SOLVENT EFFECTS ON THE INFRARED SPECTRA OF ANILINES

IV.* SECONDARY AROMATIC AMINES AND AMIDES WITH TRIFLUOROMETHYL OR PHENYL AS *ORTHO* SUBSTITUENTS

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Summary

The N–H stretching frequencies of five *N*-substituted anilines with trifluoromethyl or phenyl as *ortho* substituent have been measured in a variety of solvents. Elevation of ν(NH) by steric compression is observed. The frequency shifts observed for *N*-methyl-2-phenylaniline fit none of the three classes of solvent shift behaviour recognized for other *ortho*-substituted secondary amines. The results confirm that solvent shifts of ν(NH) cannot be used to distinguish between the steric and hydrogen bonding properties of the *ortho* substituent.

INTRODUCTION

In our previous study of solvent effects on the N–H stretching frequencies of *ortho*-substituted secondary amines,[1] it was observed that only the more basic solvents shifted ν(NH) when the *ortho* group was nitro, whereas all solvents shifted ν(NH) when the *ortho* group was methyl, bromo, or methoxy. The effect of the nitro group might arise because only the more basic solvents are capable of breaking the intramolecular hydrogen bond and thus shift ν(NH) to lower frequencies through formation of a stronger hydrogen bond between solute and solvent.

While this factor is undoubtedly important, it was also concluded that one of the lone pair orbitals on nitro oxygen plays a steric role, by preventing approach of solvent molecules seeking to present a lone pair or π-type orbital to the N–H bond. On this basis, a solvent molecule must rotate the N–H group away from the *ortho*-nitro substituent if solute–solvent association is to occur, and the aminoaromatic system will thereby lose some delocalization energy. Rotation of the amino group through 180°, which would preserve conjugation and give ready access of a solvent molecule to the N–H bond, is not possible since the *N*-substituent and the *ortho* substituent would have to overlap to an intolerable degree.

The partial rotation of the amino group required for amino group–solvent association not only causes a loss of delocalization energy, but also weakens the intramolecular hydrogen bond. These two energy losses must be offset by the energy of the new intermolecular hydrogen bond if solute–solvent association is to reach a detectable level.

* Part III, *Spectrochim. Acta*, 1966, **22**, 483.

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[1] Dyall, L. K., and Kemp, J. E., *Spectrochim. Acta*, 1966, **22**, 467.

To test the validity of these explanations, studies have now been made with trifluoromethyl and phenyl as the *ortho* substituent in secondary aromatic amines. The trifluoromethyl group does not form significant hydrogen bonds with an amino group,[2] but the lone pair orbitals on fluorine could be large enough to prevent approach of the less basic solvents to the adjacent N–H bond. The phenyl group does form a weak intramolecular hydrogen bond (see Discussion), and should also offer considerable steric hindrance to the approach of solvent molecules to the N–H bond.

In order to verify the pattern of behaviour we have already observed[3] for acetanilides, the *N*-acetyl derivatives of 2-trifluoromethylaniline and 2-aminodiphenyl have been included in the present study of solvent effects.

Experimental

All melting points are corrected. Microanalyses were carried out by the Australian Microanalytical Service, Melbourne.

Purification of Solvents

Benzonitrile was shaken with sodium carbonate and then water, and was dried over calcium chloride. The middle fraction from a distillation under reduced pressure was dried over Linde type 4A molecular sieves. Dioxan was purified by acid hydrolysis to destroy acetals, followed by drying over sodium.[4] The other solvents were purified by the methods described in previous papers.[1,3] The purity of each solvent was checked by refractive index measurement.

