for formamide and acetamide[a]

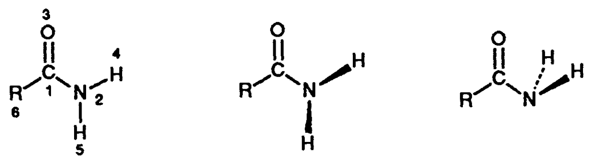
Conformer	HF/ 6-31G	HF/ 6-31G*	HF/ 6-31G**	MP2/ 6-31G*	MP2/ 6-31G**	ED[b]
Formamide, planar **1a**						
C1–N2	−0.011	−0.012	−0.012	1.360	0.000	1.368
C1–O3	−0.004	−0.031	−0.031	1.224	−0.001	1.212
N2–H4	−0.018	−0.015	−0.017	1.011	−0.006	1.027
N2–H5	−0.018	−0.015	−0.017	1.008	−0.006	1.027
C1–H6	−0.024	−0.014	−0.013	1.105	−0.005	1.125
N2–C1–O3	−0.3	0.2	0.1	124.8	0.0	125.0
N2–C1–H6	1.7	0.4	0.5	112.3	−0.2	112.7[c]
C1–N2–H4	0.5	0.3	0.0	119.0	−0.1	118.7
C1–N2–H5	0.1	0.0	−0.2	121.8	−0.2	119.7
O3–C1–N2–H4	0.0	0.0	0.0	0.0	0.0	0.0
O3–C1–N2–H5	0.0	0.0	0.0	180.0	0.0	180.0
Formamide, saddle point **1c**						
C1–N2	−0.028	−0.015	−0.017	1.442	−0.001	
C1–O3	−0.008	−0.034	−0.034	1.217	−0.001	
N2–H4, N2–H5	−0.026	−0.018	−0.019	1.023	−0.006	
C1–H6	−0.022	−0.014	−0.012	1.101	−0.005	
N2–C1–O3	−0.8	−0.4	−0.4	125.4	0.0	
N2–C1–H6	2.0	0.5	0.5	113.0	0.0	
C1–N2–H4, C1–N2–H5	9.0	1.3	1.4	107.2	−0.3	
O3–C1–N2–H4	12.7	1.4	1.5	55.7	−0.2	
O3–C1–N2–H5	−12.7	−1.4	−1.5	−55.7	0.2	
Acetamide, planar **2a**						
C1–N2	−0.010	−0.011	−0.011	1.367		1.380
C1–O3	−0.002	−0.030	−0.030	1.228		1.220
N2–H4	−0.018	−0.015	−0.017	1.010		1.022
N2–H5	−0.018	−0.015	−0.017	1.008		1.022
C1–C6	−0.009	0.000	−0.001	1.514		1.519
C6–H7	−0.011	−0.009	−0.009	1.089		1.124
C6–H8, C6–H9	−0.010	−0.008	−0.008	1.094		1.124
N2–C1–O3	−0.5	0.0	0.0	122.2		122.0
N2–C1–C6	1.4	0.4	0.5	114.5		115.1
C1–N2–H4	0.5	0.2	0.0	118.3		118.5[d]
C1–N2–H5	−0.2	−0.1	−0.2	122.8		120.0[d]
C1–C6–H7	0.5	0.4	0.4	108.5		109.8
C1–C6–H8, C1–C6–H9	−0.1	−0.2	−0.3	110.8		109.8
O3–C1–N2–H4	0.0	0.0	0.0	0.0		0.0
O3–C1–N2–H5	0.0	0.0	0.0	180.0		180.0
N2–C1–C6–H7	0.0	0.0	0.0	180.0		180.0
N2–C1–C6–H8	0.0	−0.1	−0.2	59.9		60.0[e]
N2–C1–C6–H9	0.0	0.1	0.2	−59.9		−60.0[e]
Acetamide, saddle point **2c**						
C1–N2	−0.028	−0.017	−0.019	1.455		
C1–O3	−0.006	−0.033	−0.032	1.220		
N2–H4, N2–H5	−0.024	−0.018	−0.019	1.023		
C1–C6	−0.005	0.004	0.003	1.500		
C6–H7	−0.011	−0.009	−0.009	1.090		
C6–H8, C6–H9	−0.009	−0.008	−0.008	1.093		
N2–C1–O3	−1.0	−0.4	−0.4	123.2		
N2–C1–C6	2.0	0.8	0.9	112.9		
C1–N2–H4, C1–N2–H5	8.3	1.4	1.5	106.4		
C1–C6–H7	0.2	0.0	0.0	110.5		
C1–C6–H8, C1–C6–H9	0.3	0.1	0.1	109.3		
O3–C1–N2–H4	10.7	1.4	1.5	55.0		
O3–C1–N2–H5	−10.7	−1.4	−1.5	−55.0		
N2–C1–C6–H7	0.0	0.0	0.0	180.0		
N2–C1–C6–H8	0.3	0.3	0.2	58.1		
N2–C1–C6–H9	−0.3	−0.3	−0.2	−58.1		

