Hydrogen bonding and dimeric self-association of 2-pyrrolidinone: An ab initio study

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Summary

Ab initio calculations on the different associated structures of 2-pyrrolidinone with water and with itself were carried out using 3-21G and 6-31G* basis sets at the Hartree–Fock level, including electron correlation using second-order Møller–Plesset perturbation theory. The calculated free energy changes for the intermolecular hydrogen bonded dimer and hydrated species indicated that the molecular systems with cyclic dimerization and association with two water molecules are dominant. The results are compared to the available experimental data in the literature.

Introduction

The pyrrolidinones are of interest due to their structural similarity to cyclic peptides and pharmacological use. 2-Pyrrolidinone (Scheme 1) has 3 CH_2 groups, forcing the molecule in a cis configuration. Owing to its donor–acceptor properties, it can associate with other 2-pyrrolidinone molecules by intermolecular hydrogen bonds (-C=O·······H-N-).
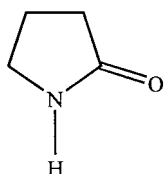
Scheme 1. Structure of 2-pyrrolidinone.

According to IR spectroscopic and dielectric measurements [1–5], the self-association of 2-pyrrolidinone is strong in the pure lactam. The cyclic dimer (with nearly zero dipole moment) is dominant in the range of low concentrations of 2-pyrrolidinone, but in high concentrations, the chain structures (with high dipole moment) have to be considered as well [3,5]. De Smet et al. studied dynamics of 2-pyrrolidinone self-association by nonlinear dielectric spectroscopy [6]. Their studies have shown that in high concentrations of 2-pyrrolidinone there is no need to introduce higher polymeric structures such as trimers or tetramers in the association model. They have also found a dipole moment value of 3.96 D for the monomer and 2.30 D for the dimer, explaining why the dimer undergoes a very rapid interconversion between open and cyclic structure.

The molecular interaction and association properties of compounds depend on their environment and structure. The acidic NH and basic CO groups of 2-pyrrolidinone allow interactions with proton accepting and proton donating solvents via hydrogen bonding. Consequently, both proton accepting (e.g. acetone, dimethyl sulphoxide or 1,4-dioxane) and proton donating solvents (such as alcohols) have a structure breaking effect on 2-pyrrolidinone association. In nonpolar solvents, the amount of self-associated species of 2-pyrrolidinone varies with the concentration of the amide [7].

In NMR studies of 2-pyrrolidinone [8], NH proton and ^{17}O NMR chemical shifts of pure 2-pyrrolidinone are 282 ppm and 7.94 ppm at 301 K. On the other

hand, the same chemical shifts of a 2-pyrrolidinone and water mixture are 271 ppm and 7.77 ppm. The results indicate that there is a molecular interaction of the NH proton and the carbonyl group of 2-pyrrolidinone with water.

Al-Azzawi et al. [9] have studied dielectric permittivities and densities of the 2-pyrrolidinone–water system. They concluded that 2-pyrrolidinone and water would be associated in a ratio of 2 mole water to 1 mole of 2-pyrrolidinone. In addition, 2-pyrrolidinone and water may form a hydrate complex in a 1:1 proportion, which is stable in the liquid state [10]. Pirila-Honkanen and Ruostesuo have also obtained the negative contributions to the molar excess volumes (V^E) [11], the electric permittivities (ε^E) [12], and ΔE_T^N values [13] of the same system in the range of 303.15–323.15 K. Their results can be ascribed to intermolecular interactions due to hydrogen bonding, because the negative values for the excess quantities are indicative of relatively strong interactions between unlike molecules.

Hydrogen bonding is one of the well-known interactions in many chemical and biological systems and it has been a research topic for many years. In strongly associated solvents, such as water, alcohols and amides, hydrogen bonding is very important. In the 2-pyrrolidinone–water mixture, the intermolecular hydrogen bonds formed between 2-pyrrolidinone molecules are broken due to the formation of hydrogen bonds between 2-pyrrolidinone and water molecules.