Preparation of Amines

(i) N-*Methyl-2-trifluoromethylaniline.*—2-Trifluoromethylaniline was treated with *p*-toluenesulphonyl chloride in pyridine solution to obtain the N-*tosyl derivative* (colorless needles from aqueous ethanol), m.p. 102·5–103·0°. This sulphonamide (13·0 g) was suspended in 10% aqueous sodium hydroxide (100 ml), and dimethyl sulphate (30 ml) was added, with stirring, during 2 hr. Stirring was continued for another hour before collecting N-*methyl*-N-*tosyl-2-trifluoromethylaniline*, which crystallized from methanol or ethanol as fluffy needles, m.p. 123–124°. Yield, 12·1 g (89%) (Found: C, 55·2; H, 4·5. $C_{15}H_{14}F_3NO_2S$ requires C, 54·7; H, 4·3%).

The following hydrolysis procedure was the most satisfactory of the numerous methods tried. The sulphonamide (8·0 g) was heated 1 hr on a steam-bath with concentrated sulphuric acid (60 ml) and water (20 ml). The solution was basified with solid sodium carbonate, and chloroform extraction recovered N-*methyl-2-trifluoromethylaniline* as a colourless oil, b.p. 177° (corr.), n_D^{20} 1·4869. Yield, 1·79 g (42%) (Found: C, 55·3; H, 4·65. $C_8H_8F_3N$ requires C, 54·9; H, 4·6%).

The amine in carbon tetrachloride solution had a single sharp ν(NH) band at 3489 cm^{-1} and an *N*-methyl band at 2828 cm^{-1} in the infrared spectrum. The structure was further confirmed by the n.m.r. spectrum (deuterochloroform solution), which had the expected singlet at 7·13 τ (2·94 protons), a broadened singlet at 5·80 τ (1·04 protons), and a complex multiplet between 2·4 and 3·5 τ (4·02 protons).

As expected, this sterically hindered amine failed to react with either acetyl chloride or *p*-toluenesulphonyl chloride in pyridine solution.

(ii) N-*Phenyl-2-trifluoromethylaniline.*—2-Trifluoromethylacetanilide (10·9 g), anhydrous potassium carbonate (8·1 g), bromobenzene (17·0 g), and freshly prepared cuprous bromide

[2] Hambly, A. N., and O'Grady, B. V., *Aust. J. Chem.*, 1962, **15**, 626.
[3] Dyall, L. K., and Kemp, J. E., *Spectrochim. Acta*, 1966, **22**, 483.
[4] Vogel, A. I., "A Text-book of Practical Organic Chemistry." p. 175. (Longmans: London 1951.)

(0·5 g) were heated 30 hr under reflux in dry nitrobenzene (50 ml). The nitrobenzene was removed by steam distillation, and ether extraction of the residue afforded a viscous tar (9·7 g). Distillation gave an oil (7·3 g), b.p. 180°/10 mm, with an amide carbonyl band at 1695 cm^{-1}. This amide was unaffected by heating 3 hr under reflux with a 1 : 1 mixture of ethanol and hydrochloric acid. Hydrolysis of the amide (7·2 g) by heating 2 hr under reflux with 10% ethanolic potassium hydroxide yielded an oil (6·0 g) which on distillation gave a head fraction (2·0 g), b.p. 112–116°/2 mm. This fraction had no carbonyl band in the infrared spectrum but did have a ν(NH) band at 3460 cm^{-1} in carbon tetrachloride solution. Higher-boiling fractions contained unchanged amide. The low-boiling fraction was redistilled to obtain *N-phenyl-2-trifluoromethylaniline*, b.p. 116°/0·7 mm, n_D^{20} 1·5656 (Found: C, 66·1; H, 4·3. $C_{13}H_{10}F_3N$ requires C, 65·8; H, 4·2%).

