The Exchange of Amino-protons in Trifluoroacetamide in Perdeuterioacetone: ^{19}F Nuclear Magnetic Resonance Study

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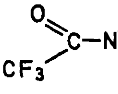
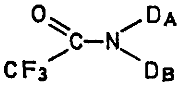
Summary ^{19}F n.m.r. spectroscopy is more useful than ^{1}H n.m.r. in the study of the exchange of hydrogen between trifluoroacetamide and $(CD_3)_2CO$.

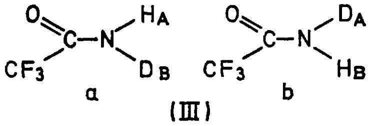
ROGERS AND WOODBREY measured the ^{19}F n.m.r. spectrum of *NN*-dimethyltrifluoroacetamide in dibromomethane in their study of hindered internal rotation in some substituted *NN*-dimethylamides.[1] We recorded the ^{19}F n.m.r. spectrum† of trifluoroacetamide (I) and observed a doublet in acetone at 34·5°. Since rotation about the C–N bond is relatively restricted even at room temperature, the coupling between fluorine nuclei and H_A gives a doublet. There is no coupling between the fluorines and H_B.‡

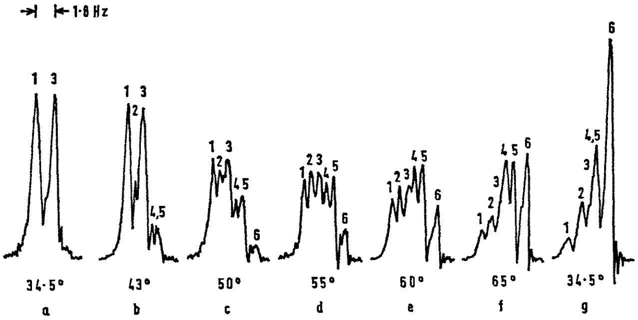

(I)


(II)

After heating the mixture of (I), (II), and (III) in ordinary acetone at 70° for 90 min., the ^{19}F n.m.r. spectrum of the solution at room temperature showed a doublet, which was the same as that due to compound (I). On the other hand, a single peak was observed after treatment of the mixture in $(CD_3)_2CO$ under the same conditions. The results reveal that the protons and deuterons in the amino-group are very labile at temperatures above 70°, and exchange takes place readily in the solutions. The doublet in acetone can be interpreted as due to the formation of compound (I) by almost complete exchange, and the single peak in $(CD_3)_2CO$ as being due to deuteriated amide (II). Although there would be couplings between fluorine nuclei and the deuterons in compound (II), no splittings due to weak coupling were detected in the single peak of very small half-width (0·5 Hz).

When the ^{19}F spectrum was measured on a solution of pure compound (I) in $(CD_3)_2CO$ freshly prepared at room temperature, a doublet was observed at 34·5° as shown in the Figure (a). This indicates that the rate of exchange between protons in the amino-group and deuterons in $(CD_3)_2CO$ is very slow at ordinary temperatures.§ The absorption peaks due to the sample solution gradually become more complicated as the temperature increases [Figure, (b—f)]. Finally, the solution was kept at 65° for about 10 min., and the spectrum was recorded [Figure (g)], after it had been cooled to room temperature. This spectrum is very similar to the spectrum of the three mixtures consisting of (I), (II), and compound (III) which has two isomers a and b due to restricted rotation. In compound (IIIa) the coupling of fluorine nuclei with H_A gives a doublet in the ^{19}F spectrum, without any coupling between fluorine D_B. In compound (IIIb) there is no coupling of fluorine nuclei with H_B and D_A; hence a single peak will appear in the ^{19}F spectrum. If we assume that in the Figure (a—g), the peaks 1 and 3 (doublet) are assigned to compound (I), 2 and 4 (doublet) to (IIIa), the single peak 5 to (IIIb), and the single peak 6 to compound (II), we can interpret the exchange process between the amino-protons and the deuterons in the solvent. The ^{19}F n.m.r. spectrum is more useful and convenient than the proton spectrum for the study of the exchange process, because of the large isotope effect on the fluorine chemical shift and the absence of appreciable broadening of the fluorine absorption bands by the electric quadrupole of the ^{14}N nucleus.


(III)



FIGURE

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† Hitachi-Perkin-Elmer R-20 Spectrometer operated at 56·456 MHz. All spectra were recorded with a sweep width of 2 p.p.m.

‡ ^{1}H n.m.r. spectrum of the amino-group of compound (I) consists of a pair of peaks below −30° in $(CD_3)_2CO$ because of the considerably hindered internal rotation about the C–N bond. Judging from the fact that the peak at lower field assigned to H_B is less broad than the peak at higher field assigned to H_A,[2] we can assume that the coupling between F and H_B is much smaller than between F and H_A. In addition to this, the fine doublets of the ^{19}F spectra of this compound at lower temperatures lead to the conclusion that the coupling between F and H_B is negligibly small. The detail was partly presented at the 8th N.M.R. Symposium at Tokyo, September 1969, and will be submitted to *J. Chem. Soc.*

§ Almost no change was observed in the ^{19}F n.m.r. spectrum during 2 hr. at room temperature, but an appreciable change was recognized in 24 hr.

[1] M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, 1962, **66**, 540.

[2] P. T. Narashimhan and M. T. Rogers, *J. Phys. Chem.*, 1959, **63**, 1338.