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SLOW ROTATION ABOUT THE C-N BOND IN THIOUREAS

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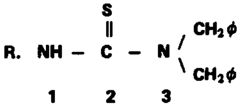
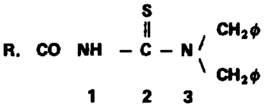
The slow rotation of the CO-N bond of amides is well known, and has been extensively studied by p.m.r. techniques (1-4). Recently, it has been shown that the C-N bonds of thioamides possess significantly greater resistance to rotation than that of the corresponding amides, due to greater contribution of the dipolar resonance form $-\overset{|S^{\ominus}}{C}=\overset{\oplus}{N}\langle$ to the structure (2,5).

As this form could also contribute to thioureas, the possibility existed that they also possessed significant torsional rigidity.



I



II

(a) R = CH_3

(b) R = Phenyl

(a) R = CH_3CH_2

(b) R = phenyl

Slow rotation has now been observed in the thioureas and acylated thioureas I and II.

The 60 MHz spectra of the benzylic protons of these compounds showed temperature dependence. Upon lowering the temperature the signals broadened, and separated into two peaks. Coalescence temperatures and calculated free energy values for rotation are presented in Table I.

It can be seen that there is a significant difference in free energy values between the thioureas I and the acylated derivatives II. In the alkyl and aryl thioureas, the rotating 2,3 C-N bonds being observed have a weaker rotational resistance than the corresponding bonds of the acyl compounds. Because the dipolar resonance may involve either nitrogen, the form A in unacylated thioureas is as equally likely to contribute as C, whereas in the acyl derivatives contributions from resonance forms such as D could be expected. To the extent that these latter structures contribute to the ground state, the barrier restricting internal rotation would be increased. All free energies obtained were lower than the value reported for dimethyl thioacetamide (ΔG^{*} ≈ 30 Kcal/mole) (2).

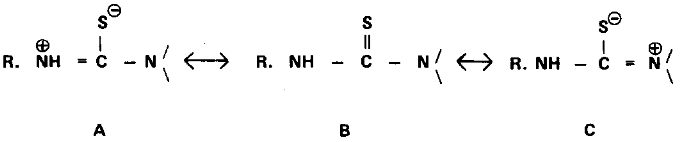
Table I

Compound	$\Delta\nu$(Hz)	Tc°K[b]	$\Delta G^{\neq}$ (kcal./mole)
I(a)	44[a]	222	10.8
I(b)	44[a]	231	11.3
II(a)	32.5	300	15.0
II(b)	32.2	310	15.5

a. estimated from line width at Tc. ± 2 Hz (6).

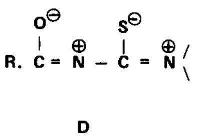
b. temperatures were calibrated using methanol spectra and are accurate to ± 2°K.

The spectrum of IIb was also observed under strongly acidic conditions. When more than an equimolar quantity of trifluoroacetic acid was added to the deuterochloroform solution, coalescence temperature was found to have increased to 318°K, while the chemical shift difference ($\Delta\nu$) decreased to 30.5 Hz. A similar effect could be achieved by the addition of p-toluenesulphonic acid, and could be reversed by addition of sodium carbonate. Formation of the conjugate acid by protonation of sulphur would be consistent with these observations (8), as protonation in this position would tend to increase the double bond character of the 2,3 C-N bond. Compound IIa (m.p. 142-145°C) is new, but prepared by standard methods (7); satisfactory analyses have been obtained. Spectra were recorded on a Varian A60D spectrometer in chloroform solutions.



$$R.\overset{\oplus}{NH}=\overset{S^{\ominus}}{\overset{|}{C}}-N< \;\longleftrightarrow\; R.\,NH-\overset{S}{\overset{\|}{C}}-N< \;\longleftrightarrow\; R.NH-\overset{S^{\ominus}}{\overset{|}{C}}=\overset{\oplus}{N}<$$

A B C



$$R.\overset{O^{\ominus}}{\overset{|}{C}}=\overset{\oplus}{N}-\overset{S^{\ominus}}{\overset{|}{C}}=\overset{\oplus}{N}<$$

D

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