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Hydrogen bonding in ε-caprolactam dimer: a quantum-chemical study

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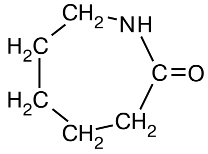
The equilibrium geometries, vibrational frequencies, and IR band intensities were calculated for the monomer and hydrogen-bonded cyclic dimer of ε-caprolactam (**1**) by the density functional B3LYP/6-311++G(d,p) method and compared with the experimental data. The gas-phase IR spectrum of monomer of **1** was first measured. The calculated hydrogen bonding enthalpy $\Delta H/2$ in the hydrogen-bonded dimer in the gas phase (−5.93 kcal/mol) is consistent with the published data. The computed scaled (scaling factor 0.97) vibrational frequencies of the monomer and dimer are in good agreement with the experimental data. The geometry of the ε-caprolactam monomer remains nearly unchanged in its dimer except for the N—H, C—O, and C—N bond lengths that respectively change from 1.012, 1.230, and 1.369 Å in the former to 1.029, 1.246, and 1.350 Å in the latter. The frequencies, eigenvectors, and IR intensities of the amide modes of the monomer and dimer differ dramatically. The calculated νNH and νCO frequency shifts due to hydrogen bonding are in good agreement with the experimental data, but theoretical intensification of the νNH IR band is much greater than that observed experimentally (by nearly 69 times *vs.* 11 times, respectively). The calculated N...O intermolecular distance in the structure of ε-caprolactam dimer equals the experimental value (2.89 Å). The influence of the basis set employed on the results of calculations is discussed.

Key words: ε-caprolactam, IR spectra, molecular structure, hydrogen bond, quantum-chemical calculations, density functional theory, hydrogen bonding enthalpy.

Recently, the number of density functional (DFT) quantum-chemical studies of vibrational spectra of complex molecules has been growing dramatically. Particularly good results were obtained in calculations with the B3LYP hybrid correlation functional, which includes the mixed Hartree—Fock and DFT exchange-correlation functionals. In contrast to Hartree—Fock calculations that require a large number of scaling factors[1] to fit the experimental data the DFT calculated frequencies should not be scaled at all or require only one or two scaling factors lying between 0.89 and 0.99 depending on the basis set employed.[2] Applicability of the B3LYP approach to calculations of the structure, energy characteristics, and vibrational spectra of H-bonded systems has been little studied as yet. The IR spectra of a few *ortho*-hydrozybenzoyl compounds with O—H...O intramolecular hydrogen bond (IHB) were reported.[3] The results obtained revealed the possibilities and limitations of the harmonic approximation in the description of spectral characteristics of intramolecularly hydrogen-bonded molecules. Theoretical prospects for quantum-chemical calculations of the vibrational spectra of H-bonded compounds and the hydrogen bonding energies of simple organic and inorganic molecules have been well documented in a monograph.[4]

The aim of this work was to investigate applicability of the B3LYP method to calculations of vibrational spectra of hydrogen-bonded molecules and to theoretically estimate the energy of hydrogen bonding taking ε-caprolactam (**1**) as an example.



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ε-Caprolactam is a convenient model for a hydrogen-bonded system, being at the same time an industrially valuable product. It is widely used in production of polymers; complexes of ε-caprolactam derivatives with transition metals are of interest as potentially bioactive compounds and catalysts.[5,6] Complexes of **1** with phenols are used in glue compositions.[7,8]

According to X-ray diffraction studies,[9,10] in the crystalline state compound **1** forms stable centrally symmetric cyclic dimers due to two intermolecular hydrogen bonds N—H...O. The IR spectra measured in solutions in CCl_4 indicate[11—14] that the equilibrium between the ε-caprolactam dimer and monomer is shifted toward the former. The H-bond enthalpy per bond, $\Delta H/2$, estimated using the empirical Iogansen rule (see a review[13]) was found to be −4.7 kcal mol^{-1},[12,13] which is close to the results of calorimetric measurements (−4.1 kcal mol^{-1}).[15] The en-

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thalpy of dimerization ($\Delta H/2$) of **1** in CCl_4 calculated using the temperature dependence of the equilibrium constant is –5.46 kcal mol^{-1}.[16] The dimerization energy ($\Delta E/2$) of molecule **1** in the crystal measured using the sublimation heat is –6.9 kcal mol^{-1}.[17] As can be seen, the estimates of the enthalpy of dimerization of **1** are scattered widely. In this work this parameter was obtained from B3LYP calculations.

