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Vibrational Spectra of Ethyleneurea and Its *C,C′*- and *N,N′*-Deuterated Derivatives

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Infrared and Raman spectra of ethyleneurea and its *C,C′*- and *N,N′*-deuterated compounds have been measured. The fundamental frequencies have been assigned by referring to isotopic frequency shifts and Raman depolarization ratios. A normal coordinate analysis has been carried out for the infrared active vibrations of a planar C_{2v} molecular model. A Urey-Bradley potential function supplemented by valence type constants for the out-of-plane deformation and the torsional coordinates has been used. The calculated frequencies based on a refined set of force constants agree well with the observed.

As a part of our serial studies on the vibrational spectra and the force field of urea derivatives,[1,2] the present work has been undertaken to deal with the infrared and Raman spectra of ethyleneurea and its *C,C′*- and *N,N′*-deuterated derivatives. It has been known that the group vibrations of monosubstituted amides, R-CONH-R′, are quite sensitive to the relative positions of the CO and the NH bonds.[3] The CN stretching and the NH in-plane deformation vibrations in the *trans* structure couple appreciably with each other, giving rise to the characteristic amide II and III frequencies, while those in the *cis* structure do not. An analogous coupling has been found for *N*-alkyl- and *N,N′*-dialkylureas which have at least one NH bond at the *trans* position of the CO bond.[4] In this respect, the behavior of the CN stretching and the NH in-plane deformation vibrations in the absence of the *trans* –CONH– structure in ethyleneurea is of interest as a clue to the correlation between the vibrational spectra and the structure of urea derivatives.

Experimental

Materials. Ethyleneurea (EU-d_0) was obtained from Tokyo Kasei Co. and was recrystallized twice from ethanol and then once from ethylacetate. For the preparation of the *C,C′*-deuterated ethyleneurea (EU-d_4), 1 ml of ethylene glycol-d_4 (Merck AG., 99%) was heated gradually with *ca.* 4 g of urea from 150 to 240 °C during 4 h.[5] The resulting resinous solid was pyrolized at 240—270 °C under reduced pressure, and EU-d_4 was distilled from the solid as it decomposed. The crystallization from ethylacetate gave *ca.* 0.21 g of EU-d_4. No indication of the re-exchange of deuterium by hydrogen in this process was detected in the infrared and the Raman spectra of this sample. The *N,N′*-undeuterated compounds were converted into the corresponding *N,N′*-deuterated compounds (EU-d_2 and EU-d_6) by the exchange reaction with heavy water.

Measurements. The infrared spectra were recorded on a JASCO IR-A2 grating infrared spectrophotometer (4000—400 cm^{-1}). The measurements were made for Nujol and hexachlorobutadiene mulls, and the observed absorption frequencies were calibrated with the standard absorptions of indene, polystyrene and ammonia. The Raman spectra were recorded on a JEOL S-1 laser Raman spectrophotometer by using the excitation line 488.0 nm of a Coherent 52G Ar^+ laser. The measurements were made for fine crystalline powder sealed in 1 mm capillary tubes, and the observed Raman frequencies were calibrated with the spontaneous emission lines of the Ar^+ laser. The depolarization measurements were made for the aqueous solutions of EU-d_0 and EU-d_4 and for the solutions of EU-d_2 and EU-d_6 in heavy water. The spectral slitwidth was 12.7 cm^{-1} for all the measurements.

The infrared spectra are shown in Figs. 1 and 2, and the Raman spectra in Figs. 3 and 4. The observed frequencies are listed in Table 1 together with approximate band intensities and assignments.

Vibrational Assignments

The crystal structure of ethyleneurea has not been determined to date. We may assume, however, that ethyleneurea takes the planar C_{2v} configuration in the crystal, since the X-ray analysis has shown that an analogous compound, ethylenethiourea, takes approximately this configuration.[6] On this assumption, EU-d_0 and its deuterated compounds should contain 30 normal vibrations which are classified as $10a_1+5a_2+6b_1+9b_2$.

In the infrared spectrum, the NH stretching band of EU-d_0 appears as a doublet but that of EU-d_4 does not. Contrarily, the ND stretching band splits for EU-d_6 but not for EU-d_2. This result indicates that the splittings observed for EU-d_0 and EU-d_6 can be attributed neither to the presence of two NH or ND bonds nor to the crystal field splitting but to anharmonic resonances. Possible candidates of the summation tones participating mainly in the weaker components of the doublets are $1423+2\times991$ (or $1376+991+1041$)≈3415 cm^{-1} for EU-d_0 and $1243+1169\approx2415$ cm^{-1} for EU-d_6.

