208. *The Infrared Absorption of Normal and* ^{18}O-*Labelled* NN′-*Di*-p-*tolylurea and* NN′-*Dicyclohexylurea.*

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The infrared absorption has been measured for solutions of normal and [^{18}O]ditolylurea and normal and [^{18}O]dicyclohexylurea in dimethyl sulphoxide and in carbon tetrachloride–dimethyl sulphoxide. The bands and the isotopic shifts of the C=O stretching frequencies are discussed. While the relative integrated absorption intensity of the ditolylurea C=O band is increased by *ca.* 80% as a result of 80% labelling with ^{18}O it is decreased by *ca.* 20% in the case of (90% labelled) dicyclohexylurea. The apparent half-width of this band is appreciably increased in each case.

The ^{18}O-content of water and many oxy-acids can be estimated spectrophotometrically after their reaction with carbodi-imides to form ureas,[1] whose carbonyl group absorbs characteristically according to the isotopic structure. For this investigation *NN′*-di-*p*-tolyl- and *NN′*-dicyclohexyl-urea were synthesized with 80 and 90 atom %, respectively, of ^{18}O labelling; their infrared spectra were studied in connexion with the effect of ^{18}O

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[1] Lapidot, Pinchas, and Samuel, *Proc. Chem. Soc.*, 1962, 109.

labelling on the spectrum of X=O compounds.[2] These ureas, however, are insoluble in the conventional solvents used for infrared absorption studies while measurements on their solid phase are more difficult to interpret owing to hydrogen bonding between the carbonyl groups and the amino-hydrogen atoms. We used dimethyl sulphoxide which affords 2% and ~1% solutions of di-*p*-tolyl- and dicyclohexyl-urea, respectively. These high solubilities seem to be due to formation of hydrogen-bonded[3] complexes such as $(Me_2SO \cdots HRN)_2CO$; in conformity a 3 : 1 mixture of carbon tetrachloride and dimethyl sulphoxide is as good a solvent for ureas as dimethyl sulphoxide itself. Table 1 gives the bands and optical densities for di-*p*-tolylurea.

TABLE 1.

Infrared absorption bands (cm.$^{-1}$) and optical densities of *NN'*-di-*p*-tolylurea.

No.	Solvent *		Concn. (g./l.)					
1	Normal	D	11·5	3450	1703	1602	1547	1511
				0·09	0·38	0·465	0·66	0·60
2	80% ^{18}O	D	3·4	3450	1659	1601	1547	1511
				—	0·47	0·55	0·76	0·46
3	Normal	CD	12	3430	1708	1599	1540	1512
				0·60	0·43	0·44	0·65	0·68
4	80% ^{18}O	CD	9	†	1688	1599	1545	1512
				—	0·30	0·39	0·48	0·77

No.							
1	—	1234		1217	1194	821	742
		0·34		0·17	0·35	0·26	0·12
2	—	1232		—	—	—	—
		0·23					
3	1293	1232		1218	1197	821	742
	0·30		0·40	0·12	0·21	0·20	0·06
4	—	—		1216	1192	—	—
	—	—		Shoulder	0·36	—	—

* D = Dimethyl sulphoxide; CD = 3 : 1 v/v carbon tetrachloride–dimethyl sulphoxide; cell thickness = 0·2 mm., but 0·5 mm. for no. 2. † Measured only over the ranges shown.

It is interesting that the N–H stretching frequency of the di-*p*-tolylureas in dimethyl sulphoxide is as high as 3450 cm.$^{-1}$ although these N–H groups are no doubt hydrogen-bonded to the solvent.[3] This value can be compared with the free acetanilide N–H group stretching[4] frequency (in carbon tetrachloride solution) at 3442 cm.$^{-1}$ and with the value of 3480 cm.$^{-1}$ for a dilute carbon tetrachloride solution of *N*-methylbenzamide,[5] and it seems that hydrogen-bonding of urea to the solvent is not strong. For the strongly hydrogen-bonded solid *NN'*-di-*p*-tolylurea this band appears[6] at about 3290 cm.$^{-1}$.

The 1703 cm.$^{-1}$ C=O stretching frequency for normal di-*p*-tolylurea shows this group to be unbonded in dimethyl sulphoxide since in the solid state[6] it absorbs at 1635 cm.$^{-1}$ and free secondary amides absorb[7] at about 1690 cm.$^{-1}$. The increase of this frequency (to 1708 cm.$^{-1}$) in carbon tetrachloride–dimethyl sulphoxide seems to result from the lower polarity of this solvent.[8]

The high intensity of the C_{ar}–C_{ar} stretching bands[9] at about[6] 1600 and 1511 cm.$^{-1}$ (the latter being usually the strongest band in the spectra of the di-*p*-tolylureas) is probably due to the effect of the polar dimethyl sulphoxide on the electron distribution in the aromatic rings.

