

On the Isomerism of Hydroxyurea

XI. Absorption Spectra in the Infra-Red

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A brief survey of the Raman and infra-red spectroscopy of urea is presented. On this background recorded infra-red spectra of the hydroxyurea isomerides are discussed and assignments of the principal absorption frequencies have been attempted. Although no rigorous proof has been furnished the results are compatible with the proposed constitutions carbamhydroxamic acid (I) and O-carbaminoyl-hydroxylamine (II), respectively.

In a preliminary communication¹ the absorption in the frequency region 3 600—600 cm^{-1} of the two isomerides were briefly described. In the present paper a first attempt has been made at a more detailed interpretation of the spectra in terms of structure.

The compounds, as well as urea, which may be regarded as the mother substance of at least one of the isomerides, belong to the medium-size molecules, which are too complicated for a complete theoretical treatment by the spectroscopist, but which are nevertheless too small to leave them entirely to the purely empirical approach of the organic chemist.

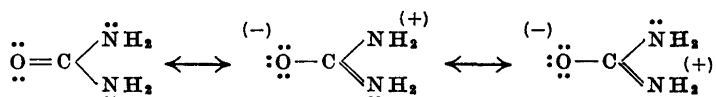
The structure of urea has been extensively studied by several authors. The Raman spectrum was recorded in 1934 by Kohlrausch and Pongratz⁴ and also investigated in 1939 by Otvos and Edsall⁵. The latter work included a comparative investigation of deuterio-urea. The absorption spectrum in the infra-red was recorded in 1941 by Kellner², who also subjected the molecule to a theoretical treatment³. Kellner found it possible to assign the observed frequencies to definite modes of vibration. The theoretical frequencies, calculated as usual from the evaluated force constants, were compared with the experimental infra-red and Raman frequencies, obtained by Kellner² and previous investigators^{4,5}. Although quite satisfactory agreement was observed, Kellner pointed out that the proposed interpretation was by no means definite. The results of Kellner are compatible with the hypothesis advanced in 1935 by

Table 1. Infra-red and Raman frequencies of urea (cm⁻¹).

	IR (Kellner ²) (solid)	Raman (Kohlrausch and Pongratz ⁴) (in H ₂ O)	Raman (Otvos and Edsall ⁵) (in H ₂ O)	Assign- ments by Kellner ²	IR (Davis & Hopkins ²⁶) (solid)	
A	3 434 3 410 3 376 3 218	3 462 (2sb) 3 383 (3sb) 3 218 (1b)	3 496 D (5b) 3 385 P (6bv) 3 235 P (5b)	N-H a-st N-H a-st N-H s-st N-H s-st first over- tone of 1680	3 444 (s) 3 348 (s)	NH ₂ a-st NH ₂ s-st
C		1 655 (0) 1 593 (2b)	1 680 P (3b) 1 604 P? (4b)	C=O st b	1 610 (s) 1 620 (m)	C=O st NH ₂ d
D		1 458 (0) 1 350 (1/2) 1 157 (1b) 1 000 (8) 685 (1b) 525 (2b)	1 478 D (2b) 1 167 P (4) 1 008 P (10) 601 D (2) 534 D (2)	C $\begin{matrix} \diagup N \\ \diagdown N \end{matrix}$ a-st b b C $\begin{matrix} \diagup N \\ \diagdown N \end{matrix}$ s-st b b	1 476 (s) 1 155 (s) 1 055 (m) 1 004 (mw) 787 (m) 712 (m) 574 (m) 559 (w)	NCN a-st NH ₂ rock NH ₂ rock NCN s-st C=O b out of plane NH ₂ torsio- nal C=O b in plane NCN d

a- asymmetric s- symmetric
st stretching b bending d deformation vibration
P polarized D depolarized
(s) strong, (m) medium (w) weak

Pauling⁸ that the urea molecule is mesomeric, two ionic structures contributing approximately 20 % each to the actual electron distribution



This picture is also in agreement with X-ray measurements of the nuclear distances⁹, $r(\text{C}=\text{O}) = 1.25 \text{ \AA}$ and $r(\text{C}-\text{N}) = 1.37 \text{ \AA}$, and with the coplanarity of the carbon, oxygen and nitrogen atoms, as first deduced from crystallographic data⁹, and later confirmed by absorption spectroscopy with polarized infra-red radiation by Keller¹⁰ and by Waldron and Badger¹¹ from more

