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Infrared Spectra of Acylureas and *NN'*-Deuterated Acylureas

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The infrared spectra of seven monoacylureas and their *NN'*-deuterated compounds have been measured in the region between 3600 and 450 cm^{-1}. A number of characteristic absorption bands of the $-CONHCONH_2$ and $-CONDCOND_2$ groups have been found and assigned by referring to the infrared spectra of related compounds and the isotopic frequency shifts. Partial deuteration by mixtures of water and heavy water has been made to distinguish the absorptions due to the NH and NH_2 groups from each other. The features of infrared spectra of monoacylureas can be explained by regarding them as composite spectra of aliphatic imides and urea. From the effect of the alkyl frame-work vibrations for the imide III frequency, it is suggested that the RCONH– group of monoacylureas takes the *trans* conformation.

The infrared spectra of monosubstituted amides and related compounds have been the subject of a large number of systematic investigation.[1] The coupling between the CN stretching vibration and the NH in-plane deformation vibration of monosubstituted amides has been proved to be related closely to the conformation of the –CONH– group. The amide II and III bands arising from this coupling are observed only for the *trans* conformation.[2] A similar effect of the structure on the vibrational coupling has been reported for the aliphatic imides in which two C=O bonds are connected to a NH bond.[3] It is desirable to extend the analysis of the amide type vibrational coupling to more complicated combinations of the C=O and NH bonds, since they are involved in many biologically important compounds.

The present paper deals with the infrared spectra of seven monoacylureas, $RCONHCONH_2$ [$R=CH_3$, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, i-C_4H_9, $(C_2H_5)_2CH$] and their *NN'*-deuterated derivatives. The assignment of the characteristic frequencies of the $-CONHCONH_2$ and $-CONDCOND_2$ groups was given on the basis of the spectral change on deuteration and comparison with related compounds such as urea,[4] monosubstituted amides[5] and aliphatic imides.[6]

Experimental

Acetylurea[7] and propionylurea[8] were prepared by heating a mixture of corresponding acid, acid anhydride, urea and trace sulfuric acid. The usual method of acylation with acyl chloride in dry benzene was used for preparing *n*-butyryl, *i*-butyryl-, *n*-valeryl, *i*-valeryl and diethylacetyl ureas.[8] These acylureas were recrystallized several times from ethyl alcohol. The *NN'*-deuterated compounds were prepared by recrystallization from a mixture of dioxane and heavy water, and partially deuterated compounds from a mixture of dioxane, water and heavy water.

The infrared spectra were recorded on a Koken DS 301 infrared spectrophotometer equipped with NaCl (4000—700 cm^{-1}) and KBr (700—450 cm^{-1}) prisms. The samples were subjected to the measurement in the form of solid dispersed in Nujol and H. C. B. (hexachlorobutadiene). The absorption frequencies are listed in Tables 1 and 2.

Results and Discussion

The Region above 2000cm^{-1}. Acylureas have both the NH_2 and NH groups, and three absorption bands due to the stretching vibrations of these groups are observed near 3430, 3320 and 3230 cm^{-1}. Watson *et al.* assigned the bands near 3420 and 3320 cm^{-1} to the NH_2 antisymmetric and symmetric stretching vibrations, respectively, and the band near 3230 cm^{-1} to the NH stretching vibration.[9]

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[4] A. Yamaguchi, T. Miyazawa, T. Shimanouchi and S. Mizushima, *Spectrochim. Acta*, **10**, 170 (1957); A. Yamaguchi, *Nippon Kayaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **78**, 1319, 1467 (1957).

