

SUBSTITUENT EFFECT ON THE IR AND PMR SPECTRA OF DIPHENYLAMINES

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Abstract—PMR chemical shifts of various *m*- and *p*-substituted diphenylamines were correlated with σ -constants. However, the N—H stretching frequencies of these amines were not linear with the σ -constants, and the irregularity in the $\nu_{\text{N-H}}$ vs σ plot was interpreted by taking into accounts the following factors: the changes in hybridization of the imino N atoms, the normal electronic effect of the substituent and the steric effect on the planarity of the amine molecules. Results on the C—N stretching absorptions were also presented.

Earlier publications concerning the substituent effect on the IR N—H spectra of various amines and amides are perplexing. The N—H stretching frequencies of substituted anilines^{1,2} and methyl-anilines¹ have been correlated with the Hammett's σ -constants, and it is shown that the N—H frequency increases as the σ -constant increases. This trend of the N—H frequencies in these amines is reversed for the O—H groups of phenols and for the N—H groups of the substituted amides.³ This apparent contradiction has been explained by considering the change in hybridization of the N atom in aniline.² Anilines were shown to exist as a nonplanar pyramidal conformation from the dipole moment measurement,⁴ and this confirms the sp^3 -like hybridization of the N atom. The electron accepting nature of the substituent would decrease the electron density on the N atom and cause the increase in the *s*-character of its sp^3 -like bonding orbital; since the decrease in electron density lessens the repulsion among the unshared and bonding electron pairs on the N atom. This favors the planar sp^2 hybridization. On the other hand, the amide has a planar conformation, and no further change in hybridization is probable. As a result, the substituent effect on the N—H frequency is normal, and the electron accepting nature of the substituent causes the decrease in electron density of the N atom, which, in turn, causes the weakening of the N—H bonds and the lowering of the N—H frequencies.

Concerning the spectral properties of the diphenylamines and related compounds, several other investigations have been reported. The UV spectra of these compounds have been dis-

cussed by Itier and Casadevall⁵ in order to determine the conjugative properties of the N atom, and the IR spectra of arylaminopyridines⁶ and nitrodiphenylamines⁷ have been determined in the solid states. The N—H stretching absorptions of 2-anilinopyridine and its nitro-substituted derivatives have been measured by the present authors,⁸ and a substituent effect similar to that found in phenols and amides was observed.

In connection with our investigations in searching the diphenylamine derivatives with pharmaceutical activity, a series of diphenylamines have been prepared and their spectral properties studied with special interest on the substituent effect.

RESULTS AND DISCUSSION

The N—H stretching absorptions of a series of diphenylamines are listed in Table 1, together with their proton chemical shifts in two solvents and the electron densities on imino N atoms obtained by HMO calculation. As shown in Fig 1, good linear correlations⁹ between the N—H chemical shifts and the Hammett's σ -constants have been obtained both in chloroform-*d* and in dimethylsulfoxide-*d*₆. The $\nu_{\text{N-H}}$ vs σ plot in Fig 2 is somewhat more complex. Diphenylamines with electron donating substituents behave like substituted anilines and N-methylanilines; i.e. the N—H stretching frequency decreases in the decreasing order of the substituent constant. On the other hand, those with electron attracting substituents exhibit a $\nu_{\text{N-H}}$ vs σ plot of negative slope. The results can be explained in the following way. The variation in the hybridization proceeds in the

Table 1. IR N—H stretching absorptions and PMR spectra of substituted diphenylamines

