SECTION B
Physical Organic Chemistry

The Nuclear Magnetic Resonance Spectra of Urethanes, Ureas, Allophanates, and Biurets

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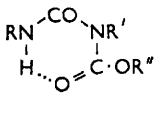
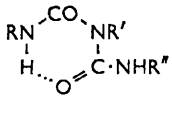
The proton magnetic resonance spectra of a number of urethanes, ureas, allophanates, and biurets are reported, and the chemical shift and multiplet splitting of the NH signal is correlated with molecular structure.

In the course of our work on the interaction of organometallic alkoxides and oxides with isocyanates,[1,2] we investigated the proton magnetic resonance spectra of a number of *N*-substituted urethanes, ureas, allophanates, and biurets. These results are now presented and discussed, particularly insofar as the chemical shift and multiplet splitting of the NH signal can provide evidence of molecular structure.

A similar investigation has been reported with the aim of identifying these structural units in polyurethane elastomers,[3] and we are very grateful to Dr. Sumi for telling us of the work of his group when ours was at an early stage. They found that, in carbon tetrachloride or chloroform at 40° and 10% (w/v) concentration, allophanates and biurets showed the resonance signal of the NH proton, but urethanes and ureas did not; all four types of compound, however, showed sharp NH signals in polar solvents such as dimethyl sulphoxide, dimethylacetamide, acetone, and pyridine. They concluded that the normal broadening effect of the ^{14}N quadrupole is probably nullified by the increase in the NH distance which results from hydrogen-bonding intramolecularly in the allophanates and biurets [(I) and (II), respectively] or intermolecularly with the solvent in the urethanes and ureas. Some of these workers' results are included with ours in the Table for comparison.



(I)



(II)

Urethanes, Ureas, and Allophanates.—We found that (at 33°) we could generally observe NH signals for the urethanes and ureas, as well as for the allophanates and biurets, in carbon tetrachloride or deuterochloroform. In isopropyl and phenyl *N*-phenylcarbamates (compounds 4 and 6), these signals might be obscured by those of the aromatic rings.

In the urethanes and ureas, the alkylNH signal occurs upfield of the arylNH signal. If a solution of a urethane in carbon tetrachloride is made more concentrated, or if the solvent is changed to dimethyl sulphoxide, the resonance shifts to lower field, as would be consistent with increasing intermolecular hydrogen-bonding. The ureas in dimethyl sulphoxide showed NH signals now about 0·5 p.p.m. to higher field than those in carbon tetrachloride. This might be taken to imply that the ureas are strongly associated by intermolecular hydrogen-bonding in carbon tetrachloride, but when the concentration of *NN'*-diethylurea was increased from 10 to 30% the NH signal moved to slightly higher field.

In both the *N*-alkylurethanes (1 and 8) and the *N*-alkylureas (10, 11, and 12), NH–CH_n coupling was apparent, the NH signal appearing as a partially resolved $(n + 1)$ multiplet. The coupling constant in all cases is about 7 c./sec., reducing to this approximate magnitude the frequency at which the NH protons can undergo exchange.

Biurets.—The structures of some mixed biurets which we obtained by treating isocyanates with organotin oxides [1] have been investigated.

3-Ethyl-1,5-diphenylbiuret (20) shows a single fairly sharp NH signal, of area equivalent to two protons, in both deuterochloroform and dimethyl sulphoxide. No splitting of the NH peak is apparent, and the CH_2 signal is a simple quartet. 5-Ethyl-1,3-diphenylbiuret (19) shows two NH signals in both solvents, separated by 5·0—5·6 p.p.m. Coupling between the NH and CH_2 groups identifies the signal at higher field as that of the EtNH group. The sequences of alkyl groups in these two compounds is therefore confirmed.

3-Ethyl-1,5-di-1-naphthylbiuret (23) gave in deuterochloroform a single NH signal of area equivalent to two protons at low field; no coupling involving the NH or CH_2 peaks was apparent. Both amide protons must therefore be on ArN groups, confirming the symmetrical structure.

