Slow Rotation in a Thiourea Detected by Proton Magnetic Resonance[1]

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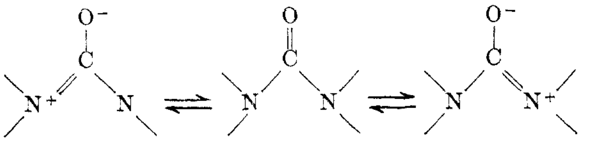
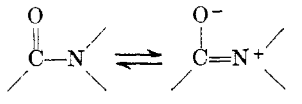
There have been many studies by proton magnetic resonance (pmr) of slow rotation in amides around the carbonyl–nitrogen bond (amide bond). However, we know of no report of slow rotation observed by pmr around the analogous bonds in ureas. The apparent lack of such slow rotation in ureas can be explained on the basis that in ureas two amide bonds must compete for delocalization energy (or double-bond character) (1), while in amides all of this effect is concentrated in one such bond (2). Recently slow rotation has been reported in N,N-dimethyl carbamates[2] in spite of competition between two bonds as in ureas—in this case between the amide and ester bonds. Apparently for the carbamates, this competition is reduced in favor of the amide bond by introducing electron-withdrawing substituents into the ester part of the molecule. Also, the barrier to rotation is known to be several kilocalories greater in thionamides[3,4] than in ordinary amides. The foregoing considerations suggest that both of these factors operating together might sufficiently enhance the barrier around one of the amide bonds in a urea for slow rotation to be observable. This communication reports such an observation with N-phenyl-N′,N′-dimethylthiourea (I).


(1)


(2)

Compound I was purchased from Columbia Organic Chemicals Co. As received, the compound gave the correct pmr spectrum, but before use was recrystallized from acetone as a precaution. The pmr measurements were made with a Varian A-60 spectrometer equipped with a variable-temperature probe. All measurements were made with 160 mg of I/ml in $CDCl_3$; immediately before use, the $CDCl_3$ was passed through a column packed with Linde Molecular Sieves. The sample was degassed and sealed under vacuum before recording the pmr spectra.

The kinetic quantities were determined by signal-shape analysis according to the equation of Gutowsky and Holm[5] as adapted by Nakagawa.[6] (We are indebted to Dr. Nakagawa for microfilms of the theoretical line shapes.) Data suitable for kinetic studies were obtained over the range −60 to −20° at 5° intervals.

In the pmr spectrum of I at −70°, the methyl signals occur as a doublet separated by 28.4 cps $|\nu_A - \nu_B|$, while the protons attached to nitrogen and the benzene ring give single signals. This value of $|\nu_A - \nu_B|$ was used throughout the analysis. One of the methyl signals is slightly broader than the other. At −40° the separate methyl signals coalesce and at −10° have become a reasonable sharp singlet ($1/T_2 = 1$ cps). Evidently, rotation around the amide bond with the two methyl groups attached is slow at low temperatures. Around the other amide bond, either the rotation is rapid or one isomer predominates to the exclusion of the other. The signal-shape analysis yielded free energy of activation ($\Delta F^*_{234°K}$) of 10.7 kcal/mole (assuming the transmission coefficient to be unity), a barrier to rotation (E_a) of 15 kcal /mole, and a log frequency factor (log A) of 15. No error limits are given for these parameters because of uncertainty in the temperature dependence of the chemical shift ($|\nu_A - \nu_B|$). Nakagawa's quantity, $\nu = 1/(2\pi T|\nu_A - \nu_B|)$, is about 0.01 for the methyl signals of I. The fit to calculated curves is insensitive to changes in the shift when ν is so small. Unfortunately, it was not possible to reach low temperatures in the slow-exchange region to obtain a temperature dependence of shift that could be extrapolated into the temperature range of intermediate exchange. As a consequence, E_a is uncertain by the amount of the unknown temperature dependence of shift. From experience with other compounds, the shift is not likely to change as much as 10% over a temperature range of 40°. On that basis, E_a is uncertain by about 1 kcal/mole. The quantity ΔF^* is generally more reliable in signal-shape analysis.[7]

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Reaction of Inorganic Cyanates with Organic Halides. III. Synthesis of Ureas and Biurets

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The reaction of *n*-butyl bromide with potassium cyanate (KNCO) in aqueous dimethylformamide (DMF) has been described by Fukui, *et al.*[1] A mixture of 1,3-di-*n*-butylurea and 1,3,5-tri-*n*-butyl isocyanurate was reported as the exclusive products. In contrast to their work, we have found that organic chlorides react with KNCO in 95% aqueous DMF at 100° to give mixtures of monosubstituted urea, 1,3-disubstituted urea, and 1,5-disubstituted biuret.

In accordance with eq 1, benzyl chloride (Ia) gives IIa, IIIa, and IVa in yields of 46, 7.3, and 20%, respectively. On the other hand, *n*-octyl chloride (Ib) pro-

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