

Vibrational Analysis and Intermolecular Hydrogen Bonding of Azodicarbonamide in the Pentamer Cluster

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Pentamer cluster of azodicarbonamide (ADA) based on the crystalline structure was investigated for the equilibrium structure, the stabilization energies, and the vibrational properties at various levels of the density functional theory. Stretching force constants of N \cdots H or O \cdots H, and angle-bending force constants of N-H \cdots N or N-H \cdots O for intermolecular hydrogen bonds in the pentamer cluster were obtained in 0.2-0.5 mdyne/Å and 1.6-2.0 mdyne/Å, respectively. The geometry of central ADA molecule fully hydrogen bonded with other four molecules shows good coincidence to the crystalline structure except the bond distances of N-H. Calculated Raman and infrared spectra of central ADA molecule in cluster represent well the experimental spectra of ADA obtained in the solid state compared to a single molecule. Detailed structural and vibrational properties of central ADA molecule in the pentamer cluster are presented.

Key Words : Vibrational analysis, Azodicarbonamide, Pentamer, Intermolecular hydrogen bonding

Introduction

Azodicarbonamide (H₂NCON = NCONH₂, ADA) is commonly used for the blowing agent through thermal decomposition, and it contains both azo and two amide groups in its chemical structure. It has some interesting structural characters, *i.e.*, a simplicity in the chemical structure, a strong molecular symmetry, and an intermolecular hydrogen bonding capability to its neighbors in the condensed phase. The *trans*-configuration as shown in the crystallographic geometry,¹⁻³ is slightly lower in energy than with *cis*-configuration. The crystallographic study of ADA revealed strong hydrogen bonding effects in molecular geometry because it is quite planar even in the crystalline state. The strong hydrogen bonding could cause a cluster formation in gas phase, in solution, or in solid state in many chemical systems. The theoretical, computational or experimental studies have been undertaken for clusters of a variety of chemical species, *e.g.*, formamide,^{4,8} thymine,⁹ trimethylamine *N*-oxide,¹⁰ carbamate,¹¹ acids,¹²⁻¹⁴ alcohols,¹⁵⁻¹⁷ amines,¹⁸ cyclodisiloxane,¹⁹ inorganics,^{20,21} liquid-crystalline oligomers,²² and cyanines.²³

Application of density functional theory (DFT) to chemistry²⁴ has received much attention recently because of a faster convergence in time than the traditional quantum mechanical correlation methods in part, and improvements in the prediction of the molecular force field, vibrational frequencies, and dipole moments. Therefore the force field from DFT calculation could be utilized with the spectroscopic data for the assignment of observed frequencies and the refinements of the molecular force field under study. The method using BP86 approximation has been successfully applied for the vibrational prediction of the azo compounds, *e.g.*, *trans*-, and *cis*-azobenzene²⁵ in particular, because it is more accurate for the vibrational frequency calculations than

any other density functional approximations. The normal mode analysis has been applied to elucidate the molecular system of chemistry and biological sciences using Wilson's *GF* matrix formulation.²⁶⁻²⁹ The matrix method has been enforced with improvements in the setup of internal coordinates, or in the computational method in the refinement procedure of the force field. It is now in progress to expand its application area to molecular dynamics studies as well as structural studies.

In the present study, the vibrational analysis of ADA molecule centered in the pentamer cluster with *trans*-configuration was investigated by normal mode analysis method using symmetry coordinates. The central ADA molecule was considered to have strong hydrogen bonding effects to its structure from four neighboring ADA molecules. It was performed using the force field obtained from DFT calculation using BP86 functional to clarify the vibrational properties in a powder state of neutral form, and also compared to the experimental spectroscopic Raman or infrared data. The hydrogen bonding effects from neighboring molecules to central ADA molecule were studied by obtaining the force constants of stretching, bending, and torsion modes and vibrational frequencies in terms of local symmetry coordinates, as well in energetic and structural points of view.

Experimental and Computation Methods

Experimental. Azodicarbonamide (ADA) was kindly donated from Kum Yang Company Limited, and used with further purifications and drying in vacuum. Its chemical structure with index numbers is shown in Figure 1. The infrared spectrum was obtained using the Bruker IFS66 machine with DTGS detector, Nernst bar light source and KBr beam splitter in the spectral resolution of 4 cm⁻¹ and

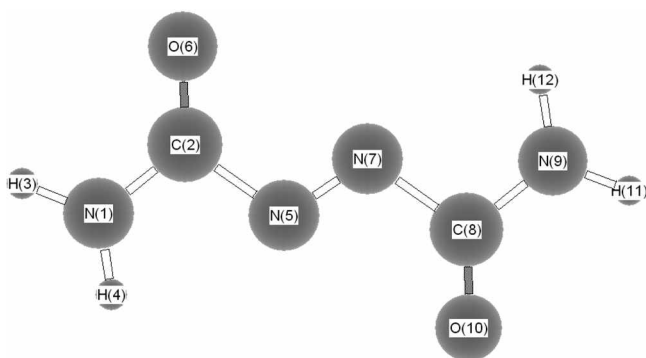


Figure 1. Chemical Structure of ADA single molecule with index numbers.

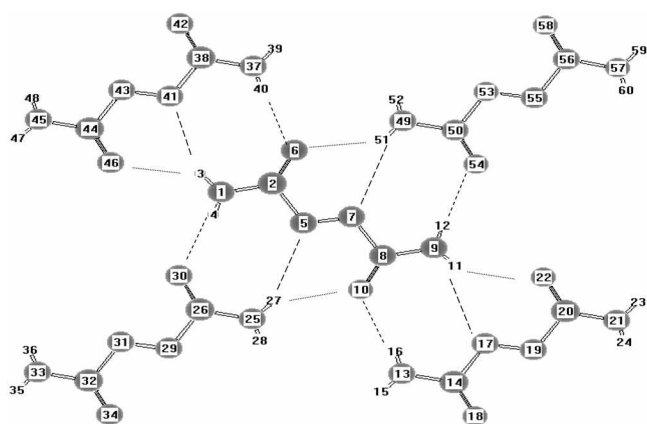


Figure 2. Pentamer cluster of ADA with index numbers and hydrogen bonds between central ADA molecule and its neighbor ADA molecules (There are three different lines indicating the hydrogen bonds, i.e., dot line, dash line, and long-dash line.)