Although there have been many experimental studies on the properties of 2-pyrrolidinone in binary mixtures [14–19], computational determinations of the molecular structures of 2-pyrrolidinone and its associated species have not been reported so far. Because structural data for the hydrogen-bonded structures of 2-pyrrolidinone–water and possible dimers of 2-pyrrolidinone are lacking, theoretical computations have been performed to examine these geometries and the energies of intermolecular interactions.

Method

The cyclic and open dimer structures and possible hydrate complex forms of 2-pyrrolidinone proposed in the literature [9,10] have been taken into consideration in the present work. All ab initio calculations [20] have been carried out using the Gaussian 94 [21] package. Full geometry optimizations were performed without symmetry restrictions at the Hartree–Fock (HF) level with the 3-21G and 6-31G* basis sets. The optimized structures at the HF/3-21G level were used as starting points for HF/6-31G* optimizations. Single point MP2 (second-order Møller–Plesset theory) calculations, correcting for electron correlation, were accomplished for all configurations on the HF/6-31G* optimized geometries with the same basis set. The stationary points were checked to be true minima by frequency analysis. The atomic charges were calculated using Mulliken population analysis included in the Gaussian 94 package.

Results and discussion

The most stable conformations predicted by ab initio computations at the HF/6-31G* level are shown in Figure 1, which also shows the numbering scheme adopted. These geometries were drawn using the program ChemOffice Pro [22]. The charge distributions from Mulliken population analysis are given in parentheses in Figure 1. The structural parameters of the HF/3-21G and HF/6-31G* optimized geometries are also listed in Tables 1–3. Bond distances are given in angstroms and bond angles in degrees. Due to the size of the systems under investigation, complete optimizations of the geometrical structures require considerable computational effort. Therefore the geometry optimizations were performed at the HF/3-21G and HF/6-31G* levels.

While computational studies on 2-pyrrolidinone indicate an almost planar molecule with all dihedral angles less than 6° [23,24], there are only two ab initio studies of 2-pyrrolidinone at the 3-21G level which gave an envelope conformation with the flap bent 27.4° out of the NC (=O) C plane [25,26].

We now present the results obtained using ab initio methods including polarization functions and electron correlation for the geometries and energies. As seen in Table 1, the calculated amide bond length for 2-pyrrolidinone (C3N1, 1.361 Å) is longer than the usual amide bond length. The C–N bond lengths are 1.319 Å and 1.336 Å in formamide and acetamide, respectively. The ring conformation of 2-pyrrolidinone is the envelope structure with a (C5C4C2N1) dihedral angle of 27.72° at the HF/6-31G* level. Because C3 and N1 are planar (C3N1O6 = 126.00°), the amide bond has a small torsion angle of −2.61°.

Comparison of our HF/3-21G optimized structural parameters to those calculated at the HF/6-31G* level shows that the optimized geometries are significantly

Table 1. Ab initio structural parameters of 2-pyrrolidinone

Parameter	HF/3-21G	HF/6-31G*	Parameter	HF/3-21G	HF/6-31G*
r (C2N1)	1.464	1.447	∠ (N1C3C5)	106.74	107.00
r (C3N1)	1.361	1.356	∠ (C2C4C5)	103.43	103.70
r (H7N1)	0.996	0.996	∠ (C3C5C4)	104.07	104.28
r (C4C2)	1.554	1.539	∠ (N1C3O6)	126.09	126.02
r (C5C3)	1.529	1.520	τ (C5C3N1H7)	176.16	169.79
r (C5C4)	1.541	1.533	τ (O6C3N1H7)	−2.61	−9.39
r (O6C3)	1.213	1.196	τ (C5C4C2N1)	27.60	27.72
∠ (C2N1C3)	115.25	114.79	τ (C4C5C3N1)	17.73	12.75
∠ (C3N1H7)	121.06	119.60	τ (C3C5C4C2)	−27.94	−25.01
∠ (N1C2C4)	101.84	102.14			

affected by the inclusion of polarization functions. For example, the calculated O6C3 and C4C2 bond lengths were found to be altered significantly by 0.017 and 0.015 Å, respectively.