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[2] Pinchas, Samuel, and Weiss-Broday, *J.*, 1962, 3968, and literature cited therein.
[3] Thompson, *J.*, 1962, 617.
[4] Russel and Thompson, *J.*, 1955, 483.
[5] Pinchas, Samuel, and Weiss-Broday, *J.*, 1961, 2666.
[6] Khorana, *Canad. J. Chem.*, 1954, **32**, 263.
[7] See, *e.g.*, Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen & Co. Ltd., London, 2nd edn., 1958, p. 205.
[8] See, *e.g.*, ref. 7, pp. 380—382.
[9] Ref. 7, p. 65.

Since Davies and Hopkins[10] assigned the 1620 cm.$^{-1}$ band of a urea mull to an NH_2 bending vibration, and since breaking the hydrogen bonds decreases such a frequency,[11,5] one expects a free urea-amino-group bending to give a band near 1570 cm.$^{-1}$. Hence, the strong bands observed with the dissolved di-*p*-tolylureas (which were shown above to be only weakly hydrogen-bonded) at about 1545 cm.$^{-1}$ must be due to their N–H bending vibrations. For solid normal di-*p*-tolylurea this band was reported[6] at 1563 cm.$^{-1}$.

The 1293 cm.$^{-1}$ band,[6] which in pure dimethyl sulphoxide solutions is masked by the solvent absorption, seems to belong to the C_{ar}–N stretching vibration, in analogy with the absorption of aromatic amines.[12] The 1233 and 1194 cm.$^{-1}$ bands may be the antisymmetrical and symmetrical N–CO–N stretching bands, respectively, since their mean value (1213) is near that (1240) of the corresponding bands for a mull of urea itself.[10]

Interaction between the individual vibrating C–N bonds is expected to be weaker in the monomeric, dissolved di-*p*-tolylureas than in the polymeric solids, the polar contributions to the structure of the latter being stabilized by strong hydrogen bonds.

Apart from the bands due to the *para*-substituted aromatic ring[13] (at 1217 and 821 cm.$^{-1}$) the only absorption observed further was at 742 cm.$^{-1}$. This seems to belong to the N–H out-of-plane bending which is shown at about 720 cm.$^{-1}$ by *N*-methylbenzamide and other secondary amides.[5] Solid urea also gives a band[10] at 712 cm.$^{-1}$; solid di-*p*-tolylurea shows[6] a doublet at about 720 and 700 cm.$^{-1}$.

Labelled di-*p*-tolylurea shows only one real spectral difference from the normal species, namely, in the location of its C=O stretching band. The frequency is decreased by 44 cm.$^{-1}$ in dimethyl sulphoxide and by 20 cm.$^{-1}$ in the mixed solvent. These values can be compared with the calculated difference[14] of $(1 - 0{\cdot}9759)1703 = 41$ cm.$^{-1}$ for a diatomic CO molecule and with the observed value of 24 cm.$^{-1}$ for various benzamides in carbon tetrachloride solution.[15]

TABLE 2.

Intensity of the CO band of *NN'*-ditolylurea.

	Solvent	Concn. (g./l.)	Apparent molar extinction coeff. (l. mole^{-1} cm.$^{-1}$)	Apparent half-width (cm.$^{-1}$)	Relative integrated absorption * (l. mole^{-1} cm.$^{-2}$)
Normal	D	12·9	480 ± 10	21	10,100 ± 500
79% ^{18}O	D	11·8	460 ± 70	42	19,000 ± 3500
Normal	CD	12·8	541 ± 10	20·5	11,100 ± 300
Normal	CD	11·9	539 ± 15	20·8	11,200 ± 400
79% ^{18}O	CD	9·2	482 ± 15 †	38·5 ‡	18,500 ± 1000

* Obtained by multiplying the apparent molar extinction by the apparent half-width. † Corrected for the presence and absorption of the light modification at the C=^{18}O frequency. ‡ With due consideration of the absorption by the normal compound.

The intensity measurements for the C=O stretching bands of normal and labelled *NN'*-di-*p*-tolylurea are collected in Table 2. This shows that labelled ditolylurea gives a doubled half-width (exactly in dimethyl sulphoxide and approximately in the mixed solvent) and, since the apparent molecular extinction coefficient is about the same for both isotopic modifications, also a relative integrated absorption which is almost doubled. *NN'*-Di-*p*-tolylurea thus shows the highest change in half-width and absorption intensity, as the result of ^{18}O-labelling, observed so far:[2] benzamides,[15] for instance, show only small variations in half-width and a rise of about 23% in intensity. The increase in the ditolylurea absorption seems to be more pronounced for dimethyl sulphoxide solutions, where the increase in half-width is also bigger, than in the mixed solvent, which may be correlated

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[10] Davies and Hopkins, *Trans. Faraday Soc.*, 1957, **53**, 1563.