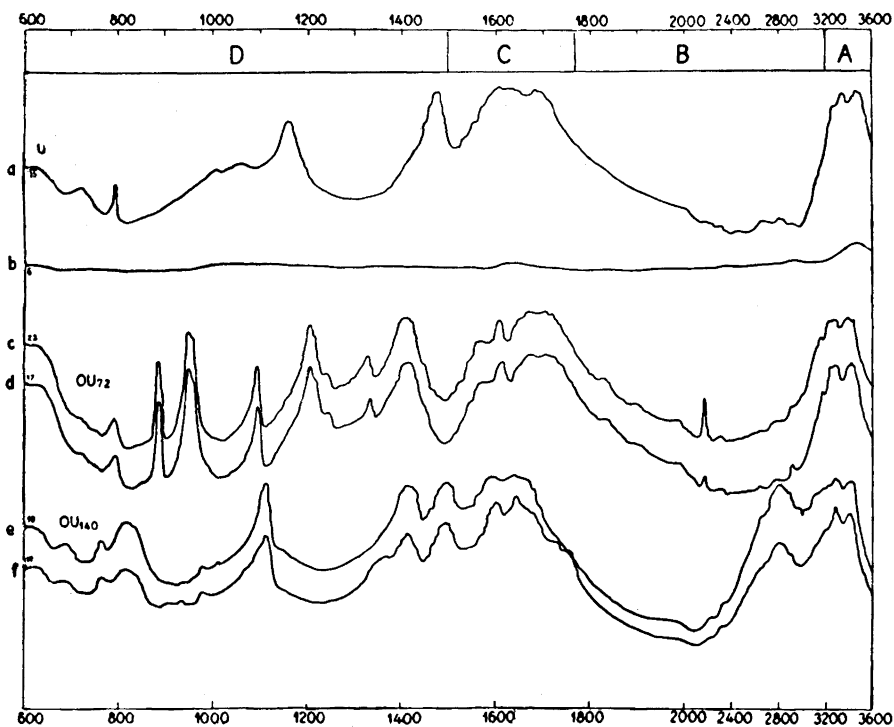


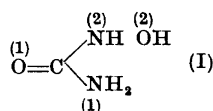
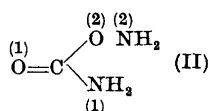
Fig. 1. Absorption spectra in the infra-red. Solid state, 1 mg substance/300 mg KBr. a, Urea; b, Potassium bromide (blank) against the atmosphere; c, «Hydroxyurea», m.p. 72°C, O-carbaminoyl-hydroxylamine, freshly prepared sample; d, As c, but sample stored at 0°C for 2½ years; e, Hydroxyurea, m.p. 140°C, carbamhydroxamic acid, prepared according to the present author²⁵; f, As e, but sample prepared according to Runti and Deghenghi²³.

accurate measurements. Further corroboration of the latter work was presented in 1953 by Robinson and Price⁶ who deduced the IR-absorption spectrum from the reflection spectrum using a single-crystal technique. Vaughan and Donohue²⁸ in 1952 obtained evidence that not only are the principle atoms coplanar but the hydrogen atoms lie in the plane of the rest of the molecule. Indications of this position had been observed in earlier work^{10,11} and the coplanarity of the entire molecule was further supported by proton magnetic resonance studies²⁹ and by neutron diffraction work²⁷. Davies and Hopkins²⁶ have recently reinvestigated the absorption of urea in the infra-red (solid and vapour state) and also recorded the spectrum of the uronium ion. Their frequency data, obtained with urea, are given in Table 1 together with the values and assignments by the previously quoted authors. Davies and Hopkins presented a detailed discussion of the bonding in urea in the solid state. The qualitative picture is in agreement with previous information, but the authors give revised values of the N—H bond lengths. They

state that only weak hydrogen bonding exists in the urea molecule, and their computation of the delocalization ("resonance"-) energy based upon the spectroscopic data yielded a value, which is considerably lower than the thermochemical value of 37 kcal/mole. The discrepancy is explained by the fact that the thermochemical value includes contributions from changes in the σ -bonds and from additional hydrogen bond energy made available by the planar configuration.

The absorption spectra of urea and of the isomeric "oxyureas", are reproduced in Fig. 1. A catalogue of frequencies of the principle absorption-bands is given in Table 2.

