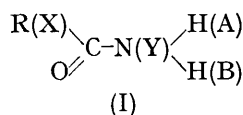


## Hindered Internal Rotation in [<sup>15</sup>N]Trifluoroacetamide

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The <sup>1</sup>H n.m.r. spectrum of [<sup>15</sup>N]trifluoroacetamide has been measured in dioxan and methyl propyl ketone from 15 to 80 °C. From the temperature dependence of the n.m.r. spectra the values for the energy barrier  $E_a$  to internal rotation about the central C–N bond were determined by means of total line-shape analysis. It has been found that the barrier was almost independent of the nature of the solvents used:  $E_a = 76.5 \pm 2.9$  in dioxan and  $77.8 \pm 2.5$  kJ mol<sup>-1</sup> in methyl propyl ketone. The other thermodynamic activation parameters  $\Delta G^\ddagger$  (298 K),  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  were calculated to be 74.0, 74.5, and 2.1 in dioxan and 73.6 kJ mol<sup>-1</sup>, 74.5 kJ mol<sup>-1</sup>, and 3.3 J mol<sup>-1</sup> K<sup>-1</sup> in methyl propyl ketone. The results obtained are compared with those for related compounds.

As reported previously,<sup>1</sup> the <sup>19</sup>F n.m.r. spectra of [<sup>14</sup>N]trifluoroacetamide (I; R = CF<sub>3</sub>) at various temperatures clearly demonstrates that internal rotation



about the C–N bond is hindered at room temperature. The evaluation of the barrier to internal rotation was, however, prevented by proton signal broadening due to the quadrupole relaxation of the <sup>14</sup>N nucleus. This broadening may be eliminated not only by proton-<sup>14</sup>N decoupling produced by the double resonance technique but also by <sup>15</sup>N substitution. In the case of spin decoupling, the interaction of the fluorine atoms with the amide protons gave an asymmetric spectrum to which the line-shape method could not be completely applied. In addition, the presence of a strong irradiation frequency field in the probe caused appreciable sample heating so

that the decoupled spectrum corresponded to a higher temperature than that of the probe. Therefore, <sup>15</sup>N substitution in the amide group was tried and found to be better. In this experiment we irradiated the fluorine nuclei at the second frequency to completely decouple them from the amide protons with a small energy, and very symmetric spectra which could be conveniently analysed by the line-shape method were obtained.

### RESULTS AND DISCUSSION

<sup>1</sup>H N.m.r. Spectrum of [<sup>15</sup>N]Trifluoroacetamide.—As shown in Figure 1, the <sup>1</sup>H n.m.r. spectrum of the compound at 33 °C consists of a pair of sharp singlets for proton A arising from spin coupling with the <sup>15</sup>N nucleus (spin  $\frac{1}{2}$ ), and a pair of quartets due to additional spin coupling with the fluorine nuclei for proton B. Pople and Schaefer<sup>2</sup> analysed the n.m.r. spectrum of an

<sup>1</sup> H. Akiyama, F. Yamauchi, and K. Ouchi, *J. Chem. Soc. (B)*, 1971, 1014.

<sup>2</sup> J. A. Pople and T. Schaefer, *Mol. Phys.*, 1960, **3**, 547.

ABR<sub>3</sub>X system, and this was very useful in considering our ABX<sub>3</sub>Y system, in which we label the fluorine atom as X and <sup>15</sup>N as Y. The values of the n.m.r. parameters

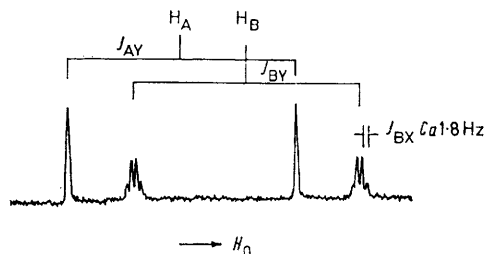


FIGURE 1 <sup>1</sup>H N.m.r. spectrum of [<sup>15</sup>N]trifluoroacetamide in MPK at 33 °C

in the two solvents are shown in Table 1 together with those for related compounds.