The compound which had been assigned the structure PhNH·CO·NMe·CO·NH(1-$C_{10}H_7$) (24) gave only a very broad NH signal at low field, which could not be integrated accurately and which we assume to consist of the two overlapping broad peaks of the PhNH and 1-naphthylNH protons. No signal that might be ascribed to an alkylNH proton near τ 3·3 could be

[1] A. J. Bloodworth and A. G. Davies, *J. Chem. Soc.* (*c*), 1966, 299; and previous Papers.
[2] A. G. Davies and G. J. D. Peddle, unpublished work.
[3] M. Sumi, Y. Chokki, Y. Nakai, M. Nakabayashi, and T. Kanzawa, *Makromol. Chem.*, 1964, **78**, 146.

detected, though it might be obscured by the complex band of the aryl groups. In carbon tetrachloride, however, the methyl group showed as a sharp singlet, with no evidence of coupling with an NH proton.

This, together with our analysis of the relative reactivity of the addendum molecules involved in the oligomerisation,[1] suggests that the methyl group is probably on the medial nitrogen atom.

From studies of infrared spectra, Sumi and his co-workers concluded that intramolecular hydrogen-bonding in the biurets is stronger than in the allophanates.[4] In order to reconcile this with the fact that the NH signal (in dimethyl sulphoxide) of 1,3,5-triphenylbiuret occurred at higher field than that of methyl *NN'*-diphenylallophanate, he suggested that rapid interconversion occurred between the two conformations (III) and (IV) (R = R' = R'' = Ph), in which the alternative hydrogen atoms were involved in exclusive hydrogen-bonding. The actual NH signal which was observed was then at the average value for the hydrogen-bonded and non-hydrogen-bonded protons.

The situation is different in an unsymmetrical biuret, where the competition between the two NH protons for hydrogen bonding will be unequal. In dimethyl sulphoxide, the PhNH signal of 1-ethyl-3,5-diphenylbiuret is now 0·92 p.p.m. downfield of that of ethyl *NN'*-diphenylallophanate (although it is still slightly

[4] M. Sumi *et al.*, unpublished work, quoted in ref. 3.

NH chemical shifts

Compound	Solvent CCl_4 (i)	$CDCl_3$ (ii)	Me_2SO (iii)
Urethanes			
1. EtNH·CO_2Me	4·7 (broad) *; 3·97 (50%) *; 3·45 (neat) *		2·85 *
2. PhNH·CO_2Me	2·08 (satd., >10%)		0·21
3. PhNH·CO_2Et			0·54 [3]
4. PhNH·CO_2Pr^i	— (satd., >10%)		0·30
5. PhNH·CO_2Bu^t	— (satd., ≪10%)	3·25 (broad)	0·55
6. PhNH·CO_2Ph	— (satd., ≪10%)	—	
7. *m*-Me·C_6H_4·NH·CO_2Et			1·34 [3]
8. EtNH·CO·O·$SnBu_3$	4·45 *		
9. PhNH·CO·O·$SnBu_3$	1·51 (50%)		
Ureas			
10. EtNH·CO·NHEt	3·58 *; 3·64 * (30%)		4·30 [3]; 4·07 * (30%)
11. MeNH·CO·NHBu	3·58 * (broad)		4·16 (20%)
12. PhN^{a}H·CO·N^{b}HEt	Insol.	Insol.	*a* 1·51; *b* 3·82 *
13. PhN^{a}H·CO·N^{b}HBu			*a* 1·67; *b* 3·94 [3]
14. PhNH·CO·NHPh	Insol.	Insol.	1·42 [3]
Allophanates			
15. PhNH·CO·NPh·CO_2Me	−0·98 (satd., <10%)	−1·12 (10% and 20%)	−0·98
16. PhNH·CO·NPh·CO_2Et		−1·28 (20%)	−0·67 [3]
17. PhNH·CO·NPh·CO_2Pr^i		−1·25 (20%)	−0·96 (20%)
18. NpNH·CO·NNp·CO_2Bu^s		−2·26 (20%)	0·40
Biurets			
19. PhNH·CO·NPh·CO·NHPh			0·40 [3]
20. PhNH·CO·NEt·CO·NHPh		0·66	−0·38
21. PhN^{a}H·CO·NPh·CO·N^{b}HEt		*a* −1·16; *b* 4·48 *	*a* −1·59; *b* 3·31 * (20%)
22. PhNH·CO·NBu·CO·NHPh			0·37 [3]
23. NpNH·CO·NEt·CO·HNNp		0·18	
24. PhNH·CO·NMe·CO·NHNp		—	−0·73 (v. broad; 15%)

