Resonance and Solvent Effects on Absorption Spectra. Part 5.[1] Substituent and Solvent Effects on Infrared Spectra of 2- and 4-Substituted Aniline Derivatives

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I.r. spectra of 2- and 4-substituted *N*-methyl- and *N*-acetylaniline derivatives in various solvents have been employed to examine intramolecular hydrogen bonding of amine hydrogen atoms with 2-substituents, or intermolecular hydrogen bonding with hydrogen-bond-acceptor (HBA) solvents. The N–H stretching frequencies, ν_{NH}, in solvents having doubly bonded oxygen HBA base centres are well correlated according to the linear solvation energy relationship (LSER), $XYZ = XYZ_0 + s\pi^* + b\beta$, where π^* and β are the solvatochromic parameters that measure solvent dipolarity–polarizability and HBA basicity. The order of susceptibilities, *b*, to solvent basicities of ν_{NH} for the compounds studied is: $CO_2Me < COCH_3 \sim CN < NO_2$, in contrast to susceptibilities of the corresponding u.v.–visible spectra, where the order is $COCH_3 \sim CN < NO_2 < CO_2Me$.

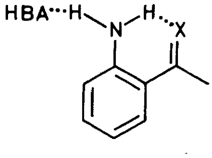
In earlier papers we have used a number of different types of spectroscopic method to study hydrogen-bonding phenomena, including i.r., n.m.r.,[2] and solvatochromic comparisons of u.v.–visible spectral shifts,[3–5] with n.m.r. and u.v.–visible spectral data playing an integral part in the original construction of the solvatochromic parameter scales. Thus, limiting ^{19}F n.m.r. shifts of 4-fluorophenol complexes with HBA bases in CCl_4, and enhanced u.v.–visible solvent shifts in HBA solvents for the HBD indicators 4-nitroaniline and 4-nitrophenol, relative to the non-HBD indicators *N*,*N*-diethyl-4-nitroaniline and 4-nitroanisole, contributed to the formulation of the β scale of HBA basicities.[3] (HBD = hydrogen-bond donor, HBA = hydrogen-bond acceptor). Similarly, enhanced u.v.–visible solvent shifts for Reichardt's $E_T(30)$ indicator 4-(2,4,6-triphenylpyridinio)-2,6-diphenylphenoxide, a strong HBA base, relative to the weak HBA indicator 4-nitroanisole, contributed to the α scale of solvent HBD acidities.[4] Where hydrogen-bonding effects were excluded, as when neither solute nor solvents were hydrogen-bond donors nor acceptors, normalized and averaged u.v.–visible solvent shifts for up to 45 indicators gave us the π^* scale of solvent dipolarity–polarizabilities.[6] A report detailing the application of the parameters to solvent-effect studies contains the most recent comprehensive collection of π^*, α, and β values.[7]

These solvatochromic parameter scales were originally intended to serve towards the correlation, rationalization, and prediction of solvent effects on many types of physicochemical properties and reactivity parameters, XYZ, through a generalized linear solvation energy relationship of the form of equation (1), where the *s*, *a*, and *b* terms represent the responses

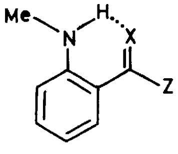
$$XYZ = XYZ_0 + s\pi^* + a\alpha + b\beta \qquad (1)$$

of the indicator or reactant solutes to the changing solvent properties. More recently the parameters have been used to correlate solute effects,[8] including solubilities in water[9] and octanol–water partition coefficients,[10] of many of the compounds treated as solvents.

In other earlier work[2,11] we also demonstrated that 4-X-2-nitroanilines undergo enhanced bathochromic shifts relative to their *N*,*N*-dimethyl derivatives in HBA solvents, and that these enhanced shifts are nicely proportional to solvent β values. With the *N*-methyl-4-X-2-nitroanilines, on the other hand (with only one proton to share), $\nu_{max.}$ values were linear, with the corresponding maxima for the *N*,*N*-dimethyl derivatives in both non-hydrogen-bonding and HBA solvents, indicating that the N–H proton prefers to remain intramolecularly hydrogen bonded to nitro, rather than forming intermolecular hydrogen bonds, even to quite strong HBA base solvents. Intramolecular hydrogen bonding is also maintained in HBA solvents by 2-acetyl-*N*-methylaniline whereas in the 2-cyano case intermolecular hydrogen bonds to the solvent are formed. The hydrogen bonding picture for the 2-nitro- and 2-acetyl-aniline derivatives is as represented by structures (A)—(C).