The IR spectra of ε-caprolactam dimer were measured in the solid phase[18,19] and in a CCl_4 solution in the 1700—100 cm^{-1} region[20] and in the region of the νNH (3600—2800 cm^{-1}) and Amide-I (1700—1600 cm^{-1}) bands.[11—14] The vibrational frequencies of ε-caprolactam dimer were assigned based on the results of calculations using the Urey—Bradley force field and taking into account the frequency shifts upon deuteration at the amide bond.[20] The structure and vibrational spectra of ε-caprolactam monomer have not been reported as yet except for the νNH frequency of a "free" N—H bond in the IR spectrum of a dilute solution in CCl_4 (3427 cm^{-1}).[11—14] This band is observed in the spectral region characteristic of free N—H bonds of *cis*-amides (3400—3430 cm^{-1}).[21] To bridge the gap, we measured the IR spectra of ε-caprolactam monomer in the gas phase and in dilute solutions in CCl_4 and calculated its equilibrium molecular structure and IR spectrum. This permitted a complete interpretation of the IR spectrum of the monomer of **1**. By comparing the spectra of the monomer and dimer we assessed the influence of dimerization on the IR spectrum of **1**. We also calculated the spectral and structural characteristics and the enthalpy of the H-bond in the ε-caprolactam dimer and compared them with the experimental data.

Results and Discussion

Vibrational spectrum and structure of ε-caprolactam monomer. According to calculations, the ε-caprolactam monomer molecule has a well-defined chair conformation with *cis*-arranged N—H and C=O bonds (Fig. 1). The calculated bond lengths, bond angles, and dihedral angles are listed in Table 1.

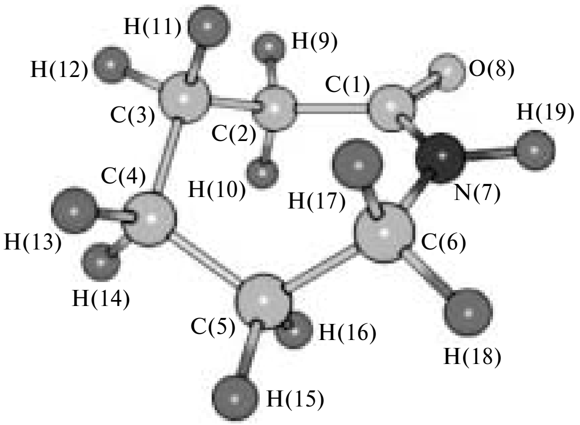

Fig. 1. Calculated structure of ε-caprolactam monomer.

Table 1. B3LYP/6-311++G(d,p) calculated geometric parameters of ε-caprolactam monomer and dimer

Parameter	Monomer	Dimer
Bond length	d/Å	
C(1)—O	1.230	1.246
C(1)—N	1.368	1.350
C(1)—C(2)	1.524	1.522
C(2)—C(3)	1.544	1.544
C(4)—C(5)	1.535	1.535
C(5)—C(6)	1.536	1.536
C(6)—N	1.462	1.461
C—H	1.096—1.100	1.096—1.100
N—H	1.012	1.029
Bond angle	ω/deg	
O—C(1)—N	120.8	121.5
O—C(1)—C(2)	121.8	120.1
N—C(1)—C(2)	117.8	118.4
C(1)—C(2)—C(3)	114.6	114.5
C(3)—C(4)—C(5)	115.6	115.5
C(4)—C(5)—C(6)	114.4	114.5
C(5)—C(6)—N	114.6	114.8
C(6)—N—C(1)	127.9	126.9
H—C—H	106—107	106—107
H—N—C(6)	118.4	117.2
H—N—C(1)	113.6	115.9
Torsion angle	φ/deg	
N—C(1)—C(2)—C(3)	62.6	62.7
C(2)—C(1)—N—C(5)	1.4	1.6
C(1)—C(2)—C(3)—C(4)	–79.42	–79.05
C(3)—C(4)—C(5)—C(6)	–60.4	–60.0
H—N—C(1)—O	1.3	1.5

The calculated and experimental vibrational frequencies and IR band intensities in the spectrum of ε-caprolactam monomer are listed in Table 2. The experimental IR spectrum of gaseous **1** shown in Fig. 2 exhibits a weak νNH band at 3442 cm^{-1} (3496 cm^{-1} obtained from calculations), three bands in the νCH region at 2974 (shoulder), 2940, and 2869 cm^{-1} and an intense νC=O band at 1712 cm^{-1} (1692 cm^{-1} obtained from calculations). In the region below 1500 cm^{-1} the spectrum exhibits weak broad overlapping bands with the frequency maxima listed in Table 2. The vibrational frequencies of the monomer (see Table 2) were assigned based on the calculated potential energy distribution (PED). No rotational band structure was observed in the spectrum of gaseous ε-caprolactam monomer obtained with a 2 cm^{-1} resolution. In the gas phase (80 °C) compound **1** exists in the monomeric form because the spectrum only exhibits bands of free NH and C=O groups at 3442 and 1712 cm^{-1}, respectively. The spectrum of a 0.007 M solution of **1** in CCl_4 simultaneously exhibits three dimer bands (at 3302, 3218 and 3086 cm^{-1})[12—14] and a monomer band at 3428 cm^{-1}

