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PHENYL GROUP MAGNETIC NONEQUIVALENCE IN SOME AROMATIC ACID NN-DIPHENYLAMIDES

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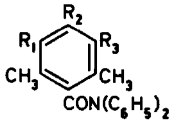
We have recently reported (1) the preparation and resistance to alkaline hydrolysis of the NN-diphenylamides of mesitoic, 2,3,5,6-tetramethylbenzoic and pentamethylbenzoic acids (I, II and III respectively). Examination of molecular (CPK) models of these sterically hindered amides suggests that rotation of the phenyl groups of the diphenylcarbamoyl ($(C_6H_5)_2NCO$) residue about the N-CO bond is restricted. As a consequence of this restricted rotation, these phenyl groups would be expected to be magnetically nonequivalent. Such nonequivalence is indeed observed in the p.m.r. spectrum* of I in CCl_4 (Fig. 1) where the signals of the aromatic protons appear as three singlets located at δ 7.23, 6.97 and 6.56 p.p.m., the proton ratio being 5:5:2 respectively (the last two protons are those of the mesitoic acid moiety). The p.m.r. spectra of II and III revealed similar phenyl group nonequivalence (see Table). For all three compounds, both the chemical shifts of the five-proton singlets and the separations ($\Delta\nu$) between these singlets are solvent-dependent. It appears that both ortho methyl groups are



I $R_1 = R_3 = H$, $R_2 = CH_3$
II $R_1 = R_3 = CH_3$, $R_2 = H$
III $R_1 = R_2 = R_3 = CH_3$

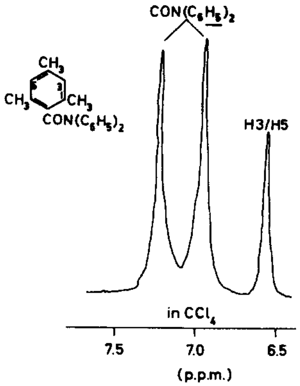


Fig.1. Aromatic region of p.m.r. spectrum of mesitoic acid NN-diphenylamide (I) at 40±1°C.

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* P.m.r. spectra were recorded at 40 ± 1°C on a Varian A60 spectrometer (60 Mc/s) for 0.25 M solutions (tetramethylsilane as internal standard).

necessary for phenyl group magnetic nonequivalence since the diphenylcarbamoyl protons of 2,4-dimethylbenzoic acid NN-diphenylamide appear as a ten-proton singlet.

So far the effect of raising the temperature of the sample on the p.m.r. spectra has been examined in only one case, namely II (in dimethyl sulphoxide solution). In this experiment it was observed that the two five-proton singlets coalesced to a single broad ten-proton singlet at 150°C* indicating that, at this temperature, the phenyl groups have become magnetically equivalent, presumably because of rapid rotation about the N-CO bond.

These results prompted us to measure the p.m.r. spectra (in CCl_4) (see Table) of NN-diphenylacetamide ($(C_6H_5)_2NCOCH_3$)+, NN-diphenyltrifluoroacetamide ($(C_6H_5)_2NCOCF_3$)+ and NN-diphenylcarbamoyl chloride ($(C_6H_5)_2NCOCl$)+. In each case only a single sharp singlet was observed for the aromatic protons and hence for these compounds there is no barrier to rotation (at 40°C) about the N-CO bond. Further spectral measurements are planned to determine whether these compounds exhibit phenyl group nonequivalence at lower temperatures.

Magnetic nonequivalence of groups (methyl and methylene) bonded to nitrogen is well known in amide chemistry (2) and has recently been reported for the methyl protons of some NN-dimethylcarbamates (3) but the present work appears to be the first reported where both the nonequivalent nuclei are phenyl groups.

At present we are endeavouring to determine accurately T_c and the activation parameters for I, II and III and are also investigating whether phenyl group magnetic nonequivalence is exhibited by other compounds containing the $(C_6H_5)_2NCO$ group.

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* Accurate determination of this coalescence temperature was rendered difficult by the broadening of the low-field five-proton singlet. Because of this broadening (partial splitting of aromatic protons?), which is particularly noticeable for solutions of I, II and III in $CDCl_3$, proton ratios were determined by planimeter measurement of the areas under the peaks.

\+ The occurrence of methyl group magnetic nonequivalence in the NN-dimethyl analogues of these compounds is well known (4).

TABLE

Chemical Shift Data of Diphenylcarbamoyl Protons of Some NN-Diphenylamides $((C_6H_5)_2NCOR)$ at 40 ± 1°C

Parent Acid	Solvent	(p.p.m.)[a]	$\Delta\nu$[b]
Mesitoic	CCl_4	6.97, 7.23	16.2
	$CDCl_3$	7.00, 7.30	18.2
	DMSO	7.15, 7.40	14.6
2,3,5,6-Tetramethylbenzoic	CCl_4	6.95, 7.25	18.6
	$CDCl_3$	7.00, 7.33	19.8
	DMSO	7.15, 7.42	16.2
Pentamethylbenzoic	CCl_4	6.97, 7.25	17.4
	$CDCl_3$	7.04, 7.37	19.6
	DMSO	7.13, 7.40	15.2
2,4-Dimethylbenzoic	CCl_4	7.03	-
	$CDCl_3$	7.15	-
	DMSO	7.23	-
Acetic	CCl_4	7.27	-
Trifluoroacetic	CCl_4	7.30	-
(NN-Diphenylcarbamoyl chloride)	CCl_4	7.25	-

[a] Where two signals are present, the proton count is 5:5; otherwise the proton count is 10.

[b] Separation (in c/s) between the singlet five-proton peaks.

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