The optimized geometrical parameters for the cyclic and open dimer structures of 2-pyrrolidinone are given in Table 2. 2-Pyrrolidinone molecules are held together by intermolecular hydrogen bonds as cited in the literature [1–6]. In the stated dimer structures, two 2-pyrrolidinone molecules are bonded to each other with one intermolecular hydrogen bond in the open structure and they are bonded to each other with two intermolecular hydrogen bonds in the cyclic structure. Boeyens et al. [27] found that the N-H···O hydrogen bond length was 1.95 Å for the symmetric dimer with an N-H···O angle of 168.6° and it was 1.68 Å for the asymmetric dimer with 173.9° for the N-H···O angle. The calculated N-H···O hydrogen bond length and N-H···O angle at the HF/6-31G* level are 1.997 Å and 171.46° for the cyclic dimer, corresponding to symmetric dimerization, and these calculated values are in good agreement with the experimental data. The obtained N–H···O bond length (which is 2.033 Å) and N-H···O angle (which is found to be 171.46°) in the open dimer structure, corresponding to asymmetric dimerization, are fairly large compared to the experimental values. Two 2-pyrrolidinone molecules associated to form the open dimer structure have a free rotation and have been optimized without symmetry restrictions. However, Boeyens et al. observed the same values in the crystalline state.

Comparing the hydrogen bond distances (N-H···O) in the dimeric structures, we saw that they were equivalent to each other in the cyclic dimer, hav-

ing a symmetric structure, and the hydrogen bond distances in the cyclic dimer were shorter than in the open dimer at all levels of theory investigated. At the same time, the hydrogen bonds are nearly linear in both dimer structures. Because of the strong hydrogen bonds, C=O and N–H bonds are longer in structure II than in structure III. The geometrical parameters of two 2-pyrrolidinone molecules in the cyclic dimer structures are the same, while the geometries of two 2-pyrrolidinone molecules are different from each other in the open dimer.