Substituent	σ	N—H stretching absorption			N—H chemical shift		pK_a	Electron density q_N
		ν_{\max} (cm ⁻¹)	$\Delta\nu$ 1/2 (cm ⁻¹)	$A \cdot 10^{-6}$ (cm/mol)	(ppm from TMS) CDCl ₃	DMSO- <i>d</i> ₆		
4-NH ₂	-0.66	—	—	—	5.72	7.28	—	1.846
4-OH	-0.36	3424.2	42.5	9.95	—	7.46	(1.8)	1.846
4-OMe	-0.268	3424.6	40.2	8.95	5.37	7.60	1.36	1.845
4-Me	-0.170	3426.0	34.7	8.52	5.49	7.75	1.20	1.841
3-OH	-0.002	3428.4	31.7	8.84	5.57	7.82	(0.7)	1.841
H	0.000	3427.2	31.5	7.51	5.56	7.91	0.78	1.841
3-OMe	0.115	3429.9	31.8	8.42	5.59	7.95	0.40	1.841
3-NO ₂	0.710	3426.1	28.4	10.9	5.82	8.52	-1.61	1.842
4-NO ₂ -4'-Me	1.10	3421.7	22.4	15.2	5.99	—	-2.93	1.823
4-NO ₂	1.27	3421.4	21.7	15.5	6.12	9.05	-3.13	1.823
4-NO ₂ -4'-F	1.332	3422.1	24.6	18.5	5.97	—	(-3.3)	1.821
4-NO ₂ -4'-Cl	1.497	3421.7	23.5	17.4	—	—	(-3.7)	1.822
4-NO ₂ -4'-Br	1.502	—	—	—	6.04	—	—	1.822
3',4-(NO ₂) ₂	1.98	3421.1	23.9	12.9	6.27	9.38	-5.19	1.824

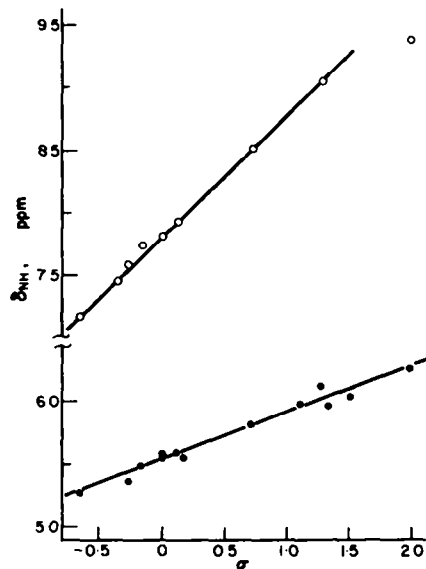


Fig 1. Substituent effect on the N—H proton chemical shifts of diphenylamines. —●— in CDCl₃ and —○— in DMSO-*d*₆.

negative σ region. However, the phenyl group of diphenylamine is more electronegative than the methyl group in N-methylaniline; thus, the hybridization of its N atom is more sp^2 -like than that of N-methylaniline. At the reflection of the ν_{N-H} (and also A_{N-H}) vs σ plot near $\sigma = +0.1$ in Fig 2, the N atom of diphenylamine takes the sp^2 hybridized state of planar conformation, and no further rehybridization proceed in the region of more positive σ -constant. However, the electron density on the N atom decreases further as the substituent becomes more strongly electron-accepting—similar

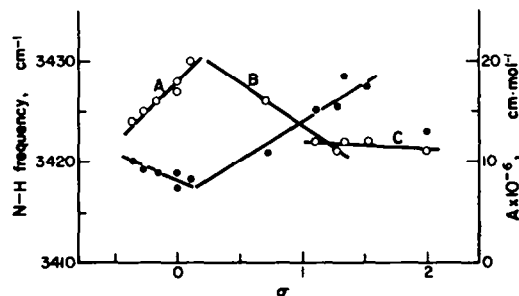
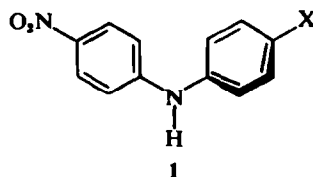


Fig 2. Substituent effect on the N—H stretching frequencies and intensities of diphenylamines. —○— denotes ν_{N-H} (in cm⁻¹), and —●— denotes A_{N-H} (in cm²·mol⁻¹).