TABLE 1

N.m.r. parameters (Hz) of [<sup>15</sup>N]trifluoroacetamide and related compounds H<sub>A</sub>H<sub>B</sub>N<sub>Y</sub>COR<sub>X</sub> at 60 MHz

R	Solvents (mol %)	t/°C	J <sub>AB</sub>	J <sub>AY</sub>	J <sub>BY</sub>	J <sub>AX</sub>	J <sub>BX</sub>	δν <sub>AB</sub>	
CF <sub>3</sub>	Dioxan (16%)	15	0.6	91.2	89.9	~0	1.8	20.4 <sup>a</sup>	
		20	0.6	91.2	90.2	~0	1.9	20.5 <sup>a</sup>	
		25	Broad	91.1	90.2	~0	1.9	20.0 <sup>a</sup>	
		33	Broad	91.1	90.5	~0	1.9	19.5 <sup>a</sup>	
		33	~0	91.2	90.4	~0	1.8	24.8 <sup>a</sup>	
Me	Dioxan (6%)	10	3.1	88.9	88.1			4.8 <sup>b</sup>	
		15	3.0	88.8	88.4	~0	0.7	5.3 <sup>b</sup>	
		MPK (7%)	10	2.9	89.2	88.1	~0	Broad	18.4 <sup>b</sup>
			25	2.8	89.2	88.1	~0	Broad	23.1 <sup>b</sup>
H	Neat		2.4	92.0	88.0	2.1	12.9	12.0 <sup>c</sup>	
		25	2.3	91.9	95.4	2.1	13.6	20.5	
	Water (8%)	28.5	2.30	91.30	86.93	2.10	13.90	22.2 <sup>d</sup>	
		25	2.9	91.0	88.0	1.7	13.5	12.8 <sup>c</sup>	

<sup>a</sup> This work. <sup>b</sup> Unpublished results; see M. Liler, *J. Magnetic Resonance*, 1971, **5**, 333 for water, acetone, and dimethyl sulphoxide solution. <sup>c</sup> Ref. 3; see A. J. R. Bourn and E. W. Randall, *Mol. Phys.*, 1964, **8**, 567 for 29.6% acetone solution. <sup>d</sup> R. J. Chuck, D. G. Gillies, and E. W. Randall, *Mol. Phys.*, 1969, **16**, 121.

<sup>1</sup>H {<sup>19</sup>F} N.m.r. Spectra of [<sup>15</sup>N]Trifluoroacetamide.—As shown in Figure 2(a) a very symmetric spectrum was observed in dioxan at 33 °C when the amide protons and the fluorine atoms were decoupled by irradiating the fluorine atoms. Although no spin interaction between protons A and B was detected at 33 °C, as shown in Figure 2(b) each singlet was split into a doublet below 20 °C. From the interval the value of J<sub>AB</sub> was found to be almost 0.6 Hz. This indicates that there is slow rotation at the lower temperature from the intrinsic effect of the non-equivalence of protons A and B. The fact that no splitting occurred due to nonequivalence of

<sup>3</sup> B. Sunners, L. H. Piette, and W. G. Schneider, *Canad. J. Chem.*, 1960, **38**, 681.

protons A and B in methyl propyl ketone (MPK) at the corresponding temperature for dioxan and even at 0 °C suggests that the coupling constant J<sub>AB</sub> is solvent dependent *i.e.* the splitting is smaller in MPK than in dioxan.

The solvent effect on the coupling constants J<sub>AY</sub> and J<sub>BY</sub> in the solvents used is virtually nil. J<sub>AY</sub> is slightly larger than J<sub>BY</sub> by *ca.* 1.3 Hz. This agrees with the results found for [<sup>15</sup>N]formamide.<sup>3</sup> A possible interpretation is that the difference of the spin-coupling constants are due to there being a longer N-H(A) bond than an N-H(B) bond.

The sharp singlets for proton A indicate that there may be no spin coupling between proton A and the fluorine atoms, or the spin interaction may be so weak that the splitting could not be resolved (J<sub>AY</sub> < 0.3 Hz, which was the resolution limit). J<sub>BX</sub> is 1.9 Hz at 33 °C, as obtained from the <sup>1</sup>H n.m.r. spectra. This is in