The parameters of the optimized hydrate structures of 2-pyrrolidinone are listed in Table 3. There are no experimental data available for 2-pyrrolidinone–water complex structures. One 2-pyrrolidinone molecule is surrounded in order to form hydrogen bonds by one, two and three water molecules in the hydrate structures. The free energy changes for the formation of structures IV, V and VI (0.67, 0.90 and 1.32 kcal mol^{-1}) indicate that structure IV is more likely to be formed. The C=O and N-H bond distances increase as the number of water molecules surrounding a 2-pyrrolidinone molecule increases. It is also noted that H···O bond distances in the hydrate structures decrease with the increasing number of water molecules, because of the repulsion of the water molecules. These changes are also outlined in Table 3. The hydrogen bonds between the N-H group of 2-pyrrolidinone and the oxygen atom of water are slightly longer than the hydrogen bonds between the C=O group of 2-pyrrolidinone and the hydrogen atom of water. The O-H bond distances which make the hydrogen bonds of water molecules in the hydrate structures are longer when compared to the other O-H bond of the same water molecule.
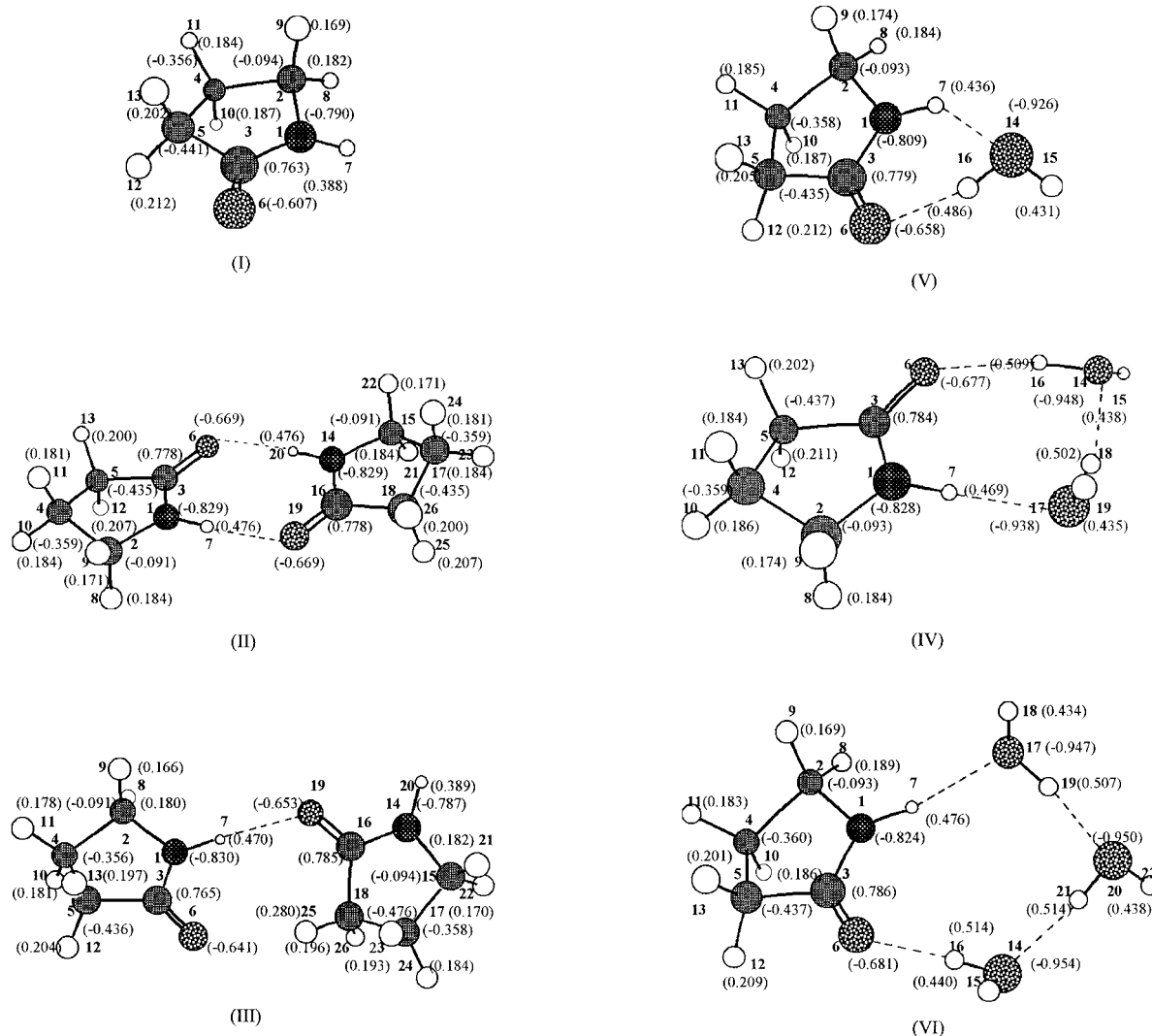
Figure 1. Optimized geometries at the HF/6-31G* level.

The calculated total energies and dipole moments at different levels are compared in Table 4. The results obtained in this way may be used in the computation of some thermodynamical properties. The calculated free energy changes for the different association processes are also summarized in Table 5. The enthalpy of the association processes, ΔH, was obtained by adding the zero-point energy correction, $\Delta(ZPE)$, and the thermal correction, $\Delta(H–H_0)$ to ΔE, and the final ΔG value was computed from the equation $\Delta G = \Delta H - T\Delta S$, where ΔS is the entropy change. The interpretation of the intermolecular interactions of the title compound was performed by means of the calculated thermodynamic properties.

