derived from the correct magnitude of the overlap integral.

The conformational dependence of the overlap integral between the $C_{2p\pi}$ and the $F_{2p\pi}$ orbitals which satisfies the conditions of maximum overlap is

$$S_{CF}{}^2(\max) = S_0{}^2 + S^2 \cos^2 \theta \qquad (1)$$

where S_0 and S are numerical constants which are easily calculated from the table of overlap integrals[9] together with the geometry of the CCF_β fragment. Assuming the C–C and C–F_β bond distances of 1.54 and 1.35 Å, respectively, and the tetrahedral value for the CCF_β bond angle, $S_0{}^2$ and S^2 are calculated to be 1.232×10^{-4} and 5.405×10^{-4}, respectively. If one assumes that the spin density $\rho_{F_{2p}}$ in the $F_{2p\pi}$ orbital is proportional to $S_{CF}{}^2$ (max), and the spin density in the F_{2s} orbital is mainly produced by the spin polarization from $\rho_{F_{2p}}$, the isotropic coupling constants should be proportional to $S_{CF}{}^2(\max)$. Therefore, the ratio $a_F(CF_3)/a_F(\theta = 90°)$ is predicted to be 3.1 from the correct magnitudes of the overlap integral. A good agreement with the observed ratio 3.2 indicates that our assumptions are reasonable.

We have further determined the proportional constants so as to give the observed principal elements[6] of the hyperfine tensor of the β-fluorine couplings in $^-OOC\text{–}\dot{C}FCF_2\text{–}COO^-$, where the conformational angle was found to be about 30° from the direction of the maximum principal element.[4,5]

$$A = (B_0 + B \cos^2 \theta)(\rho_c/\rho)$$

$$B_0 = 16 \text{ G}, B = 69 \text{ G for } A_\parallel$$

$$B_0 = 5 \text{ G}, B = 23 \text{ G for } A_\perp$$

$$B_0 = 9 \text{ G}, B = 38 \text{ G for } a_F \text{ (isotropic component)} \qquad (2)$$

where ρ is the spin density in the $C_{2p\pi}$ orbital in $^-OOC\text{–}\dot{C}FCF_2\text{–}COO^-$ and may be assumed to be 0.75–0.80,[10] while ρ_c is a spin density of the radical concerned. The conformational dependence of the coupling constants is plotted in Figure 1. Equation 2 predicts the magnitudes of a_F for $\theta = 90°$ and for the freely rotating CF_3 group in semiquinone derivatives to be 0.84 and 2.6 G, respectively, if ρ_c/ρ is assumed to be 0.07/0.75. The agreement with the observed values, 0.85 and 2.77 G, is very good.

The principal elements of the hyperfine tensor, including the anisotropic component, for the freely rotating CF_3 group were also calculated from eq 2, assuming that the direction of the $F_{2p\pi}$ orbital, that is, the direction of $A_\parallel$, varies during the rotation around the C–C bond so as to satisfy the condition for the maximum overlap with the $C_{2p\pi}$ orbital.[11] The calculated tensor is 42, 21, 21 G if $\rho_c/\rho = 1$, while the observed one for $CF_3\dot{C}FCONH_2$ is 36, 17, 14 G.[12] Although the calculated isotropic value is slightly larger than that observed, the anisotropic term (+13, −7, −7 G) shows excellent agreement with the observed one (+14, −5, −8 G).

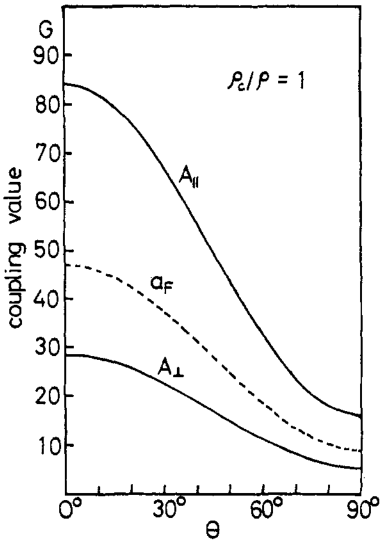

Figure 1. Conformational dependence of the principal values and the isotropic component of the β-fluorine coupling tensor.