100 times accumulated for each run. Bruker FRA106 Fourier transform spectrometer was applied in dry nitrogen purge mode to obtain Raman spectrum. It was equipped with 1064 nm cw Nd:YAG laser, a calcium fluoride beam splitter and liquid nitrogen cooled InGaAs detector for Raman scattering. The laser power was about 0.2 watt at sample. The spectral resolution was adjusted to 4 cm^{-1} and 100 times accumulated for each run. A sample powder was contained in ordinary melting point capillary tube (Drummond Scientific Co.) with tight packing for the irradiation. The infrared and Raman spectra are shown in Figures 3 and 4, respectively.

Computation. Single molecule and pentamer cluster were calculated at the theory levels of HF, B3LYP, B3P86, and BP86 using the 6-31G*, 6-31G**, and 6-311G** basis sets with the Gaussian03 program package (Gaussian, Inc.). The isotope atomic masses adapted for calculations were 12.01115 for carbon, 14.00307 for nitrogen, 15.9994 for oxygen, and 1.007825 for hydrogen, respectively. The temperature was set to 298.15 K and the pressure to 1.0 atm. The infrared and Raman spectra calculated for monomer and cluster are shown in Figures 3 and 4, respectively.

Cluster model. Initial structure of the pentamer cluster was generated using CS CHEM3D PRO (CambridgeSoft

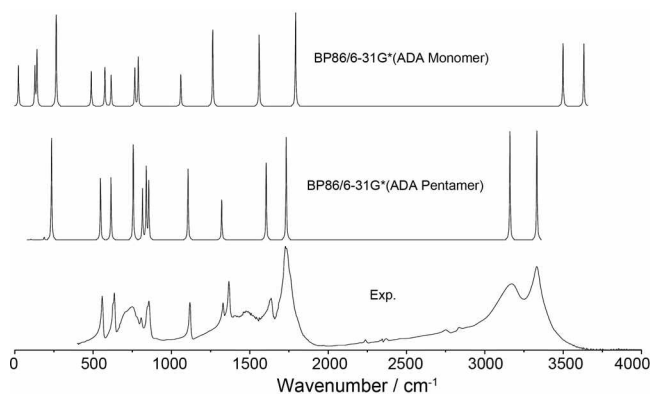


Figure 3. IR spectra of ADA. (Top: calculated spectrum of single ADA, Middle: calculated spectrum of central ADA in pentamer cluster, Bottom: experimental spectrum)

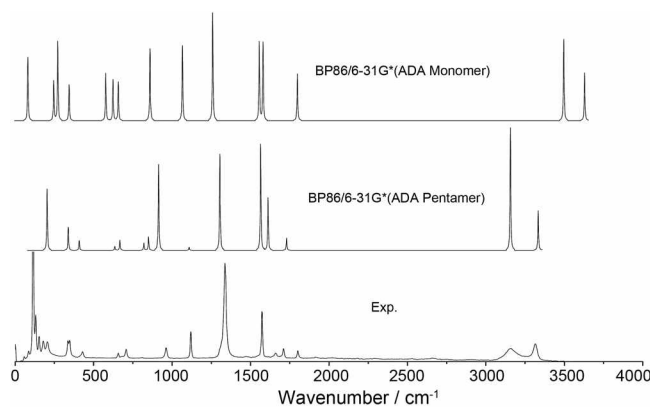


Figure 4. Raman spectra of ADA (Top: calculated spectrum of single ADA, Middle: calculated spectrum of central ADA in pentamer cluster, Bottom: experimental spectrum)

Cooperation) through ORTEP-3 windows version 1.05 according to the crystalline structure reported previously, and then transferred to the Gaussian03 program package for the optimization and the frequency calculation. First, initial optimization was performed at the AM1 level, and then optimized at higher levels of theory with mode-redundant option to force geometrical parameters of the crystalline structure as constraints. Second, further optimizations were progressed by gradually releasing the geometrical constraints. Fully optimized structure displayed in Figure 2 was obtained without any structural constraints at various levels of theory, and then employed for the calculation of Cartesian force constants and the intensities of Raman and infrared normal modes. This pentamer cluster is not positioned perfectly planar, but slightly tilted holding C_2 symmetry. However central ADA shows quite good planarity compared to its neighbors. Structural parameters of the central ADA in the pentamer cluster have been shown at various levels of theory in Table 1.

In general, the effects of hydrogen bonding have been known to be strong on a straight line in the geometry, A-H \cdots B. When the A \cdots B distance in A-H \cdots B configuration is about 2.8 to 3.0 Å, a hydrogen bond is assumed to exist between A and B atoms experimentally. Therefore, one can deduce

Table 1. Crystallographic structural parameters and Optimized molecular parameters of ADA monomer and Central ADA in pentamer cluster at various levels of theory using 6-31G*, 6-31G**, and 6-311G** basis set.