(A)



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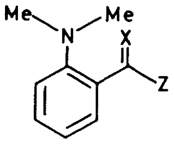


(C)

U.v.–visible solvatochromic studies have also shed light on some subtle aspects of hybridization in 2- and 4-substituted aniline derivatives. In the 4-X-anilines, the responses to solvent HBA basicity [*b* values in equation (1)] are in the order $CO_2Et > NO_2 > COPh$, with the high value for $X = CO_2Et$ rationalized on the basis that a large part of the bathochromic shift is due to rehybridization on the amine nitrogen from nearer sp^3 in non-HBA solvents to nearer sp^2 in HBA solvents (as will be discussed further later). In the 2-X-anilines, on the other hand, the *b* term follows the acidity order, $NO_2 > COCH_3 > CO_2Me$, because the intramolecularly hydrogen-bonded 2-methoxycarbonylaniline is already near sp^2-hybridized in the non-HBA solvents.[12]

Insofar as correlations of i.r. spectral data with the solvatochromic parameters are concerned, hydrogen-bonding shifts, Δν (OH free minus hydrogen bonded), of phenol, 4-fluorophenol, and methanol complexes with HBA bases have been shown[13,14] to be 'family dependent' properties, *i.e.* linear with β values within families of bases having a similar type of HBA site, but not between families. To accommodate the different families in the same correlation equation has required the use of the new co-ordinate covalency parameter ζ in combination with β, where $\zeta = -0.20$ for P=O bases, 0.00 for

C=O and S=O bases, 0.10 for C≡N bases, 0.20 for singly bonded oxygen bases, 0.60 for pyridine bases, and 1.00 for sp^3-hybridized amine bases.

Results and Discussion

In this paper we examine the effects of substituents, solvents, and intra- *versus* inter-molecular hydrogen bonding on i.r. N–H stretching frequencies of some 2- and 4-substituted *N*-methyl and *N*-acetylaniline derivatives. Solvent effects are also compared with corresponding effects on u.v.–visible spectra. Because these are 'family dependent' properties,[14] consideration is restricted to HBA bases having doubly bonded oxygen as the acceptor site, to eliminate the need for the ζ parameter in the correlation equation. Correlations involving the ζ parameter will be discussed in the next paper of this series.[15]

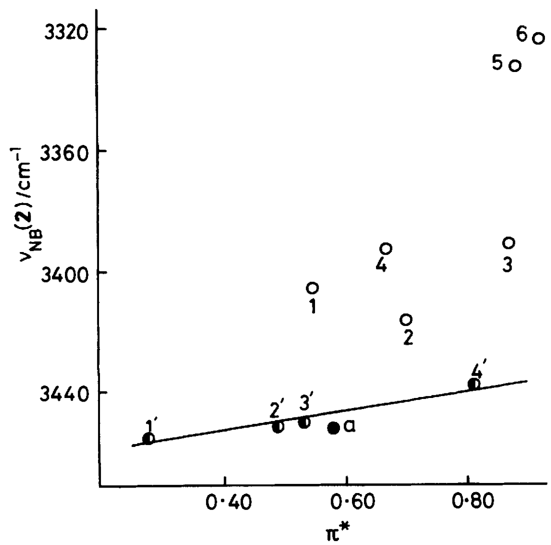
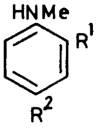


Figure 1. Plot of $\nu_{NH}(2)$ against π^* scales of solvents

The i.r. spectra of the aniline derivatives (**1**)—(**11**) were measured in the following solvents: non-HB solvents (◐ in Figures): CCl_4 (1′), Cl_3CCH_3 (2′), $Cl_2C{=}CHCl$ (3′), $ClCH_2CH_2Cl$ (4′); HBA solvents (○): ethyl acetate (1), ethyl chloroacetate (2), γ-butyrolactone (BL; 3), butan-2-one (4), *N*,*N*-dimethylacetamide (DMAc; 5), *N*-methyl-2-pyrrolidone (NMP; 6); HBD solvent (●): $CHCl_3$ (a). The N–H stretching frequencies are assembled in Tables 1 and 2 together with solvent π^*, β, and α values.