In the Raman spectra of EU-d_0 and EU-d_2 in aqueous solution, two strong and polarized bands appear at 3005 and 2908 cm^{-1}. These bands are attributed to the a_1 CH_2 stretching vibration and the overtone of the a_1 CH_2 bending vibration involved in a Fermi resonance. Similarly, aqueous solutions of EU-d_4 and EU-d_6 show two strong Raman bands at 2185 and 2145 cm^{-1} attributable to a resonance diad involving the a_1 CD_2 stretching vibration. The b_1 and the b_2 CH_2 stretching vibrations of EU-d_0 seem to give weak Raman bands at 2980 and 2915 cm^{-1}, respectively, observed only when the incident and the scattered lights are polarized perpendicularly to each other. These bands are hidden by the strong a_1 bands in the ordinary Raman spectrum.

The strong infrared band around 1660 cm^{-1} observed for EU-d_0 and EU-d_4 arises obviously from the C=O stretching vibration. The corresponding Raman band is polarized in the solution spectra as expected from the

Table 1. Observed frequencies (cm^{-1}) and assignments

IR	Raman		Assignments
Solid	Solid	Solution	
		EU-d_0	
3285 s	3310 m	—	νNH(a$_1$, b$_2$)
3000 sh	—	3005 s p	$2\times$b$_2\beta$CH$_2$(A$_1$)
—	—	2980 vw dp	νCH$_2$(b$_1$)
2960 m	2972 s	—	$2\times$a$_1\beta$CH$_2$(A$_1$)
—	—	2915 vw dp	νCH$_2$(b$_2$)
2900 m	2913 s	2908 s p	νCH$_2$(a$_1$)
1668 vs	1662 m	1665 w p	νCO+νCN(a$_1$)
1502 s	1522 m	—	βCH$_2$(b$_2$)
1485 m	1493 w	1495 vw	βCH$_2$(a$_1$)
1451 s	1450 vw	—	νCN(b$_2$)
1423 m	—	1420 sh	δNH(b$_2$)
—	1385 w	—	δNH(a$_1$)
1274 vs	—	—	ωCH$_2$(b$_2$)
1207 vw	1207 m	1215 w dp	ωCH$_2$(a$_1$), tCH$_2$(b$_1$)
1105 m	1112 w	1101 w p	νC′N(a$_1$)
1041 w	1045 m	—	νC′N(b$_2$)
991 vw	1000 s	1000 m p	νCN(a$_1$)
933 vw	934 vs	934 vs p	νC′C′(a$_1$)
768 m	—	—	πCO(b$_1$)
703 s	712 m	717 m p	δNCN+νC′N(a$_1$), πNH+τCN(b$_1$)
660 sh	—	—	δNC′C′+δCNC′(b$_2$)
511 m	502 w	—	δCO(b$_2$)
—	250 sh	230 vw dp	τCN+πNH(b$_1$)
		EU-d_4	
3303 vs	3300 w	—	νNH(a$_1$, b$_2$)
—	—	2250 w dp	νCD$_2$(b$_1$)
2215 w	2230 s	2185 m p	$2\times$b$_2\omega$CD$_2$(A$_1$)
—	2140 vs	2145 s p	νCD$_2$(a$_1$)
2125 w	—	—	νCD$_2$(b$_2$)
2090 sh	2100 vw	2120 sh p	$2\times$a$_1\nu$CN(A$_1$)
1660 vs	1654 w	1665 w p	νCO+νCN(a$_1$)
1425 s	—	—	νCN(b$_2$), δNH(b$_2$)
1377 m	1376 m	1360 vw	δNH(a$_1$)
1176 m	—	1175 vw	βCD$_2$+νC′N(b$_2$)
1145 vw	1140 m	1130 w p	βCD$_2$(a$_1$)
1122 w	—	—	νC′N+νC′C′(a$_1$)
1088 m	1082 sh	1090 sh dp	ωCD$_2$(b$_2$)
1053 w	1069 m	1070 m p	νCN(a$_1$)
924 m	928 vs	925 vs p	νC′C′+νCN(a$_1$)
901 w	—	—	ωCD$_2$(b$_2$), tCD$_2$(b$_1$)
785 sh	791 m	787 w p	ωCD$_2$+νC′C′(a$_1$)
771 m	—	—	πCO(b$_1$)
688 s	703 w	707 w p	δNCN+νC′N(a$_1$), πNH+τCN(b$_1$)
660 sh	—	—	ρCD$_2$(b$_1$)
619 vw	595 vw	—	δNC′C′+δCNC′(b$_2$)
503 m	490 vw	490 w	δCO(b$_2$)
—	225 vw	—	τCN+πNH(b$_1$)

