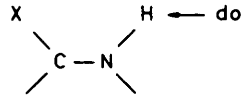
Solvent Effects on the Infrared Spectra of Nitro-*N*-methylanilines: Intra- and Inter-molecular Interactions and Molecular Configurations

Guillermo González* and Ernesto Clavijo
Department of Chemistry, Faculty of Sciences, University of Chile, Casilla 653, Santiago, Chile

The influence of various common basic solvents on the i.r. spectra of *N*-methylaniline and its *ortho*- and *para*-nitro derivatives has been studied. The behaviour of the frequency ν(N–H) depends on the donor strength of the medium. In high donor-strength media, the frequency shifts show a near linear dependence on solvent basicity; in low donor-strength media (as well as for systems exhibiting intramolecular bonding) ν(N–H) is practically constant. These results can be rationalized by considering the stabilization of species with two different configurations, the degree of planarity of which is enhanced by the donor strength of the medium.

Compounds with acidic N–H protons interact with basic solvents by formation of hydrogen bonds [see (1)]. For amide



(1)

and thioamide derivatives (X = O or S),[1–5] the strength of the solute–solvent interactions (depending mainly on the basicity of the solvent but also on its acceptor properties) can be estimated from the effect of the interactions on the N–H bond[1–5] or from their propagation along the C–N and C–X bonds.[2,3] The strength of the amide linkages and the configuration of the compounds are thus strongly affected by the nature of the solvent. Steric hindrance is usually not very important, and the possibility of intramolecular hydrogen bonding is almost non-existent. However, if X is a substituent able to interact with the N–H proton, such as a nitro group, competition between X and the solvent for the formation of the hydrogen bond should occur. Particularly appropriate for studying such processes are the *ortho*-nitroanilines. Although several studies on this topic with different nitroanilines have been reported,[6–12] the influence of the solvent on the equilibrium between intra- and inter-molecular hydrogen-bonded species has not been clearly described. In order to contribute to the knowledge of this kind of interaction, we have reinvestigated the influence of the basicity of the medium on the behaviour of *ortho*-nitro-*N*-methylaniline by observing the effect of a number of basic solvents on the frequency ν(N–H), and by comparing the frequency shifts with those observed for *para*-nitro-*N*-methylaniline and other *N*-methylaniline derivatives.

Experimental

Solvents were purified by standard techniques[13] and stored in dark bottles over molecular sieves. Solvent purity was checked by i.r. spectroscopy. *N*-Methylaniline was purified by fractional distillation from sodium pellets. *ortho*- and *para*-nitro-*N*-methylanilines were synthesized by treating the *N*-tosyl derivatives of the primary nitroanilines with dimethyl sulphate, followed by treatment of the tosyl-*N*-methyl derivatives with a mixture of sulphuric and acetic acids (2:1).[7,14]

The fundamental N–H stretching frequencies were measured with a Perkin-Elmer 621 spectrophotometer, using liquid cells with sodium chloride windows (thickness 0.5 mm). An equivalent cell with the pure solvent was used in the compensating beam. The concentrations of the amine solutions usually were in the range 0.02—0.002M. Between these limits, the N–H frequencies showed no concentration dependence. In general, the frequencies reported in this work are accurate to ±1 cm^{-1}.

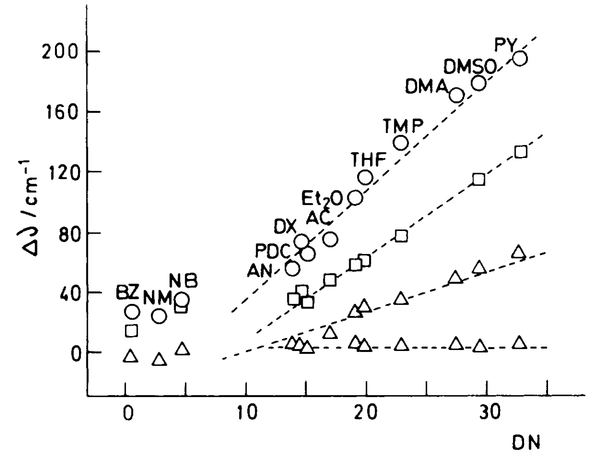


Figure 1. Influence of the medium donor strength on the N–H frequency shifts, Δν(CCl$_4$), for *ortho*-nitro-*N*-methylaniline (△), *para*-nitro-*N*-methylaniline (○), and *N*-methylaniline (□).