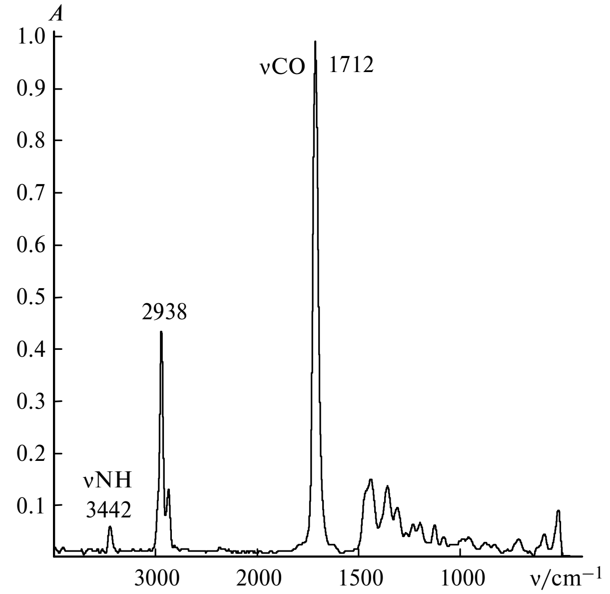

Fig. 2. IR spectrum of gaseous ε-caprolactam.

(Fig. 3) in the νNH region. The relative intensity of the last-mentioned band increases on further dilution of the solution. The νC=O band of the monomer at 1682 cm^{-1} manifests itself as a high-frequency shoulder of the dimer band at 1670 cm^{-1} (Fig. 4). It was found after deconvolution of the shape of the latter band. As the solution concentration decreases, the relative intensity of the shoulder increases. The νNH and νC=O frequencies in the spectra of ε-caprolactam monomer in the gas phase and in dilute solution in CCl$_4$ differ by about 30 cm^{-1}, which

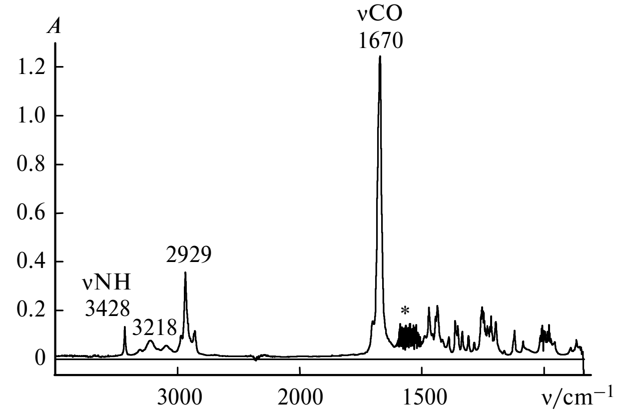

Fig. 3. IR spectrum of a dilute 0.007 *M* solution of ε-caprolactam in CCl$_4$ obtained after subtraction of the solvent bands. The results of subtraction of the solvent bands are asterisked.

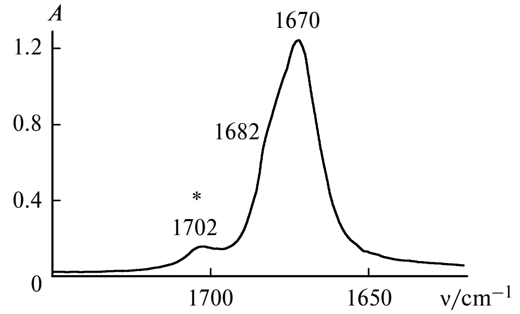

Fig. 4. Region of Amide-1 vibration in the IR spectrum of a dilute solution of ε-caprolactam in CCl$_4$. The overtone or combination tone band is asterisked.

Table 2. Scaled^a frequencies, IR band intensities (*I*), and potential energy distribution for ε-caprolactam monomer obtained from B3LYP/6-311++G(d,p) calculations

Experiment	Calculations		
$\nu_{gas}{}^b$/cm^{-1}	ν/cm^{-1}	$I \cdot 10^{-4}$ /cm mmol^{-1}	Potential energy distribution^c (%)
3442 w^d	3496	0.27	NH (99)
	3019	0.09	CH (92)
~2960 sh	2993	0.07	CH (90)
	2988	0.06	CH (76)
2938 s	2977	0.60	CH (98)
	2968	0.18	CH (95)
	2951	0.15	CH (96)
	2947	0.36	CH (89)
	2940	0.06	CH (94)
	2936	0.25	CH (83)
2869 m	2909	0.49	CH (94)
1712 vs^d	1692	4.63	C=O (76)
	1472	0.20	CH$_2$ (63) + NCH (14)

(*to be continued*)

Table 2 (*continued*)