Among the proposed constitutions, those which seem to account for most chemical and physical properties of the oxyureas are

OU₁₄₀, Carbamhydroxamic acidOU₇₂, O-Carbaminoylhydroxylamine

There is ample evidence that (I) represents the correct constitution of OU₁₄₀, *vide, e.g.*, parts III, IV, VI in the present series. Formula II was proposed by Exner¹² mainly from classical chemical arguments and on the basis of the results of the present author. It was, however, felt desirable to obtain further support by physical methods. At the time, when the preliminary communication¹ on the infra-red absorption appeared, only two O-acylated hydroxylamines were described in the literature, *viz.* O-anthranoyl-hydroxylamine³¹ and the proposed structure II for OU₇₂. Since then the preparation of further two representatives of this type of compounds³⁰ has been reported, and this adds considerably to the probability of formula II. The need for a rigorous proof and the general interest¹⁸ in the infra-red absorption of the biochemically important groupings CO—NH and NHOH is the author's justification for the following attempt at a detailed discussion of the spectra of the hydroxyureas.

The observed frequencies listed in Table 2 will be discussed with particular reference to the compatibility with the proposed constitutions I and II.

In the frequency region A all three compounds show an intense, partly resolved doublet with a slightly less intense shoulder on the low-frequency side. This is the region, where the N—H stretching vibration of amides are normally found, and the duplex nature of the peak is characteristic for the unsubstituted NH₂-group. The A-region of the urea spectrum has been carefully studied by many investigators^{2-7,11}, and there is general agreement that the frequencies are N—H stretching fundamentals *cf* Table 1. Mathis¹³ reported a characteristic, intense band at 3 μ (3 333 cm⁻¹) in the spectra of hydroxamic acids in the solid state. He too regards it as being due to N—H stretching vibrations and takes the absorption bands as a proof of the constitu-

tion $\text{R}-\text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{NHOH} \end{array}$. In 1958 Jencks³⁰ has recorded the absorption spectra

Table 2. Principle infra-red frequencies (cm^{-1}) of urea and the isomeric "oxyureas" in the solid state, cf. Fig. 1.

	$\begin{array}{c} \text{NH}_2 \\ \diagup \\ \text{O}=\text{C} \\ \diagdown \\ \text{NH}_2 \\ \text{U} \end{array}$	$\begin{array}{c} \text{NHOH} \\ \diagup \\ \text{O}=\text{C} \\ \diagdown \\ \text{NH}_2 \\ \text{(proposed)} \\ \text{OU}_{140} \end{array}$	$\begin{array}{c} \text{ONH}_2 \\ \diagup \\ \text{O}=\text{C} \\ \diagdown \\ \text{NH}_2 \\ \text{(proposed }^{12}) \\ \text{OU}_{72} \end{array}$	Proposed assignments
	Fig 1 a	Fig 1 e	Fig 1 d	
A	3 440 (s) 3 320 (s) 3 250 (s)	3 400 (s) 3 280 (s) 3 200 (s)	3 400 (s) 3 270 (s) 3 180 (s)	NH_2 a-st NH_2 s-st overtone?
B		2 800 (s)	2 170 (w)	OH (hydrogen bonded) ?
C	1 685 (s) 1 620 (s)	1 650 (s) 1 600 (s)	1 715 (s) 1 675 (s) 1 610 (s) 1 565 (m)	C=O(1) (ester) C=O (amide I) C-O(2) (?) C=O (amide I) C-N st or NH_2 d (amide II ?) ?
D	1 470 (s) 1 155 (m) 1 050 (m) 790 (w) 715 (w) 620 (m)	1 490 (s) 1 415 (s) 1 115 (s) 820 (m) 760 (m) 685 (m) 620 (m)	1 415 (s) 1 335 (m) 1 250 (m) 1 210 (s) 1 095 (m) 950 (s) 885 (m) 790 (w) 620 (s)	C-N(1) st $\begin{array}{c} \text{N} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{N} \end{array}$ st C-N(2) st C-O(2) (ester) ? NH_2 rock N-O st? C-N st ? ? ? N-O st ? C-O st ? C-O st N-O st ? ? } N-H rock ?

of various hydroxamic acids and a few O-acylhydroxylamines in chloroform solution. The data obtained with benzohydroxamic acid and O-benzoylhydroxylamine are representative and of interest in the present discussion, since the formulae of the compounds are analogous to I and II, respectively. The wave lengths, converted to wave numbers, are quoted in Table 3, and the assignments by Jencks are included. There is good agreement between the N—H stretching frequencies in Tables 2 and 3.