TABLE 1

SOLVENT DEPENDENCE OF N–H STRETCHING FREQUENCIES (cm^{-1}) OF ACETANILIDES

Acetanilide			2-Trifluoromethylacetanilide				2-Phenylacetanilide			
Solvent	ν(NH)	$\Delta\nu$	ν(NH)	$\Delta\nu$	ϵ_A	$\Delta\nu_{\frac{1}{2}}^{a}$	ν(NH)	$\Delta\nu$	ϵ_A	$\Delta\nu_{\frac{1}{2}}^{a}$
CCl_4	3445	0	3474	0	96	23	3430	0	192	12
	3398		3417sh		9		*c.* 3391sh		9	*c.* 26
PhCl	3425	20	3468	6	64	29	3424	6	126	21
	3387		*c.* 3434		19		3389		10	37
			3411sh		16					
PhH	3416	29	3470	4	61	27	3425	5	124	20
			3422sh		18		3403		17	
p-Xylene	3408	37	3475	−1	65	27	3428	2	122	17
			3422sh		17		3399	31	21	
$PhNO_2$	3394	51	3464sh	10	18		3420	10	85	
			3409	65	56		3386sh	44	64	
EtOAc	3370	75	3370	104	65	79	3365	65	67	63
PhCN	3422	23	3466		22		3424	6	44	20
	3361	84	3427		28		3354	76	76	66
			3360	114	69	78				
MeCN	3357	88	3351	123	76	95	3423sh	7	34	
							3352	78	79	74
Acetone	3356	89	3355	119	74		3423sh	7	*c.* 24	
	3290*						3352	78	75	88
Et_2O	3336	109	3477	−3	46	24	3431	−1	96	17
	3297*		3328	146	35		3325	105	35	
THF	3325	120	3474	0	16		3427	3	36	17
	3290*		3306	168	67		3310	120	60	—
			3282*		66		3293*		64	

* These bands are considered to be 2ν(C=O) borrowing intensity by Fermi resonance.

This hindered amine did not react with acetyl chloride in pyridine solution.

(iii) *N-Methyl-2-phenylaniline.*—*N*-Methyl-2-phenylacetanilide, m.p. 97–98° (lit. 98°), was obtained by methylation of the corresponding acetanilide.[5] This amide, which is known to be difficult to hydrolyse,[5] was unaffected by heating 10 hr under reflux with 10% ethanolic potassium hydroxide. Hydrolysis was achieved by heating 8 hr under reflux with 70% sulphuric acid. The *N*-methyl-2-phenylaniline obtained had b.p. 130°/1·5 mm (lit. 116°/2 mm). The infrared

[5] Popkin, A. H., Perretta, G. M., and Selig, R., *J. Am. chem. Soc.*, 1944, **66**, 833.

TABLE 2

SOLVENT DEPENDENCE OF N–H STRETCHING FREQUENCIES (cm^{-1}) OF *N*-METHYL- AND *N*-PHENYL-ANILINES

Solvent	*N*-Methylaniline*	*N*-Methyl-2-phenylaniline†						*N*-Methyl-2-trifluoromethylaniline‡						*N*-Phenyl-2-trifluoromethylaniline§					
	Solvated	Free			Solvated			Free			Solvated			Free			Solvated		
	$\Delta\nu$	$\Delta\nu$	ϵ_A	$\Delta\nu_{\frac{1}{2}}^a$	$\Delta\nu$	ϵ_A	$\Delta\nu_{\frac{1}{2}}^a$	$\Delta\nu$	ϵ_A	$\Delta\nu_{\frac{1}{2}}^a$	$\Delta\nu$	ϵ_A	$\Delta\nu_{\frac{1}{2}}^a$	$\Delta\nu$	ϵ_A	$\Delta\nu_{\frac{1}{2}}^a$	$\Delta\nu$	ϵ_A	$\Delta\nu_{\frac{1}{2}}^a$
n-Heptane	0	0	71	18				0	113	19				0	88	22			
CCl_4	4				1	50	27				4	107	20				5	84	24
PhCl	11				5	55	33				11	104	25				15	69	36
PhH	18				7	56	33				11	80	27				13	62	39
p-Xylene	24				4	48	32				10	78	32				9	58	42
$PhNO_2$	18				5	59	42				17	104	34				30	68	56
MeCN	35				13	52	60				41	91	55				63	56	95
Acetone	47				17	26	56				45	95	48	*c.* 9	17		75	59	65
Et_2O	57	0	49	27	44	21		0	43	26	61	49	48	1	47	25	105	40	112
Dioxan	55	15	38		36	39					65	91	76	*c.* 12	14		97	49	93
1,8-Cineole	78	2	54	25	69‖	7		3	71	21	62	42	*c.* 62	3	59	25	145	9	
THF	62	6	36		45	35		6	28		77	79	62	5	21		119	64	116
DMSO	118	10	35		61	41					116	105	98				171¶	49	
Pyridine	131	8	21	37	103	20		12	18		146±5	55	127	15	15		201	47	