IR	Raman		Assignments
Solid	Solid	Solution	
		EU-d_2	
3000 vw	—	3005 s p	$2\times$b$_2\beta$CH$_2$(A$_1$)
—	—	2980 vw dp	νCH$_2$(b$_1$)
2955 m	2972 m	—	$2\times$a$_1\beta$CH$_2$(A$_1$)
—	—	2915 vw dp	νCH$_2$(b$_2$)
2900 sh	2913 vs	2908 s p	νCH$_2$(a$_1$)
2460 s	2487 w	—	νND(a$_1$, b$_2$)
1652 vs	1647 m	1645 m p	νCO+νCN(a$_1$)
1502 s	1522 m	—	βCH$_2$(b$_2$)
1485 m	1494 m	1498 m p	βCH$_2$(a$_1$)
1445 s	1438 w	1445 w dp	νCN(b$_2$)
1274 vs	1273 w	—	ωCH$_2$(b$_2$)
1250 sh	—	—	ωCH$_2$+δND(a$_1$)
1202 vw	1209 vw	1210 vw p	ωCH$_2$(a$_1$), tCH$_2$(b$_1$)
1178 m	1190 sh	—	δND+νC′N(b$_2$)
1017 vw	1025 m	1015 w dp	νC′C′+νC′N(a$_1$)
925 vw	933 vs	939 vs p	νCN+νC′C′(a$_1$)
897 vw	908 m	—	δND+νC′N(b$_2$), ρCH$_2$(b$_1$)
850 vw	875 sh	—	δND+νC′C′(a$_1$)
764 s	—	—	πCO(b$_1$)
694 s	693 s	695 m p	δNCN+νC′N(a$_1$)
650 sh	—	—	δNC′C′+δCNC′(b$_2$)
510 sh	—	—	πND+τCN(b$_1$)
497 s	—	—	δCO(b$_2$)
—	250 vw	230 w dp	τCN+πND(b$_1$)
		EU-d_6	
2472 s	2513 w	—	νND(a$_1$, b$_2$)
—	—	2250 w dp	νCD$_2$(b$_1$)
2213 m	2230 s	2185 m p	$2\times$b$_2\beta$CD$_2$(A$_1$)
—	2143 m	2145 s p	νCD$_2$(a$_1$)
2125 w	—	2135 vw dp	νCD$_2$(b$_2$)
2088 w	2098 m	2105 w p	$2\times$b$_2\omega$CD$_2$(A$_1$)
1637 vs	1636 m	1640 m p	νCO+νCN(a$_1$)
1410 vs	1420 vw	—	νCN(b$_2$)
1243 m	1248 w	1242 m p	δND+νC′N(a$_1$)
1169 m	1165 vw	1165 vw	νC′N+δND(b$_2$)
1134 vw	1130 m	1120 m p	βCD$_2$+νC′C′(a$_1$)
1098 m	1089 m	1087 m dp	βCD$_2$(b$_2$), νC′N(a$_1$)
1051 m	—	—	ωCD$_2$(b$_2$)
911 sh	928 s	928 vs p	νCN(a$_1$)
901 w	—	—	tCD$_2$(b$_1$)
850 vw	863 m	862 m p	δND+ωCD$_2$(a$_1$)
830 w	840 m	835 sh dp	ωCD$_2$+δND(b$_2$)
—	786 m	778 w p	ωCD$_2$+νC′C′(a$_1$)
766 m	740 vw	—	πCO(b$_1$)
689 m	687 s	690 s p	δNCN+νC′N(a$_1$)
650 sh	—	—	ρCD$_2$(b$_1$)
595 w	592 vw	—	δNC′C′+δCNC′(b$_2$)
505 sh	—	—	πND+τCN(b$_1$)
491 s	475 vw	485 vw	δCO(b$_2$)
—	225 sh	210 vw	τCN+πND(b$_1$)

a) vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. b) p, polarized; dp, depolarized. c) ν, stretching; β, bending; ω, wagging; t, twisting; ρ, rocking; δ, in-plane deformation; π, out-of-plane deformation; τ, torsion.