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We investigated the infrared spectra of partially deuterated samples obtained by exchange reaction with the mixture of water and heavy water in various proportions, and interchanged Watson *et al.*'s assignments of the bands near 3320 and 3230 cm^{-1} on the basis of the intensity change of these bands on the progress of deuteration. One may assume that the isotopic change on the NH_2 and NH groups hardly affects the vibrational frequencies of each other, and that the intensities of the NH_2 and the NH stretching bands are determined by the total concentration of the molecules involving the corresponding group. The concentration of the NH_2 group in the partially deuterated samples decreases more steeply than that of the NH group as the concentration of heavy water in the mixed solvent increases, since the former has two exchangeable protons while the latter has one. Such difference in the rate of concentration changes is expected to give rise to the difference in the rate of intensity changes between the NH_2 and the NH stretching bands, although one must be careful in taking account of the interference of bands due to the NHD group.

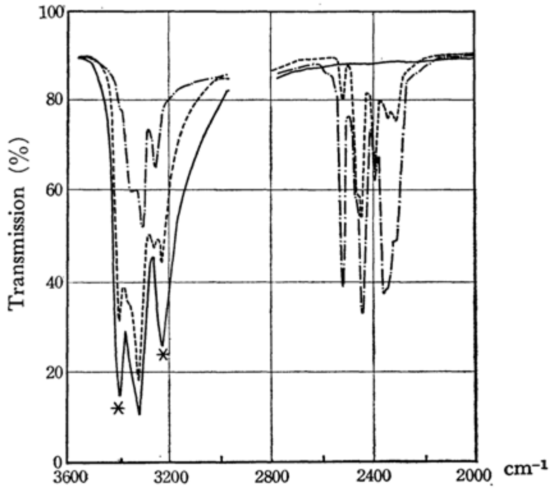

Fig. 1. Infrared spectra of propionylurea (———), partially deuterated propionylurea from 25% D_2O (---------) and partially dueterated propionylurea from 75% D_2O (—·—·—).
* the band due to the NH_2 species.

In Fig. 1, the infrared spectra of partially deuterated propionylureas between 3800 and 2200 cm^{-1} are shown. The intensities of the bands at 3424 and 3252 cm^{-1} (labeled*) decrease more rapidly than the intensity of the band at 3342 cm^{-1} on the progress of deuteration. This result suggests that the bands at 3424 and 3252 cm^{-1} are due to the NH_2 antisymmetric and symmetric stretching vibrations, respectively, and that the band at 3342 cm^{-1} is due to the NH stretching vibration. Similarly, for the deuterated compounds the bands at 2550 and 2390 cm^{-1} are assigned to the ND_2 antisymmetric and symmetric stretching vibrations, respectively, and the band at 2466 cm^{-1} to the ND stretching vibration. The intensity changes of these bands on successive deuteration are just what are expected from the concentration changes of the ND_2 and the ND groups. The bands at 3370 and 3278 cm^{-1} are observed only for the partially deuterated samples. They are attributed to the NH stretching vibrations of the NHD group, and their contributions to the peak intensities of the NH_2 and the NH stretching bands are estimated to be small. The presence of two NH stretching bands of the NHD group may be due to the presence of the NH bonds in *trans* and *cis* conformations against the C=O bond. The partially deuterated samples show also the ND stretching bands of the NHD group at 2475 and 2413 cm^{-1}.

The Region between 2000 and 1500 cm^{-1}. Figures 2—8 show the representative infrared spectra of seven monoacylureas and their *NN'*-deuterated compounds in the region between 1900 and 400 cm^{-1}. The infrared spectra between 1800 and 1500 cm^{-1} of the presently investigated acylureas may be classified into two types distinguishable from each other by the feature of the C=O stretching and the NH_2 bending absorptions. The type I spectra are shown by acetyl-, propionyl-, *i*-butyryl- and diethylacetylureas, and the type II spectra by *n*-valeryl-, *n*-butyryl- and *i*-valerylureas.