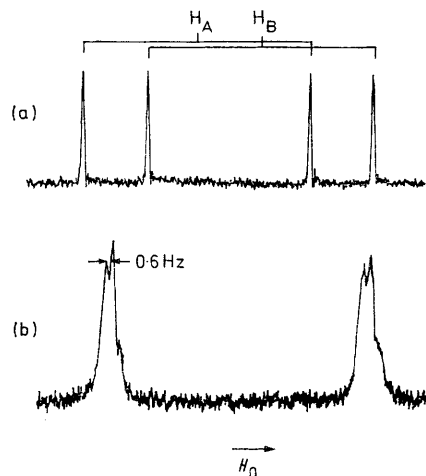


FIGURE 2 <sup>1</sup>H {<sup>19</sup>F} N.m.r. spectra of [<sup>15</sup>N]trifluoroacetamide in dioxan (a), at 33 °C (300 Hz sweep width); (b), at 15 °C (60 Hz sweep width)

accord with the value from the doublet in the fluorine spectra.<sup>1</sup>

The internal chemical shifts between protons A and B at various temperatures are listed in the last column of Table 1. A large difference was observed between the values in the dioxan and MPK solutions. In the case of [<sup>15</sup>N]acetamide the difference between the chemical shifts in the two solvents was found to be extreme. Such differences among internal chemical shifts in various solvents might be caused by solute-solute interactions as expected from the i.r. spectra.<sup>4</sup>

*Hindered Internal Rotation in [<sup>15</sup>N]Trifluoroacetamide.*—For the very symmetric <sup>1</sup>H {<sup>19</sup>F} spectra of [<sup>15</sup>N]trifluoroacetamide, total line-shape analysis can be readily applied to evaluate the barrier to internal rotation. In Figure 3, the higher field halves of the <sup>1</sup>H {<sup>19</sup>F} spectra of the amide protons A and B as observed at various temperatures are shown together with the best-fit

<sup>4</sup> R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 1947, 1248.

calculated spectra for the corresponding first-order life times  $\tau$  of the protons in sites A and B. A large number of spectra in both solvents were recorded at smaller temperature intervals over the temperature range 49–73 °C. The spectra were analysed by means of the

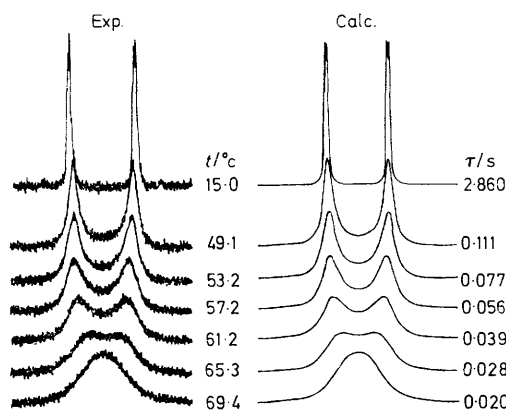


FIGURE 3 The higher field halves of the observed  $^1\text{H}$  ( $^19\text{F}$ ) spectra of the amide protons A and B, and the best-fit calculated spectra at various temperatures

computer programme for the line-shape equation presented by Heidberg *et al.*,<sup>5</sup> based upon the average-density matrix theory discussed by Kaplan<sup>6</sup> and Alexander<sup>7</sup> for the coupled AB system. The transverse relaxation time  $T_2$  was approximately estimated by measuring the observed natural line width [ $w = (\pi T_2)^{-1}$ ] of the spectra in dioxan at 15 °C; the chemical shift parameter which is defined by  $2|\delta| = \pi(\delta\nu)$  was calculated from the internal chemical shift  $\delta\nu$  of the proton A and B obtained from the lowest-temperature spectrum. In order to obtain the best-fit  $\tau$  values, a large number of calculated spectra (*ca.* 1200) were drawn by a plotter attached to an IBM computer; the calculated points

the corresponding coalescence temperatures of 68 and 72 °C in dioxan and MPK respectively.

The corresponding Arrhenius plots give the energy barrier  $E_a$  (Table 2). Although much difference was observed in the line shapes in dioxan and in MPK, the barrier is almost independent of the nature of the solvents used at *ca.* 76.5–77.8 kJ mol<sup>-1</sup>. The logarithm of the frequency factor  $\log A$  is found to be almost constant at 13.4 in both solvents. The free energy of activation  $\Delta G^\ddagger$  for each temperature was calculated by using the best-fit  $\tau$  values in terms of the Eyring equation (2) where  $\kappa$  is the transmission coefficient, assumed

$$\tau^{-1} = \kappa \frac{kT}{h} e^{-\Delta G^\ddagger/RT} \quad (2)$$

equal to 1. A plot of  $\Delta G^\ddagger$  vs.  $T$  gives a straight line with slope  $\Delta S^\ddagger$  and intercept  $\Delta H^\ddagger$  according to equation (3).

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (3)$$

The calculated activation parameters are summarised in Table 2.