[a] Calculated geometrical parameters at MP2/6-31G* level are shown. Geometrical parameters calculated at other levels are quoted relative to the MP2/6-31G* results. Bond distances are in angstrom, and bond and dihedral angles in degrees. Geometries are fully optimized with imposing C_s symmetry. [b] Ref. 109, 110. [c] Ref. 115. [d] These angles are assumed to be equal to the *r*(s) angle of formamide shown in ref. 115. [e] Assumed value.

lated using Møller–Plesset perturbation energy calculation routines[102–106] and configuration interaction energy calculation routines[107] in these programs. Harmonic vibrational frequencies were calculated using normal vibrational mode analysis routines in these programs. The calculated frequencies were scaled using a factor of 0.9 to correct the usual overestimation of vibrational frequencies at HF level.[108] The zero point and thermal vibrational energies were calculated from the scaled frequencies.

Results and Discussion

Geometrical Features.—The geometries of formamide and acetamide optimized at various theoretical levels are summar-



1a R = H
2a R = CH$_3$

1b R = H
2b R = CH$_3$

1c R = H
2c R = CH$_3$

Fig. 1 Conformation of amides

ized in Table 1 with the geometries obtained by gas-phase electron diffraction.[109,110] C_s symmetry restriction was imposed in the geometry optimizations. The absolute values of some geometrical parameters depend on the levels of calculation. The calculated C–N bond distances of planar formamide **1a** (see Fig. 1) at HF levels are 0.19–0.20 Å shorter than that obtained by electron diffraction, while the C–N bond distances calculated with electron correlation are close to the experimental value. The calculated C–O bond distance of formamide at the HF/6-31G level is 0.08 Å longer than that obtained by electron diffraction, while those at HF/6-31G* and HF/6-311G* levels are 0.19 Å shorter. The same tendency can be seen in the previous calculations of formamide at similar levels.[77,79,80,111–113] The same changes in bond distances are observed for the calculations of the planar conformer of acetamide **2a**. The calculated valence angles of the planar conformers are little affected by the level of calculation.

The agreement of the calculated geometrical parameters of these amides with those obtained from electron diffraction[109,110] is improved by the incorporation of electron correlation correction, but the calculated bond distances and valence angles are slightly different from the corresponding experimental values. The calculated geometries correspond to hypothetical vibrationless states, which are *r*(e) structures, while electron diffraction structures are vibrationally averaged thermal equilibrium structures. This difference could be the cause of the slight difference of the calculated and experimental geometrical parameters.

The dependence of the calculated geometrical parameters on the level of calculations is also found in the calculations on the saddle point conformers **1c** and **2c**. The amino group is not planar in the saddle point conformers. This pyramidalization is underestimated by HF/6-31G level calculation. The implementation of polarized functions increases the amplitude of this deformation considerably.

The calculated geometrical parameters depend on the level of calculations. However, the differences between the geometrical parameters in the planar conformer and those in the saddle point conformer are nearly the same at each theoretical level, except the HF/6-31G level. The differences between C1–N2, C1–O3, N2–H4, N2–H5 and C1–H6 bond distances of planar formamide **1a** and those of the saddle point conformer **1c** are +0.077 to +0.082 Å, −0.007 to −0.010 Å, +0.009 to +0.012 Å, +0.012 to 0.015 Å and −0.003 to −0.004 Å, respectively. The differences between N2–C1–O3, N2–C1–H6, C1–N2–H4 and C1–N2–H5 angles of **1a** and those of **1c** are 0.0 to +0.6°, +0.7 to +0.9°, −10.4 to −12.0° and −13.0 to −14.7°, respectively. Similar changes are also observed for acetamide.

These changes in the bond distances are explained by the partial double bond character of the C–N bond in the planar conformer. The C–N bond is lengthened by the cleavage of π-conjugation at the saddle point, while the C=O bond is shortened by the localization of π electrons. The s character of the C–H bond is increased and that of the N–H bond is decreased by the cleavage of the partial double bond. Thus the former bond is shortened and the latter one is lengthened at the saddle point.

The differences between C1–N2, C1–O3, N2–H4 and N2–H5 bond distances of formamide **1a** and those of acetamide **2a** are +0.007 to +0.008 Å, +0.004 to +0.006 Å, −0.001 Å and 0.0 Å, respectively. The differences between N2–C1–O3, C1–N2–H4 and C1–N2–H5 angles of **1a** and those of **2a** are −2.6 to −2.8°, −0.7 to 0.8° and +0.7 to +1.0°, respectively. The values of these differences reported from electron diffraction are +0.012 Å, +0.008 Å, −0.005 Å, −0.005 Å, −3.0°, −0.2° and +0.3°, respectively.[109,110] The calculated values are close to the experimental values.