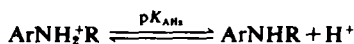
to the case of O—H groups in phenols.^{12,13} A lower electron density on the N atom consequently results in a weaker N—H bond and, hence, a lower N—H stretching frequency. A considerable deviation from the linearity is observed with 4-nitrodiphenylamines substituted at the phenyl nucleus without 4-nitro group (1). This may be attributed to the nonplanar conformation (1) in which the strong conjugation between the nitrophenyl and the imino group exists, while the other phenyl group is nonplanar with the residual part of molecule. In this molecule, the conjugation involving the nonplanar phenyl group might, at least partly, be hindered, so the effect of the second



substituent X in 1 might be suppressed to a considerable extent. Thus, the substituent effect of such di-substituted derivatives should be discussed separately. As expressed by a nearly flat line (C part of the plot in Fig 2), the N—H stretching frequency is insensitive to the second substituent.

Integrated intensities of the N—H bands are plotted in Fig 2, and the half-widths are given in Table 1. Intensity variation caused by the substituent whose σ values are less than +0.1 is the reverse order when compared with the earlier observation on aniline derivatives.^{1,2} However, the variation in the half-widths is in accordance with that of anilines.

The acidity of the N—H group could be influenced by the *s*-character of the N atom as well as by the electronic effect of the substituent. The pK_a values cannot be related directly to the ionization of the proton of the N—H group. However, a linear relation to correlate the pK_a value of the conjugate acid of an amine ($pK_{AH_3^+}$) with the pK_a values for the dissociation of the same amine to form the corresponding amide anion has been reported by Stewart and Doleman.⁹



They deduced a common equation relating acidity

and basicity of anilines and diphenylamines empirically, and its wider applicability is suggested. Therefore, the N—H stretching frequencies of some amines and amides have been plotted against their pK_a values. As a very good linear relation exists between the pK_a and σ values, ν_{N-H} vs pK_a plot of diphenylamine itself is quite similar to the former ν_{N-H} vs σ plot, and no extra information can be obtained. However, the pK_a value can be a common measure for different series of amines, and could be a useful means of comparison. The gross feature of the plot indicates that the ν_{N-H} vs pK_a plot has a negative slope when pK_a is larger than zero. Evidently, the value itself of the borderline pK_a has no significance, but the plot suggests that the sp^2 -hybridized imino group has a pK_a value lower than a borderline value near zero and that the pK_a of the imino group increases from the borderline value as the hybridization of the N atom changes from sp^2 to sp^3 -hybridized state. In short, both the slope of the ν_{N-H} vs σ plot and the pK_a values could be a guide-post for the hybridization of the amino and imino N atoms.

In order to discuss the properties of the C—N bond of diphenylamines, C—N stretching absorptions have been determined and compared with the bond orders calculated from the HMO coefficients. The results are shown in Table 2. Higher C_1 —N bond orders in 4-nitrodiphenylamines are favorable for the planar conformation of their 4-nitrophenylamino groups suggested from the behavior

Table 2. The C—N stretching frequencies and the C—N bond orders of diphenylamines

Substituent	$\nu_{C-N}^{\text{as}} (\text{cm}^{-1})^*$	Bond order		
		ρ_{C-N}	ρ_{C_1-N}	$\bar{\rho}_{C-N}$
4-NO ₂ -4'-F	1329	0.3151	0.2898	0.3025
4-NO ₂ -4'-Cl	1326	0.3151	0.2890	0.3021
4-NO ₂ -4'-Br	1331	0.3153	0.2879	0.3016
4-NO ₂	1324	0.3157	0.2838	0.2998
4-NO ₂ -4'-Me	1324	0.3160	0.2832	0.2996
3',4'-(NO ₂) ₂	1351	0.3158	0.2825	0.2992
4-NO ₂ -4'-OMe	1318	0.3184	0.2729	0.2957
H	1306	0.2835	0.2835	0.2835
3-OMe	1304	0.2834	0.2835	0.2834
3-OH	1319	0.2834	0.2834	0.2834
4-Me	1306	0.2828	0.2837	0.2832
3-NO ₂	1335	0.2835	0.2822	0.2829
4-NH ₂ -4'-F	1317	0.2693	0.2916	0.2804
4-NH ₂ -4'-Cl	1319	0.2693	0.2907	0.2800
4-NH ₂ -4'-Br	1320	0.2693	0.2894	0.2794
4-OMe	1320	0.2711	0.2849	0.2780
4-NH ₂	1311	0.2695	0.2851	0.2772
4-NH ₂ -4'-Me	1310	0.2696	0.2843	0.2769
4-OH	1314	0.2682	0.2851	0.2767