6-31G*	X-Ray	ADA Monomer				Central ADA in Pentamer Cluster			
		HF	B3LYP	BP86	B3P86	HF	B3LYP	BP86	B3P86
r(N1-C2) ^a	1.326	1.340	1.355	1.364	1.350	1.311	1.325	1.334	1.319
r(N1-H3)	0.790	0.994	1.009	1.017	1.008	1.003	1.022	1.035	1.024
r(N1-H4)	0.740	0.994	1.009	1.018	1.009	1.003	1.027	1.041	1.029
r(C2-N5)	1.479	1.465	1.493	1.508	1.484	1.463	1.487	1.496	1.477
r(C2=O6)	1.228	1.186	1.210	1.221	1.208	1.207	1.233	1.245	1.232
r(N5=N7)	1.238	1.208	1.238	1.252	1.235	1.208	1.239	1.254	1.236
θ(2,1,3)	119.4	119.28	119.67	119.92	119.77	120.27	121.19	121.20	121.22
θ(2,1,4)	117.2	120.76	120.00	119.65	119.84	120.65	120.26	120.31	120.22
θ(3,1,4)	123.1	119.96	120.32	120.43	120.39	119.07	118.55	118.49	118.55
θ(1,2,5)	109.2	108.24	106.85	106.03	106.76	110.05	109.23	108.98	109.37
θ(1,2,6)	128.3	126.70	127.05	127.26	127.19	127.80	128.44	128.61	128.57
θ(5,2,6)	122.5	125.07	126.09	126.70	126.04	122.15	122.33	122.41	122.06
θ(2,5,7)	111.5	112.61	111.43	110.69	111.24	112.58	111.64	111.00	111.40

6-31G**	X-Ray	ADA Monomer				Central ADA in Pentamer Cluster			
		HF	B3LYP	BP86	B3P86	HF	B3LYP	BP86	B3P86
r(N1-C2) ^a	1.326	1.339	1.354	1.364	1.349	1.311	1.324	1.333	1.318
r(N1-H3)	0.790	0.992	1.007	1.015	1.006	1.001	1.021	1.033	1.022
r(N1-H4)	0.740	0.992	1.008	1.016	1.007	1.002	1.026	1.041	1.029
r(C2-N5)	1.479	1.465	1.494	1.509	1.485	1.463	1.488	1.496	1.477
r(C2=O6)	1.228	1.186	1.210	1.220	1.208	1.207	1.234	1.246	1.232
r(N5=N7)	1.238	1.208	1.238	1.252	1.235	1.208	1.239	1.254	1.236
θ(2,1,3)	119.4	119.06	119.52	119.85	119.62	120.03	120.98	120.92	120.97
θ(2,1,4)	117.2	120.49	119.77	119.30	119.56	120.46	120.12	120.20	120.04
θ(3,1,4)	123.1	120.45	120.70	120.84	120.82	119.51	118.90	118.89	118.98
θ(1,2,5)	109.2	108.29	106.88	106.06	106.79	110.15	109.30	109.08	109.45
θ(1,2,6)	128.3	126.72	127.09	127.36	127.24	127.79	128.45	128.62	128.58
θ(5,2,6)	122.5	124.99	126.03	126.58	125.97	122.06	122.25	122.30	121.96
θ(2,5,7)	111.5	112.62	111.44	110.71	111.25	112.59	111.67	111.03	111.43

6-311G**	X-Ray	ADA Monomer				Central ADA in Pentamer Cluster			
		HF	B3LYP	BP86	B3P86	HF	B3LYP	BP86	B3P86
r(N1-C2) ^a	1.326	1.340	1.353	1.361	1.348	1.311	1.322	1.331	1.316
r(N1-H3)	0.790	0.992	1.006	1.014	1.005	1.001	1.020	1.032	1.021
r(N1-H4)	0.740	0.992	1.007	1.015	1.006	1.001	1.024	1.039	1.027
r(C2-N5)	1.479	1.466	1.496	1.510	1.486	1.462	1.489	1.497	1.477
r(C2=O6)	1.228	1.179	1.202	1.213	1.200	1.201	1.227	1.239	1.226
r(N5=N7)	1.238	1.203	1.231	1.245	1.228	1.204	1.232	1.248	1.230
θ(2,1,3)	119.4	119.31	119.81	120.08	119.90	119.98	120.97	120.88	120.96
θ(2,1,4)	117.2	120.22	119.45	119.03	119.27	120.33	120.14	120.17	119.99
θ(3,1,4)	123.1	120.47	120.74	120.88	120.83	119.69	118.89	118.95	119.04
θ(1,2,5)	109.2	108.08	106.66	105.85	106.57	110.12	109.33	120.88	109.48
θ(1,2,6)	128.3	127.01	127.49	127.69	127.64	127.87	128.48	120.17	128.57
θ(5,2,6)	122.5	124.91	125.85	126.45	125.79	122.00	122.19	122.30	121.95
θ(2,5,7)	111.5	112.82	111.85	111.18	111.61	112.73	111.94	111.30	111.68

^aBond lengths (r) are in Å unit, and bond angles (θ) in degree unit. The numbers are atomic index numbers shown in Figure 1.

strong hydrogen bonds in this ADA pentamer cluster at N1...O30 and O6...N37 because it is near linear, $\angle\text{NHO} \approx 172^\circ$ and comes out well below 3.0 Å to be 2.851 Å and 2.874 Å optimized at BP86/6-31G* level, respectively.