The measurement of IR spectra of formamide and acetamide has revealed that the amino groups of these molecules are planar in the stable conformer.[114–116] Our calculations for formamide agree with these experimental observations. The five levels of calculations of formamide, summarized in Table 1, show that the planar conformer **1a** corresponds to the minimum energy conformer, and the non-planar conformer **1b** does not correspond. Whereas the HF/6-31G level calculation on acetamide shows that the planar conformer **2a** is the minimum energy conformer, HF/6-31G*, HF/6-31G** and MP2/6-31G* level calculations show that the non-planar conformer **2b** is the minimum energy conformer. However, the energy differences between the planar conformer **2a** and the non-planar conformer **2b** calculated at these levels are less than 0.1 kcal mol^{-1}. These differences are very small and not significant. These calculations show that the torsional potential of acetamide is very shallow near the minimum.

Effect of Different Geometries on the Calculated Energies.—The importance of geometry optimization for the calculation of internal rotational barrier height has been claimed.[90–117] However, geometries are often optimized at a lower level and single point calculations are carried out at higher levels to reduce computational time. The effect of using geometries obtained at a lower level on the calculated barrier height is not certain. Thus we investigated this effect by performing MP2/6-31G** level calculations on formamide using the five different sets of geometries shown in Table 1. The calculated energies and internal rotational barrier heights are summarized in Table 2. The calculated barrier height for the MP2/6-31G* level geometries is close to that for the MP2/6-31G** level geometries both at the HF level and MP2 level. The calculated barrier height decreases by *ca.* 0.4 kcal mol^{-1} at the HF level and increases to 0.3 kcal mol^{-1} at the MP2 level, by the use of the HF/6-31G* and HF/6-31G** geometries, from the calculated barrier heights for the MP2/6-31G** geometries. The calculated barrier height for the HF/6-31G geometries is considerably larger than that obtained for MP2/6-31G** geometries. These calculations show a serious defect of the use of the geometries which are optimized using a basis set without polarized functions for the calculation of internal rotational barrier heights of amides.

Effect of Electron Correlation.—To evaluate the electron correlation effect on the calculated barrier heights, the 2nd, 3rd and 4th orders of the Møller–Plesset perturbation (MP2, MP3, MP4)[102–106] and configuration interaction energy calculation with all single and double substitutions (CISD)[107] were performed using the 6-31G* basis set on the MP2/6-31G* geometries of formamide and acetamide shown in Table 1. The results are shown in Table 3. The electron correlation energy correction decreases the barrier height slightly, with the exception of the MP2 correction of formamide. The MP4-(SDTQ) correction decreases the barriers of formamide and acetamide by as much as 0.42 and 1.09 kcal mol^{-1}, respectively.

Table 2 Total energies and internal rotational barrier heights of formamide using different sets of optimized geometries

Geometries	Total energies of planar conformer[a]		Internal rotational barrier height[b]	
	HF/6-31G**	MP2/6-31G**	HF/6-31G**	MP2/6-31G**
HF/6-31G	−168.939 16	−169.420 27	18.19	19.41
HF/6-31G*	−168.940 48	−169.418 99	15.97	16.71
HF/6-31G**	−168.940 49	−169.418 95	15.97	16.72
MP2/6-31G*	−168.937 90	−169.421 08	16.29	16.43
MP2/6-31G**	−168.938 36	−169.421 14	16.33	16.44

[a] Total energies in hartree. [b] Internal rotational barrier heights in kcal mol^{-1}.

Table 3 Internal rotational barrier heights calculated by various methods[a]

Molecule	Barrier heights[b]					
	HF	MP2	MP3	MP4-(SDQ)	MP4-(SDTQ)	CISD
Formamide[c]	15.99	16.55	15.20	15.12	15.57	15.78
Acetamide[d]	14.35	14.17	13.21	13.07	13.26	13.98

[a] MP2/6-31G* geometries are used. 6-31G* basis set is used for the calculations. [b] Barrier heights in kcal mol^{-1}. [c] Calculated energies of the planar conformer of formamide by HF, MP2, MP3, MP4(SDQ), MP4(SDTQ) and CISD methods are −168.928 18, −169.394 45, −169.401 52, −169.411 95, −169.427 93 and −169.360 43 hartree, respectively. [d] Calculated energies of the planar conformer of acetamide by HF, MP2, MP3, MP4(SDQ), MP4(SDTQ) and CISD methods are −207.973 56, −208.568 99, −208.586 07, −208.598 21, −208.618 37 and −208.513 47 hartree, respectively.