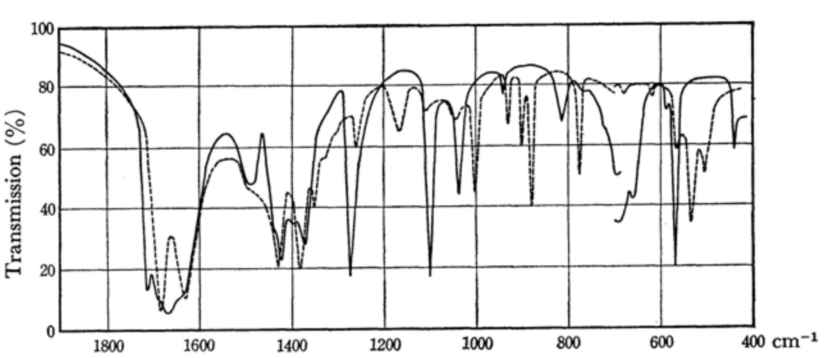

Fig. 2. Infrared spectra of acetylurea (solid line) and acetylurea-d_3 (broken line).

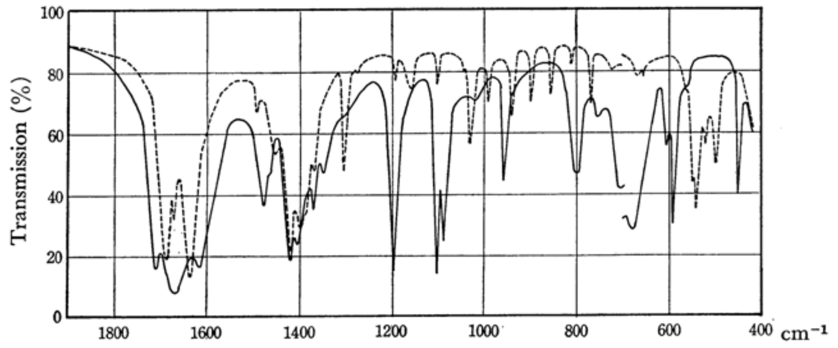

Fig. 3. Infrared spetra of propionylurea (solid line) and propionylurea-d_3 (broken line).

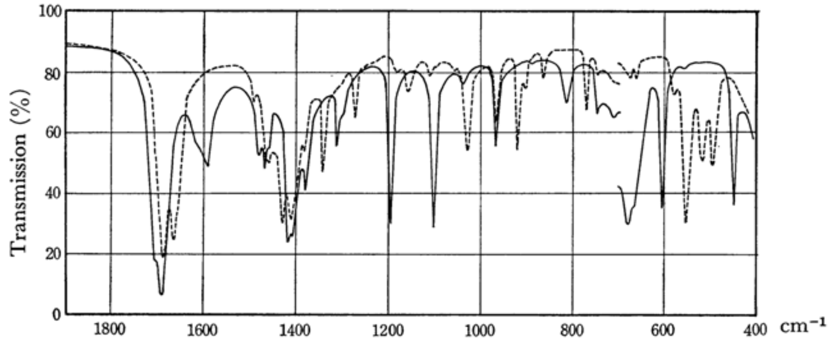

Fig. 4. Infrared spectra of *n*-butyrylurea (solid line) and *n*-butyrylurea-d_3 (broken line).

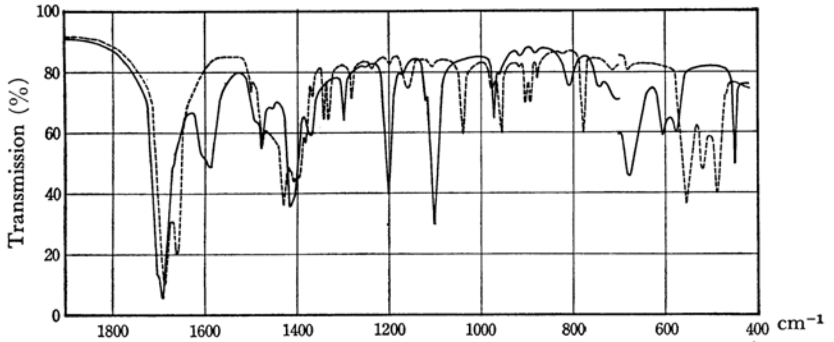

Fig. 5. Infrared spectra of *i*-butyrylurea (solid line) and *i*-butyrylurea-d_3 (broken line).