The ν_{NH} values of 4-acetyl-*N*-methylaniline (**2**) in non-HBA, HBD ($CHCl_3$), and HBA solvents are plotted against π^* values in Figure 1. The correlation pattern appears to be similar to patterns we have observed earlier[16] when the 'stepwise solvatochromic comparison method' was used to unravel solvent dipolarity–polarizability and hydrogen-bonded effects on the u.v.–visible spectra of some aniline derivatives. The following may be seen in the Figure. (i) The $\nu_{NH}(2)$ values in non-HB solvents are linearly correlated with π^* with very shallow slope, indicating a low sensitivity of $\nu_{NH}(2)$ to solvent dipolarity–polarizability. (ii) The data point for $CHCl_3$ is displaced slightly from the correlation line towards higher wavenumber; the small but probably real effect is consonant with hydrogen bonding by $CHCl_3$ to the acetyl group increasing its electron-withdrawing ability and hence exerting a purely second-order effect on the remote N–H bond. This effect is also observed for most of the other indicators in Table 1. (iii) The data points for the HBA solvents are displaced from the correlation line towards lower

Table 1. I.r. spectral data, ν_{NH}/cm^{-1},[a] of 4- and 2-substituted *N*-methylaniline derivatives (**1**)—(**6**)

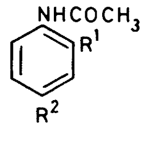


	R^1	R^2
(**1**)	H	CO_2Me
(**2**)	H	$COCH_3$
(**3**)	H	CN
(**4**)	H	NO_2
(**5**)	$COCH_3$	H
(**6**)	CN	H

Solvent	(**1**)	(**2**)	(**3**)	(**4**)	(**5**)	(**6**)	π^*	β
1′ CCl_4	3 409	3 455	3 453	3 457	3 320	3 437	0.28	0.00
2′ Cl_3CCH_3	3 406	3 451	3 452	3 453	3 324	3 435	0.49	0.00
3′ $Cl_2C{=}CHCl$	3 406	3 450	3 451	3 452	3 325	3 434	0.53	0.00
4′ $ClCH_2CH_2Cl$	3 399	3 439	3 438	3 439	3 331	3 424	0.81	0.00
1 AcOEt	3 382	3 407	3 402	3 389	3 328	3 395	0.55	0.45
2 $ClCH_2CO_2Et$	3 390	3 418	3 414	3 407	3 330	3 408	0.70	0.35
3 BL[b]	3 370	3 392	3 383	3 368	3 331	3 382	0.87	0.49
4 MeCOEt[c]	3 376	3 394	3 391	3 383	3 330	3 393	0.67	0.48
5 CH_3CONMe_2	3 350	3 334	3 329	3 299	3 331	3 339	0.88	0.76
6 NMP[d]	3 346	3 325	3 325	3 297	3 328	3 335	0.92	0.77
a $CHCl_3$[e]	3 412	3 452	3 454	3 453	3 334	3 437	0.58	0.00

[a] Measured with a Hitachi 260–50 spectrometer using 0.05—0.3M-solutions and 0.1—1 mm cell width. [b] γ-Butyrolactone. [c] The HBD acidity of MeCOEt is observed only with much stronger bases than those discussed here. [d] *N*-Methyl-2-pyrrolidone. [e] HBD Acidity, α = 0.44.

Table 2. I.r. spectral data, ν_{NH}/cm^{-1}, of 4- and 2-substituted *N*-acetylaniline derivatives (7)—(11)



	R^1	R^2
(7)	H	H
(8)	H	COCH$_3$
(9)	H	CN
(10)	COCH$_3$	H
(11)	CN	H

Solvent	(7)	(8)	(9)	(10)	(11)
1′ CCl$_4$	3 445	*a*	*a*	3 258	3 421
2′ Cl$_3$CCH$_3$	3 439	3 432	3 432	3 257	3 418
3′ Cl$_2$C=CHCl	3 438	3 432	3 432	3 257	3 418
4′ ClCH$_2$CH$_2$Cl	3 420	3 416	3 411	3 252	3 406
1 AcOEt	3 370	3 357	3 354	3 257	3 338
2 ClCH$_2$CO$_2$Et	3 377	3 369	3 366	3 255	3 358
3 BL[b]	3 343	3 334	3 334	3 256	3 316
4 MeCOEt	3 357	3 351	3 344	3 257	3 333
5 CH$_3$CONMe$_2$	3 276	3 265	3 261	3 253	3 251
6 NMP[b]	3 273	3 261	3 257	3 252	3 247
a CHCl$_3$	3 439	3 433	3 433	3 254	3 420