We found that the best-fit  $\tau$  values in both solvents, and therefore the  $E_a$  values, were dependent on the magnitude of  $T_2$ . It was impossible to get a spectrum in dioxan solution at much lower temperatures where rotation around the C–N bond would be completely frozen and the uncertainty in  $T_2$  from an expanded spectrum at 15 °C in dioxan was relatively large due to the fine splitting between the amide protons A and B. On the other hand, the determination of  $T_2$  could not be obtained from any high temperature spectrum above 80 °C because of thermal decomposition. Three different  $T_2$  values, 0.50, 0.65, and 0.80 s, were therefore chosen with some uncertainty from the natural line-width of the spectrum at 15 °C and from nearly 200 up to 300 theoretical spectra for each  $T_2$  value were calculated. The line shapes were very much less sensitive to

TABLE 2

Activation parameters for hindered internal rotation about the C–N bond in [<sup>15</sup>N]trifluoroacetamide

Solvent	$T_2/s$	$E_a/\text{kJ mol}^{-1}$	$\log A$	$\Delta G^\ddagger(298 \text{ K})/\text{kJ mol}^{-1}$	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J mol}^{-1} \text{K}^{-1}$	$t_c/^\circ\text{C}^a$
Dioxan <sup>b</sup>	0.65	$76.5 \pm 2.9$	$13.4 \pm 0.6$	$74.0 \pm 2.9$	$74.5 \pm 3.3$	$2.1 \pm 9.6$	68
MPK <sup>b</sup>	0.50	$80.3 \pm 2.5$	$13.9 \pm 0.4$	$74.0 \pm 2.5$	$77.8 \pm 2.0$	$11.7 \pm 6.3$	72
	0.65	$77.8 \pm 2.5$	$13.5 \pm 0.4$	$73.6 \pm 2.5$	$74.5 \pm 3.3$	$3.3 \pm 3.3$	72
	0.80	$77.4 \pm 2.5$	$13.4 \pm 0.4$	$73.6 \pm 2.5$	$74.5 \pm 2.0$	$2.8 \pm 0.6$	72

<sup>a</sup> Coalescence temperature ( $\pm 2$  °C). <sup>b</sup> Errors were obtained at the 95% confidence level by the least squares method.

were first normalised to the experimental spectra to facilitate visual comparison. Final values were chosen as those giving the best superposition of calculated curves on the observed spectra.

One can also estimate the  $\tau$  values at the coalescence temperatures in terms of the approximate equation (1).<sup>8</sup> The calculated  $\tau_c$  values are 0.018 and 0.023 s at

$$\tau_c = \frac{2^{\frac{1}{2}}}{\pi(\delta\nu^2 + 6J_{AB}^2)^{\frac{1}{2}}} \quad (1)$$

<sup>5</sup> J. Heidberg, J. A. Weil, G. A. Janusonis, and J. K. Anderson, *J. Chem. Phys.*, 1964, **41**, 1033.

<sup>6</sup> J. Kaplan, *J. Chem. Phys.*, 1958, **28**, 278; 1958, **29**, 462.

such differences in  $T_2$  in the coalescence region and no choice of an actual  $T_2$  value was possible. However, only by choosing  $T_2$  to be 0.65 s could we reproduce the low temperature spectrum. Although the above method was not entirely adequate, this seemed to us the only feasible procedure for determining  $T_2$ . From Table 2, it would be estimated that a change of  $T_2$  by 0.15 s caused a change in  $E_a$  of at most 2.5 kJ mol<sup>-1</sup>, higher  $E_a$  values being obtained for lower values of  $T_2$ .

<sup>7</sup> S. Alexander, *J. Chem. Phys.*, 1962, **37**, 967, 974; 1963, **38**, 1787.

<sup>8</sup> D. Kost, E. H. Carlson, and M. Raban, *Chem. Comm.*, 1971, 656.

The energy barriers for internal rotation in formamide and substituted *NN*-dimethylformamides are reported by many authors.<sup>9</sup> We can find that the energy barrier is lowered by 2.5 kJ mol<sup>-1</sup> by the substitution of the CF<sub>3</sub> group, in comparison with the  $E_a$  value 80.3 kJ mol<sup>-1</sup> for formamide.<sup>10</sup> The substitution effect by CF<sub>3</sub> is thus found only to be close to zero, judging from the range of errors. Considering the large electron-withdrawing power of the CF<sub>3</sub> group, the absence of the effect by this group on the internal rotation seems to be rather striking. In the cases of *NN*-dimethylformamide,<sup>11</sup> and *NN*-dimethyltrifluoroacetamide,<sup>12</sup> the barriers for rotation  $E_a$  are reported as 85.8 and 86.2 kJ mol<sup>-1</sup> respectively, but for *NN*-dimethyltrichloroacetamide<sup>13</sup> a considerable lowering at *ca.* 20.9 kJ mol<sup>-1</sup> in the energy barrier was observed on the substitution by the CCl<sub>3</sub> group.

