

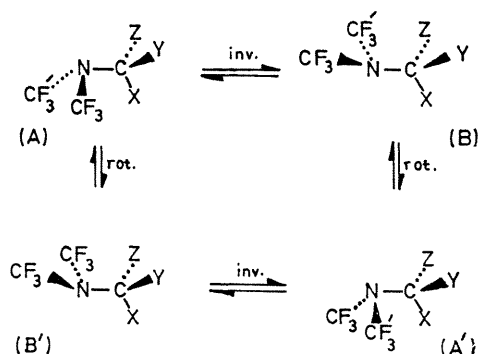
## Magnetic Nonequivalence of Trifluoromethyl Groups in *NN*-Bistrifluoromethylalkylamines

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**Summary** Below their coalescence temperatures, *NN*-bistrifluoromethylalkylamines of the type  $(\text{CF}_3)_2\text{N}\cdot\text{CXYZ}$ , show magnetic nonequivalence of their trifluoromethyl groups, which coalesce with free energies of activation in the range 8.4–15.8 kcal./mole.

VARIOUS compounds containing heteroatoms (O, N, S, P, Cl, Br) adjacent to a nitrogen atom have been studied by n.m.r. spectroscopy<sup>1,2</sup> and the observed changes in spectra have been ascribed as arising from either hindered inversion



at the nitrogen or hindered rotation about the bond to the heteroatom. No reports of hindered inversion at the nitrogen have appeared for acyclic amines containing no adjacent heteroatom, although substantial barriers to inversion are apparent in strained cyclic amines,<sup>2</sup> and the rate of inversion for *NN*-dibenzylmethylamine has been deduced from the pH dependence of the spectrum of the protonated amine in aqueous solution.<sup>3</sup>

We now report a study of the <sup>19</sup>F n.m.r. spectra of a series of *NN*-bistrifluoromethylalkylamines<sup>4</sup> of the type  $(\text{CF}_3)_2\text{N}\cdot\text{CXYZ}$ , where the adjacent carbon is chiral. These show a single absorption due to the trifluoromethyl groups at high temperatures, two coupled absorptions of equal intensity ( $J_{\text{CF}_3, \text{CF}_3}$  ca. 10 Hz.) at low temperatures. The coalescence temperature,  $T_c$  and rates,  $k_c$ , and free energies of activation at coalescence,  $\Delta G_c^\ddagger$ , calculated for the various compounds by the usual methods, are listed in the Table.

For compounds with a single halogen at the  $\alpha$ -carbon  $\Delta G_c^\ddagger$  increases with increasing size of the halogen, while introducing a second halogen [compare compounds (I)–(IV) with (IX) and (X)] apparently reduces the barrier slightly. Changing substituents on the  $\beta$ -carbon has a much smaller effect. There is, however, a distinct difference in  $\Delta G_c^\ddagger$  for the *erythro*- and *threo*-isomers of compounds (XIII) and (XIV).

The coalescence of the  $\text{CF}_3$  absorptions at high temperatures requires the occurrence of both inversion at the nitrogen and rotation through 180° about the N–CXYZ bond, not necessarily as separate and distinct processes. The series of interconversions  $A \rightleftharpoons B \rightleftharpoons A' \rightleftharpoons B' \rightleftharpoons A$  represent these processes for a particular conformation, but (B), (B') may not be directly on the reaction profile.

The observed nonequivalence and high-temperature coalescence of the  $\text{CF}_3$  absorptions may be explained on the following basis: (i) rotation is free but inversion is hindered—it is difficult to explain the changes in  $\Delta G_c^\ddagger$  with varying  $\alpha$ -substituents on this basis; (ii) one conformation is highly favoured,  $\Delta G_c^\ddagger$  being largely associated with hindered rotation—unlikely to be true for all the compounds studied; or (iii) inversion is hindered, but  $\Delta G_c^\ddagger$  is associated in part

Spectral data and free energies of activation  $\Delta G_c^\ddagger$ <sup>a</sup> for  $(CF_3)_2N\cdot R$ 

| Compound <sup>b</sup> | R                                   | $\Delta\nu$ (Hz.) | $T_c$ | $k_c$ (sec. <sup>-1</sup> ) | $\Delta G_c^\ddagger$ (kcal./mole) |            |
|-----------------------|-------------------------------------|-------------------|-------|-----------------------------|------------------------------------|------------|
| (I)                   | CHF·CF <sub>2</sub> Cl              | 243               | -54°  | 540                         | 9.6 ± 0.5                          |            |
| (II)                  | CHF·CF <sub>2</sub> I               | 244               | -57°  | 540                         | 9.5 ± 0.5                          |            |
| (III)                 | CHF·CHFBr <sup>c</sup>              | 263               | -64°  | 583                         | 9.2 ± 0.5                          |            |
| (IV)                  | CHF·CFCIBr <sup>c</sup>             | 203               | -43°  | 447                         | 10.2 ± 0.5                         |            |
| (V)                   | CHBr·CH <sub>2</sub> Br             | 359               | +24°  | 797                         | 13.2 ± 0.3                         |            |
| (VI)                  | CHBr·CHFBr <sup>c</sup>             | 366               | +40°  | 813                         | 13.3 ± 0.3                         |            |
| (VII)                 | CHBr·CF <sub>2</sub> Br             | 408               | +85°  | 907                         | 15.8 ± 0.3                         |            |
| (VIII)                | CHI·CH <sub>2</sub> CF <sub>3</sub> | 416               | +68°  | 921                         | 15.0 ± 0.3                         |            |
| (IX)                  | CFCl·CFCIBr <sup>d</sup>            | 79.5              | -78°  | 176                         | 8.6 ± 1.5                          |            |
|                       |                                     | 87.5              | -78°  | 194                         | 8.6 ± 1.5                          |            |
| (X)                   | CFCl·CFBr <sub>2</sub>              | 78.2              | -77°  | 173                         | 8.6 ± 1.5                          |            |
| (XI)                  | CHMe·CH <sub>2</sub> Cl             | 451               | -75°  | 1001                        | 8.4 ± 0.4                          |            |
| (XII)                 | CHMe·CH <sub>2</sub> Br             | 441               | -74°  | 977                         | 8.5 ± 0.4                          |            |
| (XIII)                | CHMe·CHCIME                         | erythro           | 406   | -40°                        | 904                                | 10.1 ± 0.4 |
|                       |                                     | threo             | 421   | -72°                        | 932                                | 8.7 ± 0.4  |
| (XIV)                 | CHMe·CHBrMe                         | erythro           | 397   | -40°                        | 880                                | 10.1 ± 0.4 |
|                       |                                     | threo             | 426   | -65°                        | 943                                | 8.9 ± 0.4  |

<sup>a</sup> Measurements at 56.46 MHz.; Perkin-Elmer R10 spectrometer.

<sup>b</sup> Containing CFCl<sub>3</sub>, except compounds (V) and (VII) (neat), and (VIII) (in CCl<sub>4</sub>).

<sup>c</sup> Mixture of two diastereoisomers, showing very similar coalescence behaviour.

<sup>d</sup> Two diastereoisomers.

with steric hindrance from bulky substituents at the  $\alpha$ -carbon—this explanation is preferred since it seems to account for the observed variations in  $\Delta G_c^\ddagger$ .

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