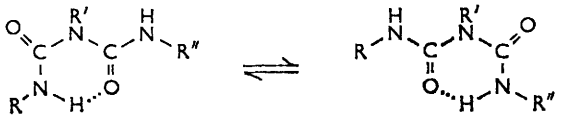
Np = 1-Naphthyl. — indicates that the NH resonance could not be detected. * Indicates that coupling was apparent between the NH group and the alkyl group.

Characteristic resonances of alkyl groups are summarised below. The code number of the compound and of the solvent is followed by the relevant alkyl group, its τ value, and (in parentheses) its multiplicity.

1. i CH_3CH_2 8·86(3), CH_3CH_2NH 6·67(5), OCH_3 6·32†
1. iii CH_3CH_2 8·87(3), OCH_3 6·39
4. i $(CH_3)_2CH$ 8·74(2), $(CH_3)_2CH$ 4·88(7)
4. iii $(CH_3)_2CH$ 8·72(2)
5. i $(CH_3)_3$ 8·38
5. ii $(CH_3)_3$ 8·46
5. iii $(CH_3)_3$ 8·49
8. i CH_3CH_2NH 6·82(5)
10. i CH_3CH_2 8·74(3), CH_3CH_2NH 6·73(5)
10. ii CH_3CH_2 8·92(3), CH_3CH_2NH 6·84(5)
10. iii CH_3CH_2 9·02(3)
11. i CH_2NH 7·23(2)
12. iii CH_3CH_2 8·93(3)
15. i OCH_3 6·24
16. ii CH_3CH_2 8·83(3), CH_3CH_2 5·71(4)
17. ii $(CH_3)_2CH$ 8·85(2), $(CH_3)_2CH$ 4·87(7)
17. iii $(CH_3)_2CH$ 8·85(2), $(CH_3)_2CH$ 4·91(7)
20. ii CH_3CH_2 8·63(3), CH_3CH_2 6·00(4)
21. ii CH_3CH_2 8·94(3), CH_3CH_2NH 6·78(5)
21. iii CH_3CH_2 8·96(3)
23. ii CH_3CH_2 2·59(3), CH_3CH_2 5·90(4)
24. ii CH_3 6·52

† (independent of concentration)

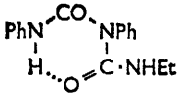
upfield, by about 0·1 p.p.m., in deuterochloroform). The separation between the PhNH and EtNH signals is very large, much larger than that observed in *N*-ethyl-*N'*-phenylurea, and the PhNH signal occurs some



(III) (IV)

2·0 p.p.m. downfield of that which Sumi *et al.* observed in triphenylbiuret. The position of the EtNH signal is relatively sensitive to a change of solvent, shifting downfield by about three times as much as that of the PhNH signal on changing from deuterochloroform to dimethyl sulphoxide.

It appears then that the PhNH proton at low field is heavily involved in intramolecular hydrogen-bonding, and the EtNH proton at high field is relatively free to enter into hydrogen-bonding association with the solvent, *i.e.*, that the biuret in solution is substantially in the conformation shown in structure (V).



(V)

EXPERIMENTAL

Materials.—The urethanes **1**, **2**, and **6** were prepared from the appropriate isocyanate and alcohol or phenol, using tributyltin methoxide or triethylamine as a catalyst as required. The urethanes **4** and **5**, and the allophanates **17** and **18** were prepared from the appropriate aluminium alkoxide and isocyanate.[2] The ureas **10**, **11**, and **12** were obtained from the appropriate amine and isocyanate. The sources of the other compounds have been described in ref. 1.

Spectra.—Proton magnetic resonance spectra were recorded at 33·5° on a Perkin-Elmer R-10 spectrometer operating at 60 Mc./sec. Unless stated otherwise, concentrations are 10% (w/v) as used in ref. 3. Chemical shifts are quoted in τ-units.

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