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SLOW ROTATION AROUND THE BENZENE-TO-CARBONYL BOND IN A BENZAMIDE*

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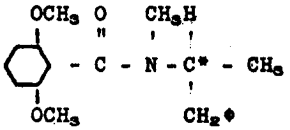
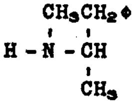
Rotation around the carbonyl-to-nitrogen bonds in many amides$^{(1,2)}$ is slow on the proton magnetic resonance (PMR) time scale. Recently, slow rotation around the benzene-to-nitrogen bond in o-substituted aryl amides was observed in PMR studies in this Laboratory$^{(3,4,5)}$. The purpose of this letter is to report evidence for slow rotation around the benzene-to-carbonyl bond in the di-o-substituted benzamide,



(I).

Compound I was prepared by adding a mixture of the amine,  $H-\overset{CH_3}{\overset{|}{N}}-\underset{\underset{CH_3}{|}}{\overset{CH_2\Phi}{\overset{|}{CH}}}$, and triethyl amine (included as a scavenger for HCl)

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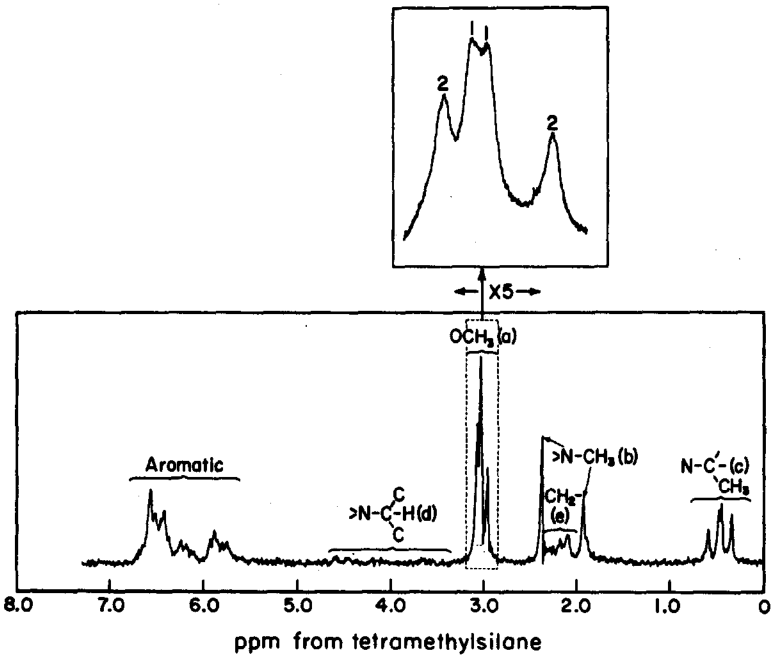
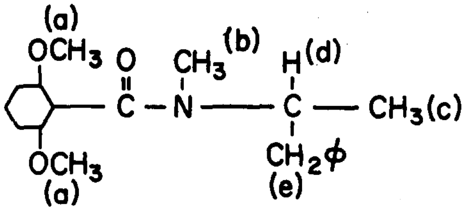
to a solution of di-o-methoxybenzoyl chloride in dichloromethane. After standing overnight, the product solution was washed sequentially with water, a solution of Na_2CO_3, and water again; then the dichloromethane was removed under vacuum. The product was purified by molecular distillation at 170°C and $<1 \times 10^{-3}$ mm Hg and purified further by crystallizing the uranyl nitrate adduct from a mixture of methylcyclohexane and dichloromethane. The adduct was redissolved in dichloromethane, the uranyl nitrate was stripped away from the amide with water and Na_2CO_3 washes, and the dichloromethane was removed under vacuum. PMR spectrograms taken after molecular distillation only and after distillation plus further purification by adduct crystallization were identical. Calculated for I: C = 72.7, H = 7.63, N = 4.47; found: C = 71.9, H = 7.65, N = 4.46.

Figure 1 is the PMR spectrum of I, as a 15 volume % solution in $CDCl_3$. The general appearance of this spectrum is consistent with the coexistence of two amide isomers due to slow rotation around the carbonyl-to-nitrogen (amide) bond, with one amide isomer being slightly more abundant than the other. However, instead of the two signals that would be expected for the methoxy protons (one for each isomer), two pairs of signals are observed. An acetone solution of the uranyl nitrate adduct of I gives qualitatively the same spectrum, including the four methoxy signals.

In t-butylbenzene as the solvent at 60°C, the same general features are observed as in $CDCl_3$ at 40°C. However, as the temperature is raised to 100°C, all signals broaden (as would be expected as the rate of rotation around the amide bond



PMR SPECTROGRAM OF



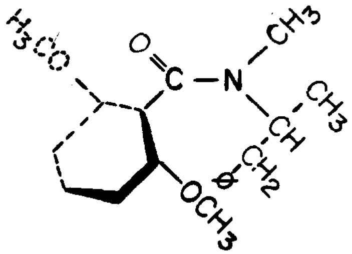
in $CDCl_3$ at 40°C

FIG. 1

is increased) and coalescence of signals from the separate amide isomers is approached. At 130°C the methoxy signals have coalesced into a reasonably sharp doublet and even ring slightly on the 500 cps scale. At 145°C the methoxy signals are a poorly resolved doublet with no ringing, but at 165° have become a sharp singlet. Apparently these signals go through two discrete stages of coalescence - from a quartet to a doublet and finally to a singlet.

It seems likely that the barrier to rotation around the benzene-to-carbonyl bond is 20 kilocalories/mole or greater. On the basis of studies with related amides we believe that the first stage of coalescence should be assigned to the onset of rapid rotation around the amide bond. This leaves the second stage of coalescence to the onset of rapid rotation around the benzene-to-carbonyl bond. By comparison with the coalescence temperatures for other amides and their kinetic quantities for rotation(2), the barrier to rotation around the amide bond in I must be about 20 kilocalories/mole. Thus the barrier to rotation around the benzene to carbonyl bond may be greater than 20 kilocalories/mole. Even if our assignment is the reverse of the correct one, the barri is at least 20 kilocalories/mole.

A reasonable choice of ground state for the molecules of I (one amide isomer) is shown below.



There is a loss of electron delocalization energy because the benzene ring is not in the plane of the carbonyl group. However, this provides steric considerations favorable to preserving the larger delocalization energy of the amide framework.

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