Experiment	Calculations		
$\nu_{gas}{}^{b}$/cm^{-1}	ν/cm^{-1}	$I \cdot 10^{-4}$ /cm mmol^{-1}	Potential energy distribution^{c} (%)
1468 m	1465	0.16	CH_2 (63)
	1455	0.08	CH_2 (76)
	1445	0.31	CH_2 (40) + CNH (19) + CN (8) + C=O (5) + CCH (3)
	1436	0.09	CH_2 (64)
1438 m	1434	0.25	CH_2 (67)
	1376	0.19	CNH (25) + CN (12) + CC (7) + C=O (3) + CCH (17) + NCH (11)
	1358	0.03	CCH (72) + CC (16)
	1350	0.14	CCH (62) + CC (9) + NCH (6)
1356 m	1339	0.44	CCH (60) + CC (12) + CN (5) + NCH (5)
1305 m	1322	0.40	CCH (55) + CC (13) + CN (7) + NCH (6)
	1266	0.04	CCH (48) + CN (15)
	1245	0.01	CCH (70) + NCH (15)
	1212	0.05	CCH (41) +NCH (26)
1224 m	1210	0.47	CCH (53) + NCH (8) + CN (6) + CC (3)
1191 m	1183	0.21	CCH (60) + CC (11)
	1153	0.01	CCH (59) + NCH (20) + CN (4)
1121 w	1105	0.11	CC (50) + CN (21)
	1084	0.02	CCH (54) + NCH (8) + CC (9) + CN (4)
1076 w	1051	0.08	CC (42) + CN (16) + CCH (5)
980 w	993	0.03	CC (64)
958 w	962	0.06	CCH (60) + CN (3) + CC (2) + τ (2)
	943	0.02	CCH (48) + NCH (5) + CC (4) + χC=O (4)
873 w	888	0.05	CCH (48) + CC (15) + χC=O (4)
825 w	857	0.08	CC (57) + CN (5) + NCO (4)
	805	0.01	CC (46) + CCH (12) + χC=O (8)
	775	0.04	CCH (52) + CC (24) + τ (6)
	696	0.01	CC (31) + CN (21)
	650	0.40	χC=O (41) + ρNH (11)
581 w	593	0.25	CCH (30) + ρNH (12) + CN (13) + CNC (10) + τ (9) + CCN (5) + NCO (4) + χC=O (5) + CNH (3)
513 m	547	0.25	τ (26) + ρNH (11) + CCC (10) + χC=O (9)
	497	0.59	CCC (28) + χC=O (19) + τ (9) + ρNH (24)
	464	0.06	NCO (45) + CC (13) + CN (5) + CCC (6)
	341	0.04	CCN (38) + CCC (15)
	320	0.03	CCC (41) + NCO (5) + CCN (5) + τ (5)
	261	0.01	τ (43)
	235	0.01	τ (65) + ρNH (17) + CCC (7)
	235	0.01	τ(76) + CCC (8)
	127	0.01	τ(65) + ρNH (17)
	64	0.0	τ(44)

[a] Obtained with a scaling factor of 0.97.

[b] Notations of line intensities in the experimental spectrum: s is strong, m is medium, w is weak, v is very, and sh is shoulder.

[c] Notations of vibrations: τ is torsional skeletal vibration, ρ is out-of-plane bending vibration of the NH bond, and χ is out-of-plane bending vibration of the C=O bond.

[d] 3428 and 1682 cm^{-1} in the spectrum of a dilute (0.007 mol L^{-1}) solution in CCl_4.

indicates the interaction between the monomer and the solvent.

Vibrational spectrum and structure of ε-caprolactam dimer. The experimental and calculated vibrational frequencies of ε-caprolactam dimer are listed in Table 3. The frequencies were compared taking into account the assignment proposed earlier.[20] The scaled vibrational frequencies of the ε-caprolactam dimer obtained using a scaling factor of 0.97 are in good agreement with experimental data. The largest deviations from the experimental

Table 3. Scaled^a frequencies, IR band intensities (I), and potential energy distribution (PED) for ε-caprolactam dimer^b obtained from B3LYP/6-311++G(d,p) calculations