Table 4 Internal rotational barrier heights calculated with several basis sets[a]

Basis sets	Energies[b]		
	HF	MP2	MP3
Formamide			
3-21G	20.28	19.42	17.88
6-31G	22.84	21.45	20.14
6-31G*	15.99	16.55	15.20
6-31G**	16.29	16.43	15.16
6-311G*	16.16	16.79	15.38
6-311G**	15.98	15.79	14.47
6-311 + +G**	16.32	16.19	14.86
6-311G(2d,p)	15.53	16.03	14.78
6-311G(2d,2p)	15.65	16.18	14.96
Acetamide			
6-31G	21.34	18.93	18.16
6-31G*	14.35	14.17	13.21
6-31G**	14.60	14.02	13.16
6-311G**	14.23	13.33	12.45
6-311 + +G**	14.59	13.83	12.87
6-311G(2d,2p)	13.96	14.03	

[a] Using MP2/6-31G* geometries. [b] Barrier heights in kcal mol^{-1}.

Whereas the barrier heights given by the MP3, MP4(SDQ) and CISD corrections are close to those with the MP4(SDTQ) correction, the barrier heights of formamide and acetamide with the MP2 correction are *ca.* 1.0 kcal mol^{-1} larger than those with the MP4(SDTQ) correction.

Basis Set Effect.—The internal rotational barrier height of formamide has been measured in liquid phase by NMR spectroscopy.[1–3,6] Sunners *et al.* have reported that the rotational barrier height of formamide in acetone solution is 18 ± 3 kcal mol^{-1}.[1] Kamei has reported that ΔE_a values of formamide neat, in water, in acetone and in dioxane solutions are 18.9 ± 1.0, 21.3 ± 1.3, 16.9 ± 1.9 and 16.8 ± 1.0 kcal mol^{-1}, respectively.[2] Drakenberg and Forsen have reported that the $\Delta H^\ddagger$ of formamide in dimethyl glycol dimethyl ether and methyl propyl ketone solution are 19.0 ± 0.2 and 18.5 ± 0.2 kcal mol^{-1}, respectively.[3] Chan *et al.* have measured the barrier height in a polystyrene matrix.[6] The $\Delta H^\ddagger$ of 13.9 kcal mol^{-1} reported by them is 3–7 kcal mol^{-1} smaller than those obtained in the liquid phase.

As mentioned above, the internal rotational barrier height of formamide has been estimated by various levels of *ab initio* molecular orbital calculations.[75–81] The calculated barrier heights at HF level using double-zeta type basis sets with full geometry optimization are 18–19 kcal mol^{-1}.[76–79] These values are close to the experimental barrier heights measured in the liquid phase,[1–3] while some early calculations gave larger barrier heights due to the lack of sufficient geometry optimization.[75] The calculated barrier heights at the HF level using polarized basis sets are 14–16 kcal mol^{-1},[79–81] which are significantly smaller than those using double-zeta basis sets. Jansen *et al.*[79] and Wiberg and Laidid[80] have reported calculations using polarized basis sets with electron correlation correction. The incorporation of the electron correlation correction further decreases the barrier height. But the decreases due to the electron correlation correction are less than 1.0 kcal mol^{-1}. Jansen *et al.* have reported that the zero point vibrational energy correction for the barrier height of formamide is only 0.1–0.2 kcal mol^{-1}.[79]

We calculated the internal rotational barrier height of formamide using several basis sets, up to 6-311G(2d,2p) basis set, on the MP2/6-31G* geometries shown in Table 1 with the MP3 electron correlation correction. The results are shown in Table 4. The calculated barrier heights using polarized basis sets decrease by 0.7–1.5 kcal mol^{-1} from the values calculated at HF level, by the incorporation of the MP3 electron correlation correction. The calculated barrier heights with the MP2 correction are 1.3–1.4 kcal mol^{-1} larger than the corresponding values calculated with the MP3 correction. The calculated barrier heights using 3-21G and 6-31G basis sets are considerably larger than those using polarized basis sets as well as previous calculations.[76–81] The calculated barrier heights using polarized basis sets with the MP3 level electron correlation correction are 14.5–15.4 kcal mol^{-1}. The effect of the addition of polarized functions on hydrogen atoms is not large. The augmentation of multiple polarized functions and diffuse functions also has little effect on the calculated barrier height. Normal vibrational frequencies of the planar **1a** and saddle point **1c** conformers were calculated at the HF/6-31G* level. The results are shown in Table 5. Zero point and thermal vibrational energies were calculated based on the scaled frequencies. Zero point vibrational energy correction decreases the barrier height by only 0.23 kcal mol^{-1}. This value is close to the correction reported by Jansen *et al.*[79] On the other hand, the thermal vibrational energy correction for 298.15 K decreases the barrier height by as much as 0.52 kcal mol^{-1}. These corrections and the MP3/6-311G(2d,2p)//MP2/6-31G* level barrier height of 14.92 kcal mol^{-1} lead to the $\Delta H^\ddagger$ of 14.21 kcal mol^{-1}. Whereas this barrier height is considerably smaller than the experimental barrier heights obtained in the liquid phase,[1–3] it is close to the barrier height of $\Delta H^\ddagger$ = 13.9 kcal mol^{-1} measured in a polystyrene matrix.[6]