In Table 5, the MP2/6-31G* energy differences (ΔE) and free energy changes (ΔG) are compared with the HF/6-31G* energies. At a higher level of theory used in this study, MP2/6-31G*, the ΔG value for the cyclic dimer is -6.16 kcal mol^{-1}. On the other hand, Walmsley [2] performed a study on 2-pyrrolidinone in benzene up to 0.5 mol L^{-1} and determined a dimerization constant of $K = 33 \pm 5$ M^{-1} for the cyclic dimer. Using the dimerization constant would allow us to predict ΔG ($\Delta G = -RT\ln K$) to be -2.07 kcal mol^{-1}, which is close to the calculated value of -1.33 kcal mol^{-1} at the HF/6-31G* level. Interestingly, the improvement in the level of electron correlation results in an increase in the ΔE

Table 2. Ab initio structural parameters of the cyclic and open dimer of 2-pyrrolidinone

Parameter[a]	II		III	
	HF/3-21G	HF/6-31G*	HF/3-21G	HF/6-31G*
r (C2N1), r (C15N14)	1.465	1.447	1.464(1.468)	1.446(1.449)
r (C3N1), r (C16N14)	1.337	1.338	1.345(1.350)	1.345(1.348)
r (C4C2), r (C17C15)	1.554	1.539	1.553(1.554)	1.539(1.539)
r (C5C3), r (C18C16)	1.528	1.519	1.530(1.521)	1.521(1.516)
r (C5C4), r (C18C17)	1.542	1.533	1.541(1.542)	1.533(1.534)
r (O6C3), r (O19C16)	1.230	1.209	1.224(1.225)	1.203(1.205)
r (H7N1), r (H20N14)	1.014	1.005	1.010(0.997)	1.003(0.996)
∠ (C3N1C2), ∠ (C16N14C15)	114.67	114.66	114.72(114.89)	114.57(114.58)
∠ (C2N1H7), ∠ (C15N14H20)	123.63	123.53	122.00(123.74)	122.92(123.82)
∠ (N1C3C5), ∠ (N14C16C18)	108.12	107.90	107.63(107.79)	107.55(107.61)
∠ (N1C2C4), ∠ (N14C15C17)	102.35	102.66	102.32(101.78)	102.59(102.13)
∠ (C3C5C4), ∠ (C16C18C17)	103.55	103.88	103.70(103.68)	104.03(103.95)
∠ (C2C4C5), ∠ (C15C17C18)	103.23	103.57	103.12(103.73)	103.46(103.99)
∠ (N1C3O6), ∠ (N14C16O19)	126.55	126.52	126.78(125.01)	126.59(125.21)
τ (C4C2N1H7), τ (C17C15N14H20)	−194.35	171.43	166.85(165.7)	173.68(172.93)
τ (O6C3N1H7), τ (O19C16N14H20)	−1.60	−6.12	−3.28(−1.93)	−8.67(−7.04)
τ (C4C5C3N1), τ (C17C18C16N14)	17.24	14.09	17.49(17.42)	13.59(13.44)
τ (C5C4C2N1), τ (C18C17C15N14)	26.70	26.13	27.45(26.70)	27.11(26.47)
τ (C2C4C5C3), τ (C15C17C18C16)	−26.78	−24.61	−27.44(−27.12)	−24.97(−24.61)
r (O19· · · · · · ·H7)	1.832	1.997	1.874	2.033
r (O6· · · · · · ·H20)	1.832	1.997		
∠ (C3O6H20), ∠ (H7O19C16)	121.48	120.70	(122.25)	(121.28)
∠ (O6H20N14), ∠ (N1H7O19)	170.34	171.46	(173.65)	(175.49)
τ (N1H7O19C16)	1.87	9.25	37.10	67.97
τ (N1C3O6H20)	0.447	1.42		

[a] If the second geometrical parameters given after the comma in the first column are different from the first geometrical parameters, their values are given in parentheses in the table.