These bonds are drawn with dash lines in Figure 2. Other two possible hydrogen bonds are bent in angle, and a bit longer in distance. Hydrogen bonds, $\angle\text{NHO} \approx 141^\circ$, of N25...O10 2.883 Å and N1...O46 2.945 Å obtained at the same

Table 2. Stabilization Energy (kJ/mol) at 298 K per single ADA molecule of Pentamer cluster to ADA Monomer at various levels of theory

	HF			B3LYP			BP86			B3P86			
	6-31G*	6-31G**	6-311G**	6-31G*	6-31G**	6-311G**	6-31G*	6-31G**	6-311G**	6-31G*	6-31G**	6-311G**	
ADA Monomer	EE ^a	-445.56	-445.58	-445.68	-448.04	-448.05	-448.18	-448.06	-448.07	-448.20	-449.11	-449.12	-449.24
	ZPE	-445.47	-445.49	-445.59	-447.96	-447.97	-448.09	-447.98	-447.99	-448.12	-449.03	-449.04	-449.16
	ΔH	-445.46	-445.48	-445.59	-447.95	-447.96	-448.08	-447.97	-447.98	-448.11	-449.02	-449.03	-449.15
	ΔG	-445.50	-445.52	-445.63	-447.99	-448.00	-448.13	-448.02	-448.03	-448.15	-449.06	-449.07	-449.19
Pentamer	EE	-2227.89	-2227.97	-2228.50	-2240.30	-2240.37	-2240.98	-2240.41	-2240.47	-2241.08	-2245.65	-2245.72	-2246.30
	ZPE	-2227.43	-2227.51	-2228.04	-2239.88	-2239.95	-2240.56	-2240.00	-2240.07	-2240.67	-2245.22	-2245.29	-2245.87
	ΔH	-2227.38	-2227.46	-2228.00	-2239.83	-2239.90	-2240.51	-2239.95	-2240.02	-2240.63	-2245.18	-2245.24	-2245.82
	ΔG	-2227.53	-2227.61	-2228.15	-2239.98	-2240.05	-2240.66	-2240.10	-2240.17	-2240.78	-2245.32	-2245.39	-2245.97
Stabilization	$\Delta(\Delta E)^b$	-39.47	-39.83	-38.73	-49.86	-50.11	-46.88	-49.03	-49.75	-46.33	-50.31	-51.01	-48.32
	$\Delta(\Delta H)$	-33.96	-34.17	-35.49	-49.52	-49.66	-46.29	-48.81	-49.44	-45.87	-50.00	-50.64	-47.86
	$\Delta(\Delta G)$	-12.67	-13.13	-0.45	-12.93	-13.27	-10.06	-12.42	-11.43	-9.81	-11.31	-11.83	-9.23

^aEE (electronic energy), ZPE (zero point energy), ΔH and ΔG are in hartree unit. ^bThe stabilization energies $\Delta(\Delta E)$, $\Delta(\Delta H)$ and $\Delta(\Delta G)$ are in kJ/mol unit, and defined as $[\Delta(\text{pentamer}) - 5 \Delta(\text{monomer})]/5$.

Table 3. Diagonal force constants in symmetry coordinates (mdyne/Å or equivalent unit for deformation or torsion) of ADA monomer and Central ADA in pentamer

Symmetry Coordinate ^a	Symmetry Species ^b	BP86/6-31G*		BP86/6-31G**		BP86/6-311G**	
		ADA	CADA	ADA	CADA	ADA	CADA
N-C Stretching	Ag (ip)	7.134	8.691	7.113	8.695	7.006	8.544
N-H3 Stretching	Ag (ip)	7.134	6.116	7.214	6.129	7.133	6.109
N-H4 Stretching	Ag (ip)	7.041	5.600	7.112	5.490	7.042	5.547
C-N Stretching	Ag (ip)	2.938	3.731	2.924	3.708	2.824	3.584
C=O Stretching	Ag (ip)	12.446	10.919	12.476	10.866	12.380	10.751
N=N Stretching	Ag (ip)	10.780	10.784	10.799	10.789	10.786	10.727
N-C Stretching	Bu (ip)	7.129	8.629	7.106	8.630	7.003	8.487
N-H3 Stretching	Bu (ip)	7.132	6.098	7.214	6.111	7.132	6.092
N-H4 Stretching	Bu (ip)	7.040	5.596	7.111	5.486	7.041	5.544
C-N Stretching	Bu (ip)	3.150	3.546	3.139	3.545	3.061	3.454
C=O Stretching	Bu (ip)	12.486	10.934	12.519	10.886	12.418	10.777
NH ₂ Rocking	Ag (ip)	0.497	0.616	0.484	0.609	0.490	0.602
NH ₂ Scissoring	Ag (ip)	0.448	0.505	0.433	0.493	0.432	0.489
NCN Bending	Ag (ip)	1.159	1.413	1.156	1.417	1.169	1.397
NC=O Bending	Ag (ip)	1.042	1.353	1.042	1.346	1.040	1.329
CN=N Bending	Ag (ip)	1.560	1.888	1.557	1.880	1.529	1.846
NH ₂ Rocking	Bu (ip)	0.494	0.618	0.480	0.611	0.486	0.604
NH ₂ Scissoring	Bu (ip)	0.447	0.502	0.432	0.490	0.431	0.486
NCN Bending	Bu (ip)	1.098	1.594	1.097	1.593	1.109	1.564
NC=O Bending	Bu (ip)	0.992	1.262	0.992	1.260	0.992	1.246
CN=N Bending	Bu (ip)	1.430	3.365	1.440	3.349	1.395	3.250
NH ₂ Wagging	Bg (op)	0.009	0.089	0.010	0.089	0.012	0.085
C=O Deformation	Bg (op)	0.610	0.652	0.608	0.647	0.626	0.655
NH ₂ Wagging	Au (op)	0.010	0.099	0.011	0.099	0.013	0.094
C=O Deformation	Au (op)	0.654	0.787	0.653	0.778	0.672	0.779
NH ₂ Torsion	Au (op)	0.340	0.670	0.338	0.667	0.342	0.638
N-C Torsion	Au (op)	0.029	0.747	0.029	0.744	0.031	0.702
N=N Torsion	Au (op)	0.367	0.574	0.365	0.572	0.358	0.553
NH ₂ Torsion	Bg (op)	0.334	0.649	0.332	0.646	0.336	0.618
N-C Torsion	Bg (op)	0.024	0.095	0.021	0.092	0.019	0.087

^aNumbers side to the atomic symbols are the atomic numberings employed in ADA. ^bSymmetry species of symmetry coordinates (ip: in-plane, op: out-of-plane)

Table 4. Calculated Frequencies of ADA monomer and Central ADA in pentamer at BP86 level, and experimental frequencies of solid ADA with Assignments and Vibrational numbering.