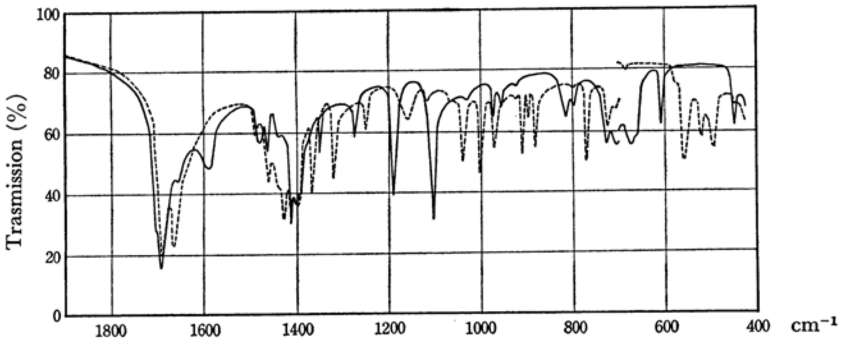

Fig. 6. Infrared spectra of *n*-valerylurea (solid line) and *n*-valerylurea-d_3 (broken line).

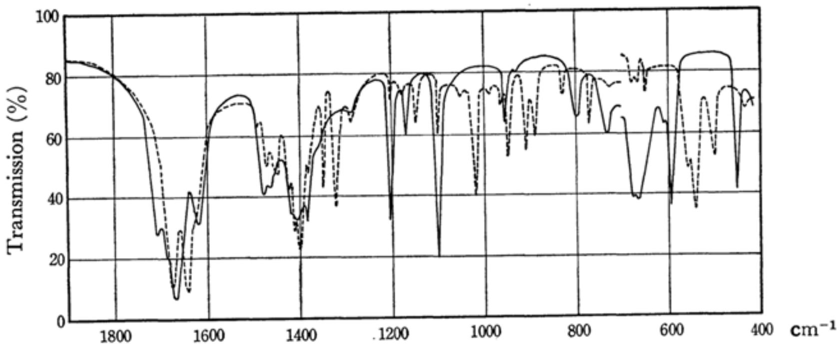

Fig. 7. Infrared spectra of *i*-valerylurea (solid line) and *i*-valerylurea-d_3 (broken line).

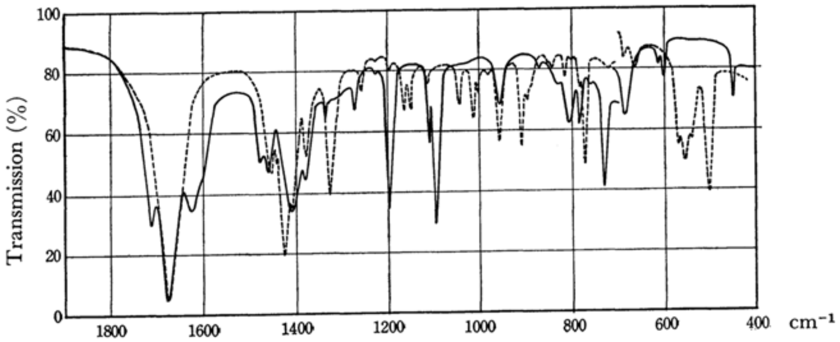

Fig. 8. Infrared spectra of diethylacetylurea (solid line) and diethylacetylurea-d_3 (broken line).