Results

The N–H fundamental frequencies [ν(N–H)] for *N*-methylaniline and its *ortho*- and *para*-nitro derivatives measured in different solvents at room temperature are reported in Table 1. In general, the solvent shift Δν(N–H) (measured with respect to CCl$_4$) increases with increasing basicity of the solvent. The dependence of Δν on the solvent donor strength (expressed as the Donor Number, DN[15]) is shown in Figure 1. The frequency values as well as the shifts Δν are in general in good agreement with those reported by Dyall and Kemp.[7] The dependence of the N–H frequencies on the aniline concentration in the concentration range used was negligible, and the deviations were within experimental error in the determination of the band maxima.

Unlike the behaviour of *N*-methylaniline and its *para*-nitro derivative, for which a single and relatively sharp N–H band is always observed, the spectra of *ortho*-nitro-*N*-methylaniline in the more basic solvents show a splitting of the N–H absorption

Table 1. Solvent effects on the N–H stretching frequency in *N*-methylaniline and its nitro derivatives

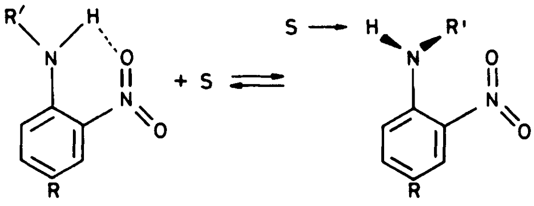
		N-Methylaniline		*para*-Nitro-*N*-methylaniline		*ortho*-Nitro-*N*-methylaniline	
Solvent	DN[a]	ν(N–H)	$\Delta\nu$(CCl$_4$)	ν(N–H)	$\Delta\nu$(CCl$_4$)	ν(N–H)	$\Delta\nu$(CCl$_4$)
Carbon tetrachloride (CCl$_4$)		3 457	0	3 464	0	3 410	0
Benzene (BZ)	0.1	3 445	12	3 435	29	3 411	−1
Nitromethane (NM)	2.7			3 437	27	3 412	−2
Nitrobenzene (NB)	4.4	3 428	29	3 427	37	3 409	1
Acetonitrile (AN)	14.1	3 420	37	3 409	55	3 404	6
Dioxane (DX)	14.8	3 417	40	3 390	74	3 405	5
Propane-1,2-diol carbonate (PDC)	15.1	3 425	32	3 400	64	3 409	1
Acetone (AC)	17.0	3 409	48	3 390	74	3 399	11
Diethyl ether (Et$_2$O)	19.2	3 399	58	3 363	101	3 405	5
						3 384	26
Tetrahydrofuran (THF)	20.0	3 396	61	3 348	116	3 408	2
						3 380	30
Trimethyl phosphate (TMP)	23.0	3 380	77	3 325	139	3 408	2
						3 375	35
N,N-Dimethylacetamide (DMA)	27.8			3 295	169	3 406	4
						3 360	50
Dimethyl sulphoxide (DMSO)	29.8	3 342	115	3 286	178	3 407	3
						3 355	55
Pyridine (PY)	33.0	3 326	131	3 270	194	3 405	5
						3 345	65

[a] Solvent donor numbers from ref. 16.

into two bands with different sensitivities to solvent. The band at higher frequency remains practically unaltered, while the lower one shifts to lower frequencies with increasing solvent donor strength. Although the relative intensities of the two bands depend on the donor strength of the medium, the overlap of the bands prevents any quantitative determination of this effect.

Discussion

Solute–solvent interactions for *ortho*-nitroanilines and *ortho*-nitrophenols in basic solvents are determined by both the ability of the aniline to form intramolecular hydrogen bonds and the donor strength of the solvent (Scheme 1). Thus, in *ortho*-nitro-*para*-*N*-methyltoluidine the intramolecular interaction is very strong and the equilibrium in Scheme 1 is displaced to the left in all common basic solvents.[12] For *ortho*-nitrophenol, on the other hand, intermolecular solute–solvent interactions[12] predominate. Nevertheless, the i.r. spectra of *ortho*-nitro-*N*-methylaniline in the more basic solvents, with two bands in the N–H stretching region, indicate the occurrence of such an equilibrium regulated by the donor strength of the solvent. As can be observed in Figure 1, at low donor strength the formation of intramolecular hydrogen bonds prevails, so that only one band, not dependent on DN, is observed. In strong donor solvents, a second band appears which shows a dependence on solvent basicity characteristic of intermolecular hydrogen bonds. The solvation pattern observed in Figure 1 thus agrees with the behaviour expected for *ortho*-derivatives able to undergo intramolecular interactions; however, the comparison of the solvation pattern of *ortho*-nitro-*N*-methylaniline with those of *para*-nitro-*N*-methylaniline and *N*-methylaniline points to a more complicated phenomenon. Since the solvation patterns for the three anilines observed in Figure 1 are qualitatively the same, the clearly different behaviour observed for the stretching frequency of the N–H bond at high and low solvent donor strengths could be interpreted, at least to a first approximation, as resulting from an equilibrium between two molecular configurations of the solute governed by the co-ordinative properties of the medium. In solvents with low donor strength, species with a configuration (which we will call configuration I) having a relatively low tendency to interact with the solvent would predominate. In a high donor-strength medium, on the other hand, the species would have a configuration more sensitive to the solvent, configuration II. Although those two configurations, I and II, are clearly distinguishable by their solvation patterns (Figure 1), nothing can be said at this point about their molecular structures. As an approximation for understanding the nature of configurations I and II, the following analysis of the features in the solvation of these and other species may be attempted.