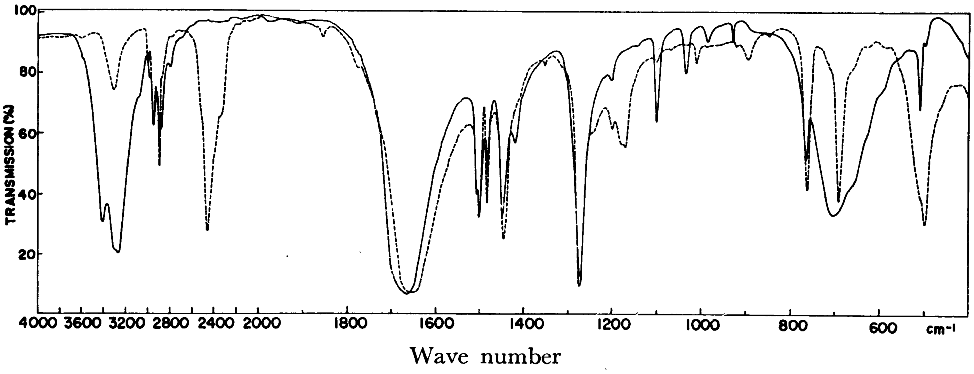

Fig. 1. Infrared spectra of EU-d_0 (——) and EU-d_2 (----).

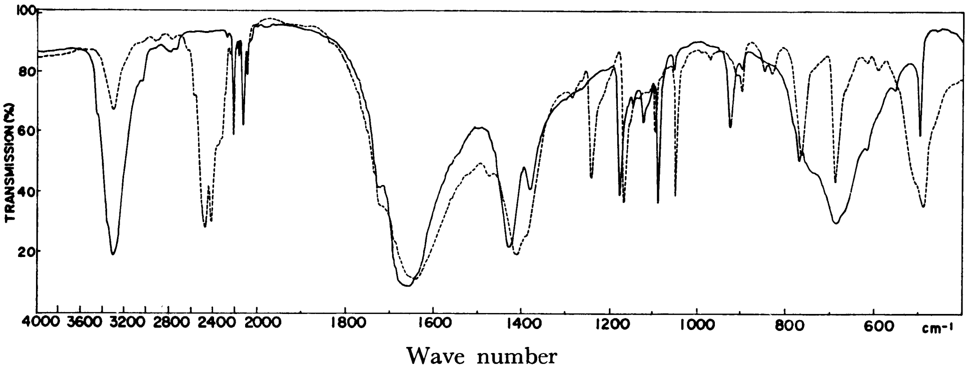

Fig. 2. Infrared spectra of EU-d_4 (——) and EU-d_6 (----).

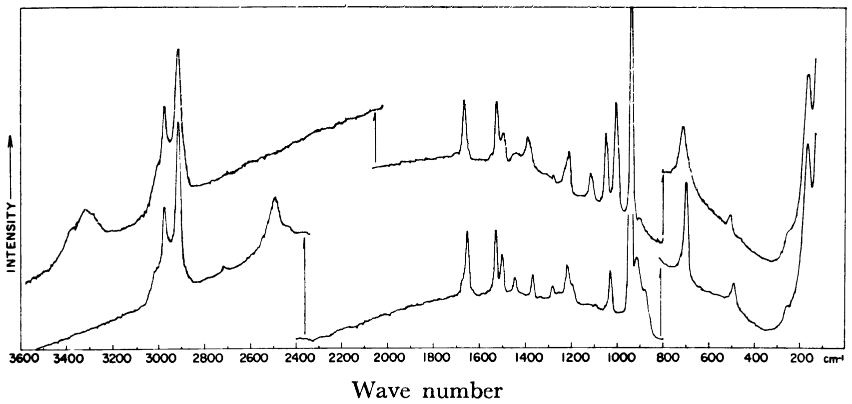

Fig. 3. Raman spectra of EU-d_0 (above) and EU-d_2 (below).