and ∆G values. The MP2 energy overestimates the ∆G value, while the HF energy is in good accord with the experimental value. However, the cyclic dimer and water complexes of 2-pyrrolidinone are preferred over the open dimer structure at both the MP2 and HF levels. When we look at the calculated ∆G values in Table 5, 2-pyrrolidinone molecules self-associate rather than associating with water molecules at the HF level, while 2-pyrrolidinone molecules prefer to form a trihydrate complex (Vl) at the MP2 level. The experimental studies [9,10] suggested that 2-pyrrolidinone–water complexes were formed predominantly in proportions of 1:1 and 1:2, which is in good agreement with our HF/6-31G* energies. Consequently, we chose to use the HF level energies instead of the MP2 energies.

The concentration of 2-pyrrolidinone is important in the 2-pyrrolidinone–water mixtures. It may be worth mentioning that Ruostesuo and Pirila-Honkanen [12] obtained excess dielectric permittivity (ε^E) data for 2-pyrrolidinone–water which showed a clear maximum at a mole fraction of about 0.5, suggesting that when 2-pyrrolidinone and water are mixed in the main contributions, the interactions between 2-pyrrolidinone and water molecules are broken up. Although it has been reported in the literature that 2-pyrrolidinone and water molecules were associated in both proportions of 1:1 and 1:2 [9,10], we here also considered a trihydrate complex structure in order to see the effect of the number of water molecules on the stabilization of complexes. As seen from the calculated free energy changes (∆G) given in Table 5, the dihydrate structure IV is favorable. The negative excess molar volumes (V^E) which suggest strong hydrogen bonding between unlike molecules were measured for the 2-pyrrolidinone–water system, as was already mentioned [9]. In the region of 0.39 mole fraction of 2-pyrrolidinone, each curve exhibits a minimum that

Table 3. Ab initio structural parameters of 2-pyrrolidinone–water complexes

Parameter	V		IV		VI	
	HF/3-21G	HF/6-31G*	HF/3-21G	HF/6-31G*	HF/3-21G	HF/6-31G*
r (C2N1)	1.463	1.448	1.467	1.449	1.469	1.449
r (C3N1)	1.343	1.344	1.333	1.338	1.330	1.336
r (C4C2)	1.556	1.539	1.554	1.539	1.553	1.539
r (C5C3)	1.525	1.518	1.527	1.518	1.528	1.518
r (C5C4)	1.543	1.534	1.541	1.533	1.541	1.533
r (O6C3)	1.229	1.206	1.234	1.209	1.234	1.210
r (H7N1)	1.007	1.000	1.023	1.005	1.028	1.005
∠ (C3N1C2)	114.93	114.67	114.34	114.54	114.29	114.66
∠ (C2N1H7)	126.32	124.32	122.97	122.93	121.38	122.24
∠ (N1C3C5)	107.99	107.70	108.48	107.95	108.50	107.95
∠ (N1C2C4)	102.04	102.41	102.51	102.68	102.69	102.75
∠ (C3C5C4)	103.60	103.00	103.56	103.94	103.48	103.87
∠ (C2C4C5)	103.51	103.69	103.13	103.53	103.00	103.51
∠ (N1C3O6)	125.48	126.15	126.90	126.75	127.42	126.86
τ (C4C2N1H7)	167.48	173.35	166.26	171.56	165.19	170.70
τ (O6C3N1H7)	−2.52	−7.40	−2.00	−6.36	−1.43	−5.90
τ (C4C5C3N1)	16.49	13.19	16.71	13.88	17.74	14.75
τ (C5C4C2N1)	26.61	26.67	26.70	26.25	26.49	25.86
τ (C2C4C5C3)	−26.38	−24.51	−26.41	−24.57	−26.81	−24.81
r (H16O14)	0.978	0.956	0.989	0.959	0.990	0.959
r (H15O14)	0.966	0.947	0.964	0.947	0.963	0.947
r (H21O20)					1.001	0.960
r (H22O20)					0.964	0.947
r (H19O17)			0.965	0.948	0.999	0.959
r (H18O17)			0.994	0.959	0.965	0.947
∠ (H16O14H15)	108.65	105.47	109.83	105.59	109.86	105.39
∠ (H21O20H22)					109.89	105.60
∠ (H19O17H18)			109.01	105.31	109.00	105.11
r (O6···H16)	1.855	2.01	1.680	1.891	1.645	1.873
r (O14···H18)			1.627	1.889		
r (O17···H7)			1.734	2.005	1.690	1.980
r (O14···H21)					1.573	1.850
r (O20···H19)					1.592	1.872
r (O14···H7)	1.935	2.20				
∠ (C3O6H16)	105.12	107.53	126.01	128.42	137.57	137.44
∠ (O6H16O14)	148.67	151.23	167.81	168.54	176.02	173.32
∠ (O14H18O17)			163.20	161.54		
∠ (O14H21O20)					170.28	170.93
∠ (O20H19O17)					171.89	169.97
∠ (H18O17H7)			98.74	96.01	116.44	118.96
∠ (O17H7N1)			171.65	174.72	175.81	169.72
τ (C3O6H16O14)	−13.51	−13.72	26.33	41.07	132.07	146.21
τ (O6H16O14H15)	−108.68	−110.46	102.52	85.96	−17.48	5.73
τ (H16O14H18O17)			−12.73	−20.48		
τ (H16O14H21O20)					−12.65	−30.20
τ (H21O20H19O17)					23.77	38.16
τ (H18O17H7N1)			−13.95	−5.29		
τ (H19O17H7N1)			102.29	105.51	−178.72	−158.35