Drakenberg has reported that the internal rotational barrier heights ($\Delta H^\ddagger$) of acetamide in dimethyl formamide and acetone solution are 20.1 and 18.2 kcal mol^{-1}, respectively.[4] Umemoto

Table 5 HF/6-31G* harmonic vibrational frequencies of formamide[a]

Structure	Symmetry of vibration	Harmonic frequencies	E_{ZP}[b]	E_{th}[c]
Planar	A′	618, 1160, 1379, 1563, 1789, 1999, 3214, 3838, 3973	27.66	0.73
	A″	106, 674, 1183		
Saddle point	A′	642, 1026, 1214, 1549, 1787, 2033, 3259, 3695	27.43	0.21
	A″	(505i), 965, 1381, 3774		

[a] Frequencies in cm^{-1}, and energies in kcal mol^{-1}. [b] Zero point vibrational energies are calculated based on scaled frequencies corrected by a factor of 0.9. [c] Thermal energies at 298.15 K calculated from the scaled frequencies.

and Ouchi have reported that the barrier heights ($\Delta H^{\ddagger}$) in dimethyl sulphoxide, methyl propyl ketone, 1,3-dioxane and 1,4-dioxane are 18.7 ± 0.4, 19.3 ± 0.8, 18.9 ± 0.4 and 20.5 ± 0.8 kcal mol^{-1}, respectively.[5] Chan *et al.* have reported a lower barrier height of $\Delta H^{\ddagger} = 13.4$ kcal mol^{-1} in a polystyrene matrix.[6]

The internal rotational barrier height of acetamide has been calculated at the HF level.[77,79,81,82] The calculated barrier heights at the HF level using double-zeta basis sets are 17–18 kcal mol^{-1}.[77,79,81,82] The barrier heights using polarized basis sets are 12–13 kcal mol^{-1},[79] which are much lower than those using double-zeta basis set, as well as the calculations on formamide.

The calculated internal rotational barrier heights of acetamide using various basis sets are shown in Table 4. The calculated barrier heights using polarized basis sets are decreased by as much as 1.1–1.8 kcal mol^{-1} by the incorporation of the MP3 electron correlation correction from those obtained at the HF level. The calculated barrier heights at the MP2 level are 0.9–1.0 kcal mol^{-1} larger than the corresponding values with the MP3 level correction. The calculated barrier height using the 6-31G basis set is larger than those using polarized basis sets, as well as previous calculations.[77,79,81,82] The calculated barrier heights using polarized basis sets with the MP3 level electron correlation are 12.5–13.2 kcal mol^{-1}. The changes in the calculated barrier height due to the augmentation of multiple polarized functions and diffuse functions are not large. The basis set and electron correlation effects on the calculated internal rotational barrier height of acetamide are close to those of formamide. The calculated barrier heights of acetamide using polarized basis sets are smaller than the experimental barrier heights in the liquid phase, but are close to the barrier height obtained in a polystyrene matrix.[6]

Whereas the calculated barrier heights of formamide and acetamide depend on the level of calculations, the difference in the barrier heights for two amides is nearly independent of the basis set at all levels of calculations. The differences in the barrier heights for the two amides calculated at HF, MP2 and MP3 levels are 1.50–1.75, 2.15–2.52 and 1.98–2.02 kcal mol^{-1}, respectively.

Conclusion

The basis set effect on the internal rotational barrier heights of formamide and acetamide was studied using several basis sets up to 6-311G(2d,2p) with electron correlation correction. The calculated barrier heights using double-zeta basis sets were 5–6 kcal mol^{-1} higher than those obtained using polarized basis sets. The calculated barrier heights were little affected by further augmentation of multiple polarized functions and diffuse functions. The barrier heights calculated with polarized basis sets were decreased by the incorporation of electron correlation at the MP3 level by as much as 1–2 kcal mol^{-1}. The calculated barrier heights were considerably lower than the experimental barrier heights measured in the liquid phase. The further improvement of the basis set and the incorporation of electron correlation correction, which we had done, did not improve the agreement of the calculated values with the experimental values measured in the liquid phase. However, the calculated barrier heights using polarized basis sets were close to the barrier heights measured in a polystyrene matrix by NMR spectroscopy. The high barrier heights measured in the liquid phase can be rationalized if the intermolecular interaction in the liquid phase increases the internal rotational barrier height.