[a] Too sparingly soluble for measurement. [b] See Table 1.

wavenumbers (lower energy), as is characteristic of correlation patterns involving hydrogen bonding between HBD indicators and HBA solvents.[16] (iv) The $\Delta\Delta\nu_{NH}$ values (vertical displacements from the correlation line in Figure 1) for the HBA solvents are in the HBA basicity order, *i.e.* NMP ~ DMAc > BL ~ MeCOEt ~ CH$_3$CO$_2$Et > ClCH$_2$CO$_2$Et.

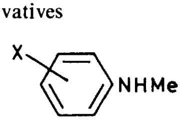
If ν_{NH}(**2**) were a 'family independent' property,[14] a logical next step would be to combine the data for the ten non-HB and HBA solvents in Table 1 to derive an equation for ν_{NH}(**2**) as a function of π^* and β by the stepwise or multiple linear regression version of the solvatochromic comparison method.[16] This would not be correct for a 'family dependent' property, however, as it would carry with it the implicit assumption that the solvent property measured by the co-ordinate covalency parameter, ζ, is the same for the chloro compounds (1′)—(4′) as for the C=O compounds, (1)—(6). We believe this property to be nil for the non-HBA solvents, but not for the doubly bonded oxygen bases, despite the fact that we have assigned to them a ζ value of 0.00. The latter value was not intended to suggest that co-ordinated covalency is nil for C=O bases, but rather that this family serves as the benchmark against which the co-ordinate covalency property is measured for the other families.

The contribution of co-ordinate covalency to ν_{NH}(**2**) in the C=O solvents is seen when we compare correlation of ν_{NH}(**2**) with π^* of the four non-HBA solvents [equation (2)] and with π^* and β of the six HBA solvents [equation (3)]. The 48 cm^{-1}

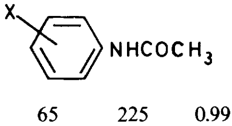
$$\nu_{NH}(\mathbf{2}) = 3\,465 - 31\pi^* \text{ (cm}^{-1}\text{) (in non-HB solvents)} \quad (2)$$
$$n = 4, r = 0.979, \text{s.d.} = 1.2$$

$$\nu_{NH}(\mathbf{2}) = 3\,513 - 27\pi^* - 207\beta \text{ (cm}^{-1}\text{)}$$
$$\text{(in doubly bonded oxygen base solvents)} \quad (3)$$
$$n = 6, r = 0.994, \text{s.d.} = 4.2$$

Table 3. Terms of the LSER equations, $\nu_{NH} = \nu_0 + s\pi^* + b\beta$, of 4- and 2-substituted aniline derivatives



X	ν_0	$-s$	$-b$	r	s.d.	χ[a]
4-CO$_2$Me	3 433	23	86	0.993	2.1	2.832
4-COCH$_3$	3 513	27	207	0.994	4.2	2.864
4-CN	3 509	37	194	0.999	1.1	3.208
4-NO$_2$	3 525	42	246	0.998	3.3	3.421
2-CN	3 484	27	160	0.996	2.7	



X	ν_0	$-s$	$-b$	r	s.d.	χ[a]
4-H	3 505	65	225	0.996	4.0	
4-COCH$_3$	3 496	55	238	0.994	5.1	
4-CN	3 488	43	248	0.995	4.7	
2-CN	3 474	44	242	0.998	3.8	

[a] Ref. 18.

difference in intercept between equations (3) and (2) is the contribution of the co-ordinate covalency property to ν_{NH}(**2**) in doubly bonded oxygen base solvents.