* ν(NH) 3446 cm^{-1} in n-heptane. † ν(NH) 3440 cm^{-1} in n-heptane. ‡ ν(NH) 3493 cm^{-1} in n-heptane. § ν(NH) 3465 cm^{-1} in n-heptane. ‖ ±4. Another band (ϵ_A 11) had $\Delta\nu$ 30±3 cm^{-1}. ¶ Another band (ϵ_A 49) which had $\Delta\nu$ 190 cm^{-1} is considered to arise from Fermi resonance.

spectrum of a carbon tetrachloride solution had the expected single ν(NH) band (at 3429 cm^{-1}), and an *N*-methyl band at 2805 cm^{-1}.

(iv) *Acetanilides.*—2-Phenylacetanilide, m.p. 121·0–121·5° (lit. 121°), and 2-trifluoromethylacetanilide, m.p. 95–96° (lit. 94°), were prepared from commercial samples of the primary amines by standard acetylation methods.

Measurement of Spectra

Solid compounds were dried *in vacuo* over phosphorus pentoxide, and liquids were dried over Linde type 4A molecular sieves, prior to measurement of infrared spectra.

Infrared spectra were measured with a Unicam SP700 spectrophotometer as described previously.[1,3] Frequencies, ν, and band widths, $\Delta\nu_{\frac{1}{2}}^{a}$, are reported in cm^{-1}, and apparent extinction coefficients in units of cm^2 $mole^{-1}$.

The spectra of the acetanilides are presented in Table 1, and the spectra of the *N*-methyl- and *N*-phenyl-anilines in Table 2. In Table 2, "free" N–H refers to N–H groups which are not hydrogen-bonded to solvent, while "solvated" N–H describes N–H groups which are hydrogen-bonded to solvent molecules. Both bands are observable in some solvents.

TABLE 3

N–H STRETCHING FREQUENCIES (cm^{-1}) OF *N*-SUBSTITUTED ANILINES IN CARBON TETRACHLORIDE SOLUTION

Compound	ν(NH)	Compound	ν(NH)
Acetanilide	3445	*N*-methylaniline	3442
2-Methylacetanilide	3460	2,*N*-dimethylaniline	3453
2-Trifluoromethylacetanilide	3474	4,*N*-dimethylaniline	3437*
2-t-Butyl-5-chloroacetanilide	3495	*N*-methyl-2-trifluoromethylaniline	3489
2-Phenylacetanilide	3430	*N*-methyl-4-trifluoromethylaniline	3451*
Diphenylamine	3434	*N*-methyl-2-phenylaniline	3439
2-Trifluoromethyldiphenylamine	3460	*N*-methyl-4-phenylaniline	3443*

* These values are either taken from the data of Krueger, P. J., and Thompson, H. W., *Proc. R. Soc.* A, 1957, **243**, 143, or are estimated (to ± 1 cm^{-1}) from the correlation of ν(NH) with Hammett σ found by these authors for *para*-substituted *N*-methylanilines.