ADA		Central ADA in Pentamer		Exp	Sym ^a	Assignments and Vibrational numbering
6-31G*	6-31G*	6-31G**	6-311G**			
3639	3341	3345	3339	3316	Ag	N-H3 Stretch 12
3638	3338	3342	3336	3338	Bu	N-H3 Stretch 11
3505	3166	3137	3152	3172	Bu	N-H4 Stretch 13
3505	3164	3135	3149	3158	Ag	N-H4 Stretch 14
1797	1737	1734	1721	1734	Bu	C=O Stretch - N-C Stretch 15
1806	1736	1734	1720	1710	Ag	C=O Stretch - N-C Stretch 16
1564	1619	1605	1600	1661	Ag	NH ₂ Scissor - C=O Stretch 17
1564	1609	1595	1589	1636	Bu	NH ₂ Scissor - C=O Stretch 18
1587	1571	1568	1562	1573	Ag	N=N Stretch 19
1269	1326	1322	1311	1330	Bu	N-C Stretch + NC=O Bend + NH ₂ Rock 111
1267	1312	1307	1298	1337	Ag	N-C Stretch + NC=O Bend + NH ₂ Rock 110
1073	1116	1109	1109	1117	Ag	NH ₂ Rock - C=O Stretch - N-C Stretch 112
1065	1111	1103	1102	1115	Bu	NH ₂ Rock - C=O Stretch - N-C Stretch 113
867	920	920	916	961	Ag	CN=N Bend + C-N Stretch 114
619	860	859	844	856	Au	NH ₂ Torsion 122
584	856	856	842		Bg	NH ₂ Torsion 123
268	843	840	802	840	Au	NH ₂ Wag 124
252	826	822	805	810	Bg	NH ₂ Wag 125
793	820	816	826	807	Bu	C-N Stretch + NC=O Bend 115
770	760	760	765	750	Au	C=O Deform + NH ₂ Wag - N=N Torsion 126
631	673	673	671	704	Ag	NC=O Bend + C-N Stretch + NH ₂ Rock 116
664	642	641	648	657	Bg	C=O Deform 127
580	618	618	618	628	Bu	NC=O Bend + NCN Bend - CN=N Bend 117
492	552	552	551	555	Bu	NCN Bend - NC=O Bend - CN=N Bend 118
350	415	415	413	420	Ag	NCN Bend 119
278	345	342	338	337	Ag	C-N Stretch + CN=N Bend + NC=O Bend 120
132	238	236	234		Bu	CN=N Bend + NCN Bend 121
87	209	207	205	205	Bg	N-C Torsion 128
145	191	190	189		Au	N=N Torsion 129
28	108	108	107		Au	N-C Torsion 130

^aSymmetry of each vibration (Ag and Bu: in-plane vibrations (ν_1 - ν_{21}), Bg and Au: out-of-plane vibrations (ν_{22} - ν_{30}), g: Raman active, u: IR active)

level are drawn with dot lines in Figure 2. Other possible, but weak hydrogen bonds, $\angle\text{NHN} \approx 155^\circ$, are at N25...N5 3.248 Å and N1...N41 3.332 Å drawn with long-dash lines. Overall 12 hydrogen bonds between central ADA and 4 neighbors are shown in Figure 2. These hydrogen bonds are classified into 3 different kinds, indicated with a dash line (near linear and close enough $\text{NH}\cdots\text{O}=\text{C}$), a dot line (angled and a bit long $\text{NH}\cdots\text{O}=\text{C}$), and a long-dash line (angled and comparatively long $\text{NH}\cdots\text{N}=\text{N}$).

Normal mode analysis. The symmetry coordinates of single ADA molecule (C_{2h} point group) was composed of 11 stretching (6 Ag + 5 Bu symmetry), 10 in-plane bending (5 Ag + 5 Bu symmetry), 4 out-of-plane deformation (2 Bg + 2 Au symmetry), and 5 torsion (2 Bg + 3 Au symmetry) modes. Among them, all stretching and in-plane bending modes are in-plane modes, and others out-of-plane modes. Vibrations belonging to Ag and Bg symmetry species are Raman active, and to Au and Bu infrared active. To extract vibrations of central ADA, the pentamer cluster was treated in 150 modes in total five times of single ADA in the

symmetry coordinates because five monomers are separated in fact. The diagonal force constants and vibrational frequencies obtained are listed in Tables 3 and 4 at the level of BP86 approximation using three different basis sets, respectively.

To obtain vibrational properties of hydrogen bonds in the pentamer cluster, each monomer molecule was configured to be connected each other through four hydrogen bonds representing hydrogen bonding of the same kind, *e.g.*, dot lines, dash lines, or long-dash lines in Figure 2. This reconfiguration results in 3 sets of clusters shaped like a propeller connected in the same line. Each of three screw-like clusters was then treated by the local symmetry coordinates of its own. Because this cluster is connected each other through hydrogen bonds to a large molecule of 60 atoms, in the local symmetry coordinate there are 174 modes in all. It consists of 59 stretching, 58 in-plane bending, 20 out-of-plane deformation, and 37 torsion modes. The structural parameters and force constants in the local symmetry coordinates are listed in Table 5 at the level of BP86 approximation using three

Table 5. Optimized structural parameters and Calculated force constants in local symmetry coordinates (mdyne/Å or Equivalent unit for bending or torsion) of hydrogen bonds in ADA pentamer at BP86 level using three different basis set