Brown *et al.*<sup>14</sup> reported that the integrated intensities in the i.r. spectra of the carbonyl bond for formamide, trifluoroacetamide, and trichloroacetamide were 4.22, 4.04, and 3.37 (l mol<sup>-1</sup> cm<sup>-1</sup> × 10<sup>-4</sup>) respectively, there being no particular effect of the CF<sub>3</sub> group on the intensity but a strong reduction by the CCl<sub>3</sub> group. They suggested that the intensity was considerably lowered in those compounds where a bulky group was situated *cis* to the carbonyl group and the resonance form which possessed a formal negative charge on the oxygen was inhibited by the repulsion of non-bonding electrons in the substituted group and the oxygen atom. Although this may give one of the explanations for the effect of the CF<sub>3</sub> group on the energy barrier to the rotation, the essential feature of the CF<sub>3</sub> group as a substituent in comparison with the other amides is not yet clear.

<sup>9</sup> W. E. Stewart and T. H. Siddall, *tert*, *Chem. Rev.*, 1970, **70**, 517.

<sup>10</sup> T. Drakenberg and S. Forsén, *J. Phys. Chem.*, 1970, **74**, 1.

<sup>11</sup> M. Rabinovitz and A. Pines, *J. Amer. Chem. Soc.*, 1969, **91**, 1585.

<sup>12</sup> K. H. Abramson, P. T. Inglefield, E. Krackower, and L. W. Reeves, *Canad. J. Chem.*, 1966, **44**, 1685.

#### EXPERIMENTAL

[<sup>14</sup>N]Trifluoroacetamide was obtained from Tokyo Kasei and was recrystallised from MPK. [<sup>15</sup>N]Trifluoroacetamide (over 96% enriched) was obtained from Merck and used without further purification. MPK and dioxan were distilled over 3A molecular sieves using a 100 cm column; the middle fractions were taken. N.m.r. samples were prepared in a dry-box and sealed under vacuum after treating by the 'pump and thaw' technique.

The <sup>1</sup>H and <sup>19</sup>F n.m.r. spectra were obtained with a Hitachi R-20 spectrometer operating at 60.0 and 56.4 MHz. Spectra were recorded (several times) on 40 cm charts at 300, 120, and 60 Hz sweep widths and calibrated using a Corona-425 frequency counter. The second irradiation frequencies for the <sup>1</sup>H {<sup>14</sup>N} and <sup>1</sup>H {<sup>19</sup>F} spectra were set at 4.334936 and 56.456253 MHz by a frequency synthesiser, Takeda TR-3130. The temperature dependence study was done with the Hitachi VR-202 probe. Samples were allowed 10 min to attain thermal equilibrium at each temperature before the spectra were recorded. Sample temperature was calibrated with an ethylene glycol internal thermometer, which was examined separately on our equipment by the m.p. method.<sup>15</sup> In the case of the <sup>1</sup>H {<sup>14</sup>N} spectra, due to the intense irradiation a rapid temperature increase was observed and it was rather difficult to determine the correct thermal equilibrium. However, no temperature increase was observed for the <sup>1</sup>H {<sup>19</sup>F} spectra, due to the weak irradiation in that case.

The theoretical spectra were calculated by means of the IBM 1130 system with a 1627 plotter. After normalisation *ca.* 1200 spectra were calculated. The intervals for the  $\tau$  values were first-set roughly at 0.01 and then at 0.001, approaching the best-fit  $\tau$  values.

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<sup>13</sup> T. Drakenberg, K. Dahlqvist, and S. Forsén, *Acta Chem. Scand.*, 1970, **24**, 694.

<sup>14</sup> T. L. Brown, J. F. Regan, R. D. Schetz, and J. C. Sternberg, *J. Phys. Chem.*, 1959, **63**, 1324.

<sup>15</sup> O. Yamamoto and M. Yanagisawa, *Analyt. Chem.*, 1970, **42**, 1463.