Evidence for Slow Rotation around the Benzene-to-Carbonyl Bond in a *meta*-Substituted Benzamide†

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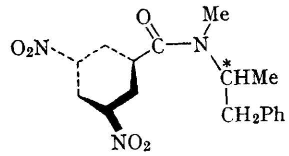
SLOW rotation around the benzene-to-carbonyl bond has been reported[1] for *ortho*-substituted benzamides. This Communication reports for the first time evidence for slow rotation around this bond in a *meta*-substituted benzamide. Compound (I) was prepared by reacting 3,5-dinitrobenzoyl chloride with the amine (with Et_3N as a scavanger for HCl) and purified by repeated crystallization. ^1H nuclear magnetic resonance scans were obtained with a Varian A-60 spectrometer fitted with a variable temperature probe.



(I)

The benzamide (I) is capable of the *cis–trans*-isomerism that results when rotation is slow around the carbonyl-to-nitrogen (amide) bond: the methyl group may either be *cis* to the carbonyl oxygen as shown or *trans* to oxygen after a 180° rotation around the amide bond. At $-10°$ in acetone, two complete sets of ^1H n.m.r. signals are observed, consistent with the co-existence of two isomers in an abundance ratio of 3 : 1, as shown in the top scan in the Figure (100 c./sec. expansion for the *ortho*- and *para*-proton signals from the nitrated benzene ring). The doublet ($J_{\mathrm{H,H}} = 2{\cdot}0_1$ c./sec.) is for the *ortho*-protons in the major isomer and the smaller doublet ($J_{\mathrm{H,H}} = 2{\cdot}0_1$ c./sec.) at lower field is for the *ortho*-protons of the minor isomer. The *para*-protons give two overlapping triplets ($J_{\mathrm{H,H}} = 2{\cdot}0_1$ c./sec.) at lowest field, one triplet from each isomer. At $-40°$, the larger doublet is broadened into a hump. (Second scan). At $-60°$, the larger (major) doublet is so broad that it is lost in the noise (not shown). At $-90°$, all signals are broad (third scan) from viscosity broadening, but the larger doublet signal has reappeared at *half* intensity *between* the smaller doublet and the overlapping triplets. The other half of this signal is lost in the more intense pattern from the protons of the other benzene ring more than one p.p.m. upfield. We interpret this behaviour as the change of the signals of the *ortho*-protons in the major isomer from an A_2 pattern at $-10°$ to an AB pattern with a chemical shift of more than one p.p.m. at $-90°$. From rough application of the equation of Meiboom[2] the A $\rightarrow$ B exchange process has a rate of 50 sec.$^{-1}$ at $-20°$. This corresponds to an exchange barrier of 9 kcal./mole with a frequency factor of 10^{10} or 13 kcal./mole if the frequency factor is as much as 10^{14}. The higher values are more consistent with the rotations observed in amides.[3]

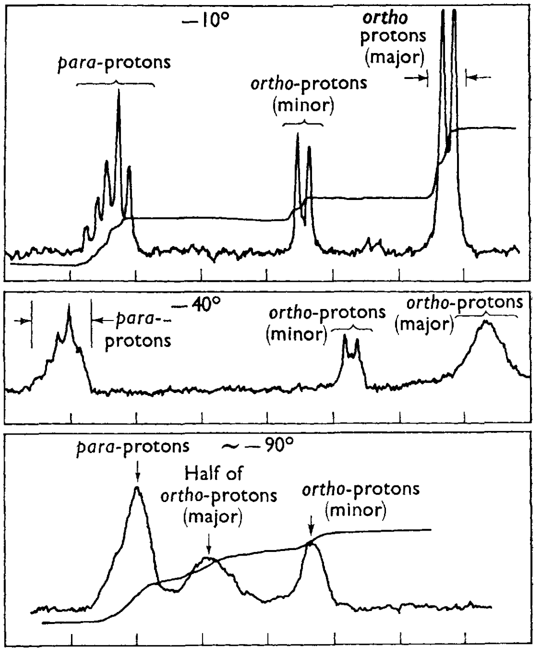


FIGURE. ortho- *and* para-*Proton signals from nitrated ring in* N-*methyl*-N-(1-*methyl-2-phenylethyl*)-3,5-*dinitrobenzamide.* (250 mg./ml. in acetone; scan 100 c./sec. wide)

The only obvious exchange process to account for these observations is slow rotation around the benzene-to-carbonyl bond. With slow rotation at this bond and with the nitrated benzene ring in a ground state that is rotated out of the amide plane, the *ortho*-protons are non-equivalent, as observed

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in the major isomer. The only symmetry operation[4] that makes them equivalent is rotation around the benzene-to-carbonyl bond, and this rotation has become slow on the ^1H n.m.r. time scale. Evidently, either rotation is more rapid in the minor amide isomer or the field gradient between the *ortho*-protons is near zero.[4] The first explanation is probably correct; the minor isomer places the *N*-methyl group *trans* to oxygen and *cis* to the nitrated ring. Because of the smaller size of the $-CH_3$ group as compared to $CH_3{-}\dot{C}H{-}CH_2Ph$ the barrier to rotation around the benzene-to-carbonyl bond in the minor isomer would be smaller.

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[4] T. H. Siddall, tert., *J. Phys. Chem.*, 1966, **70**, 2249.