Scheme 1.

The nearly linear dependence of $\Delta\nu$ on DN in the more basic solvents, which can be described to a good approximation by the relationship (1), permits us to evaluate the hypothetical

$$\Delta\nu = a_0 + a_1\mathrm{DN} \qquad (1)$$

N–H frequency of a particular aniline, with configuration II, in an inert medium (DN = 0), thus allowing us to compare the vibrational characteristics of the N–H bonds corresponding to the two configurations under the same conditions. In order to study the dependence of the configuration on the nature of the substituents, we have also analysed the data reported by Dyall

Table 2. Substituent effects on the solvation of some *N*-methylanilines; ν(N–H) in an inert medium and regression parameters from their behaviour in high donor-strength media

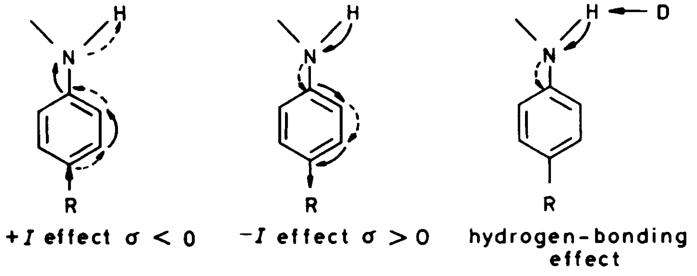
		ν(N–H) in inert medium[a]		Regression parameters for Δν *vs.* DN[e] in high donor-strength media		
Aniline substituent	$\sigma_p{}^b$	$\nu_{01}{}^c$	$\nu_{01}'{}^d$	a_0	a_1	r
H	0.00	3 457	3 504	−46.8	5.42	0.998
ortho-NO_2	0.71	3 410	3 438	−26.8	2.76	0.997
para-NO_2	0.71	3 461	3 500	−38.8	7.30	0.988
ortho-Br	0.86	3 433	3 475	−42.4	4.68	0.998
para-Br	0.86	3 444	3 492	−47.6	5.91	0.999
ortho-Me	−0.14	3 453	3 502	−50.2	4.74	0.997
ortho-Br, *para*-NO_2	0.97	3 432	3 471	−39.0	5.88	0.983
ortho-NO_2, *para*-NO_2	1.42	3 384	3 438	−53.7	7.02	0.996
ortho-MeO, *para*-NO_2	0.59	3 455	3 494	−39.0	5.88	0.983

[a] From frequency values reported in this work and in ref. 7. [b] Hammett constants from ref. 17. [c] Frequency values in CCl_4. [d] Frequency values estimated at DN = 0 from aniline behaviour in high donor-strength media. [e] In solvents with DN > 17 for *ortho*-nitro derivatives and DN > 14.1 for the other compounds.

and Kemp[7] for other *N*-methylanilines, which present solvation patterns similar to those shown in Figure 1.

Besides the N–H frequencies for the anilines in CCl_4, ν_{01}, Table 2 also shows statistical data associated with the behaviour of Δν(N–H) at high donor strength, and the derived hypothetical values of the frequencies at null donor strength, ν_{01}'.

As an approach to understanding the nature of configurations I and II we have analysed the influence of the substituents on the N–H frequencies as well as on the solvent shifts by using the Hammett substituent constants σ_p.[17] However, this analysis is not simple, becuase of the dependence of the frequencies on a number of factors: (i) electron-attracting substituents ($-I$ effects) will produce a decrease in ν(N–H); (ii) intra- or inter-molecular interactions of the N–H protons with donors shift the N–H absorption to lower frequencies; and (iii) the *s* character of the nitrogen hybrid orbitals in the N–H bond increases with increasing degree of coplanarity in the system, shifting ν(N–H) to higher values. Moreover, these effects are always interrelated; thus, according to the bond-length variation rules,[16] $-I$ effects and the formation of hydrogen bonds both induce an increase in the degree of planarity in the molecule, but produce opposite effects on ν(N–H) (Scheme 2). In view of the complexity of such a system, it is not surprising that no correlation between ν_{01}(N–H) or ν_{01}'(N–H) and the inductive characteristics of the substituent can be found. Nonetheless, the parameters a_1 and a_0, related to the influence of the solvent on the frequency shifts, show some interesting trends connected with the nature of the substituents.