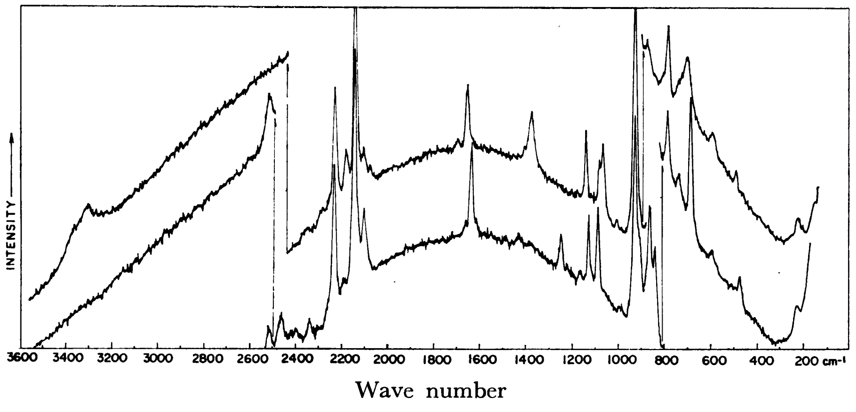

Fig. 4. Raman spectra of EU-d_4 (above) and EU-d_6 (below).

assignment. A slight low-frequency shift was observed for this band on the *N,N′*-deuteration, revealing a small coupling between the C=O stretching and the a_1 NH in-plane deformation vibrations.

In the infrared and Raman spectra of EU-d_0 and EU-d_2, the bands due to the CH_2 bending vibrations around 1500 cm^{-1} and those due to the CH_2 wagging vibrations around 1270 and 1200 cm^{-1} were easily assigned because they disappeared on the *C,C′*-deuteration. According to the normal coordinate analysis, the b_1 CH_2 twisting vibration may also contribute to the bands around 1200 cm^{-1}. The infrared and the Raman bands due to the CH_2 rocking vibrations of EU-d_0 and EU-d_2, and those due to the CD_2 bending, wagging, twisting and rocking vibrations of EU-d_4 and EU-d_6 were not obvious and we picked them up tentatively by referring to the calculated frequencies for the initial force constants.

In contrast to the cases of methylurea[2,7] and *N,N′*-dimethylurea,[8] EU-d_0 and EU-d_4 show no infrared bands in the region between 1550 and 1510 cm^{-1} where the amide II frequency is expected. Instead, EU-d_0 shows a strong infrared band at 1451 cm^{-1}, which persists on the *N,N′*-deuteration with a small low-frequency shift, and a weak band at 1423 cm^{-1} which disappears on the *N,N′*-deuteration. From analogy with urea[1,9] and *cis*-monosubstituted amides,[3,10] the 1451 cm^{-1} and the 1423 cm^{-1} bands are assigned to the CN stretching and the NH in-plane deformation vibrations, respectively, in the b_2 species. The a_1 NH in-plane deformation vibration is thought to give rise to the Raman band at 1385 cm^{-1}. For EU-d_4, the infrared absorptions due to the CN stretching and the NH in-plane deformation vibrations in the b_2 species seem to overlap at 1425 cm^{-1}, and the a_1 NH in-plane deformation band appears around 1377 cm^{-1} both in the infrared and the Raman spectra. For EU-d_2, and EU-d_6, the a_1 and the b_2 ND in-plane deformation vibrations are likely to contribute to the Raman band around 900 cm^{-1} and the infrared band around 1200 cm^{-1}, respectively. A weak Raman band was observed at 1360 cm^{-1} for EU-d_2 but was left unassigned since no fundamental frequencies were expected around this frequency.

In the infrared spectrum, EU-d_0 shows four bands at 1105, 1041, 991, and 933 cm^{-1} attributable to the skeletal stretching vibrations. From intensities and depolarization ratios of the corresponding Raman bands, the 1105, 991, and 933 cm^{-1} bands are assigned to the a_1 species and the 1041 cm^{-1} band to the b_2 species. Shifts of these bands on the *N,N′*- and the *C,C′*-deuterations suggest that the skeletal stretching vibrations couple complicatedly with the CD_2 and the ND deformation vibrations. Particularly, one of the a_1 skeletal stretching vibrations couples strongly with the a_1 ND in-plane deformation vibration, and gives rise to an infrared band around 1240 cm^{-1} for EU-d_2 and EU-d_6.