		BP86/6-31G*			BP86/6-31G**		BP86/6-311G**	
Atoms ^a		X-Ray ^b	Structure ^c	Force Constant	Structure ^c	Force Constant	Structure ^c	Force Constant
Stretching	r(H3...O46)	2.255	2.069	0.236	2.075	0.228	2.083	0.219
	r(O6...H51)	2.240	2.024	0.294	2.023	0.285	2.012	0.279
	r(H3...N41)	2.629	2.419	0.339	2.411	0.326	2.441	0.314
	r(N7...H51)	2.629	2.329	0.387	2.325	0.370	2.370	0.353
	r(H4...O30)	2.169	1.816	0.432	1.796	0.413	1.809	0.393
	r(O6...H40)	2.162	1.841	0.370	1.826	0.354	1.837	0.339
Bending	θ(1,3,46)	140.08	140.93	1.782	140.65	1.666	142.38	1.586
	θ(6,51,49)	141.05	138.72	2.084	138.80	1.946	141.32	1.853
	θ(1,3,41)	155.31	146.68	1.676	146.89	1.564	146.02	1.497
	θ(7,51,49)	154.91	147.32	1.961	147.17	1.843	145.42	1.747
	θ(1,4,30)	170.62	171.92	1.636	171.88	1.712	172.10	1.318
	θ(6,40,37)	171.68	174.37	1.911	174.18	1.888	174.46	1.745
Torsion	τ(1,3,46,44)	-173.68	171.06	0.276	171.24	0.265	171.77	0.291
	τ(2,6,51,49)	178.51	164.10	0.143	164.58	0.140	162.79	0.148
	τ(1,3,41,43)	163.38	-168.67	0.276	-168.68	0.278	-170.02	0.279
	τ(5,7,51,49)	178.27	-165.27	0.270	-165.86	0.279	-165.35	0.260
	τ(1,4,30,26)	157.77	-130.62	0.509	-133.09	0.497	-122.01	0.486
	τ(2,6,40,37)	-178.04	146.48	0.551	146.47	0.530	137.64	0.533

^aThe numbers are atomic index numbers shown in Figure 2. ^bObtained from Ortep-3 drawing based on the crystal data in *J. Chem. Phys.* **1974**, *60*, 176. ^cHydrogen bond lengths (r) are in Å unit, and bond angles (θ) and torsion angles (τ) in degree unit.

different basis sets.

Single molecule and the pentamer cluster have 12 and 60 atoms in total, respectively. The force constants matrix in the Cartesian coordinate generated through *ab initio* or density functional calculation has 666 elements for single molecule and 16290 elements for the pentamer cluster overall which are composed of all the diagonal and half the off-diagonal elements. Using these elements, the force constants in the local symmetry coordinates, the frequencies, and potential energy distributions were obtained using Wilson's *GF* matrix method. The scaling factors are now well recognized to be transferable for the group frequencies. In this study, however, we did not apply any scaling factor, e.g., 0.96, etc., for the frequency calculations.

Results and Discussion

Optimized structure of central ADA in pentamer cluster.

Fully optimized geometry parameters of central ADA in the pentamer cluster at the level of HF, B3LYP, BP86, and B3P86 using 6-31G*, 6-31G**, and 6-311G** basis set have been presented in Table 1 along with those of fully optimized ADA monomer and X-ray crystallographic data. The central ADA molecule is almost planar both in crystallographic geometry and in the optimized geometry. The backbone dihedral angle through C2-N5-N7-C8 was obtained to be 180.0°, the dihedral angle through N1-C2-N5-N7 near 175.0° as shown below calculated at BP86/6-31G* which is compared to the crystal geometry and ADA monomer optimized. Geometry parameters of ADA crystal

structure were obtained from Ortep-3 drawing based on the crystal data reported previously.

Dihedral Angle	Crystal	BP86/6-31G*	
		ADA monomer	Central ADA in pentamer
H3-N1-C2-N5	179.7°	180.0°	-177.4°
H3-N1-C2-O6	-1.0°	0.0°	2.4°
H4-N1-C2-N5	-0.9°	0.0°	2.2°
H4-N1-C2-O6	178.4°	180.0°	-177.9°
N1-C2-N5-N7	170.4°	180.0°	174.9°
O6-C2-N5-N7	-9.0°	0.0°	-4.9°
C2-N5-N7-C8	-179.0°	180.0°	180.0°

The amine and carbonyl moieties of amide group CONH₂ in ADA molecule are planar both in crystal and in the optimized geometries at various levels of theory shown in Table 1. The distance of N1-C2 bond is about 0.16 Å shorter than that of C2-N5 bond as shown in crystallographic parameters, 0.153 Å. The atomic charge, -0.77 of N1 atom was calculated at BP86/6-31G* much stronger in negative than that of N5 atom, -0.23. The distances of N1-C2 and C2-N5 bonds are a bit shorter in central ADA due to intermolecular hydrogen bonding than in ADA monomer, nonetheless the carbonyl bond has been lengthened about 0.02 Å. But, the azo moiety, N=N bond does not show any significant change in the bond distance due to hydrogen bonding. The distances of N-H bonds were weakly lengthened as much 0.02 Å due to hydrogen bonding, but the

optimized are much longer about 0.23 Å than crystal parameters. These results are not clear to explain, but partly because the crystallographic bond distance of hydrogen atom might not be accurate, or partly because, for crystal, the distance of hydrogen atom inherently comes shorter through the crystal packing.

The optimized angles of C2-N1-H3, C2-N1-H4, and H3-N1-H4 also show a discrepancy from crystal parameters, but the optimized angles of N1-C2-O6, N1-C2-N5, and O6-C2-N5 of central ADA in pentamer cluster show very good coincidence with crystal parameters. The optimized angle of C2-N5-N7 is close to the crystal parameter for all density functional theory using every basis set utilized in this study.