DISCUSSION

(*a*) *Effects of* ortho *Substituents on N–H Stretching Frequencies*

The modification of the observed ν(NH) frequency of an *ortho*-substituted secondary aromatic amine by the electronic, steric, direct field, and hydrogen bonding effects of the substituent has been discussed in a previous paper.[1]

Steric compression of the N–H bond can be minimized by rotation of the amino group out of the plane of the aromatic ring, and also by buckling of the ring itself. Certain *ortho* substituents, such as nitro, can alleviate the compression by rotation away from the amino group. Nevertheless, the residual compression can be considerable for some *ortho* substituents, and raises the infrared stretching frequency of the N–H bond, as shown by the data listed in Table 3. Only the dominant ν(NH) band is tabulated for the acetanilides; it is attributed to the *trans* conformer of these compounds.[3]

In the *N*-methyl-, *N*-phenyl-, and *N*-acetyl-anilines, the *ortho*-trifluoromethyl group considerably raises ν(NH), and the effect is greater than that observed with an *ortho* methyl group. It is known that electrical effects of substituents do not affect ν(NH) of acetanilides,[6,7] and it is evident from Table 3 that the ν(NH) frequency increases caused by *ortho*-trifluoromethyl in the other two series of anilines likewise do not arise in this way.

The frequency increases parallel the effective size ($Bu^t > CF_3 > CH_3 > H$) of the *ortho* substituents, and we therefore believe that the compressional effect on frequency is more important than any direct field effect which these substituents might exert on the N–H group.

It is well known from ultraviolet spectral data[8–11] that an *ortho* substituent in diphenyl increases the angle between the two aromatic ring planes. Stereomodels of *N*-methyl-2-phenylaniline indicate that, provided the interplanar angle is not too close to 90°, there will be compression between the N–H bond and one lobe of the π orbitals of the adjacent ring. This stereochemical arrangement is however suitable for hydrogen bond formation. The ν(NH) values in both the acetanilide and *N*-methylaniline series are actually *lowered* by *ortho* phenyl, which indicates that this substituent forms an intramolecular hydrogen bond strong enough to offset the compressional effect on frequency.

(*b*) *Solvent Effects on ν(NH) of Acetanilides*

There is only slight association of the less basic solvents (chlorobenzene, benzene, xylene) with the N–H group of the two *ortho*-substituted acetanilides studied here, and it is not clear which conformers of the solute are responsible for some of the weak, broad shoulders on the main absorption peak. Nitrobenzene, and solvents more basic than nitrobenzene, shift ν(NH) to lower frequencies. A plot of these seven $\Delta\nu$ values against $\Delta\nu$(H) for acetanilide in the same solvents is linear for both 2-trifluoromethylacetanilide and 2-phenylacetanilide, and least squares treatment yields the following correlations:

$$\Delta\nu(CF_3) = 1{\cdot}44\Delta\nu(H) - 6{\cdot}8 \quad (1)$$
(av. deviation 2·7 cm^{-1})

$$\Delta\nu(Ph) = 1{\cdot}16\Delta\nu(H) - 16{\cdot}6 \quad (2)$$
(av. deviation 6·1 cm^{-1})

For both these *ortho*-substituted acetanilides, the extrapolation of these frequency shifts in basic solvents back to carbon tetrachloride as reference solvent (i.e. $\Delta\nu(H) = 0$) yields a ν(NH) frequency slightly higher than the experimental value in this solvent. The present results therefore parallel our previous ones for other *ortho*-substituted acetanilides,[3] and confirm that the *trans* conformer present

[6] Nyquist, R. A., *Spectrochim. Acta*, 1963, **19**, 1595.
[7] Moccia, R., and Thompson, H. W., *Spectrochim. Acta*, 1957, **10**, 240.
[8] Beaven, G. H., and Hall, D. M., *J. chem. Soc.*, 1956, 4637.
[9] Beaven, G. H., and Johnson, E. A., *Spectrochim. Acta*, 1959, **14**, 67.
[10] Braude, E. A., Sondheimer, F., and Forbes, W. F., *Nature*, 1954, **173**, 117.
[11] Friedel, R. A., Orchin, M., and Reggel, L., *J. Am. chem. Soc.*, 1948, **70**, 199.

in basic solvents has slightly different geometry from that present in carbon tetrachloride solution. The results also confirm that solvent shifts of ν(NH) do not distinguish the weak intramolecular hydrogen bond present in such amides as 2-phenylacetanilide from other effects of *ortho* substituents.[3]

The *ortho* substituent reveals its presence chiefly by preventing complete association of the N–H bond even with basic solvents. The *ortho*-phenyl substituent shields the N–H bond so effectively that even such a small solvent molecule as acetonitrile is unable to form hydrogen bonds with all the available N–H groups.