Experiment		Calculations		
$\nu_{solid}{}^c$ (cm^{-1})	$\nu_{solv}{}^d$ (cm^{-1})	ν/cm^{-1}	$I \cdot 10^{-4}$ /cm mmol^{-1}	Potential energy distribution (%)
3305	3302 m.sh	3224	19.76	N—H (96)
3224	3218 m.sh			
3081	3086 m.sh			
3190		3183	0.0	N—H (96)
		3027	0.23	C—H (99)
		3012	0.38	C—H (96)
2960 s		2982	1.63	C—H (86)
		2977	0.36	C—H (79)
2929 s		2967	1.36	C—H (90)
		2940	0.56	C—H (92)
		2936	0.40	C—H (92)
		2935	0.23	C—H (90)
2853 s		2919	1.05	C—H (78)
		2911	0.36	C—H (76)
1664 vs	1670 vs	1677	10.32	C=O (52) + C—N (10)
1636^e	1633^e	1646	0	C=O (42) + C—N (8) + δNH...O (13) + CNH (20)
1495^e	1495^e	1507	0	C=O (28) + δNH...O (28) + CNH (25) + δC=O...H (6)
1487 s	1485 m	1497	0.53	C=O (18) + δNH...O (28) + CNH (31) + δC=O...H (4)
		1469	0	CH$_2$ (50) + NCH (14)
1466 s	1470 m	1466	0.48	CH$_2$ (56)
1455 s	1450 sh	1457	0.15	CH$_2$ (65)
1443 s	1440 s	1448	0.21	CH$_2$ (69)
1428 m	1418 m	1439	0.51	CH$_2$ (72)
		1436	0.04	CH$_2$ (69)
1418 s	1412 s	1413	1.01	C—N (22) + CC (10) + CH$_2$ (16) + CCH (11)
1395 sh	1395 sh	1358	0.30	CCH (56) + NCH (10) + CC (7) + C—N (2)
1366 s	1372 s	1349	0.19	CCH (49) + NCH (8) + CC (9)
1351 sh	1356 sh	1345	0.33	CCH (64)+ CC (9)
1333 m	1340 m	1327	0.17	CCH (64) + CC (6)
1316 w	1320 w	1307	0.11	CCH (62)
1291 m	1290 m	1276	0.27	CCH (45) + NCH (26)
1257 m	1265 m	1248	0.18	CCH (56) + NCH (4)
1239 w	1238 w	1220	0.08	CCH (45) + NCH (18) + C—N (4) + CC (2)
1199 s	1209 s	1188	0.34	CCH (67) + C—N (4)
1169 vw	1165 vw	1148	0.04	CCH (50) + NCH (10)+ C—N (8)
1125 s	1130 s	1109	0.38	C—N (28) + CC (10) + CCH (6)
1087 m	1090 m	1069	0.08	CCH (34) + CC (26)
1021 w	1020 w	1060	0.05	CC (50) + C—N (9) + CCH (6)
		999	0.01	CC (27) + C—N (22) + CCH (15) + CCC (4)
983 m	985 m	965	0.18	CCH (35) + CC (13) + NCH (5) + CCC (3)
963 w	965 w	943	0.06	CCH (48) + CC (13) + CCC (4)
883 w	897 w	874	0.0	CCH (26) + CC (21) + CCN (2) + CCC (5) + χC=O (4)
824 s	825 m	856	0.86	ρNH (78)
		806	0	ρNH (75)
807 s	770 s	850	0.26	CC (42) + C—N (8) + ρNH (6) + CCH (22)
867 w	848 w	825	0.18	CCH (52) + τ (6) + χC=O (4)
848 sh		798	0.04	CC (56) + C—N (4) + CCH (4)
		795	0	CC (32) + ρNH...O (32)
693 w	695 m	725	0.04	CC (32) + C—N (6) + CCH (10) + τ (4) + χC=O (10)
		678	0.04	χC=O (36) + CC (8) + C—N (6)

(*to be continued*)

Table 3 (*continued*)

Experiment		Calculations		
$\nu_{\text{solid}}{}^{c}$	$\nu_{\text{solv}}{}^{d}$	ν/cm^{-1}	$I\cdot 10^{-4}$ /cm mmol^{-1}	Potential energy distribution (%)
cm^{-1}				
583 m	580 m	566	0.15	C—N (10) + CCN (8) + CNC (5) + NCO (8) + CNH (2) + CCN (5) + CCH (10) + χC=O (7)
506 s	505 s	490	0.71	CCO (44) + NCO (6) + CCH (4) + τ (4) + NH...O (10)
490 w	490 w	471	0.02	CCC (24) + CCN (5) + CCH (18) + χC=O (6)
399 m	398 m	379	0.11	CCN (19) + CCC (12) + τ (23) + ρNH (4)
338 w	323 m	326	0.00	τ (48) + CCC (20)
325 m		313	0.14	CCC (44) + χC=O (4) + CNH (8) + δCO...N (4)
259 w		232	0.03	τ (56) + CCC (10)
195 w		177	0.05	τ (48) + CCC (8)
		123	0	NH...O (82)
		111	0.0	τ (64)
		105	0.02	τ (71)
		74	0.13	NH...O (82)
		34	0.01	NH...O (46)+ τ (40)
		18	0.03	τ (60)

[a] Obtained with a scaling factor of 0.97.

[b] For notations of vibrations, see note to Table 1.[12,14,20]

[c] Data taken from the IR spectra of solid **1**.[18—20]

[d] Data taken from the IR spectra of a solution of compound **1** in CCl_4.

[e] Data taken from the Raman spectra of solid **1** and its aqueous solution.[22,23]

values are observed in the high-frequency region of highly anharmonic N—H and C—H vibrations. The formation of centrally symmetric ε-caprolactam dimer (Fig. 5) results in splitting of each monomer vibration into two vibrations, a Raman active vibration, which is symmetrical with respect to the center of symmetry of the dimer, and an IR active antisymmetrical vibration. In most cases the symmetrical and antisymmetrical vibrations have nearly equal frequencies except for the amide bond frequencies, namely, the νNH (~3220 cm^{-1}), Amide-I (~1670 cm^{-1}), Amide-II (~1500 cm^{-1}), and Amide-IV (ρNH ~800 cm^{-1}) frequencies in the spectrum of ε-caprolactam dimer. The splitting between the Raman active and IR active components can be as high as 50 cm^{-1} for the Amide-IV mode. The frequencies and intensities of the IR active modes of ε-caprolactam dimer and the corresponding frequencies of the Raman active modes are listed in Table 3. The experimental frequencies of the Raman active amide modes were taken from the Raman spectra of solid compound **1** [22] and its aqueous solution.[23]