Energetics of ADA pentamer cluster. Intermolecular hydrogen bonding would generate significant stabilization energies to form the cluster. Table 2 shows these results at various level of theory using three different basis set under 1.0 atm and 298 K. Stabilization ($\Delta(\Delta E)$ and $\Delta(\Delta H)$) per a single ADA molecule in electronic energy and enthalpy has been calculated in the range of about 50 kJ/mol as shown in Table 2. However the free energy of stabilization is less small as much about 10 kJ/mol because the entropy change became reduced due to clustering.

Force constants of central ADA molecule in the symmetry coordinates. Diagonal elements of force constants of force constant matrix in the symmetry coordinates were listed for ADA monomer and central ADA molecule in Table 3. The symmetry coordinates were divided into several blocks, e.g., stretching, deformation (in-plane and out-of-plane bending), and torsion.

Stretching. The force constants of N-H stretching were about 6.1 and 5.6 mdyn/Å. The force constants were smaller than those of monomer, due to hydrogen bonding. The difference of force constants between two stretching (N-H3 and N-H4) was due to strength of hydrogen bond. The H3 formed angled hydrogen bond with two different atoms, N and O, but the H4 formed one linear hydrogen bond with O. Then strength of hydrogen bond of H4 was stronger than that of H3 as explained above. The force constants of N-C stretching increased to about 8.6 mdyn/Å due to hydrogen bonding, but force constants of C=O stretching decreased to about 10.9 mdyn/Å. Whereas, the force constant of N=N stretching was not changed to maintain the same magnitude as ADA monomer, 10.8 mdyn/Å.

In-plane bending. These modes include both scissoring and rocking modes of NH₂, and skeletal bending modes of N-C-N, N-C=O, and C-N=N. The force constants of NH₂ scissoring and rocking modes were not much changed to maintain at 0.5 and 0.6 mdyn/Å from near 0.5 mdyn/Å of ADA monomer. The force constants of N-C=O and N-C-N bending were increased to 1.4 mdyn/Å from near 1.0 mdyn/Å of ADA monomer due to hydrogen bonding. The force constant of bending of C-N=N was increased to 1.9 mdyn/Å from 1.5 mdyn/Å of ADA monomer.

Out-of-plane deformation. These modes include wagging mode of NH₂, and out-of-plane deformation of C=O. The force constants of NH₂ wagging mode were significantly

increased to about 0.09 mdyn/Å from 0.01 mdyn/Å of ADA monomer due to hydrogen bonding. However, the force constant of C=O deformation was slightly increased to 0.65 and 0.78 mdyn/Å from 0.65 mdyn/Å of ADA monomer.

Torsion. The force constants of NH₂ torsion modes were comparatively increased to about 0.7 mdyn/Å from 0.3 mdyn/Å of ADA monomer. The force constants of N-C modes were drastically increased to about 0.7 mdyn/Å from 0.02 mdyn/Å of ADA monomer. The torsion mode of N=N was slightly increased due to their hydrogen bonding because it maintains the skeletal structure in the central position.

Vibrational analysis of central ADA molecule. The calculated frequencies of ADA monomer and central ADA in pentamer cluster at BP86 level with experimental frequencies of solid ADA with assignments were shown in Table 4. The vibrations of central ADA molecule were analyzed in each region of interest.

Vibrations of N-H stretching region. Stretching frequencies of N-H where the hydrogen atoms were hydrogen bonded to neighboring oxygen or nitrogen atoms were calculated at 3341, 3338, 3166, and 3164 cm⁻¹. These frequencies were similar to the experimental values, 3316, 3338, 3172, and 3158 cm⁻¹ as shown in Table 4. These frequencies were down shifted from those of the ADA monomer due to strong hydrogen bonding. In particular, the latter two bands are mainly attributed from N-H4 stretching while the former two bands mainly from N-H3 stretching. This indicates that the hydrogen of N-H4 part makes stronger hydrogen bond as shown in Table 4. This could be conformed from the IR spectrum experimentally obtained which is shown in the bottom of Figure 3. The band at 3172 cm⁻¹ (N-H4 stretching, Bu) is much broader than a band at 3338 cm⁻¹ (N-H3 stretching, Bu). This indicates that the hydrogen of N-H4 makes stronger hydrogen bonding than that of N-H3 because it is connected to oxygen atom of carbonyl group in the way of almost linear.

Vibrations of C=O stretching region. Stretching frequencies of C=O were calculated at 1737 and 1736 cm⁻¹. These values were similar to 1734 and 1710 cm⁻¹ of experimental values as shown in Table 4, also down-shifted compared to the ADA monomer. This band is usually considered as Amide I band in the peptide system. This carbonyl band is coupled weakly with N-C stretching mode. There are two bands at 1661 and 1636 cm⁻¹ which are from carbonyl band coupled with NH₂ scissoring mode. These are slightly apart from calculated 1609 and 1619 cm⁻¹, which are considered as Amine II band in the peptide system. This discrepancy can be proposed to be partly from reduced C=O stretching and enhanced NH₂ scissoring contributions due to strong hydrogen bonding in the cluster. The IR spectrum experimentally obtained shown in the bottom of Figure 3 displays a broad carbonyl band at 1734 cm⁻¹, where the broadening indicates the hydrogen bonding.

Vibrations of N=N stretching region. Stretching frequencies of the azo group N=N for all cases are not much changed despite to hydrogen bonding. Only a few wavenumbers are down-shifted compared to the ADA monomer, but the

frequency of N=N stretching, 1571 cm^{-1} , was similar to 1573 cm^{-1} of experimental value.

Vibrations of N-C stretching region. Stretching modes of the N1-C2 bond are strongly coupled to the C=O bond to form Amide band. This mode was dispersed in several bands from 1111 to 1737 cm^{-1} region. The major contribution makes two bands at 1326 and 1312 cm^{-1} with coupling of NC=O bending and NH₂ rocking modes, experimentally observed at 1330 and 1337 cm^{-1} which are considered as Amide III band in the peptide system. Stretching modes of C2-N5 next to azo moiety bond was calculated at 820 and 345 cm^{-1} , which are much near to experimental values.