The spectral patterns for (**1**), (**3**), (**4**), (**6**), (**7**), (**8**), (**9**), and (**11**) are quite similar to that of (**2**) in the solvents studied, but this is not the case for the 2-acetyl derivatives (**5**) and (**10**). For the latter indicators, it is seen in Tables 1 and 2 that the ν_{NH} values cover a rather narrow range and are not significantly different in non-HB and HBA solvents. This is almost certainly because these indicators use their single hydrogen atoms to form strong intramolecular hydrogen bonds, which are not disrupted even in strong HBA base solvents. A minor response to solvent HBA basicity in the u.v.–visible spectrum of (**5**) (Table 4) is consonant with this conclusion.

The ν_0, s, and b values in equation (1) for the other indicators are assembled in Table 3, together with the r and s.d. measures of statistical goodness of fit. The results indicate the following. (i) When the correlations are confined to doubly bonded oxygen bases, the multiple regressions with π^* and β are of excellent statistical quality. (ii) Unlike the 2-acetyl derivatives, the 2-cyano compounds show significant response to solvent HBA basicity (Table 3). This indicates that intramolecular hydrogen bonding by an aromatic amine to an *ortho*-cyano group, if it occurs at all, must be quite weak. Again this is confirmed by the b values in the u.v.–visible spectral correlations (Table 4). (iii) Apart from their effects on the hydrogen-bonding interaction, substituent effects on ν_{NH} in the non-HB solvent (1′)—(4′) are quite small for all 4-substituted compounds except the 4-CO$_2$Me derivative (**1**). Thus, for (**2**)—(**4**) ν_{NH} values in CCl$_4$ range from 3 453 to 3 457 cm^{-1}, as compared with 3 409 cm^{-1} for (**1**). (This will be seen later to be quite important, as it suggests that the force constant for the N–H stretch becomes larger as hybridization on amine nitrogen changes from sp^3 to sp^2.) (iv) The order of response to solvent HBA basicity follows solute HBD acidity, *i.e.* the b values increase in the order CO$_2$Me < COCH$_3$ < CN < NO$_2$, which corresponds to the σ_p^- or σ^- order of electron-withdrawing ability (as distinct from σ_R or σ_R^-, where COCH$_3$ > NO$_2$). (v) Consonant with (iv), the b values for the stronger HBD *N*-acetyl derivatives are greater than those for the corresponding *N*-methyl derivatives. (vi) Most interestingly, it is seen in Table 3 that, as compared with the b values for the other *para*-substituted compounds, the response of the 4-CO$_2$Me derivative (**1**) to solvent HBA basicity

Table 4. Terms of the LSER equations, $\nu_{max.} = s\pi^* + b\beta$, of 4- and 2-substituted aniline derivatives

X	$-s$	$-b$	r	X	$-s$	$-b$	r
4-CO_2Et[b]	1.64	1.51	0.991	4-CO_2Et[a]	1.30	3.01	0.996
4-$COCH_3$[c]	1.66	0.79	0.998	4-COPh[a]	1.74	2.21	0.995
4-CN[b]	1.58	0.66	0.989	4-CN[b]	1.54	1.39	0.983
4-NO_2[b,c]	3.22	1.35	0.999	4-NO_2[a]	3.14	2.79	
2-CO_2Me[b]	0.31	0.03	0.980	2-CO_2Me[b]	0.30	0.70	0.981
2-$COCH_3$[c]	0.37	0.03	0.980	2-$COCH_3$[b]	0.42	0.64	0.991
2-CN[b]	0.73	0.58	0.985	2-CN[b]	0.65	0.65[d]	0.992
2-NO_2[b]	1.61	0.12	0.994	2-NO_2[b]	1.54	1.20	0.997

[a] Ref. 16. [b] Ref. 11. [c] Present study. [d] Since 2-cyanoaniline forms two hydrogen bonds to HBA solvents, the value given is for $b/2$.