[11] Ref. 7, pp. 217, 219.

[12] Ref. 7, p. 249.

[13] Ref. 7, p. 65.

[14] Halmann and Pinchas, *J.*, 1958, 1703.

[15] Pinchas, Samuel, and Weiss-Broday, *J.*, 1961, 3063.

with the exceptionally high isotopic shift for the dimethyl sulphoxide solutions noted above. The molar extinction coefficient and half-width of the labelled ditolylurea increased even more (see Table 2) on further dilution of its dimethyl sulphoxide solution.

TABLE 3.

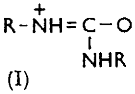
Infrared absorption bands (cm.$^{-1}$) and optical densities of *NN'*-dicyclohexylurea.

	Solvent *	Concn. (g./l.)									
Normal	CD	3·7	3430	2920	2570	1990	1668	1548	1252	1221	888
			0·20	0·14	0·02	0·03	0·28	0·34	0·08	0·08	0·34
~90% ^{18}O	CD	6·6	3430	2920	2580	1990	1647	1548	1252	1221	890
			0·72	0·30	0·05	0·11	0·53	0·39	0·18	0·16	0·15
Normal †	D	4·8					1660	1548			
							0·38	0·20			
~90% ^{18}O †	D	Satd.					1627	1550			

* See Table 1; cell-thickness 0·2 mm., except 0·5 mm. in the last case. † Measured only in the 1730—1480 cm.$^{-1}$ region.

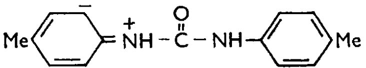
The bands observed for *NN'*-dicyclohexylurea are reported in Table 3. They can be compared with those that Stewart and Muenster[16] observed for the strongly hydrogen-bonded solid normal[6] and [^{18}O]dicyclohexylurea at 1628, 1575, and 1611, 1575 cm.$^{-1}$, respectively.

The lower values for the C=O frequencies of the dicyclohexylureas than of the ditolylureas (see Table 1), *e.g.*, 1668 cm.$^{-1}$ for the normal alicyclic urea (in the mixed solvent), compared with 1708 cm.$^{-1}$ for its aromatic analogue, must be due to higher contributions from polar structures, such as (I) to the state of the alicyclic ureas. In the aromatic ureas these contributions are lower because of conjugation of the aromatic rings to the NH groups which results in resonating structures (II) which oppose the polarization of the C=O group. This effect of the aromatic conjugation is also reflected in the C=O stretching frequency of amides. Thus, unbonded acetanilide in carbon tetrachloride has this band[17] at 1705 cm.$^{-1}$ while free *N*-ethylacetamide[18] absorbs at 1687 cm.$^{-1}$.



$R{-}\overset{+}{N}H{=}\underset{NHR}{\underset{|}{C}}{-}O^-$

(I)



(II)

The greater contribution of structures such as (I) seems also to be the reason for the higher frequencies of the (O=)C–N stretching bands of alicyclic than of aromatic ureas. These bands, probably, appear at 1252 (antisymmetric) and 1221 cm.$^{-1}$ (symmetric) for the alicyclic and at 1233 and 1194 cm.$^{-1}$ for the aromatic ureas. The effect of a greater (I) (double-bond) character of the (O=)C–N bonds on their stretching frequencies is thus appreciable.

The 890 cm.$^{-1}$ band of the alicyclic ureas (which is not given by the ditolylureas) seems to be due to the " breathing " vibrations of the cyclohexyl group, by analogy with the similar vibrations of tetrahydrofuran (913 cm.$^{-1}$), alkylcyclobutanes (910 cm.$^{-1}$), and cyclopentanes[19] (890 cm.$^{-1}$). That this vibration is active in the infrared region, in contradistinction to the cyclopentanes[19] case, can be due to the lower symmetry of the cyclohexyl derivatives, especially in view of the effect of the polar substituent and in the hydrogen-bonding solvent. Cyclohexane itself also shows strong bands[20] at about 870 and 910 cm.$^{-1}$.

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[16] Stewart and Muenster, *Canad. J. Chem.*, 1961, **39**, 401.

[17] Barrow, *J. Chem. Phys.*, 1953, **21**, 2008.