Vibrations of NH₂ in-plane-bending region. Scissoring mode of NH₂ group was calculated at 1619 and 1609 cm^{-1} which were down-shifted from 1661 and 1636 cm^{-1} of experimental values as mentioned above. Rocking mode of NH₂ group was calculated at 1116 and 1111 cm^{-1} . These frequencies were almost the same to the experimental values, and coupled with C=O stretching and N-C stretching modes.

Vibrations of skeletal in-plane bending region. The skeletal frame of C-N=N-C has its in-plane deformation modes with O and N connected, which are C-N=N bending, N-C=O bending, and N-C-N bending. These modes are scattered in the region of 920 to 238 cm^{-1} . The N-C=O bending mode is considered as Amide IV band in the peptide system. Two bands at 673 and 618 cm^{-1} is attributed from this N-C=O mode coupled with other modes.

Vibration of NH₂ out-of-plane-bending and torsion region. In the pentamer system, the out-of-plane mode of NH₂ group is greatly hindered due to hydrogen bonding in the cluster. This effect makes NH₂ torsion and NH₂ wagging modes to very strong. The NH₂ torsions are calculated to 860 and 856 cm^{-1} , and wagging to 843 and 826 cm^{-1} close to experimental values. The NH₂ torsions are considered as Amide V band in the peptide system.

Vibrations of C=O out-of-plane deformation region. The deformation modes were calculated at 642 and 760 cm^{-1} . The calculated frequencies were similar to experimental values. This band is considered as Amide VI band in the peptide system.

Vibrations of skeletal torsion region. The torsion modes were calculated below 210 cm^{-1} . The N-C torsion is calculated to 209 cm^{-1} , N=N torsion to 191 cm^{-1} , and N-C torsion to 108 cm^{-1} .

Force constants of hydrogen bonds in the local symmetry. The optimized structural parameters and calculated force constants in local symmetry coordinates of hydrogen bonds in ADA pentamer cluster at BP86 level at different basis sets are shown in Table 5 along with crystalline structural parameters. Because the calculated spectra using the basis set 6-31G* fits well the experimental infrared and Raman spectra, the force constants calculated from the basis set 6-31G* are discussed as following.

Stretching of hydrogen bonding. Force constants of bent H \cdots O bonds (H3 \cdots O46 and O6 \cdots H51) which were drawn with dot lines in Figure 2, came out to 0.236 and 0.294 mdyn/\AA . Force constants of H \cdots N bonds (long-dash lines,

H3 \cdots N41 and N7 \cdots H51) were came out to 0.339 and 0.387 mdyn/\AA . Force constants of linear H \cdots O bonds (dash lines, O6 \cdots H40 and H4 \cdots O30) came out 0.370 and 0.432 mdyn/\AA . This values several times larger than the stretching force constants of C=O \cdots H-N in the polyglycine peptide system,²⁸ about 0.125 mdyn/\AA . We can count this fact to strong hydrogen bonding, consequently shorter distance of 2.16 \AA as shown in Table 5. This distance is much less than 2.4 \AA calculated in the hydrogen bonded system³⁰ of ammonia-acetylene dimer, H₃N \cdots HC \equiv CH. These values for the linear H \cdots O hydrogen bonding system were also much larger than 0.0582 mdyn/\AA observed from a hydrogen-bonded dimer³¹ formed between trimethylamine and acetylene, (CH₃)₃N \cdots HC \equiv CH, in gas phase by Fourier-transform microwave spectroscopy. The hydrogen bonding proton stretching mode³³ in polyglycine I at 20 K studied by inelastic neutron scattering spectroscopy shows at 2960 cm^{-1} , with double minimum potential wells which is far below the normal N-H stretching vibrational frequency indicating strong hydrogen bonding.

In-plane bending of hydrogen bonding. Force constants of N1-H3 \cdots O46 and N1-H3 \cdots N41 bending modes came out about 1.7 mdyn/\AA , of O6 \cdots H51-N49 and N7 \cdots H51-N49 bending modes to about 2.0 mdyn/\AA . Force constants of N1-H4 \cdots O30 and O6 \cdots H40-N37 bending mode came out 1.636 and 1.911 mdyn/\AA , respectively. These values are quite large compared to 0.030 mdyn/\AA of C=O \cdots H-N bending³² obtained from the calculation of crystalline anti-parallel chain pleated sheet polyglycine I. However, the bending mode³³ of hydrogen bonding proton perpendicular to the mean plane of the peptide unit of polyglycine I was observed at about 700 cm^{-1} which suggests firm rigidity in the chain structure of polyglycine. Our structure has two hydrogen atoms forming strong hydrogen bonding with next molecules in the cluster, therefore these bending modes are very rigid to make in-plane bending motion.

Torsion of hydrogen bonding. Force constants of torsion modes of bent hydrogen bonding came out about 0.3 mdyn/\AA , but of linear hydrogen bonding to about 0.5 mdyn/\AA . These values are also larger than the usual torsion force constants adapted in analysis of polyglycine I system. This is mainly due to the rigidity in the pentamer cluster.

Conclusions

The equilibrium structure, the stabilization energies, and the vibrational properties were studied using a pentamer cluster of azodicarbonamide molecules. Stabilization enthalpy from a pentamer formation of about 48.75 kJ/mol calculated using BP86/6-31G* theory level is rather large compared to other molecules. This implies that ADA molecules form very strong hydrogen bonded cluster. Using the force constant matrix calculated for pentamer, vibrational analysis shows successful to explain the experimental Raman and infrared spectrum of ADA solid state. The stretching and angle-bending force constants of intermolecular hydrogen bonds were obtained.

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