Scheme 2.

The parameter a_1 corresponds to the susceptibility of the N–H protons of the anilines with the configuration II to form hydrogen bonds with the solvent. As shown in Figure 2, such 'acidity' of the N–H protons increases with increasing σ value, as can be predicted from the charge displacements indicated by the arrows in Scheme 2. This relationship does not follow for derivatives with *ortho*-substituents such as Br and NO_2, able to form hydrogen bonds. The influence of intramolecular interactions on solvent shifts in these compounds was not observed by Dyall and Kemp because of the solvent effects on the configuration of the *N*-methylaniline used as reference in the Bellamy plots by which the analysis was made.[7] The same problem could appear, to a greater or lesser extent, if the reference of the solvent donor-strength scale used for analysing the observed solvent shifts behaved in a way similar to that of the substrate (for instance on the scale proposed by Kamlet and Taft[9] using phenol and aniline derivatives as reference).

The parameter a_0, the intercept in the plot of Δν *vs.* DN, corresponds to the difference between ν_{01} and ν_{01}' at DN = 0, *i.e.* to the difference in strengths of the N–H bonds for the two configurations. The variation of a_0 with the σ values of the substituents is shown in Figure 3. A clear tendency for a_0 to grow with increasing $-I$ effects (σ < 0) of the substituents is observed in spite of the relatively high dispersion in the plot. The straight line in Figure 3 (being drawn in the light of the additional effects expected for *ortho*-NO_2 derivatives because of potential intermolecular hydrogen bonding) should be seen only as a guide for observing the aforementioned tendency. If we consider that, as already stated, an increase in the $-I$ effect would favour a planar system, the pattern observed in Figure 3 should indicate that the difference between the configurations I

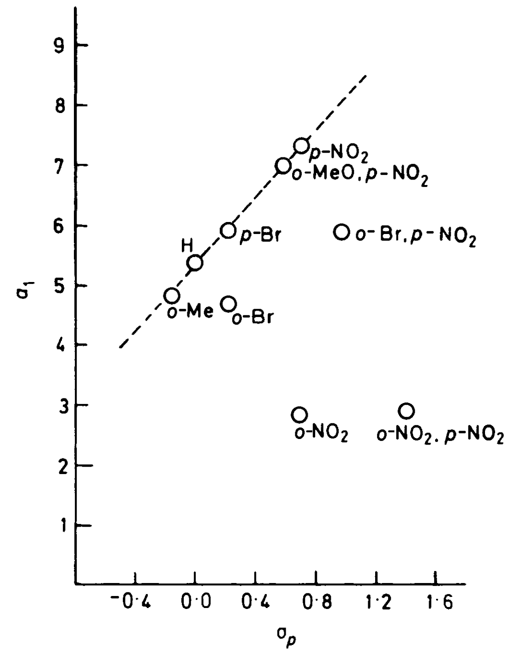


Figure 2. Influence of the substituent on the sensitivity to solvent of the different *N*-methylanilines [a_1 from relationship $\Delta\nu(CCl_4) = a_0 + a_1DN$ obtained in strong donor media]

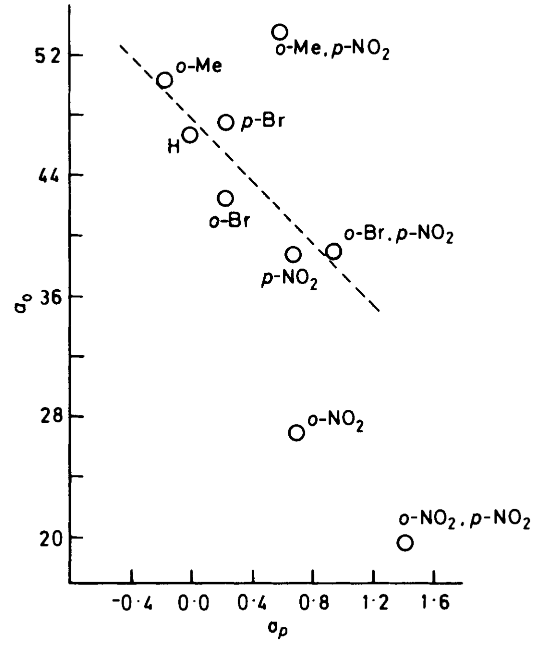


Figure 3. Substituent effect on the intercept a_0 from the relationship $\Delta\nu(CCl_4) = a_0 + a_1DN$ obtained for various anilines in strong donor media (*i.e.* influence of the aniline substituent on the difference between the high and low donor-strength medium configurations)