References

1 B. Sunners, L. H. Piette and W. G. Schneider, *Can. J. Chem.*, 1960, **38**, 681.
2 H. Kamei, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 2269.
3 T. Drakenberg and S. Forsen, *J. Phys. Chem.*, 1970, **74**, 1.
4 T. Drakenberg, *Tetrahedron Lett.*, 1972, 1743.
5 K. Umemoto and K. Ouchi, *Org. Magn. Reson.*, 1981, **15**, 13.
6 B. Chan, J. P. Shukla and S. Walker, *J. Mol. Struct.*, 1983, **102**, 165.
7 H. S. Gutowski and C. H. Holm, *J. Chem. Phys.*, 1956, **25**, 1228.
8 G. Fraenkel and C. Franconi, *J. Am. Chem. Soc.*, 1960, **82**, 4478.
9 M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, 1962, **66**, 540.
10 A. Allerhand and H. S. Gutowsky, *J. Chem. Phys.*, 1964, **41**, 2115.
11 A. Mannschreck, *Tetrahedron Lett.*, 1965, 1341; R. M. Hammaker and B. A. Gugler, *J. Mol. Spectrosc.*, 1965, **17**, 356.
12 R. C. Neuman, Jr. and L. B. Young, *J. Phys. Chem.*, 1965, **69**, 2570.
13 K. H. Abramson, P. T. Inglefield, E. Krakower and L. W. Reeves, *Can. J. Chem.*, 1966, **44**, 1685.
14 D. G. Gehring and W. A. Mosher, *J. Org. Chem.*, 1966, **31**, 3436.
15 D. M. Lynch and W. Cole, *J. Org. Chem.*, 1966, **31**, 3337.
16 T. H. Siddall, III and R. H. Garner, *Can. J. Chem.*, 1966, **44**, 2387.
17 H. A. Staab and D. Lauer, *Tetrahedron Lett.*, 1966, 4593.
18 R. M. Moriarty and J. M. Kliegman, *J. Org. Chem.*, 1966, **31**, 3007.
19 S. R. Johns, J. A. Lamberton and A. A. Sioumis, *J. Chem. Soc., Chem. Commun.*, 1966, 480.
20 A. Mannschreck, A. Mattheus and G. Rissmann, *J. Mol. Spectrosc.*, 1967, **23**, 15.
21 R. C. Neuman, Jr., D. N. Roark and V. Jonas, *J. Am. Chem. Soc.*, 1967, **89**, 3412.
22 T. Matsuo, *Can. J. Chem.*, 1967, **45**, 1829.
23 G. Isaksson and J. Sandstrøm, *Acta Chem. Scand.*, 1967, **21**, 1605.
24 F. Conti and W. v. Philipsborn, *Helv. Chim. Acta*, 1967, **50**, 603.
25 H. Kessler and A. Rieker, *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.*, 1967, **22B**, 456.
26 H. Kessler and A. Rieker, *Justus Liebigs Ann. Chem.*, 1967, **708**, 57.
27 H. S. Gutowsky, J. Jonas and T. H. Siddall, III, *J. Am. Chem. Soc.*, 1967, **89**, 4300.
28 J. A. Weil, A. Blum, A. H. Heiss and J. K. Kinnaird, *J. Chem. Phys.*, 1967, **46**, 3132.
29 J. P. Chupp and J. F. Olin, *J. Org. Chem.*, 1967, **32**, 2297.
30 H. Paulsen and K. Todt, *Chem. Ber.*, 1967, **100**, 3397.
31 G. Fraenkel, M. P. Cava and D. R. Dalton, *J. Am. Chem. Soc.*, 1967, **89**, 329.
32 V. A. Mannschreck and H. Munsch, *Angew. Chem.*, 1967, **79**, 1004.
33 H. Gunther and R. Wenzl, *Tetrahedron Lett.*, 1967, 4155.
34 P. T. Inglefield, E. Krakower, L. W. Reeves and R. Stewart, *Mol. Phys.*, 1968, **15**, 65.
35 A. Pines and M. Rabinovitz, *Tetrahedron Lett.*, 1968, 3529.
36 R. C. Neuman, Jr. and V. Jonas, *J. Am. Chem. Soc.*, 1968, **90**, 1970.
37 T. H. Siddall, III, W. E. Stewart and A. L. Marston, *J. Phys. Chem.*, 1968, **72**, 2135.
38 M. Rabinovitz and A. Pines, *J. Am. Chem. Soc.*, 1969, **91**, 1585.
39 W. E. Stewart and T. H. Siddall, III, *Chem. Rev.*, 1970, **70**, 517.
40 T. H. Siddall, III, W. E. Stewart and F. D. Knight, *J. Phys. Chem.*, 1970, **74**, 3580.
41 M. Frucht, A. H. Lewin and F. A. Bovey, *Tetrahedron Lett.*, 1970, 3707.
42 L. W. Reeves, R. C. Shaddick and K. N. Shaw, *Can. J. Chem.*, 1971, **49**, 3683.
43 A. Komoriya and C. H. Yoder, *J. Am. Chem. Soc.*, 1972, **94**, 5285.
44 G. Montaudo, P. Maravigna, S. Caccamese and V. Librando, *J. Org. Chem.*, 1974, **39**, 2806.

