Proton Magnetic Resonance Studies of Trichloroacetamides

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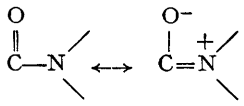
ROGERS and WOODBREY[1] showed the rate of rotation around the carbonyl-to-nitrogen bond (amide bond) to be much greater and the signal coalescence temperature much lower in *NN*-dimethyltrichloroacetamide (I) than in *NN*-dimethylacetamide (II) [$\Delta F^0_{298\cdot2}$ = 14·9 kcal./mole for (I) as against 17·4 for (II)]. We have observed the reverse situation for the corresponding di-2-propyl derivatives, (III) and (IV). We have not determined kinetic values for (III) and (IV) quantitatively; however the coalescence temperature is 10° higher for (III), even though the chemical shift between methyl groups is greater for (IV) (see Table). The $CHCl_3$ proton signal for the equimolar solution of (IV) is at 8·2 p.p.m. at 0°, while it is at 7·3 p.p.m. for (III). From these last two data, (III) must be a much poorer base than (IV), and resonance form (B) must be much less important for (III) than for (IV).



(A) (B)

TABLE

*Proton magnetic resonance data**

	Signal position at 0° (25 vol % in $CDCl_3$)		
Compound	N–CH_3	CH–N	$(CH_3)_2C$–N
(I) Me_2N–CO–CCl_3	3·39, 3·12	—	—
(II) Me_2N–CO–CH_3	3·05, 2·94	—	—
(III) Pr^i_2N–CO–CCl_3	—	4·70, 3·52	1·43, 1·31
(IV) Pr^i_2N–CO–CH_3	—	3·93, 3·52	1·38, 1·23

* Obtained with a Varian A-60 spectrometer, all shifts in p.p.m. from tetramethylsilane.

This indication of less double bond character in the amide bond of (III) than in (IV) is directly opposite to the indication from signal coalescence. Finally, one signal set for the proton(s) α to nitrogen is shifted very much downfield for (I) and (III) compared to (II) and (IV).

These various observations can be explained if (a) it is assumed the α-proton(s) of the alkyl group *trans* to oxygen is close to one or more chlorine atoms and (b) this proximity produces a strongly attractive potential-energy term for (III). Such an attractive term has already been suggested for the N–H proton in *N*-substituted chloroacetamides.[2] Close proximity is known to deshield protons.[3] A strong attraction between the carbon-to-proton dipole and the chlorine-to-carbon dipole(s) would stabilize (III) in its planar ground state. In that event, there might be considerably less double bond character in the amide bond than coalescence behaviour indicates, which in turn is consistent with (III) being a relatively weak base. We are currently attempting a quantitative determination of this attractive term. From discussion above, the value of this term may be as much as two or three kcal., which seems exceptionally large.

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[1] M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, 1962, **66**, 540.
[2] R. D. McLachlan and R. A. Nyquist, *Spectrochim. Acta*, 1964, **20**, 1397.
[3] A. D. Buckingham, *Canad. J. Chem.*, 1960, **38**, 300.