Table 5. U.v.–visible spectral data, $10^3\ \nu_{max.}/cm^{-1}$, of 4- (**2**) and 2-acetyl-*N*-methylaniline (**5**)

Solvent	(**2**)	(**5**)	π^*	β
1′ C_6H_{12}	33.04	26.62	0.00	0.00
2′ n-C_6H_{14}	33.26	26.68	−0.08	0.00
3′ Cl_3CCH_3	32.26	26.47	0.49	0.00
4′ $ClCH_2CH_2Cl$	31.77	26.34	0.81	0.00
1 AcOEt	31.89	26.45	0.55	0.45
2 BL[a]	31.28	26.35	0.87	0.49
3 THF	31.76	26.47	0.58	0.55
4 Bu_2O	32.31	26.56	0.24	0.46
5 $HCONMe_2$	31.04	26.35	0.88	0.69
6 NMP[a]	30.97	26.32	0.92	0.77
7 $(CH_3)_2SO$	30.79	26.26	1.00	0.76

[a] See Table 1.

is much smaller than would be predicted from any single or multiple parameter correlation with any of the various sigma constants. This is most interesting because (**1**) was also out-of-line in (iii), and in the u.v.–visible spectral correlations mentioned at the beginning and discussed further later. (vii) A trend of s values for 4-substituted *N*-methylanilines with dipole moments or substituent electronegativities is evident in Table 3, but the range of the responses to solvent π^* values (42—49 = 23) is too small to merit detailed analysis.

Comparison with U.v.–visible Spectral Correlations.—To understand better the intricacies of solvent effects on $\nu_{NH}(\mathbf{1})$, it is useful to consider again the effects of solvent dipolarity–polarizability and HBA basicity on the u.v.–visible spectra of 2- and 4-acetyl-*N*-methylanilines [(**2**) and (**5**)]. Data from the present study are combined with earlier findings in Table 4. The experimental $\nu_{max.}$ data for (**2**) and (**5**) are in Table 5; the solvatochromic equations (excluding the data for $CHCl_3$) are given by equations (4) and (5).

$$\nu(\mathbf{2})_{max.} = 33.10 - 1.66\pi^* - 0.79\beta \times 10^3\ (cm^{-1}) \quad (4)$$
$$n = 11,\ r = 0.998,\ s.d. = 0.05 \times 10^3$$

$$\nu(\mathbf{5})_{max.} = 26.65 - 0.37\pi^* + 0.03\beta \times 10^3\ (cm^{-1}) \quad (5)$$
$$n = 11,\ r = 0.980,\ s.d. = 0.03 \times 10^3$$

Considering first the correlation equation for the 2-X-*N*-methylaniline derivatives in Table 4, it is seen that the b values are negligible for 2-CO_2Me, 2-$COCH_3$, and 2-NO_2, but not for 2-CN. This indicates that the single hydrogen bonds of the first three compounds are intramolecular, but that for the fourth is intermolecular. Going next to the 2-X-aniline derivatives, it is seen that b values for 2-CO_2Me and $COCH_3$ and the $b/2$ value for CN are quite similar to one another and lower than b for 2-NO_2; these results are roughly consonant with the acidity order. This is because all four 2-X-$C_6H_4NH_2$ compounds are near sp^2-hybridized on nitrogen in all solvents. The intramolecular hydrogen bonding favours sp^2 over sp^3 hybridization as shown in the one-bond N–H coupling, $^1J(^{15}NH)$, obtained by Axenrod and his co-workers;[17] $^1J(^{15}NH)$ values for 4-nitroaniline are 86.4 Hz in $CDCl_3$ (non-HBA) and 89.4 Hz in $(CD_3)_2SO$ (HBA), while those for 2-nitroaniline are 90.3 and 91.0 Hz, respectively. It is known that $^1J(^{15}NH)$ values are well correlated with s character of nitrogen, and the foregoing values indicate that an intramolecular hydrogen bond favours sp^2 over sp^3 hybridization. Further, $^1J(^{15}NH)$ values of 88.1 and 89.3 Hz in $CDCl_3$ and $(CD_3)_2SO$ for 2-benzoylaniline[17b] show favoured sp^2 over sp^3 also in 2-COR-substituted anilines.