45 R. C. Neuman, Jr. and V. Jonas, *J. Org. Chem.*, 1974, **39**, 925.

46 C. Nagata and S. Tanaka, *Nippon Kagaku Kaishi*, 1975, 579.

47 R. Drakenberg and R. E. Carter, *Org. Magn. Reson.*, 1975, **7**, 307.

48 M. D. Wunderlich, L. K. Leung, J. A. Sandberg, K. D. Meyer and C. H. Yoder, *J. Am. Chem. Soc.*, 1978, **100**, 1500.

49 R. Rauchschwalbe, G. Völkel, E. Lang and H.-D. Lüdemann, *J. Chem. Res. (S)*, 1978, **448**.

50 J. Hauer, G. Völkel and H.-D. Ludemann, *J. Chem. Res. (S)*, 1980, 16.

51 C. H. Yoder and R. D. Gardner, *J. Org. Chem.*, 1981, **46**, 64.

52 U. Berg and Z. Blum, *J. Chem. Res. (S)*, 1983, 206.

53 A. Gryff-Keller, J. Terpinski and E. Zajaczkowska-Terpinska, *J. Chem. Res. (S)*, 1984, 330.

54 M. Feigel, *J. Chem. Soc., Chem. Commun.*, 1980, 456.

55 B. D. Ross, N. S. True and D. L. Decker, *J. Phys. Chem.*, 1983, **87**, 89.

56 M. Feigel, *J. Phys. Chem.*, 1983, **87**, 3054.

57 B. D. Ross and N. S. True, *J. Am. Chem. Soc.*, 1984, **106**, 2451.

58 B. D. Ross, N. S. True and G. B. Matson, *J. Phys. Chem.*, 1984, **88**, 2675.

59 B. D. Ross, L. T. Wong and N. S. True, *J. Phys. Chem.*, 1985, **89**, 836.

60 C. B. LeMaster and N. S. True, *J. Phys. Chem.*, 1989, **93**, 1307.

61 I. Suzuki, *Bull. Chem. Soc. Jpn.*, 1962, **35**, 540.

62 T. Miyazawa, *Bull. Chem. Soc. Jpn.*, 1961, **34**, 691.

63 R. C. Neuman, Jr., W. R. Woolfenden and V. Jonas, *J. Phys. Chem.*, 1969, **73**, 3177.

64 T. Drakenberg, K.-I. Dahlqvist and S. Forsen, *J. Phys. Chem.*, 1972, **76**, 2178.

65 A. Calzolari and F. Conti, *J. Chem. Soc. B*, 1970, 555.

66 T. Drakenberg and S. Forsen, *J. Chem. Soc., Chem. Commun.*, 1971, 1404.

67 K. C. Ramey, D. J. Louick, P. W. Whitehurst, W. B. Wise, R. Mukherjee and R. M. Moriarty, *Org. Magn. Reson.*, 1971, **3**, 201.