Effect of dimerization on the IR spectrum of ε-caprolactam. The calculated equilibrium structure of the

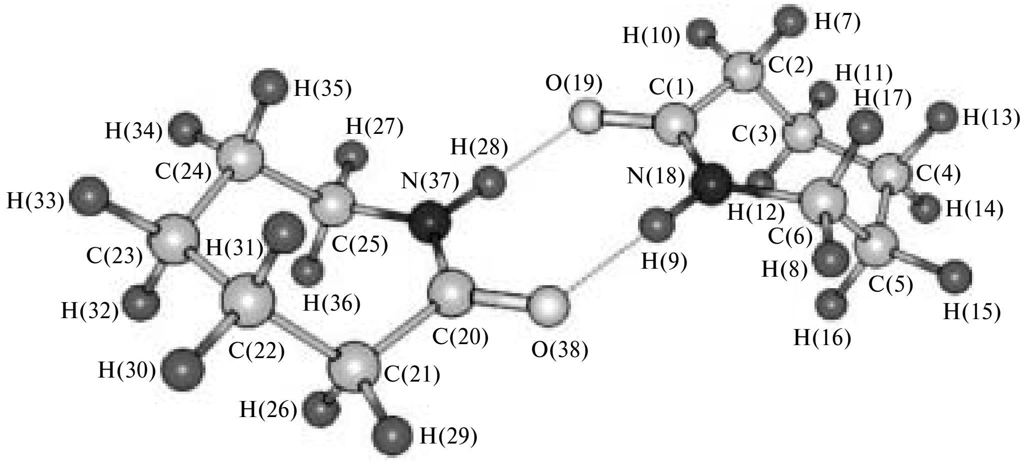

Fig. 5. Calculated structure of ε-caprolactam dimer.

ε-caprolactam dimer is shown in Fig. 5. Selected bond lengths, bond angles, and torsion angles are listed in Table 1. In the dimer the seven-membered rings retain the chair conformation. The geometric parameters of isolated molecule **1** and of the monomer unit in the dimer are very similar except for the amide bond parameters. On going from monomer to the dimer the C=O and N—H bond lengths increase from 1.230 to 1.246 Å and from 1.012 to 1.029 Å, respectively, the C—N bond is shortened from 1.368 down to 1.350 Å, and the C—N—H angle changes from 113.6 to 115.9°. Other bond angles and torsion angles change by at most one degree, which indicates a sufficient rigidity of the seven-membered ring of molecule **1**. A similar conclusion was also drawn in an X-ray study[24] on the crystal structure of a molecular complex of **1** with 4-chlororesorcin.

Though the calculated and experimental N—H bond lengths in the ε-caprolactam dimer differ by 0.03 Å (1.029 *vs.* 1.06 Å), the computed N....O hydrogen bond length (2.895 Å) nearly coincides with the experimental values (2.89—2.90 Å,[9,10] see Table 4). A comparison of the data listed in Tables 2 and 3 shows that dimerization strongly influences the vibrational frequencies and band intensities of the amide bonds. The pattern of changes in the IR spectrum is characteristic of the formation of intermolecular H-bonds N—H...O. The calculated and experimental spectral characteristics of the H-bond in the ε-caprolactam dimer are listed in Table 5. According to calculations, dimerization causes a decrease in the νNH frequency by 272 cm^{-1} and the νNH band becomes nearly 69 times more intense than the corresponding band in the IR spectrum of the monomer. Indeed, the IR spectrum of a solution of compound **1** in CCl_4 exhibits a weak narrow νNH band of the monomer at 3427 cm^{-1} (intensity $I = 0.52 \cdot 10^4$ cm mmol^{-1})[12] and broad νNH bands of the dimer with an integrated intensity I of $5.6 \cdot 10^4$ cm mmol^{-1} at lower frequencies.[12] The νNH bands in the IR spectra of ε-caprolactam dimer in solutions and in the solid phase have complex shapes in which one can distinguish three broad components with maxima at 3302, 3218, and 3086 cm^{-1}. The complex νNH band structure is a Fermi resonance band;[14] therefore, in Table 5 we present the frequency of the center of gravity of this band. The calculated shift of the νNH frequency (272 cm^{-1}) upon the formation of the N—H...O bond is close to the experimental value (247 cm^{-1}), whereas theoretical intensification ($I_{\text{dimers}}/I_{\text{monomer}}$) of the ν(NH) IR band much exceeds that observed experimentally (by nearly 70 times *vs.* 11 times, respectively).