Table 3. Infra-red frequencies of benzoyl-hydroxylamines in chloroform-solution. Data and assignments by W. P. Jencks³⁰.

	$\begin{array}{c} \text{NHOH}_2 \\ \diagup \\ \text{O}=\text{C} \\ \diagdown \\ \text{C}_6\text{H}_5 \end{array}$ Benzohydroxamic acid	$\begin{array}{c} \text{ONH}_2 \\ \diagup \\ \text{O}=\text{C} \\ \diagdown \\ \text{C}_6\text{H}_5 \end{array}$ O-Benzoylhydroxyl- amine	
A	3 400 (m) N—H 3 180 (m) OH	3 290 (m) N—H 3 180 (w) N—H	
C	1 660 (s) C=O (amide)	1 730 (s) C=O (ester) 1 640 (w) (?) 1 533 (m) (?)	
D	1 385 (m) C—N st 895 (m) N—O (?)	1 454 (s) (?) 1 317 (m) (?) 1 180 } (s) C—O ester 1 280 } 925 (m) N—O (?)	

The assignment of the third (low-frequency) band is uncertain. In the urea molecule (*cf.* Table 1) it has been interpreted as the first overtone of the frequencies around $1\,600\text{ cm}^{-1}$. In benzohydroxamic acid on the other hand (*cf.* Table 3) a corresponding band has been assigned to a hydrogen bonded O—H group and in O-benzoyl hydroxylamine to a hydrogen bonded N—H group. It is emphasized that the latter assignments refer to solution spectra.

Since it is virtually impossible to distinguish between N—H and O—H bonds in this region the presence of a hydroxy-group in OU_{72} is not directly disproved; it is, however, unlikely for chemical reasons.

In the frequency-region B there is a broad band at $2\,800\text{ cm}^{-1}$ in the spectrum of OU_{140} . It is one of the most intense bands in the spectrum and is absent or extremely weak in U and OU_{72} . It has therefore tentatively been assigned to the hydroxy-group¹. Since this assignment would rule out all the possible formulations of OU_{72} containing free hydroxy-groups and would be in favour of the set of formulae I/II its validity has to be carefully considered. The normal stretching vibration of the unassociated O—H group is found at much higher frequencies in the A region. It is, however, well known¹⁴ that the frequency is very considerably lowered by hydrogen bonding, of which there are ample possibilities in OU_{140} . For the O—H...O bond in the crystalline state the O—H frequency shift has been shown to be a monotonic and nearly linear function of the H...O distance^{15,16}. Similar regularities have been demonstrated¹⁷ for a number of other "straight" hydrogen bonds, such as OH...N, NH...O, NH...N, which may also be present in crystals of OU_{140} . The linear relationship is valid only up to a distance of *ca.* 2.8 Å. For short,

i. e. strong hydrogen bonds the OH frequency is reduced very considerably. When straight OH...O bonds are involved, stretching frequencies of the O—H bond as low as 2 000 cm^{-1} have in fact been recorded in the crystalline state. The observed frequency of 2 800 cm^{-1} is, therefore, by no means exceptionally low. Taking 3 700 cm^{-1} as the normal frequency of the non-hydrogen-bonded O—H group, 2 800 cm^{-1} would correspond¹⁷ to a hydrogen bond distance OH...O of 2.67 Å.

The flattened shape of the maximum at 2 800 cm^{-1} in Fig. 1 is also in accordance with general experience concerning the hydrogen-bonded OH group in this frequency region^{17, Fig. 2}.

Mathis¹³ has recorded the IR-spectra of a number of hydroxamic acids, which are, of course, closely related to the proposed formula (I) for OU₁₄₀. He reported "une bande d'absorption intense et très large" at 3.6 μ corresponding very closely to 2 800 cm^{-1} . This band is visible in the solid state only, *cf* Table 3. In carbon tetrachloride solution it disappeared and was replaced by a new, intense band at 3 450 cm^{-1} (2.9 μ). From these observations Mathis concluded that the 2 800 cm^{-1} band was *not* due to a hydrogen-bonded OH group and assigned it tentatively to a C—H stretching vibration, perturbed by the proximity of an oxygen atom, a proximity, which Mathis assumed to exist in the solid state only. The new band at 3 450 cm^{-1} , appearing in solution, was assigned to a hydrogen bonded hydroxy-group, intermolecular hydrogen bonds being postulated in solution only.