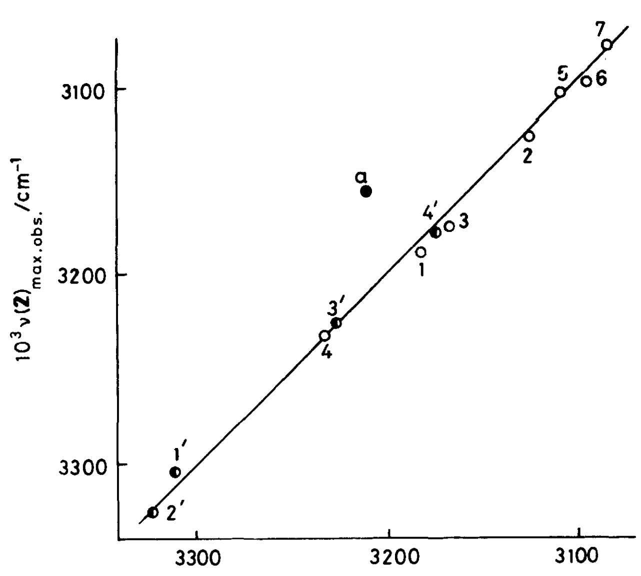
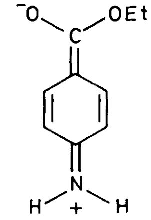


Figure 2. Plot of experimental $\nu(\mathbf{2})_{max.}$ values against values calculated through equation (4)

The situation is quite different for the 4-X-aniline and 4-X-*N*-methylaniline derivatives of Table 4, where the order of b values is 4-CO_2Et > 4-NO_2 > 4-COR > 4-CN. That the 4-ethoxycarbonyl compounds show higher responses of $\nu_{max.}$ to solvent HBA basicity than the more acidic 4-nitro compounds has been rationalized on the basis that the former are near sp^3-hybridized on amine nitrogen in non-HB solvents* and nearer sp^2-hybridized in HBA solvents, whereas the latter are near sp^2-hybridized in all solvents. Rehybridization from sp^3 to sp^2 should be strongly bathochromic, as it increases the contribution of canonical structure (**12**) to the electronic excited



(**12**)

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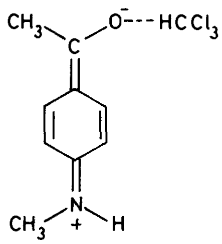
* $^1J(^{15}NH)$ for 4-CO_2Et can be calculated to be 82.6 Hz in $CDCl_3$ from the correlation of $^1J(^{15}NH)$ with σ_p^-.

state. Thus the *b* values for the 4-NO_2 derivatives reflect only the effects of hydrogen bonding, whereas the *b* values for the 4-CO_2Et derivatives reflect the combined effects of hydrogen bonding and rehybridization and are correspondingly higher.

With the foregoing as background, we can now explain why the *b* coefficient in the solvatochromic equation for ν_{NH} of 4-MeO_2C-C_6H_4-NHMe (**1**) is so much lower than the corresponding coefficients for (**2**)—(**4**). (*a*) From the u.v.–visible correlations we infer that hybridization on the amine nitrogen of (**1**) goes from nearer sp^3 to nearer sp^2 as HBA basicity of the solvent increases. (*b*) From the ν_{NH} values in the non-HB solvents [(iv) above] we infer that the force constants for the stretch frequencies are larger (higher ν_{NH}) for sp^2- as compared with sp^3-hybridized amines. (*c*) Hydrogen bonding to HBA bases leads to lower ν_{NH} values. (*d*) The same molecular effects, rehybridization and hydrogen bonding, influence the u.v.–visible and i.r. solvent shifts. (*e*) Hence, unlike the u.v.–visible spectra, where rehybridization and hydrogen bonding shift $\nu(\mathbf{1})_{max.}$ in the same direction, the effects on i.r. maxima are in opposite directions; hydrogen bonding shifts $\nu_{NH}(\mathbf{1})$ to lower wavenumbers, rehybridization to higher wavenumbers. The consequence is that the *b* value for (**1**) is lower than it would have been in the absence of rehybridization.

Effect of HBD *Solvent on U.v.–Visible Spectrum of* (**2**).—A plot of $\nu(\mathbf{2})_{max.}$ against values calculated through equation (4) is shown in Figure 2, where it is seen that, unlike the effect on the i.r. spectrum, hydrogen bonding by $CHCl_3$ to the C=O group of (**2**) leads to a significant bathochromic shift. This is because here the hydrogen bonding is to an atom at the chromophore terminus, where it leads to important stabilization of the electronic excited state (**13**). To incorporate this effect in the total solvatochromic equation would require that we add a term in *a*α to equation (4).



(**13**)

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