In the type II spectra, the C=O stretching absorptions, observed as a sharp and strong band near 1690 cm^{-1} and its shoulder near 1705 cm^{-1}, are separated clearly from the NH_2 bending absorption near 1590 cm^{-1} which disappears on *NN'*-deuteration. In the type I spectra, on the other hand, the C=O stretching and the NH_2 bending absorptions overlap with each other and give rise to a strong composite band with three peaks near 1710, 1680 and 1620 cm^{-1}. The spectral change on *NN'*-deuteration gives no definite clue to identify the absorption due to the NH_2 bending vibration. We tentatively assigned the 1620 cm^{-1} peak to this vibration from analogy to the type II spectra. The difference between the type I and II spectra may result from the difference in the scheme of hydrogen bonds involving the C=O and the NH_2 groups. Although this spectral difference is rather empirical at the present stage, it should be noted that a preliminary survey of infrared spectra of a number of α-brominated acylureas has also shown the presence of the two types I and II. The C=O stretching absorption of the *NN'*-deuterated acylureas splits mostly into two distinct peaks, around 1680 and 1640 cm^{-1} for the type I and around 1690 and 1665 for the type II. Only diethylacetylurea shows a single peak at 1681 cm^{-1}.

The Region between 1500 and 850 cm^{-1}. The spectral change on *NN'*-deuteration is complicated in this region since many deformation vibrations of the NH_2, NH, ND_2 and ND groups show their frequencies in this region and they couple often with other vibrations. Acetylurea shows a medium band at 1485 cm^{-1} and two sharp and fairly strong bands at 1260 and 1098 cm^{-1}, all of which disappear on *NN'*-deuteration. The 1485 cm^{-1} and the 1098 cm^{-1} bands persist in the spectra of other acylureas, but the 1260 cm^{-1} band is replaced by a similar band near 1200 cm^{-1} on the change of the acyl group from acetyl to the others. In some cases involving large acyl groups, the presence of the 1480 cm^{-1} is obscured by the overlap of the CH_3 and CH_2 deformation absorptions, and is confirmed only by the comparison with the corresponding *NN'*-deuterated compounds. Instead of these bands, the *NN'*-deuterated acylureas show commonly four weak to medium bands around 1330, 1170, 1050 and 900 cm^{-1}. We assigned the 1100 cm^{-1} band of the undeuterated compounds to the NH_2 rocking vibration from analogy to acetamide,[10] urea[4] and biuret,[11] and the 1170 cm^{-1} band and the 900 cm^{-1} band of *NN'*-deuterated compounds to the ND_2 bending and ND_2 rocking vibrations, respectively, from analogy to

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TABLE 1. THE INFRARED CHARACTERISTIC FREQUENCIES OF $-CONHCONH_2$ GROUP

CH_3-	CH_3CH_2-	$CH_3CH_2CH_2-$	$(CH_3)_2CH-$	$CH_3(CH_2)_3-$	$(CH_3)_2CH_2CH_2-$	$(C_2H_5)_2CH-$	Assignment
3425 vs*	3424 vs	3419 vs	3414 s	3408 s	3419 s	3394 s	NH_2 asym. stretching
3354 vs	3342 vs	3338 vs	3325 vs	3335 s	3339 s	3321 s	NH stretching
3232 s	3252 s	3238 m	3248 m	3232 m	3238 m	3230 m	NH_2 sym. stretching
1712 s	1712 vs	1707 vs	1705 vs	1704 vs	1705 vs	1714 vs	C=O stretching
1674 vs	1680 vs	1693 vs	1668 vs	1690 vs	1690 vs	1681 s	C=O stretching
1637 s	1620 s	1595 m	1619 s	1593 m	1593 m	1624 m	NH_2 bending
1485 m	1476 m	1479 m	1481 m	1480 w	1483 w	1476 m	Imide II band
1414 vs	1407 vs	1415 s	1410 s	1414 s	1412 m	1412 s	CN stretching (?)
1260 s	1198 vs	1193 s	1203 s	1187 s	1198 vs	1198 s	Imide III band
1098 s	1098 s	1098 s	1100 s	1098 s	1100 s	1096 s	NH_2 rocking
942 vw	956 m	966 m	953 w	971 w	968 w	957 w	CN stretching
815 w	800 m	815 w	802 w	815 w	812 w	808 w	C=O out-of-plane deformation (urea part)
725 695 mb	700 mb	710 mb	735 mb	732 704 mb	715 mb	740 mb	NH out-of-plane deformation
660 mb	680 mb	680 mb	675 665 mb	680 mb	680 mb	685 mb	NH_2 wagging
589 vw 569 vs	607 vw 595 s	650 m	609 vw 593 m	608 m	603 w 577 w	600 w	CO in-plane or out-of-plane deformation (amide part)