In the opinion of the present author the observations of Mathis might equally well be explained by assigning the band at 2 800 cm^{-1} to a hydrogen-bonded OH group in the crystalline state. Since the N—H group too may be involved in hydrogen bonds in the crystalline state, it would be reasonable to assume, that the new band appearing at 3 450 cm^{-1} in solutions of hydroxamic acids represents the normal frequency of either the non-bonded OH group or of an unassociated N—H group.

Unfortunately the insolubility of OU₁₄₀ in non-polar solvents prevents the recording of a solution spectrum, which might otherwise throw further light upon the origin of the 2 800 cm^{-1} band. Some further support for the assignment of the band at 2 800 cm^{-1} to a strongly hydrogen-bonded hydroxy-group is provided by observations by Nightingale and Wagner³⁴. They reported a broad, intense band at 2 876 cm^{-1} in the infra-red spectrum of solid hydroxylamine at low temperature and attributed it to the O—H stretching vibration. The surprisingly low frequency was interpreted as indicating extremely strong hydrogen bonding in the crystal.

In the double-bond region C urea as well as the two oxyureas show an intense, broad absorption band, consisting of two incompletely resolved maxima.

This feature corresponds closely to what is known from amides of the general formula



in which the R groups must have a carbon adjacent to the amide group and cyclic connections by way of the R groups must be absent. These compounds all display two typical bands in the double-bond region. One is located at approximately 1 650 cm^{-1} ("Amide I") and is assigned to the carbonyl stretch-

ing vibration. For the other one at approximately $1\ 550\text{ cm}^{-1}$ ("Amide II") three different explanations have been proposed, the most probable one assigning it to the stretching vibrations of the C—N bond, which is supposed to be enhanced in bond strength by a mesomerism involving the adjacent C=O bond ²⁵.

Hydroxamic acids similarly show an intense absorption in this region. In benzohydroxamic acid (*cf.* Table 3) the frequency of $1\ 666\text{ cm}^{-1}$ ($6.0\ \mu$) has been reported in the solid state ¹³ and $1\ 660\text{ cm}^{-1}$ in solution ³⁰. Both authors assigned it to carbonyl stretching vibration.

In urea a Raman frequency, which has been assigned to C=O, occurs at $1\ 680\text{ cm}^{-1}$, other authors report the value of $1\ 665\text{ cm}^{-1}$ (*cf.* Table 1). Thompson *et al.*¹⁸ have demonstrated that in the infra-red spectra of nearly all mono-, di- and tetra-substituted ureas the C=O absorption is located close to $1\ 660\text{ cm}^{-1}$. The normal frequency in aldehydes, ketones and fatty acids is approximately $1\ 700\text{ cm}^{-1}$. The reason for the value being considerably lower in amides, hydroxamic acids and ureas obviously is the weakening of the C=O bond by delocalisation.

We assume that the high frequency component of the intense, broad bands in OU₇₂ and OU₁₄₀ similarly represents a C=O stretching frequency. According to the above hypothesis the fact that in OU₁₄₀ the high frequency component is $1\ 650\text{ cm}^{-1}$, very close to the urea value, suggests that the delocalization and hence the bond length $r(\text{C}=\text{O})$ are nearly equal. In OU₇₂, on the other hand, the supposedly corresponding band is located at a considerably higher frequency than in urea, in fact very close to the normal value of $1\ 700\text{ cm}^{-1}$, observed for simple ketones. Consequently the C=O bond should be very nearly a pure double bond. This trend might be expected from the proposed constitutions, since the symmetrical arrangements of two equivalent C—N bonds in urea and OU₁₄₀ in all probability will cause more delocaliza-

tion of the C=O bond than will the $\text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{N} \end{array}$ arrangement in OU₇₂. On the assumption that formula II represents the correct constitution of OU₇₂, the carbonyl bond is in fact of the ester-type and the location of its frequency fit quite well with general experience. Furthermore the observation of a strong absorption at $1\ 730\text{ cm}^{-1}$ in O-benzoylhydroxylamine (*cf.* Table 3) assigned to the carbonyl group ³⁰ may be taken as further corroboration of the assignment of the frequency.