[18] Klemperer, Cronyn, Maki, and Pimentel, *J. Amer. Chem. Soc.*, 1954, **76**, 5846.

[19] Jones and Sandorfy in " Technique of Organic Chemistry," Interscience Publ. Inc., New York, 1956, Vol. IX, p. 576.

[20] Shell Development Co., " Documentation of Molecular Spectra Catalogue," Butterworths Scientific Publns., London, 1958, compound card No. 1289.

Labelling the carbonyl group with ^{18}O is again seen (Table 3) to result in a decrease of about 20 cm.$^{-1}$ only (1668—1647) for a carbon tetrachloride–dimethyl sulphoxide solution but appreciably more (33 cm.$^{-1}$) for a pure dimethyl sulphoxide solution. The latter isotopic shift, although higher than usual [14,15,21,22] ($\sim$30 cm.$^{-1}$), is still less than the 44 cm.$^{-1}$ observed for ditolylurea in pure dimethyl sulphoxide.

The isotopic C=O shift of dimethyl sulphoxide solutions was, however, found to be less than that for carbon tetrachloride solutions in the case of benzophenone [14] (1652 and 1627 cm.$^{-1}$ for the C=^{16}O and C=^{18}O frequencies, respectively) and benzamide [23] (1679 and 1664 cm.$^{-1}$, respectively; N–H bending 1577 and 1570 cm.$^{-1}$).

The relative absorption intensities for normal and labelled *NN'*-dicyclohexylurea (Table 4) show that ^{18}O labelling also markedly increases the half-width of its C=O band, although not as much as for ditolylurea (in the mixed solvent, 32% compared with 88%). The intensity of the alicyclic urea band, however, decreases on labelling instead of increasing as for the aromatic urea. Such a decrease, of about 20%, was also observed for benzophenone,[14] triphenylphosphine oxide,[24] monomeric benzoic acid,[21] and methyl benzoate,[21] while in a number of very polar compounds ^{18}O-labelling increased the C=O band absorption.[2] It was therefore even suggested [2] that there exists a correlation between the high polarity of an X=O compound (X = C or S) and the direction of the effect of ^{18}O-labelling on the intensity of its X=O absorption band. That dicyclohexylurea with the lower C=O stretching frequency (hence, higher polarization) gives an ^{18}O-induced decrease in intensity while ditolylurea gives an increase shows that this problem is more complex.

TABLE 4.

Intensity of the CO band in the isotopic *NN'*-dicyclohexylureas.

Material	Solvent	Concn. (g./l.)	Apparent molar extinction coeff. (l. mole^{-1} cm.$^{-1}$)	Apparent half-width (cm.$^{-1}$)	Relative integrated absorption (l. mole^{-1} cm.$^{-2}$)
Normal	CD	3·7	730 ± 15	30	22,000 ± 500
$\sim$90% ^{18}O	CD	15·2	435 ± 22 *	39·5 †	17,200 ± 1000
Normal	D	4·8	870 ± 50	54·5	47,500 ± 3000
$\sim$90% ^{18}O ‡	D	—	—	—	—

* Corrected for the presence and absorption of the light modification. † After subtraction of the absorption due to the normal modification. ‡ The C=O absorption is interfered with by that of the solvent.

EXPERIMENTAL

[^{18}O]*Di*-p-*tolylurea*.—^{18}O-Enriched water (from the separation plant of the Weizmann Institute) in excess was added to a solution of di-*p*-tolylcarbodi-imide in dioxan through which dry hydrogen chloride was then bubbled to saturation. The crystals of di-*p*-tolylurea which separated were washed several times with dioxan and dry ether.

Normal Di-p-*tolylurea*.—The normal compound was prepared similarly with ordinary water.

[^{18}O]*Dicyclohexylurea and Normal Dicyclohexylurea*.—These substances were prepared analogously from dicyclohexylcarbodi-imide.

Isotope Analyses.—The labelled urea was sealed with copper bronze (previously dried for 1 hr. in a stream of hydrogen at 300—400°) under a vacuum in a break-seal tube and heated [25] at 320° for 30 min. The carbon dioxide formed was analysed without further purification, by means of a Consolidated Engineering Corp. model 21-401 spectrometer.

The optical measurements were carried out as already described.[23]

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[21] Pinchas, Samuel, and Weiss-Broday, *J.*, 1961, 2382.
[22] Karabatsos, *J. Org. Chem.*, 1960, **25**, 315.
[23] Pinchas, Samuel, and Weiss-Broday, *J.*, 1961, 1688.
[24] Halmann and Pinchas, *J.*, 1958, 3264.
[25] Halmann, *J.*, 1959, 305.