TABLE 2. PRODUCT AND SUM RULES

Product rule[a)]		d_0/d_2	d_0/d_4	d_0/d_6
a_1	theor.	1.975	2.761	5.458
	obsd[b)]	1.988	2.626	5.304
b_2	theor.	1.934	2.653	5.139
	obsd[b)]	1.957	2.609	5.249
b_1	theor.	1.396	2.625	3.665
	obsd[b)]	1.394[c)]	2.683	3.678

Sum rule[d)]	$\Delta\lambda(d_0-d_2)$	$\Delta\lambda(d_4-d_6)$	$\Delta\lambda(d_0-d_4)$	$\Delta\lambda(d_2-d_6)$
a_1[b)]	3.443	3.434	3.290	3.294
b_2[b)]	3.452	3.493	3.356	3.385
b_1[b)]	0.150[c)]	0.133		

a) $d_i/d_j=\Pi\nu(\text{EU-}d_i)/\Pi\nu(\text{EU-}d_j)$. b) The observed frequencies in Table 5 were used. c) The unobserved fundamental frequency in the b_1 species was replaced by the calculated frequency, 898 cm^{-1}. d) $\Delta\lambda(d_i-d_j)=10^{-5}\times 4\pi^2c^2\{\sigma(\text{EU-}d_i)-\sigma(\text{EU-}d_j)\}/N$ (10^{-5} s^{-2}), where c is the velocity of light and N is the Avogadro number.

In the Raman spectrum between 800 and 400 cm^{-1}, EU-d_0 shows two bands at 712 and 502 cm^{-1} which persist on both the *N,N′*- and the *C,C′*-deuterations without large frequency shifts. Based on the depolarization ratio, the 712 cm^{-1} and the 502 cm^{-1} bands were assigned to skeletal vibrations in the a_1 and the b_2 species, respectively. In the infrared spectra, the corresponding bands around 700 cm^{-1} of EU-d_0 and EU-d_4 and around 500 cm^{-1} of EU-d_2 and EU-d_6 are markedly broadened and intensified by overlapping absorptions due to the NH and the ND out-of-plane deformation vibrations, respectively, in the b_1 species. EU-d_0 shows an infrared band at 768 cm^{-1} which is almost insensitive to both the *N,N′*- and the *C,C′*-deuterations and is assigned to the C=O out-of-plane deformation vibration. The weak Raman band at 250 cm^{-1} of EU-d_0 and EU-d_2 is depolarized in the solution spectra and shifts to 225 cm^{-1} on the *C,C′*-deuteration. This band is thus assigned reasonably to the b_1 skeletal torsional vibration. Throughout whole the investigated region of infrared and Raman spectra, no bands assignable to the a_2 species are observed for any of EU-d_0, EU-d_2, EU-d_4, and EU-d_6.

In order to check isotopic consistency in the assignment, the product rule[11] and the sum rule[12] were applied to the observed fundamental frequencies after correcting a few for anharmonic resonances. The results are given in Table 2. Denoting the sum of the squared frequencies of the isotope A over the species Γ by $\sigma(\text{A}, \Gamma)$, we may write the sum rule relations as

$$\sigma(\text{EU-}d_0, a_1) - \sigma(\text{EU-}d_2, a_1) = \sigma(\text{EU-}d_4, a_1) - \sigma(\text{EU-}d_6, a_1)$$

and similar expressions for the b_2 and the b_1 species. According to the modified sum rule for symmetrical isotopic molecules,[13] one more independent relation

$$\sigma(\text{EU-}d_0, a_1) - \sigma(\text{EU-}d_2, a_1) = \sigma(\text{EU-}d_0, b_2) - \sigma(\text{EU-}d_2, b_2)$$

holds provided that the force field includes no interaction terms between the two NH groups, and similarly we have

$$\sigma(\text{EU-}d_0, a_1) - \sigma(\text{EU-}d_4, a_1) = \sigma(\text{EU-}d_2, b_2) - \sigma(\text{EU-}d_6, b_2)$$

in the absence of interaction terms between the two

CH_2 groups. In support of the assignments, all these relations are satisfied fairly well by the observed frequencies.