The relation between bond length and stretching frequency of the carbonyl group has been studied by Rundle *et al.*¹⁹. For bond lengths ranging from 1.13 to 1.31 Å the points were found to fit a smooth curve, from which the C=O bond lengths in OU₁₄₀ and OU₇₂ may be read as 1.25 Å and 1.22 Å, respectively; that of urea is 1.26 Å.

Although the assignment of the high frequency absorption bands in region C to a carbonyl group is compatible with the formulae I and II it should be pointed out that no direct proof is delivered. This should be particularly emphasized with respect to formula II. The reason for this is that the C=N bond is known to produce a stretching frequency in the same region and of similar intensity, and it is virtually indistinguishable from that of C=O.

Molecular structures containing a C=N bond instead of a C=O bond, which have been proposed for both oxyureas, are therefore not entirely ruled out by the present results. Relatively few investigations have been carried out on the infra-red absorption of acyclic C=N compounds. Bonino and Manzoni-Ansidei²⁰ reported an absorption band at 1 650—1 660 cm⁻¹ in acyclic oximes and assigned it to the C=N bond. Mathis¹³ similarly observed a characteristic band at 5.95—6 μ (1 680—1 666 cm⁻¹) in acyclic oximes and made the same assignment. Duyckaerts²¹ reported the value 1 630 cm⁻¹ in free oximes and assigned it to the C=N—OH group without specification; in salts and complexes of oximes he observed a band at 1 550 cm⁻¹, which he assigned to $\overset{+}{\text{N}}-\overset{-}{\text{O}}$. Borello and Henry²² have investigated glyoximes and assigned a frequency at 1 625 cm⁻¹ to the C=N bond. Some iminoethers and guanidines have also been investigated. It appears from the above and is generally agreed that the C=N absorption occurs at somewhat lower frequencies (1 625—1 650 cm⁻¹) than that of the C=O group, although values up to 1 683 cm⁻¹, have been found (acetoxime, Ref.²⁵, p. 182). It will be noticed that some of the values reported of the C=N frequency are very close to the low frequency component of the composite bands in region C in Table 2. This component at 1 620, 1 610 and 1 600 cm⁻¹, respectively, has therefore tentatively been assigned to the C—N bond, which is assumed to be enhanced in bond strength by mesomerism involving the carbonyl group. It may possibly be identified with the "Amide II" band, for which a similar interpretation has been presented²⁵. The fact that in OU₇₂ the supposed "Amide II" band is distinctly separate from the C=O band, whereas in U and OU₁₄₀ it is poorly resolved, may be correlated with the smaller degree of bond delocalization or "resonance" in the OU₇₂ molecule as discussed above.

The alternative explanations²⁵ of the "Amide II" band may also be considered as a possibility, particularly the one assigning the band to NH₂ deformation, *cf.* Table 1.

As an aid in the assignment of the frequencies in region C the absorption of O-methyl-isourea might be of interest, since the contribution from structures containing C=N double bonding should be even more pronounced in this compound than in urea and the oxyureas. The Raman spectrum of an aqueous solution containing 50 % by weight of O-methylisouronium chloride has been determined by Edsall²³, but the results obviously refer to the cation, in which the delocalization of the C=N bonds is large, and no assignments have been made by the author except for some lines arising from the methyl-group. Investigations of the infra-red spectrum of the base are in progress in this laboratory.

Finally in the C region there is a shoulder at 1 565 cm⁻¹, also observed in O-benzoylhydroxylamine (*cf.* Table 3). In benzohydroxamic acid it is absent.

It is obvious from the discussion that at present a completely reliable assignment of the bands in the double-bond region C is hardly possible from the spectroscopic data alone, and the possibility is left open that the bands may

be entirely or partly due to C=N stretching vibrations and deformation of NH_2^* .

In the frequency region D urea and OU_{140} display certain similarities, whereas the absorption curve of OU_{72} is much more complex. This is to be expected on the basis of the formulae I and II since it is the region, in which the C—N and C—O stretching frequencies normally appear, and with respect to these bonds U and OU_{140} are related and fundamentally different from OU_{72} .

At 1470 cm^{-1} an intense band is noticed in urea (Table 2). It probably corresponds to the Raman lines observed at 1458 and 1478 cm^{-1} , respectively, by two different investigators (Table 1). These lines have been assigned to

$\text{C} \begin{array}{l} \swarrow \text{N} \\ \searrow \text{N} \end{array}$ asymmetric stretching. It is probably this band that reappears in OU_{140} at 1490 cm^{-1} , but is absent or considerably displaced in OU_{72} in accordance with formula II, containing one C—N only.