(c) *Solvent Effects on ν(NH) of* ortho-*Substituted Secondary Aromatic Amines*

A comparison of the solvent shifts, $\Delta\nu$, of ν(NH) of *ortho*-substituted secondary aromatic amines with the shifts for the unhindered amine (*N*-methylaniline)[1] reveals three classes of behaviour.

Class A.—The *ortho* substituent introduces delocalization and intramolecular hydrogen bond energy terms (see Introduction) which offset the intermolecular hydrogen bond energy gained when the solute associates with solvent. The *ortho* substituent thus favours the unsolvated amine over the solvent-bonded species, and there is no detectable association in the less basic solvents. The solvent shifts produced by the more basic solvents follow the hydrogen-bond accepting power of the solvent as measured by $\Delta\nu$ for an unhindered amine.

Class B.—If the *ortho* substituent does not introduce sufficient steric hindrance, or form a strong intramolecular hydrogen bond, there is a detectable level of solute–solvent association in even the less basic solvents. The frequency shifts measured for the associated species parallel the shifts for an unhindered amine in the same series of solvents, and the Bellamy-type plot[1] of one set of shifts against the other is therefore linear.

Class C.—The *ortho* group introduces non-bonding interactions which are determined partly by the size of the group and of the solvent molecule, and partly by the types of orbitals coming into contact. These interactions clearly affect the extent of the solute–solvent association, and may also prevent solvent molecules approaching within normal hydrogen bonding range. The intermolecular hydrogen bond will then be long and weak, and the frequency shift will be small compared with the shift obtained for the same solvent with an unhindered amine. These solvents producing class C behaviour will appear as deviant points on the Bellamy-type plot.

We have previously observed class A behaviour for the *ortho*-nitro substituent, and class B behaviour when the *ortho* substituent was bromo, methyl, or methoxy. Class C behaviour was found for benzene and *p*-xylene solvents when the *ortho* substituent in *N*-methylaniline was bromo or methoxy.[1]

(i) *Trifluoromethyl as* ortho *Substituent*

The Bellamy-type plot of $\Delta\nu(CF_3)$ for *N*-methyl-2-trifluoromethylaniline against $\Delta\nu$(H) for *N*-methylaniline yields a straight line defined by equation (3).

$$\Delta\nu(CF_3) = 1{\cdot}11\Delta\nu(H) - 0{\cdot}88 \quad (3)$$

(av. deviation 2·6 cm^{-1})

All solvents shift ν(NH) for this substituted amine, so that this amine clearly falls into class B. Together with our previous example[1] of 2-bromo-*N*-methylaniline, it serves to define the conditions required for class A or class B behaviour. The *ortho*-bromo group forms a weak intramolecular hydrogen bond, but provides only small steric shielding of the N–H group to approach by a solvent molecule. The *ortho*-trifluoromethyl group provides substantial steric hindrance to solvent approach, but forms no significant intramolecular hydrogen bond. In neither instance are the unfavourable energy terms introduced sufficient to prevent even the least basic solvents from forming an intermolecular hydrogen bond. Class A behaviour requires that the sum of steric and hydrogen bond terms introduced by the *ortho* substituent be sizable, as it is for the nitro group.

The $\Delta\nu$ values for benzene, *p*-xylene, cineole, and DMSO deviate by 7, 15, 24, and 14 cm^{-1} respectively from equation (3), and this behaviour is interpreted as being class C. These are solvents which either have a large hydrogen-bond accepting orbital (benzene, *p*-xylene), or have a highly sterically shielded bonding site (cineole), or possess a highly negative bonding site (DMSO) which is repelled by the lone pair orbitals. All these solvents might therefore be expected to form unusually long, and therefore weak, hydrogen bonds. Other solvents with sterically shielded bonding sites (diethyl ether, tetrahydrofuran, pyridine) produce normal frequency shifts, but a sizable fraction of the solute is unassociated with solvent. The "free" N–H stretching frequencies show small solvent shifts (Table 2) which are not clearly related to solvent polarization or polarizability.