Normal Coordinate Analysis

Based on the assumed symmetry of the point group C_{2v}, the ***G*** matrices were set up by using structure parameters transferred from the crystallographic data for urea[14] and ethylenethiourea,[6] the former being referred to only with respect to the C=O bond-length. They are shown in Fig. 5. The tetrahedral redundancy around each CH_2 group was eliminated analytically by introducing an orthogonal set of local symmetry coordinates.[15] The out-of-plane vibrations of the -NHCONH- group were described by the NH and the CO out-of-plane deformation coordinates and the internal rotation coordinates[16] around the C–N and the N–C′ bonds (Table 3). The redundant coordinates associated with the ring (2 in a_1, 1 in b_2 and 2 in b_1) were eliminated numerically on diagonalizing the ***G*** matrices.[17]

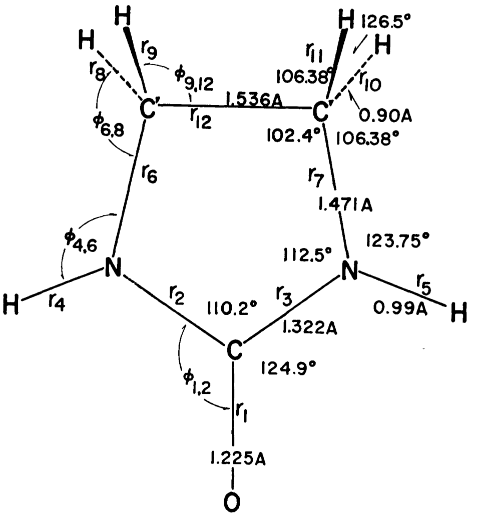

Fig. 5. Structural parameters and internal coordinates.

TABLE 3. OUT-OF-PLANE INTERNAL COORDINATES OF THE -NHCONH- GROUP

Coordinate	description[a)]
$S_1=\Delta\pi_1$[b)]	πCO
$S_2=\Delta\pi_4$[b)]	πNH
$S_3=\Delta(\tau_{124}+\tau_{126}+\tau_{324}+\tau_{326})/4$	τCN
$S_4=\Delta\sum_{j=8,9,12}(\tau_{46j}+\tau_{26j})/6$	τNC′
$S_5=\Delta\pi_5$[b)]	πNH
$S_6=\Delta(\tau_{135}+\tau_{137}+\tau_{235}+\tau_{237})/4$	τCN
$S_7=\Delta\sum_{j=10-12}(\tau_{57j}+\tau_{37j})/6$	τNC′

a) See footnote c), Table 1. b) The out-of-plane deformation coordinates were defined to be positive when the end atoms (O for S_1 and H for S_2 and S_5) move toward the observer from the plane of Fig. 5.

A simple Urey-Bradley force field including 25 force constants was employed for the a_1 and the b_2 vibrations. The initial values of the force constants were transferred from methylurea.[2] On refining the force constants, the observed frequencies were mostly taken from the infrared data. In the first step of the refinement, the stretching and the bending constants were adjusted by referring to the Jacobian matrix elements, and then by the least squares method in which K(NH) and K(CH) were fixed. In the next step, the stretching and the bending constants were fixed at the final values in the above process, and the repulsion constants were refined by the least squares method. Finally, the force constants except K(NH), K(CH), H(NC′C′) and F(HC′H) were refined by the least squares method, the last two being fixed because of large uncertainties.

The potential function for the b_1 vibrations was written as the sum of a simple Urey-Bradley type force field for the CH_2 group and a valence type force field for the torsional and the out-of-plane deformation vibrations. The values of the Urey-Bradley type constants were transferred from the converged set obtained in the treatment of the a_1 and the b_2 vibrations. The values of the diagonal constants were taken initially to be the observed frequency parameters divided by the corresponding ***G*** matrix elements for EU-d_0. These diagonal constants were adjusted first by referring to the Jacobian matrix elements and then by the least squares method. The off-diagonal constants $f(\pi$NH, τC′N) and $f(\pi$NH, πCO), were then added with the initial values zero, and all the constants were refined by the least squares method.

