Geminal Proton Nonequivalence in Some *NN*-Diethylbenzamides

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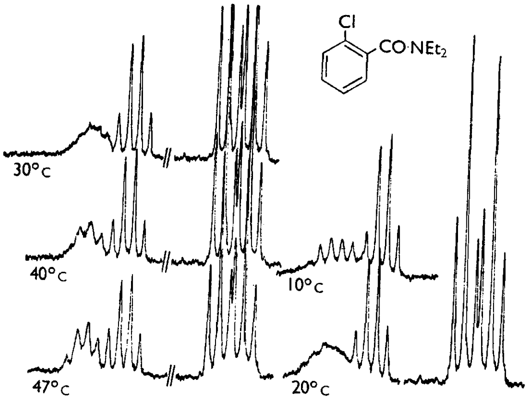
A RECENT Paper[1] on the p.m.r. spectra of some *N*-substituted *N*-arylamides in which, when one *N*-substituent is an *ortho*-substituted aryl group and the other contains an α-methylene group, the methylene protons are nonequivalent, prompts us to report some preliminary observations on the spectra of *NN*-diethylbenzamides.

The p.m.r. spectrum[2] of *o*-chloro-*NN*-diethylbenzamide at room temperature showed two quartets for the methylenes, the signals for the lower-field quartet being appreciably broadened. On raising the temperature of the solution it was observed that the lower-field signals sharpened into a quartet and then broadened again as they coalesced with the up-field quartet. The two methyl triplets were sharp signals at room temperature and coalesced at the same temperature as the ethyl quartets. On cooling the solution, the signals for the low-field quartet became broader and at 10°c a sixteen-line pattern, being the AB part of an ABX_3 pattern, was observed. The methyl signals remained as two distinct triplets. Some of these spectra are shown in the Figure. In the Table are listed a series of *ortho*-substituted NN-diethylbenzamides in which this phenomenon was observed together with the chemical shift $(\nu_A - \nu_B)$ measured at -50°c between the two methylene protons and the temperature T_c (AB) at which the ABX_3 pattern appeared to collapse to an A_2X_3 pattern. By a double resonance experiment[3] it was shown that the lower-field quartet was associated with the lower-field triplet. It has been shown[4] that in unsymmetrically substituted *NN*-dialkylalkylamides the preferred conformation is that in which the bulkier alkyl substituent is *cis*-orientated to the carbonyl group. A p.m.r. spectrum of *N*-ethyl-*N*-methylbenzamide showed the presence of two conformers and that the preferred conformer had the methyl singlet at lower field and the quartet for the ethyl methylene at higher field. Thus it is the ethyl group *cis* to the phenyl ring that gives rise to the ABX_3 pattern in *ortho*-substituted *NN*-diethylbenzamides.

Our results suggest that there is a steric interaction between the *ortho*-substituents and the ethyl group *cis* to the phenyl ring causing unequal population of the three possible rotameric conformations of the methylene of the ethyl group and thus unequivalent average environment of the methylene protons. We think that restriction of rotation around the benzene-to-carbonyl bond similar to that postulated between the benzene-to-nitrogen bond in *N*-alkyl-*N*-phenylamides[1] is probably a small factor in the magnetic nonequivalence of the methylene protons since a symmetrically *ortho*-di-substituted benzamide (*i.e.*, 2,6-dichloro-*NN*-diethylbenzamide) also exhibited the same phenomenon and *meta*-substituted benzamide analogues do not show this effect.



FIGURE

It is interesting to note in the Table that neither ($\nu_A - \nu_B$) nor T_c (AB) appears to be directly related to the bulk of the *ortho*-substituent. Further the *ortho*-methoxyl analogue did not exhibit any broadening of the low-field ethyl quartet even down to −60°C.

By examination of the line shape of the two ethyl quartets as they approach their coalescence temperature it was possible to get a measure of the energy barrier for rotation about the amide bond using the method of Gutowsky and Holm.[5] Although the values for this energy barrier for the *ortho*-substituted amides (E_A = 10—14 kcal.) were greater than for the analogous *para*- (E_A = 6—9 kcal.) and *meta*- (E_A = 4—5 kcal.) substituted *NN*-diethylbenzamides, and indicate that steric factors probably influence this energy barrier, it is not considered that this is a significant factor in causing the nonequivalence of the methylene protons since the *ortho*-methoxyl derivative and *NN*-diethylthionobenzamide have high energy barriers (E_A~11 kcal.) but do not show the none-equivalent methylene protons at temperatures as low as −60°C.

TABLE

Chemical shift ($\nu_A - \nu_B$) *and coalescence temperatures* T_c (*AB*) *of the methylene protons in some* ortho-*substituted* NN-*diethylbenzamides*

Substituent	($\nu_A - \nu_B$)c./sec.	T (AB) °K	J_{AB} c./sec.
2-Fluoro	14·8	241	13·5
2-Chloro	32·1	303	13·5
2-Nitro	35·8	264	13·5
2-Methyl	36·4	280	13·3
2,6-Dichloro	33·4	297	13·3

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[1] T. H. Sidall and C. A. Prokaska, *J. Amer. Chem. Soc.*, 1966, **88**, 1172.

[2] Spectra were determined in *ca.* 10% $CDCl_3$ solution on a Varian Associates model A-60 spectrometer equipped with a V-6040 variable temperature controller.

[3] Double-resonance spectra were obtained on a Varian Associates model HA-100 spectrometer equipped with a Muirhead–Wigan decade oscillater D-890A.

[4] L. A. La Planche and M. T. Rogers, *J. Amer. Chem. Soc.*, 1963, **85**, 3728.

[5] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, 1956, **26**, 1228.