68 I. Ando, N. Jinno and A. Nishioka, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 2639.

69 J. C. Woodbrey and M. T. Rogers, *J. Am. Chem. Soc.*, 1962, **84**, 13.

70 A. G. Whittaker and S. Siegel, *J. Chem. Phys.*, 1965, **42**, 3320.

71 W. Egan, T. E. Bull and S. Forsen, *J. Chem. Soc., Chem. Commun.*, 1972, 1099.

72 W. E. Waghorne, A. J. I. Ward, T. G. Clune and B. G. Cox, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 1131.

73 B. M. Rode and R. Fussenegger, *J. Chem. Soc., Faraday Trans. 2*, 1975, **71**, 1958.

74 R. Fussenegger and B. M. Rode, *Chem. Phys. Lett.*, 1976, **44**, 95.

75 D. H. Christensen and R. N. Kortzeborn, *J. Chem. Phys.*, 1970, **53**, 3912.

76 R. F. Nalewajski, *J. Am. Chem. Soc.*, 1978, **100**, 41.

77 J. O. Williams, C. V. Alsenoy and L. Schäfer, *J. Mol. Struct. (THEOCHEM)*, 1981, **76**, 171.

78 A. J. Duben and S. Miertus, *Chem. Phys. Lett.*, 1982, **88**, 395.

79 P. G. Jasien, W. J. Stevens and M. Krauss, *J. Mol. Struct. (THEOCHEM)*, 1986, **139**, 197.

80 K. B. Wiberg and K. E. Laidig, *J. Am. Chem. Soc.*, 1987, **109**, 5935.

81 K.-T. Lim and M. M. Francl, *J. Phys. Chem.*, 1987, **91**, 2716.

82 V. J. Klimkowski, H. L. Sellers and L. Schäfer, *J. Mol. Struct.*, 1979, **54**, 299.

83 V. S. Dimitrov and J. A. Ladd, *J. Mol. Struct.*, 1987, **159**, 107.

84 K. Tasaki and U. W. Suter, *J. Phys. Chem.*, 1988, **92**, 5886.

85 K. Raghavachari, *J. Chem. Phys.*, 1984, **81**, 1383.

86 K. B. Wiberg and M. A. Murcko, *J. Am. Chem. Soc.*, 1988, **110**, 8029.

87 N. L. Allinger, R. S. Grev, B. F. Yates and H. F. Schaefer III, *J. Am. Chem. Soc.*, 1990, **112**, 114.

88 K. B. Wiberg and M. A. Murcko, *J. Comput. Chem.*, 1988, **9**, 488.

89 B. Wiberg and K. E. Laidig, *J. Am. Chem. Soc.*, 1987, **109**, 5935.

90 S. Tsuzuki and K. Tanabe, *J. Chem. Soc., Faraday Trans.*, in press (paper 1/01986D).

91 J. S. Binkley, M. J. Frisch, D. J. DeFrees, R. Krishnan, R. A. Whiteside, H. B. Schlegel, E. M. Fluder and J. A. Pople, *GAUSSIAN 82*, Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA 1982.

92 M. J. Frisch, J. S. Binkley, H. B. Schlegel, K. Raghavachari, C. F. Melius, R. L. Martin, J. J. P. Stewart, F. W. Bobrowicz, C. M. Rohlfing, L. R. Kahn, D. J. Defrees, R. Seeger, R. A. Whiteside, D. J. Fox, E. M. Fleuder and J. A. Pople, *GAUSSIAN 86*, Carnegie–Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA 1986.

93 J. S. Binkley, J. A. Pople and W. J. Hehre, *J. Am. Chem. Soc.*, 1980, **102**, 939.

94 M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro and W. J. Hehre, *J. Am. Chem. Soc.*, 1982, **104**, 2797.

95 W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257.

96 P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213.

97 M. S. Gordon, *Chem. Phys. Lett.*, 1980, **76**, 163.

98 R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650.

99 P. C. Hariharan and J. A. Pople, *Chem. Phys. Lett.*, 1972, **16**, 217.

100 M. J. Frisch, J. A. Pople and J. S. Binkley, *J. Chem. Phys.*, 1984, **80**, 3265.

101 T. Clark, J. Chanrasekhar, G. W. Spitznagel and P. v. R. Schleyer, *J. Comput. Chem.*, 1983, **4**, 294.

102 C. Møller and M. S. Plesset, *Phys. Rev.*, 1934, **46**, 618.

103 J. S. Binkely and J. A. Pople, *Int. J. Quantum Chem.*, 1975, **9**, 229.

104 J. A. Pople, J. S. Binkley and R. Seeger, *Int. J. Quantum Chem. Symp.*, 1976, **10**, 1.

105 R. Krishnan and J. A. Pople, *Inter. J. Quant. Chem.*, 1978, **14**, 91.

106 R. Krishnan, M. J. Frisch and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 4244.

107 J. A. Pople, R. Seeger and R. Krishnan, *R. Int., J. Quant. Chem. Symp.*, 1977, **11**, 149.

108 J. A. Pople, H. B. Schlegel, R. Krishnan, D. J. DeFrees, J. S. Binkley, M. J. Frisch, R. A. Whiteside, R. F. Hout and W. J. Hehre, *Int., J. Quant. Chem. Symp.*, 1981, **15**, 269.

109 M. Kitano and K. Kuchitu, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 67.

110 M. Kitano and K. Kuchitu, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 3048.

111 G. Fogarasi, P. Puley, F. Török and J. E. Boggs, *J. Mol. Struct.*, 1979, **57**, 259.

112 L. Schäfer, C. V. Alsenoy and J. N. Scarsdale, *J. Mol. Struct. (THEOCHEM)*, 1982, **86**, 349.

113 J. E. Boggs and Z. Niu, *J. Comput. Chem.*, 1985, **6**, 46.

114 S. T. King, *J. Phys. Chem.*, 1971, **75**, 405.

115 E. Hirota, R. Sugisaki, C. J. Nielsen and G. O. Sorensen, *J. Mol. Spectrosc.*, 1974, **49**, 251.

116 R. A. Kydd and A. R. C. Dunham, *J. Mol. Struct.*, 1980, **69**, 79.

117 W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory*, John Wiley, New York, 1986.

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