TABLE 4. FORCE CONSTANTS

Urey-Bradly type constants (in mdyn/Å)							
K(NH)	5·50	K(CH)	4.44	K(CN)	$5.059_0(0.127_8)$[a)]	K(NC′)	$2.734_0(0.172_5)$
K(C′C′)	$2.307_0(0.170_8)$	K(C=O)	$5.892_0(0.444_3)$	H(HC′H)	$0.382_1(0.006_3)$	H(C′C′H)	$0.201_4(0.028_2)$
H(NC′H)	$0.175_7(0.037_7)$	H(NC′C′)	0.308_1	H(C′NH)	$0.200_6(0.046_3)$	H(CNH)	$0.275_8(0.070_0)$
H(CNC′)	$0.092_9(0.091_8)$	H(NCN)	$1.108_0(0.271_7)$	H(NCO)	$0.171_3(0.060_3)$	F(HC′H)	0.084_7
F(C′C′H)	$0.340_2(0.031_3)$	F(NC′H)	$0.482_4(0.041_8)$	F(NC′C′)	$0.421_0(0.084_2)$	F(C′NH)	$0.358_0(0.079_7)$
F(CNH)	$0.492_0(0.141_2)$	F(CNC′)	$0.849_0(0.277_4)$	F(NCN)	$0.669_0(0.216_0)$	F(NCO)	$1.644_0(0.186_8)$
κ(C′)	$0.013_6(0.033_9)$ mdyn Å						
Valence type constants (in mdyn Å/rad²)[b)]							
$f(\pi$NH, πNH)	$0.123_4(0.022_2)$[a)]	$f(\tau$NC′, τNC′)	$0.046_8(0.033_0)$	$f(\pi$CO, πCO)	$0.796_1(0.014_4)$		
$f(\tau$CN, τCN)	$0.473_9(0.077_2)$	$f(\pi$NH, τNC′)	$0.034_0(0.013_2)$	$f(\pi$NH, πCO)	$0.081_3(0.008_1)$		

a) ( ); dispersion. b) The relevant internal coordinates are shown in the parentheses; π, out-of-plane deformation coordinate; τ, internal rotation coordinate.

Table 5. Fundamental frequencies of ethyleneurea and its deuterated derivatives

	$(CH_2NH)_2CO$		$(CH_2ND)_2CO$		$(CD_2NH)_2CO$		$(CD_2ND)_2CO$	
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
a_1	3303[a]	3299	2900	2916	3303	3299	2460[b]	2415
	2900	2915	2460	2415	2125	2096	2125	2096
	1668	1669	1652	1645	1660	1667	1637	1643
	1485	1496	1485	1494	1377	1375	1243	1239
	1385	1376	1250	1261	1145	1146	1134	1135
	1207	1212	1202	1187	1122	1123	1098	1093
	1105	1111	1017	1022	1053	1049	911	905
	991	1000	925	929	924	910	850	862
	933	928	850	857	785	787	786	783
	703	703	694	697	688	685	689	681
b_2	3303[a]	3296	2915	2925	3303	3296	2460[b]	2406
	2915	2925	2460	2406	2125	2110	2125	2110
	1502	1499	1502	1498	1425	1433	1410	1427
	1451	1438	1445	1430	1425	1417	1169	1201
	1423	1417	1274	1279	1176	1158	1098	1104
	1273	1277	1178	1177	1088	1073	1051	1050
	1041	1029	897	917	901	894	830	830
	660	653	650	643	619	620	595	612
	511	512	497	500	503	502	491	492
b_1	2980	3006	2980	3006	2250	2243	2250	2243
	1207	1160	1202	1160	901	852	901	852
		898	897	896	771	765	766	764
	768	770	764	769	688	707	650	664
	703	699	510	503	660	655	505	502
	250	243	250	243	225	231	225	230

a) The value for EU-d_4 was used as the unperturbed frequency. b) The value for EU-d_2 was used as the unperturbed frequency.

The final values of the force constants are listed in Table 4. The magnitudes of the stretching constants are reasonable in comparison with the corresponding constants of urea,[1,9] methylurea[2] and diketopiperazine,[17,18] being correlated well with the assumed bond-lengths. For the b_1 vibrations, both the diagonal and the off-diagonal force constants are of comparable magnitudes with the corresponding constants of methylurea.[2] The frequencies calculated from the final set of force constants are shown in Table 5. The agreement between the observed and the calculated frequencies is excellent throughout the four isotopic ethyleneureas.

It is well known for amide and urea derivatives containing a *trans* -CONH- group that the NH in-plane deformation and the CN stretching vibrations couple strongly with each other and give rise to the amide II and III bands in infrared spectra.[3,4] According to the present calculation, such a coupling does not occur for EU-d_0 and EU-d_4 which contain a -NHCONH- group in the *cis-cis* conformation (Table 1).

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