At 1415 cm^{-1} there is an intense band common to OU_{72} and OU_{140} but absent in U. If this band too be assigned to a C—N stretching vibration a reasonable explanation of the four bands appearing in the region 1490 — 1415 would be, that the two separate peaks in the "unsymmetric" OU_{140} are due to the two C—N bonds (formula I), and that these peaks in the symmetrical urea molecule coincide at the intermediate frequency 1470 . In OU_{72} in accordance with formula II there is one C—N band at 1415 (in common with OU_{140}). The fact that all these frequencies are displaced from the normal C—N stretching frequency region (900 — 1300 cm^{-1}) toward the double bond region may be understood as a result of the partial double bond character of the existing C—N bonds in all three compounds. In reasonable accordance with the results deduced from the C-region the relative displacement of the C—N frequencies indicate considerable bond delocalization in U and OU_{140} and much less in OU_{72} .

The low frequency part of the fingerprint-region D is still more difficult to interpret, and only vague suggestions may be attempted.

It would be reasonable to assign the bands located round 1100 cm^{-1} in OU_{140} and OU_{72} to N—O stretching vibrations. Some support for this assignment is provided by investigations of Borello and Henry²² who assigned a frequency at 1150 cm^{-1} in a glyoxime to the N—O bond. Some evidence against this assignments is, however, found in the fact that absorption at 1100 cm^{-1} is not completely absent in urea, the formula of which is devoid of N—O bonds. The frequency in question is of course in the normal position of C—N stretching vibrations (900 — 1300) and this should be taken into account as an alternative assignment. A symmetrical stretching vibration of C—N has been reported at 1000 cm^{-1} in urea (Table 1).

* Added in proof. A publication in Czech by O. Exner (*Chem. Listy* 52 (1958) 1613) has come to the author's knowledge after this paper had been delivered for publication. Exner has recorded the IR-absorption in the carbonyl-region of a number of hydroxylamine derivatives, *inter alia* the hydroxyureas. Exner reports a carbonyl frequency of 1750 cm^{-1} in OU_{72} and a double band at 1680 and 1695 cm^{-1} , respectively, in OU_{140} . The numerical deviations from the values reported in Table 2 are probably due to the fact that Exner's measurements are carried out on dioxane solutions.

Formula II requires C—O single bond frequencies to exist in OU_{72} , and since this bond has no equivalent in the conventional formula of urea and probably not in that of OU_{140} either, any frequency assignable to C—O should be chosen amongst OU_{72} -bands, which are absent in U and OU_{140} . Three intense bands meeting these requirements, fall within the normal region of C—O stretching vibrations, namely those at $1\ 210\text{ cm}^{-1}$, 950 cm^{-1} and at 885 cm^{-1} , respectively. It should be pointed out, however, that a band at 950 cm^{-1} observed in β -oximes in the solid state has been assigned to the N—O bond²⁴. Since furthermore the band at $1\ 210\text{ cm}^{-1}$ has an equivalent in O-benzoyl-hydroxylamine (Table 3) we suggest that this band be assigned to the C—O stretching vibrations.

Finally the *E*-region is the one in which N—H rocking is normally observed and the band around 800 cm^{-1} observed in all three compounds may tentatively be assigned accordingly.

Summarizing the discussion of the absorption spectra it may be said that no details have been found, which are incompatible with the formulae I and II. Some observations are in favour of them, but no unambiguous proof has been delivered as far as absorption spectroscopy in the infra-red is concerned.

EXPERIMENTAL

The preparation and characterization of the hydroxyureas (Fig. 1, curves *c*, *d*, and *f*) have been described in a previous communication³². The sample of the higher melting isomeride employed for the recording of curve *e* was prepared according to Runti and Deghenghi³³. It is regarded as having a higher degree of purity than that used for curve *f*. The urea sample was a commercial analytical-grade product.

All results in Fig. 1 and Table 2 refer to the crystalline state. The pressed disc technique was used and the disc contained 1 mg substance dispersed in 300 mg of potassium bromide. The instrument was a Perkin Elmer double beam infra-red spectrophotometer model 21, equipped with sodium chloride optics. Resolution 927, response 1, gain 6.5, speed 5, suppression 2.

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