and II is minimal when both correspond to nearly planar structures. On the other hand, the fact that the species with the high donor-strength configuration II always presents N–H frequencies (ν_{01}') higher than the corresponding species with the low donor-strength configuration (I) should indicate a higher degree of planarity for configuration II than for I. Thus, from this analysis it could be concluded that for anilines interactions *via* N–H hydrogen bonding with the medium in general induce a greater planarity of the molecule. However, this analysis is valid probably only for *para-* and *ortho-*derivatives which do not form intramolecular hydrogen bonds. For the *ortho*-nitro and to some extent also for the *ortho*-bromo derivative, the frequencies measured (ν_{01}) as well as those estimated (ν_{01}') for an inert medium certainly do not depend only on the inductive effects of the substituents; they also depend on the strength of the intramolecular hydrogen bond. Since the formation of an intramolecular hydrogen bond also affects the planarity of the system, opposite effects on the N–H frequency [ν(N–H) would decrease with hydrogen bonding and increase with increasing molecular planarity] should be observed. The occurrence of such intramolecular interactions in both kinds of configuration (I and II) could explain the relatively low susceptibility to the solvent (low a_1 values in Figure 2) as well as the greater similarity (low a_0 values in Figure 3) of the two configurations in an inert medium. Consequently, the perhaps simplistic interpretation of the behaviour of *ortho*-nitro-*N*-methylaniline (Figure 1) on the basis of only intra- or inter-molecular interactions in low and high donor-strength medium, respectively, should be improved by taking into account the possibility that intramolecular interactions can also contribute to the configurational behaviour in media of high donor strength.

Acknowledgements

This work was partially supported by the 'Departamento de Investigación y Bibliotecas' of the University. We thank Mrs. M. A. Santa Ana and Mrs. I. Chadwick for discussions.

References

1 G. González and J. Granifo, *Inorg. Chim. Acta*, 1979, **35**, 209.
2 J. Manzur and G. González, *Z. Naturforsch., Teil B*, 1981, **36**, 763.
3 G. González and I. Chávez, *J. Chem. Soc., Faraday Trans. 2*, 1981, **77**, 2231.
4 G. González, B. Bogdanov, N. Yutronic, and J. Manzur, *Spectrochim. Acta, Part A*, 1982, **38**, 591.
5 G. González and N. Yutronic, *Spectrochim. Acta, Part A*, 1983, **39**, 269.
6 L. K. Dyall, *Spectrochim. Acta*, 1961, **17**, 291.
7 L. K. Dyall and J. E. Kemp, *Spectrochim. Acta*, 1966, **22**, 467.
8 S. Millefiori, G. Favini, A. Millefiori, and D. Grasso, *Spectrochim. Acta, Part A*, 1977, **33**, 21.
9 M. J. Kamlet and R. W. Taft, *J. Am. Chem. Soc.*, 1976, **98**, 377.
10 T. Yokoyama, R. W. Taft, and M. J. Kamlet, *J. Am. Chem. Soc.*, 1976, **98**, 3233.
11 M. E. Jones, R. W. Taft, and M. J. Kamlet, *J. Am. Chem. Soc.*, 1977, **99**, 8452.
12 M. J. Kamlet and R. W. Taft, *J. Org. Chem.*, 1982, **47**, 1734.
13 J. Riddick and W. B. Bunger, 'Techniques of Chemistry,' ed. A. Weissberger, Wiley-Interscience, New York, 1970, vol. II.
14 E. H. Usherwood and N. H. Whitely, *J. Chem. Soc.*, 1963, 1069.
15 V. Gutmann and E. Wychera, *Inorg. Nucl. Chem. Lett.*, 1966, **2**, 257.
16 V. Gutmann, 'The Donor-Acceptor Approach to Molecular Interactions,' Plenum Press, New York, 1978.
17 O. Exner, 'Correlation Analysis in Chemistry; Recent Advances,' ed. N. B. Chapman and J. Shorter, Plenum Press, New York and London, 1978.

Received 5th February 1985; *Paper* 5/205