* ν_{C-N}^{as} denotes the asymmetric stretching frequency of C—N—C bonds. The symmetric C—N stretching band could not be assigned because of the complexity of the spectra in 1200–1000 cm^{-1} region.

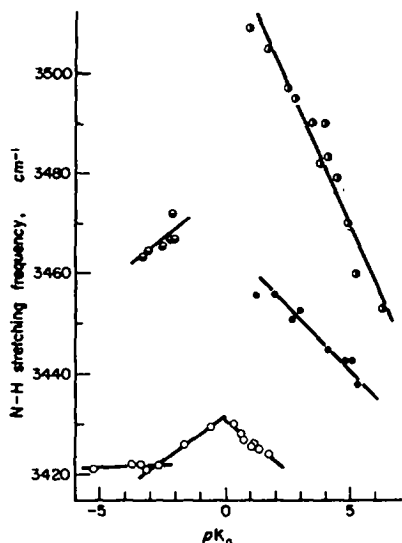


Fig 3. The ν_{N-H} vs pK_a plots for various amines. —○—: diphenylamines, —●—: N-methylanilines^{1,14}, —●—: ν_{NH} of anilines,¹ —●—: N-methylbenzamides.³

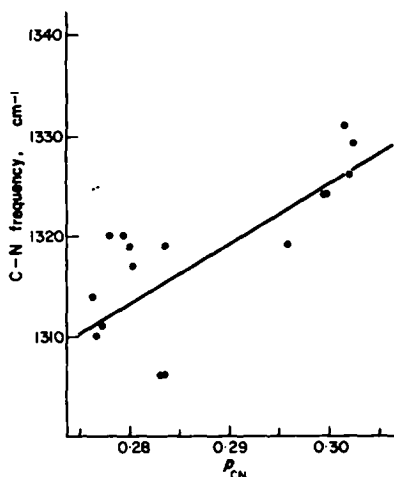


Fig 4. The ν_{C-N} vs p_{C-N} (bond order) plot for diphenylamines.

in the N—H stretching region. A linear relation (Fig 4) is observed between the mean bond orders and the C—N frequencies, but the linearity is rather unsatisfactory ($r = 0.683$). The ν_{C-N} vs σ plot also gives a poor linear relation. This could be due to vibrational coupling and other unmeasurable interactions among skeletal vibrational modes and, to a lesser extent, to the roughness of the HMO approximation.*

*The N—H chemical shift vs. electron density plot gives much reliable results ($r = 0.950$ for δ_{N-H} in chloroform-*d* and $r = 0.923$ for δ_{N-H} in DMSO-*d*₆).

EXPERIMENTAL

The IR spectra were recorded with a Hitachi Model 225 grating infrared spectrophotometer, and the absorption frequencies were calibrated by the absorption bands of water (vapor) at 3447.09 and 3442.41 cm^{-1} in order to keep the accuracy of the wave number within 0.5 cm^{-1} (usually within 0.2 cm^{-1}). The measurements were carried out in dilute chloroform soln for the N—H stretching region and in solid state (KBr pellet) for the C—N stretching region. The PMR spectra were obtained with a JEOL JNM C-60H spectrometer. The HMO calculations were carried out by a NEAC 2230 digital computer by employing the coulomb and resonance integrals given in the literatures.¹⁵

The diphenylamines were prepared by the usual methods, and the preparation has been reported in other publications.¹⁶⁻¹⁹ The solvent was carefully purified by the routine procedure.

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