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INFRARED ABSORPTION OF SUBSTITUENTS—XI[1]

THE STRUCTURE OF UREAS AND THIOUREAS

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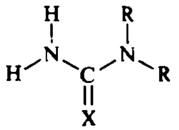
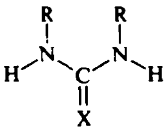
Abstract—The technique of partial deuteration has been extended to distinguish between N,N′- and N,N-disubstituted ureas and thioureas.

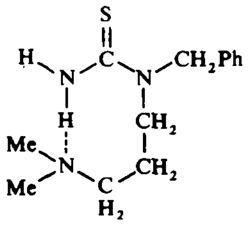
A PRIMARY amino group can be identified by the presence of a triplet in the NH-stretching region of the spectrum of the partially deuterated derivative.[2,3] The N—H stretch of the uncoupled NHD group appears between the symmetrical and the anti-symmetrical NH stretch of the NH_2 group. This technique has previously been applied to the structural classification of potentially tautomeric amino-imino compounds.[1,4,5] We now show that it may also be used to distinguish between isomeric disubstituted ureas (I/III) and thiourea (II/IV).



(I, X = O)
(II, X = S)



(III, X = O)
(IV, X = S)



(V)

The problem originally arose in the course of the investigation of the alkylation of amides and carbodiimides prior to hydration was not possible, and it thus became necessary to find a convenient method to distinguish between symmetrically and asymmetrically disubstituted ureas.

RESULTS AND DISCUSSION

Results are recorded in Table 1.

Three of the compounds of known structure contained an NH_2 group. For N,N-dimethylurea (Table, No. 1) and for acetone 2-methylthiosemicarbazone (No. 2) the IR spectrum was as expected: the usual doublet before deuteration, changing to a triplet with the two outermost peak positions essentially unchanged after partial deuteration. The spectra of N-benzyl-N-(3-dimethylamino-*n*-propyl) thiourea (No. 3) is anomalous, showing two bands both before and after deuteration. However this is explained by intramolecular hydrogen bonding in this compound (V) which causes the force constants of the two NH groups to be significantly different, and the bands to be far less coupled. The low frequency of one of the bands (3280 cm^{-1}) supports this explanation.

TABLE 1. INFRARED SPECTRAL MAXIMA* (cm^{-1}) FOR CCl_4 SOLUTIONS IN THE NH STRETCHING REGION

No	$R_1R_2NC(X)NR_3R_4$					Initial spectra		After partial deuteration		
	R_1	R_2	X	R_3	R_4					
1	Me	Me	O	H	H	3527	3427	3522	3467	3422
2	Me	N:CMe_2	S	H	H	3517	3387	3527	3442	3392
3	CH_2Ph	$(CH_2)_3NMe_2$	S	H	H	3472	3282 (w)	3472	3277(w)	
4	H	Ph	O	Ph	H	3432(sh)		3427(sh)		
5	H	CH_2Ph	O	CH_2Ph	H	3447		3442		
6	H	Ph	O	CPh_3	H	3432	3412	3432	3412	
7	H	CH_2Ph	O	CPh_3	H	3437		3437		
8	H	Et	O	2,6-dimethyl-phenyl	H	3437		3432		
9	H	Ph	S	Ph	H	3417	3382	3412	3377	
10	H	$CH(Ph)_2$	S	CPh_3	H	3423	3387	3427	3392	
11	H	Ph	S	$CH(Me)_2$	H	3422	3392	3417	3387	
12	H	Ph	S	$CH(Ph)_2$	H	3412	3387	3412	3387	
13	H	$C(Ph)_3$	O	2,6-dimethyl-phenyl	H	3422		3417		

* All band positions are accurate to ±5 cm^{-1}.
w = weak band. sh = band with shoulder.

Five ureas (Nos. 4–8) and four thioureas (Nos. 9–12) of known structure containing two different NH groups were available. All these compounds show either one band, or two bands with a fairly narrow separation ($\leqslant 35$ cm^{-1}), and in each case no new band appears on deuteration, confirming the absence of appreciable coupling and therefore the absence of an NH_2 group. Two bands can arise when the N- and N′-substituents are different, which presumably implies different force constants for the two NH groups; however in certain cases two bands (No. 9) or a band with a shoulder are found where the two substituents are identical. The latter situation probably arises from rotational isomers about the C(:X)—N bonds.

The compound of previously unknown structure (No. 13) could clearly be assigned the N,N′-disubstituted structure on the basis of the criterion previously established.

EXPERIMENTAL

Compounds Nos. 4, 5 and 9 (cf. Table 1) were prepared by standard methods and had m.ps agreeing with quoted values. Thioureas Nos. 10, 11[8] and 12[9] were made[6] by reaction of an amine and isothiocyanate. Reaction of the corresponding thiourea with mercuric oxide and water, by the method of ref. 6, gave N-*ethyl*-N'-(2,6-*dimethylphenyl*)*urea* (No. 8) which formed colourless needles, m.p. 224–225°, from ethanol. (Found: C, 68·8; H, 8·3; N, 14·9. $C_{11}H_{16}N_2O$ requires C, 68·7; H, 8·4; N, 14·6).

Ureas Nos. 6 and 7 were prepared by hydration of the authentic carbodiimide.[6] Compounds Nos. 1[11] and 3[10] were made by the literature methods indicated.

Acetone (*N-thiocarbamoyl-N-methyl*)*hydrazone* (No. 2)

Prepared from the corresponding methylthiosemicarbazide, formed colourless prisms, m.p. 150–151° (from acetone). (Found: C, 41·4; H, 7·3; S, 21·7. $C_5H_{11}N_3S$ requires C, 41·4; H, 7·6; S, 22·0%).

Compound No. 13, of uncertain structure, was prepared[6] by the tritylation of 2,6-dimethylphenyl cyanamide.

Spectra were obtained of carbon tetrachloride (molecular sieve dried) solutions in matched 4 cm path length cells (as many of the compounds were highly insoluble, and to exclude intermolecular hydrogen-bonding) on a Perkin–Elmer 257 grating spectrometer.

Deuteration was affected by refluxing the compound in dry dioxan–deuterium oxide mixture under nitrogen for periods of up to 1 hr. The solvent was removed *in vacuo* and the compound dried for 24 hr under high vacuum. The extent of deuteration was checked by the 4000–1500 cm^{-1} Nujol mull spectra.

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