The proposed $\cos^2 \theta$ rule seemingly accounts for the conformational dependence of β-fluorine coupling constants obtained in solutions as well as in single crystals. In conclusion, the direct overlap between the half-filled $C_{2p\pi}$ orbital and the $F_{2p\pi}$ lone-pair orbital is considered to be the most important mechanism in β-fluorine couplings. The details of this treatment will be given elsewhere.[13]

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(10) M. Iwasaki, S. Noda, and K. Toriyama, *Mol. Phys.*, **18**, 201 (1970).

(11) It should be noticed that the simple average of $\cos^2 \theta$ in eq 2 is only valid for the isotropic couplings and it does not give a correct answer for the anisotropic couplings.

(12) R. J. Lontz, *J. Chem. Phys.*, **45**, 1339 (1966).

(13) M. Iwasaki, *Mol Phys.*, in press.

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Acyclic Conformational Analysis. Direct Observation of Rotation about the Carbon–Nitrogen Single Bond in *tert*-Butyldimethylamine

Sir:

Although a respectable amount of data regarding rotation about formally single carbon–nitrogen bonds is available, the barriers obtained from microwave and thermodynamic studies[1] give only the enthalpy of activation ($\Delta H^{\ddagger}$) and no information concerning the entropy of activation ($\Delta S^{\ddagger}$) for the rotation process. In many of the instances in which variable-temperature nmr spectroscopy has been used to determine activation parameters ($\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$) for C–N bond rotation, the C–N bonds possess greater than single bond order due to electronic delocalization.[2] It has not been demonstrated previously that variable-temperature nmr spectroscopy can be used to study rotation about a legitimate single C–N bond.

This paper deals with the direct observation of rotation about a single C–N bond in *tert*-butyldimethylamine (I). I was selected for this study because slow nitrogen inversion does not generate a center of asym-

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(1) D. R. Lide and D. E. Mann, *J. Chem. Phys.*, **28**, 572 (1958); E. B. Wilson, Jr., *Advan. Chem. Phys.*, **2**, 367 (1959); D. J. Millen, *Progr. Stereochem.*, **3**, 138 (1962).

(2) C. H. Bushweller, P. E. Stevenson, J. Golini, and J. W. O'Neill, *J. Phys. Chem.*, **74**, 1155 (1970), and references therein.

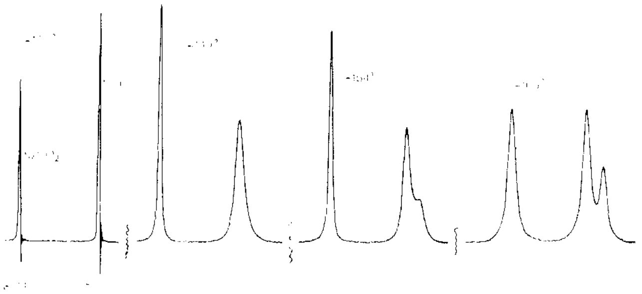
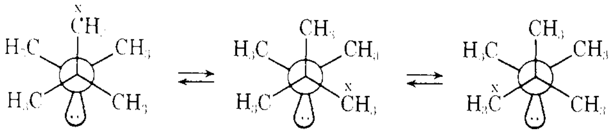


Figure 1. The pmr spectrum (60 MHz) of *tert*-butyldimethylamine (10% by volume in CH_2CHCl) as a function of temperature.

metry[3] and rotation is the only rate process which would be expected to affect the nmr spectrum.

Examination of the pmr spectrum (60 MHz) of I (15% by volume in CH_2CHCl) at −100° revealed two sharp singlet resonances due to the *tert*-butyl (δ 1.00) and methyl (δ 2.14) groups (Figure 1). Upon lowering the temperature, the *tert*-butyl resonance (δ 1.00) broadens and separates into two overlapping peaks with an area ratio of 1:2 (Figure 1). The shape of the $N(CH_3)_2$ peak (δ 2.14, Figure 1) is essentially independent of temperature except for some broadening due most likely to viscosity effects and ^{14}N quadrupole relaxation.