TABLE 2. THE INFRARED CHARACTERISTIC FREQUENCIES OF $-CONDCOND_2$ GROUP

CH_3-	CH_3CH_2-	$CH_3CH_2CH_2-$	$(CH_3)_2CH-$	$CH_3(CH_2)_3-$	$(CH_3)_2CH_2CH_2-$	$(C_2H_5)_2CH-$	Assignment
2544 s	2550 s	2545 m	2551 s	2542 m	2542 m	2545 m	ND_2 asym. stretching
2474 m	2466 s	2466 m	2466 s	2468 m	2468 m	2465 m	ND stretching
2393 s	2390 m	2377 m	2396 s	2379 m	2380 m	2386 m	ND_2 sym. stretching
1682 vs	1691 vs	1691 vs	1680 vs	1690 vs	1687 vs	1681 vs	C=O stretching
1637 vs	1640 vs	1666 s	1641 vs	1666 vs	1664 vs		C=O stretching
1425 s	1421 vs	1430 s	1415 s	1430 s	1431 s	1425 s	CN stretching (?)
1348 m	1307 s	1342 m	1319 m	1321 s	1332 m	1328 m	Imide II′ band
1169 vw	1160 vw	1159 vw	1156 w	1158 w	1167 w	1170 w	ND_2 bending
1112 vw	1032 m	1030 w	1021 w	1041 m	1038 m	1047 m	Imide III′ band
933 w	946 w	964 w	950 w	967 m	955 m	957 m	CN stretching
879 m	899 w	904 m	908 w	910 m	906 w	910 m	ND_2 rocking
772 w	770 w	772 w	772 w	771 m	773 m	773 m	C=O out-of-plane deformation (urea paprt)
534 wb	549 sh 542 s	551 s	563 m 548 m	559 s	558 m	573 m	C=O in-plane or out-of-plane deformation (amide part)
563 w	518 m	521 w	544 m	517 m	525 w	554 s	ND out-of-plane deformation
505 m	495 m	496 m	501 w	495 s	494 s	501 s	ND_2 wagging

* vs; very strong, s: strong, m: medinm, w: weak, vw: very weak, b: broad

acetamide-d_2[10] and urea-d_4.[4] The remaining deuteration sensitive absorption frequencies are quite analogous to those reported for aliphatic acylic imides, RCONHCOR′ (R, R′=alkyl), and their *N*-deuterated derivatives.[6] The imide II band near 1500 cm^{-1} and the imide III band between 1240 and 1180 cm^{-1} of aliphatic acylic imides are replaced on deuteration by the imide II′ band near 1330 cm^{-1} and the imide III′ band near 1000 cm^{-1}. By the normal coordinate analysis of diacetamide,[3] it has been confirmed that the imide II and III bands arise from the coupling between the NH in-plane deformation vibration and the CN stretching vibrations of the –CONHCO– group, just as in the well known case of the amide II and III bands of monosubstituted amides. The imide II′ band of the deuterated acylic imides is mainly due to the CN stretching vibration and the imide III′ band due to the ND in-plane deformation vibration. From the structural analogy between acylureas and acylic imides, the 1480 cm^{-1} band of the presently investigated acylureas is identified immediately as the imide II band and the 1260 cm^{-1} of acetylurea and the 1200 cm^{-1} band of the other acylureas as the imide III band. The 1330 cm^{-1} and the 1050 cm^{-1} bands of the *NN′*-deuterated acylureas correspond probably to the imide II′ and III′ bands, respectively. These empirical assignmengs of the deuteration sensitive bands of acylureas are given support to by the infrared spectra of the partially deuterated samples. On the increase of the relative amount of heavy water in the solvent for the exchange reaction, the 1100 cm^{-1} band shows faster intensity decrease than the 1480 cm^{-1} band and the 1200 cm^{-1} band (1280 cm^{-1} for acetylurea), whereas the 1170 cm^{-1} and the 900 cm^{-1} bands show slower intensity increase than the 1330 cm^{-1} and the 1050 cm^{-1} bands. The partially deuterated samples show only a few additional absorptions appearing as satellite peaks of the above mentioned bands, although these samples are mixtures of many isotopic molecules with respect to the number and positions of deuterium atoms.