Table 4. Calculated energies, dipole moments, ZPE, H–H$_0$ and S at room temperature (298.15 K)

Structure	HF/3-21G E (Hartree)	HF/6-31G* E (Hartree)	ZPE[a] (kcal mol^{-1})	μ (D)	H–H$_0$ (kcal mol^{-1})	S (cal mol^{-1} K^{-1})	MP2/6-31G* E (Hartree)
I	−283.29180	−284.87975	75.09	4.28 (4.00)[b]	3.81	73.09	−285.72374
II	−566.61978	−569.78099	151.72	0.23 (0)[c]	7.94	111.62	−571.47667
III	−566.60907	−569.77343	151.23	2.17 (2.30)[c]	8.18	115.63	−571.46686
IV	−434.52858	−436.93499	109.06	2.91	7.46	103.37	−438.15955
V	−358.90603	−360.90631	92.01	3.67	5.69	88.54	−361.94070
VI	−510.14387	−512.96007	125.63	2.61	9.49	122.09	−514.37295

[a]Scaled by 0.9. Experimental values for the dipole moments are given in parentheses ([b]Ref. 19 and [c]Ref. 6). Energies for H$_2$O molecule: E (HF/6-31G*) = −76.01075 Hartree, E (MP2/6-31G*) = −76.19596 Hartree, ZPE = 14.42 kcal mol^{-1}, H–H$_0$ = 2.37 kcal mol^{-1}, S = 44.99 cal mol^{-1} K^{-1}.

Table 5. Calculated free energy changes[a,b] for the different association processes

Association type	ΔE[c]	ΔE[d]	Δ(ZPE)	−TΔS	Δ(H–H$_0$)	ΔG[c]	ΔG[d]
I + I → II	−13.49	−18.32	1.54	10.30	0.32	−1.33	−6.16
I + I → III	−8.74	−12.16	1.05	9.11	0.56	1.98	−1.44
I + H$_2$O → V	−9.92	−13.18	2.50	8.81	−0.49	0.90	−2.36
I + 2 H$_2$O → IV	−21.17	−27.54	5.13	17.80	−1.09	0.67	−5.70
I + 3 H$_2$O → VI	−30.16	−38.49	7.28	25.63	−1.43	1.32	−7.01

[a] Δ(ZPE), Δ(H–H$_0$), ΔS were calculated using the HF/6-31G* geometries.
[b] ΔE, scaled Δ(ZPE), Δ(H–H$_0$), ΔS and ΔG are in kcal mol^{-1}.
[c] The HF/6-31G* energies were used in deriving ΔE and ΔG.
[d] The MP2/6-31G* energies were used in deriving ΔE and ΔG.

decreases with an increase in temperature and shifts slightly toward a higher 2-pyrrolidinone concentration. Therefore, it was concluded that 2-pyrrolidinone and water will be associated in the proportion of 1:2.