Since slowing of the nitrogen inversion process does not generate a center of asymmetry in I as it does in dibenzylmethylamine,[3] slow inversion cannot account for the spectral transitions described in Figure 1. The most plausible rationalization is a slowing of rotation about the *tert*-butyl–nitrogen bond. Perusal of eq 1 indicates that in any of the three equivalent rotamers (Newman projection looking down the central *tert*-butyl carbon–nitrogen bond), the *N*-methyls always experience equivalent environments and should display an nmr spectrum independent of any rate process save CH_3–N rotation. However, for the *tert*-butyl group in any given rotamer (eq 1), there are two equivalent methyls bisected by the nitrogen lone pair and one other different methyl which bisects the $N(CH_3)_2$ group. In the event of slow rotation of *tert*-butyl (eq 1), the *tert*-butyl resonance should consist of two singlets of relative intensity 1:2 as observed (Figure 1). It is also clear from eq 1 that the three methyls of the *tert*-butyl group do indeed exchange environments *via* rotation and that rapid rotation on the nmr time scale will result in a singlet resonance.



(1)

Total line-shape analyses[4] for the *tert*-butyl resonance over the temperature range from −161 to −137° have been performed. It is clear from the nmr spectra (Figure 1) that the width at half-height ($W_{1/2}$) of the $N(CH_3)_2$ resonance (δ 2.14) increases as the temperature is lowered, especially from *ca.* −110 to −166°. This is due to a lowering of the spin–spin relaxation time (T_2) due to viscosity and ^{14}N quadrupole relaxation. However, examination of the nmr spectrum of I at −80° (fast exchange conditions) shows that $W_{1/2}$ for the $N(CH_3)_2$ resonance is equal to $W_{1/2}$ for the *tert*-butyl peak. In addition, perusal of the nmr spectrum of I at −166° (Figure 1) reveals equal intensities for the larger of the two *tert*-butyl resonances and the $N(CH_3)_2$ peak. Since these peaks should have an area ratio of 1:1, the data strongly imply equal widths at half-height. Indeed, the best "fit" of theoretical to experimental spectra for the *tert*-butyl resonances at −166° was obtained using $W_{1/2}$ equal to that of the $N(CH_3)_2$ peak. In all subsequent line-shape calculations at different temperatures it was assumed therefore that the $N(CH_3)_2$ $W_{1/2}$ accurately reflected the C–CH_3 $W_{1/2}$. In addition, it is observed that the chemical shift of the *tert*-butyl resonance under conditions of fast exchange (*e.g.*, −80°) is predicted accurately using the properly weighted chemical shifts of the two *tert*-butyl peaks observed at −166°, *i.e.*, the chemical shifts of the *tert*-butyl resonances are essentially independent of temperature. A series of rate constants (k = first-order rate constant for the disappearance of any methyl of the *tert*-butyl group from any one of the three sites; eq 1) as a function of temperature was obtained by matching calculated[4] to experimental nmr spectra. A least-squares treatment of ln k *vs.* $1/T$ (correlation coefficient = 0.998) gave $E_a = 6.4 \pm 0.2$ kcal/mol, $\Delta H^{\ddagger} = 6.2 \pm 0.2$ kcal/mol, $\Delta G^{\ddagger} = 6.0 \pm 0.1$ kcal/mol at −153°, and $\Delta S^{\ddagger} = 1.3 \pm 1.5$ eu.

The above results indicate clearly that barriers to rotation about C–N single bonds can be determined by variable-temperature nmr spectroscopy and that total nmr line-shape analysis will give all the activation parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, $\Delta G^{\ddagger}$, E_a) for such a process. It is also clear that the barriers to inversion and rotation in simple acyclic trialkylamines are similar and that either process may be detected depending on the structure of the amine.[3]

We are investigating steric effects on the rotational barriers in simple amines and these results will be reported in due course.

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[3] M. J. S. Dewar and W. B. Jennings, *Tetrahedron Lett.*, 339 (1970); C. H. Bushweller and J. W. O'Neil, *J. Amer. Chem. Soc.*, **92**, 2159 (1970).

[4] C. H. Bushweller, J. Golini, G. U. Rao, and J. W. O'Neil, *ibid.*, **92**, 3055 (1970). See ref 5 in the above paper.

[5] Supported by a NASA Traineeship, 1969–1970.

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Copper(II) Propionate-*p*-Toluidine. A Cupric Carboxylate Adduct of Novel Polymeric Structure

Sir:

Many studies of copper(II) carboxylates have been stimulated by interest in the nature of the metal–metal interaction exhibited by some of these compounds.[1-5]

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[1] M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, **64**, 99 (1964).