For aliphatic acylic imides it has been reported that the vibrations of alkyl groups contribute to the imide III band through the coupling with the CN stretching vibrations, and this coupling gives rise to the low frequency shift of the imide III frequency of aliphatic acylic imides from 1240 cm^{-1} to 1180 cm^{-1} on the change of alkyl frameworks from methyl to ethyl and larger alkyl groups. Similarly, the effect of the alkyl framework on the imide III frequency of acylureas presently observed indicates that the CN stretching vibration of the RCONH– group of acylureas couples with the NH in-plane deformation vibration as well as with the vibrations of the alkyl framework. It is well known that the coupling between the CN stretching and the NH in-plane deformation vibrations occurs only for the trans –CONH– group.[2] Accordingly, the RCONH– group of acylureas is probably in the trans conformation.

Besides the CN stretching vibration of RCONH– group participating in the imide II and III bands, acylureas have two more degrees of freedom for those arising from the –$NHCONH_2$ group. We assigned the weak or medium band near 950 cm^{-1} observed commonly for the presently investigated acylureas and their *NN′*-deuterated compounds to one of these two CN stertching vibrations. This absorption frequency is comparable with the CN symmetric stretching frequency of urea itself at 1000 cm^{-1}.[4] The remaining CN stretching band is then supposed to appear around 1450 cm^{-1} by analogy with the CN antisymmetric stretching frequency of urea (1660 cm^{-1}).[4] The interference of the CH deformation bands of alkyl groups makes it difficult, however, to identify this band. The strong bands near 1410 cm^{-1} for acylureas and near 1440 cm^{-1} for the *NN′*-deuterated compounds were tentatively assigned to this CN stretching vibration.

The Region between 850 and 450 cm^{-1}. For the undeuterated acylureas, four bands around 810, 700, 680 and 570 cm^{-1} are commonly observed between 850 and 450 cm^{-1}. Referring to the C=O out-of-plane deformation frequency of urea, we assigned the slightly broad band near 810 cm^{-1} of undeuterated acylureas to the corresponding vibration of the –$NHCONH_2$ group. On *NN′*-deuteration, this band is replaced by the sharp band at 770 cm^{-1}, the frequency being almost independent of the alkyl group. The broad bands around 700 and 680 cm^{-1} of acylureas disappear on deuteration and are assigned to the NH_2 wagging and the NH out-of-plane deformation, vibration respectively, from analogy with urea and aliphatic imides. For the *NN′*-deuterated compounds, the corresponding ND_2 wagging and the ND out-of-plane deformation bands are found near 550 and 500 cm^{-1}, respectively. These assignments were given support to again by the change in the relative intensities on partial *NN′*-deuteration.

The group frequencies so far left unassigned in this region are the C=O in-plane and out-of-plane deformation vibrations of the RCONH– group and the C=O in-plane deformation vibration of the –$NHCONH_2$ group. By comparison with the available data for monosubstituted amides,[5] imides[6] and urea,[4] these vibrations are expected to have their frequencies around 600 cm^{-1}. The strong band near 570 cm^{-1} of acylureas may therefore be taken as an overlapped absorption contributed by these vibrations. The corresponding band for *NN′*-deuterated compounds is observed around 530 cm^{-1}.

Thanks are due to the members of the Microanalytical Center of Kyoto University for elemental analysis.