Table 4. Calculated and experimental bond lengths and bond angles of the peptide bond in ε-caprolactam monomer and dimer

Parameter	Monomer Calculations	Dimer	
		Calculations	Experiment
Bond length		d/Å	
C(6)—N	1.462	1.461	1.470[a], 1.466[b]
C(1)—C(2)	1.524	1.522	1.513, 1.515
C=O	1.230	1.246	1.250, 1.250
C(1)—N	1.369	1.350	1.340, 1.331
N—H	1.012	1.029	1.06
N...O	—	2.89	2.90, 2.89
Bond angle		ω/deg	
H—N—C(1)	113.6	115.9	122(2)
N—C(1)—O	120.8	121.5	120.9, 121.0

[a] Data taken from Ref. 9.

[b] Data taken from Ref. 10.

Table 5. Spectral characteristics of hydrogen bond in ε-caprolactam dimer

Characteristic	Experiment			Calculations	
	Monomer		Dimer[a]	Monomer	Dimer
	GP[a]	Solution[b]			
Frequency			ν/cm^{-1}		
νNH	3442	3428	3180[c]	3496	3224
νC=O	1712	1682	1670	1693	1677
νNH...O					74
		$\Delta\nu = \nu_{\text{monomer}} - \nu_{\text{dimer}}$			
ΔνNH		247		272	
ΔνC=O		12		16	
Intensity		$I \cdot 10^{-4}$/cm mol^{-1}			
I(NH)		0.52[12]	5.6[12]	0.27	18.76
I(C=O)				4.63	10.32
		$\Gamma = I_{\text{dimer}}/I_{\text{monomer}}$			
Γ(NH)		10.8		69.5	
Γ(C=O)				2.2	

[a] Gas phase.

[b] A soluiton in CCl_4.

[c] For ε-caprolactam dimer we present the frequency of the center of gravity of the complex νNH band.

The calculated 16 cm^{-1} low-frequency shift of the intense Amide-I band of the ε-caprolactam dimer at 1670 cm^{-1} with respect to the monomer band is close to the experimental value (12 cm^{-1}), the calculated band intensity being increased by a factor of 2.2; this is close to the increase in the νC=O band intensities by 1.5 times upon dimerization of carboxylic acids.[13] The coupling degree of this mode is also changed. Indeed, the Amide-I mode of the monomer of **1** is well localized with a 76% contribution of the C=O mode, whereas for the dimer this mode is coupled with the C—N stretching and C—N—H bending modes.

The behavior of the Amide-II mode upon dimerization is worth noting. The corresponding vibrational frequency in the IR spectrum of the dimer is observed at ~1500 cm^{-1}, the Amide-II mode being a coupled mode with a 31% contribution of the C—N—H bending mode and a 18% contribution of the C=O stretching mode. This band is shifted to 1445 cm^{-1} in the spectrum of *N*-deuterated compound **1**.[20] The IR spectrum of the monomer exhibits two low-frequency bands at 1376 cm^{-1} and 1445 cm^{-1} that can be assigned to Amide-II modes. Both of them are coupled modes with a nearly 20% contribution of the C—N—H bending mode and certain contributions of the C—C—H and H—C—H bending modes and the C—N and C=O stretching modes. Even stronger coupled is the Amide-III mode with predominant contribution of the C—N mode. The corresponding band is observed near 1290 cm^{-1} in the spectra of secondary amides.[21] The C—N stretching modes make contributions from 15 to 20% to the vibrations at 1413, 1109, and 999 cm^{-1} in the IR spectrum of the dimer and to the vibrations at 1376, 1266, 1105, 696, and 593 cm^{-1} in the IR spectrum of the ε-caprolactam monomer. The out-of-plane bending vibration ρNH (Amide-IV) of the ε-caprolactam dimer at 856 cm^{-1} with a calculated intensity of 0.86 cm $mmol^{-1}$ is well localized (78%). Indeed, the IR spectrum of solid compound **1** exhibits a broad, rather intense band at 820 cm^{-1}, which is low frequency shifted to 710 cm^{-1} in the spectrum of *N*-deuterated compound **1**.[20] As should be expected upon breaking the N—H...O bond, the ρNH modes are shifted to lower frequencies (650—500 cm^{-1}) in the spectrum of ε-caprolactam monomer, being strongly coupled.

The IR spectra of ε-caprolactam dimer recorded in the solid phase and in CCl_4 solution exhibit an intense band near 500 cm^{-1} assigned[20] to the in-plane bending vibration δC=O. The results of our calculations confirmed this assignment. Noteworthy is that the out-of-plane vibration χC=O (the case in point is the plane of centrally symmetric dimer $(NH...O=C)_2$) is characterized by a higher frequency (~690 cm^{-1}). The corresponding vibrational frequencies in the IR spectrum of ε-caprolactam monomer are nearly 40 cm^{-1} lower (464 and 650 cm^{-1}, respectively).

