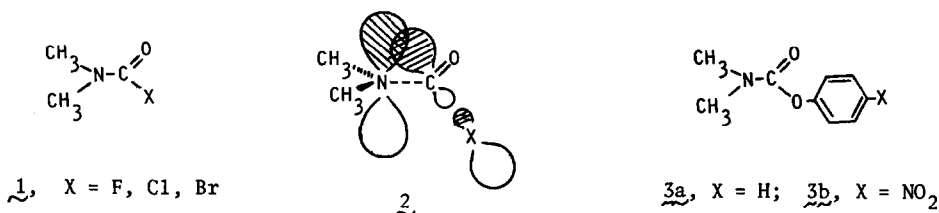


THE ROLE OF HYPERCONJUGATION IN AMIDE ROTATION. TORSIONAL
BARRIERS IN ARYL N,N-DIMETHYLCARBAMATES

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The concept of hyperconjugation has gained new interest in recent years,¹ since the discussion of organic structural phenomena in terms of perturbational molecular orbital (PMO) theory has become widespread.² Within the PMO framework, any two electron (stabilizing) interaction between orbitals of σ and π type symmetries may be termed 'hyperconjugation'. Recently lone pair - polar bond hyperconjugation has been invoked to account for the observed order of amide rotational barriers in N,N-dimethylcarbamoyl halides (1).³ Thus, the torsional transition state (2), in which the nitrogen lone pair is properly oriented for overlap with the C-X σ^* orbital, is increasingly stabilized in the order F < Cl < Br following the order of decreasing σ_{C-X}^* orbital energies (F > Cl > Br). The observed order of barriers (F > Cl > Br) may therefore result from this transition state interaction.³



While excellent correlations with other phenomena associated with the C-X bond seem to support this view,³ the current understanding of amide rotation⁴ focuses on the effects of substituents on the rotational *ground state*. In fact, the same trend in the barriers for series 1 can also be rationalized in terms of ground state effects: steric destabilization of the ground state, the effect of substituent electronegativity, as well as the π donor ability of the halogens at the ground state may all lead to the same observation. We therefore undertook to study more critically the importance of transition state hyperconjugation in the rotation of amides and related systems. The system chosen was the *para*-substituted phenyl N,N-dimethylcarbamate (3).

This communication describes preliminary results of a DNMR study of free energies of activation for rotation in 3a and 3b. Previous attempts to study substituent effects on torsional barriers in carbamates⁵ were unsuccessful, due to the small chemical shift nonequivalence of the N-

TABLE. Free energies of activation and 100 MHz DNMR data.^a

Compound	ρ^b	$T_c, ^\circ K^c$	$\Delta\nu_c, Hz^d$	$k_c, e^{-1} sec^{-1}$	$\Delta G_c^\ddagger, Kcal/mol^f$
<u>3a</u>	0.24	332	43.5	96	16.5
	0.30	335	54.0	120	16.5
<u>3b</u>	0.22	342	38.0	84	17.1
	0.31	347	60.0	133	17.0

a. Bromobenzene solution. b. ILSR/[substrate]. c. Coalescence temperature. d. $\Delta\nu_c$ taken as the width at half height of the coalescence spectrum. e. $k_c = \pi\Delta\nu_c/\sqrt{2}$. f. From Eyring's equation.

methyl groups. In order to overcome this difficulty, spectra were recorded in presence of a lanthanide shift reagent (LSR), $Eu(fod)_3$.⁶ The LSR caused the room temperature spectra, which otherwise showed a singlet for the N-methyl groups, to split substantially and enable reliable ΔG^\ddagger measurements (Table). It has been shown that added LSR has no significant effect on the barrier in carbamates.^{6b,c} In addition, equal ρ 's ($\rho = [LSR]/[carbamate]$) were used, so that any possible effect would be minimized upon comparing the barriers. The Table shows that the barrier for 3b is higher than that for 3a.

The effect of the p-nitro group is to lower various MO's in its vicinity,² including the σ_{C-O}^* orbital. As a result, the stabilizing hyperconjugation of the transition state should increase, due to the smaller energy gap between the lone pair and the σ_{C-O}^* orbitals.³ This, however, is in disagreement with the observed order of barriers. On the other hand, our findings are readily understood in terms of the usual ground state substituent effect picture:⁴ the enhanced electronegativity of the phenoxy oxygen introduced by the nitro group further stabilizes the conjugated ground state of the amide function, and hence the higher barrier.

We therefore conclude that in the present system hyperconjugation cannot explain the order of barriers, and that, in fact, ground state effects on amide rotation are dominant over transition state hyperconjugation.

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