The calculated dipole moment values (Table 4) of the species under investigation are in good agreement with the experimental data. The dipole moment predicted for the cyclic dimer is significantly smaller than that for the open dimer. The associated species with larger dipole moments could be expected to be more stable than those having smaller dipole moments in an environment with high dielectric constant. At the HF/6-31G* level, the calculated intermolecular interaction energies for the associated species of 2-pyrrolidinone indicate that hydrogen bonds contribute to the stabilization of the associated species by 6.75, 8.74, 4.96, 7.06 and 7.54 kcal mol^{-1} for formation of one hydrogen bond in structures II, III, IV, V and VI, respectively.

The results of Mulliken population analysis with the use of 6-31G* at the HF level are given in Figure 1. The calculated Mulliken charges are consistent with the expected charges in the intermolecular hydrogen-bonded associates. The charges of the oxygens and hydrogens are considerably larger than the corresponding atoms in the 2-pyrrolidinone and H$_2$O (O, −0.869; H, 0.434) molecules. The oxygen atoms gain charge, while the hydrogen atoms lose it. Consequently, the oxygens could be classified as hydrogen acceptor. The bond distance between O6 and H25 atoms is 2.44 Å in structure III. When the charge distributions on O6 and H25 are compared to isolated 2-pyrrolidinone, the charge is transferred from hydrogen to a carbonyl oxygen, which shows a weak interaction between O6 and H25. In the hydrate structures, these gains and losses of charge increase when the number of water molecules increases. The shortening of the C-O bond with increasing number of water molecules is one consequence of this charge distribution.

Conclusions

We performed a theoretical evaluation of the contributions of the intermolecular hydrogen bonds to

structural stability by use of ab initio molecular orbital calculation methods. The calculations reported here, except for 2-pyrrolidinone at the HF/3-21G level, are the first ab initio studies on these systems. The following conclusions were drawn from the study:

1. The MP2/6-31G* free energy changes (ΔG) are higher than the HF/6-31G* ΔG values. It is clear from these results that the HF method provides much better results than MP2 for these systems. Thus, high-level electron-correlation methods beyond the second-order Møller–Plesset perturbation theory are required to obtain adequate results.

2. The study of dimerization of 2-pyrrolidinone requires a larger basis set with the addition of polarization functions to hydrogens and an accurate description of the solute/solvent interactions.

3. The effect of hydrogen bond formation caused the same geometrical changes of 2-pyrrolidinone in all associated species.

4. At the HF/6-31G* level, the calculated free energy change (ΔG) for cyclization of 2-pyrrolidinone was found to be -1.33 kcal mol^{-1}, which was lower than for the open dimer structure, suggesting the cyclic structure was more favorable.

5. The intermolecular hydrogen bonds in the cyclic dimer are stronger than that in the open dimer. Therefore, the intermolecular hydrogen bonds were also expected to contribute to the stability of structure II.

6. In the presence of water molecules, 2-pyrrolidinone associates with the water molecules in order to form various hydrate complexes. According to the HF/6-31G* energies, complex IV was the most stable structure among them and 2-pyrrolidinone prefers the association to itself instead of water molecules.

7. In order to make firm predictions, computations on the dimeric self-association of 2-pyrrolidinone are currently being performed using the larger basis sets in the gas phase and in solution.

8. We hope that this study provides an interpretation to literature data and establishes grounds for possible future work.

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