Calculation of the enthalpy of dimerization of ε-caprolactam. The enthalpy of hydrogen bond in the ε-caprolactam dimer was calculated by the B3LYP method using the computed enthalpies of ε-caprolactam dimer and monomer following a known procedure.[4a]*

The enthalpy of dimerization of compound **1** at room temperature ($\Delta H_{298}/2$) was calculated per N—H...O hydrogen bond using the relationship

$$\Delta H_{298}/2 = (H_{\text{dimer}} - 2H_{\text{monomer}})/2 =$$
$$= -(730.397710 - 2 \cdot 365.189408)/2 = -0.0094 \text{ hartree} =$$
$$= -\ 5.93 \text{ kcal mol}^{-1}.$$

The dimer and monomer enthalpies (H_{dimer} and H_{monomer}, respectively) at 298 K were taken from the Gaussian-98 output listing. No BSSE correction was applied. The calculated enthalpy of the NH...O hydrogen bond (−5.93 kcal mol^{-1}) exceeds the value calculated according to Iogansen´s rule for ε-caprolactam dimer in CCl_4 solutions (−4.7 kcal mol^{-1})[12] by nearly 1.2 kcal mol^{-1}. Dimerization of compound **1** and, consequently, the ΔH value can be disturbed by the solvent (CCl_4) due to (i) the interaction between the solvent and molecule **1** and (ii) possible presence of not only cyclic dimers but also other associates in solutions. Because of this, the enthalpy of the H-bond in the dimer in solution is always lower than in the gas phase.[13,25] For instance, the experimental $\Delta H_{298}/2$ value for dimers of carboxylic acids in the gas phase (−7.0±0.5 kcal mol^{-1})[13,25,26] is 1.6 kcal mol^{-1} higher than that obtained for solutions of the same acids in CCl_4 (5.4±0.5 kcal mol^{-1}).[12,13] Thus, the calculated enthalpy of hydrogen bond in ε-caprolactam dimer, −5.93 kcal mol^{-1}, seems to be quite realistic.

Effect of the basis set on the results of calculations. The equilibrium structure, vibrational frequencies, IR band intensities, and the enthalpy of hydrogen bond were calculated with two basis sets, 6-31+G(d,p) and 6-311++G(d,p). (Listed in the text and in Tables 1—5 are the results obtained from calculations in the extended basis set 6-311++G(d,p).) A comparison of the results obtained in both basis sets showed that the size of the basis set has a little effect on the geometric and spectral parameters of the ε-caprolactam monomer and dimer but strongly overestimates the enthalpy of the hydrogen bond in the latter (−9.85 kcal mol^{-1} obtained with the 6-31+G(d,p) basis set).

$$\Delta H_{298}/2 = -(730.242557 - 2 \cdot 365.105576)/2 =$$
$$= -0.0314/2 = -\ 0.0157 \text{ hartree} = -9.85 \text{ kcal mol}^{-1}.$$

The enthalpy of hydrogen bond is calculated as a difference between two very large numbers; therefore, even a small difference in the enthalpies of the ε-caprolactam dimer and monomer computed with different basis sets has a strong (nearly twofold) effect on the results of calculations. Calculations in the extended basis set are more correct, as follows from the decrease in the corresponding numerical values. For instance, the enthalpy of ε-caprolactam dimer calculated with inclusion of thermal correction is −730.397710 (6-311++G(d,p) basis set) and −730.242557 hartree (6-31+G(d,p) basis set). Thus, the geometry and vibrational spectra of molecular complexes can be calculated using a standard basis set, whereas the energies of H-bonded complexes or the enthalpies of bonding should be calculated in the extended basis set augmented with polarization and diffuse functions.

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* The sources of errors in calculation of the enthalpy of H-bond including the basis set superposition error (BSSE) were also analyzed in that study.[4b]

Experimental

The spectrum of gaseous compound **1** in the spectral region 4000—400 cm^{-1} was measured in a tailor-made heated gas cell 10 cm long with KBr windows at ~80 °C and a pressure of ~10^{-2} Torr. Spectra of a solution of compound **1** in CCl_4 with subtraction of the solvent bands were measured at concentrations of 0.007 and 0.001 mol L^{-1} in a cell 3 mm thick in the spectral region 3400—3000 cm^{-1} and in a cell 1.2 mm thick in the spectral region 1700—1500 cm^{-1}. The spectra were measured on a Magna IR 750 IR Fourier spectrometer (Nicolet, USA) with a 2 cm^{-1} resolution.

ε-Caprolactam (GOST 7850-74) was twice recrystallized from anhydrous benzene, dried, and stored in a vacuum desiccator at 40 °C (3 Torr); m.p. 68.5—69 °C.

Deconvolution of the shape of the Amide-I band was performed using the PE-GRAMS program assuming Lorentzian contours of spectral components.

Quantum-chemical calculations were carried out by the B3LYP method in the 6-31+G(d,p) basis set and in the 6-311++G(d,p) extended basis set using the "Gaussian-98" program suite.[2] The starting geometry of ε-caprolactam monomer was optimized by the molecular mechanics method; the starting geometric parameters of ε-caprolactam dimer was taken as Cartesian atomic coordinates from the X-ray diffraction data for a single crystal of **1** at room temperature.[9] All the computed frequencies were scaled using a scaling factor of 0.97. Normal coordinate analysis was carried out in Cartesian system. The results obtained were converted in the system of internal coordinates using the NCA99 program complex.[27]

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