N-Phenyl-2-trifluoromethylaniline parallels the behaviour of the *N*-methyl compound. The linear Bellamy-type plot is described by equation (4).

$$\Delta\nu(CF_3) = 1{\cdot}88\Delta\nu(H) - 3{\cdot}6 \quad (4)$$
(av. deviation 2·9 cm^{-1})

This time, class C behaviour is exhibited when the solvent is benzene, *p*-xylene, DMSO, or pyridine; the deviations from equation (4) are respectively 17, 31, 47, and 41 cm^{-1}. It is possible that Fermi resonance is partly responsible for the unusually small solvent shifts produced by DMSO and pyridine.[1]

(ii) *Phenyl as* ortho *Substituent*

The modified Bellamy plot for *N*-methyl-2-phenylaniline is shown in Figure 1. The solvents increasing in basicity from n-heptane to acetone define class B behaviour; only *p*-xylene falls into class C. In cineole solution there are two solvent-bonded solute species. The smaller frequency shift falls near the plot for the weakly basic solvents. The larger frequency shift for cineole, together with those of the other three ethers and pyridine, roughly define another linear plot, with scattering from class C intrusions. The frequency shift produced by DMSO does not fall into either group of solvent shifts.

The much larger frequency shifts produced by the most basic solvents indicate that a change in type of solvated species occurs between acetone and dioxan in the solvent series.

This change is attributed to a substantial increase in the degree of rotation of the methylamino group from the aminoaryl ring plane, so that the weak non-linear hydrogen bond formed by less basic solvents is replaced by the stronger linear type. A virtually complete rotation of the methylamino group may not be energetically prohibitive in this amine, since the phenyl group would then be able to rotate back closer to the plane of the aminoaryl ring and thus conjugate more strongly.

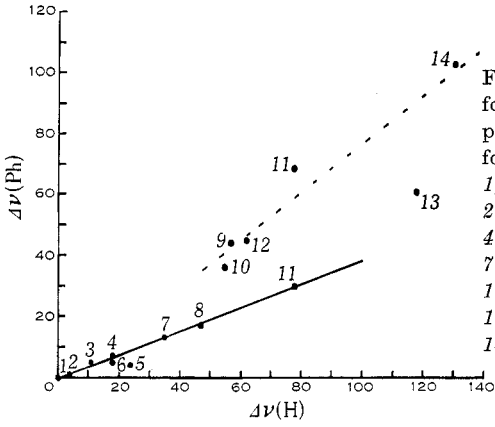

Fig. 1.—Frequency shifts ($\Delta\nu$(Ph)) for *N*-methyl-2-phenylaniline plotted against corresponding shifts ($\Delta\nu$(H)) for *N*-methylaniline.
1, n-Heptane; *2*, carbon tetrachloride; *3*, chlorobenzene; *4*, benzene; *5*, *p*-xylene; *6*, nitrobenzene; *7*, acetonitrile; *8*, acetone; *9*, diethyl ether; *10*, dioxan; *11*, 1,8-cineole; *12*, tetrahydrofuran; *13*, dimethyl sulphoxide; *14*, pyridine.

Conclusions

A number of energy terms determine whether or not a detectable level of association will occur between a solvent and the N–H bond of an *ortho*-substituted secondary aromatic amine. These terms include intermolecular and intramolecular hydrogen bonds, the delocalization energy of the aminoaromatic system, and non-bonding interactions between the solvent and the *ortho* substituent.

In favourable cases, the frequency shifts parallel those for an unhindered amine, and may be considered as a measure of the intermolecular hydrogen bond strength. The other energy factors then determine the position of the equilibrium between those solute molecules bonded to solvent and those which are not, and two types of behaviour (classes A and B above) can be observed. The comparison of nitro, bromo, and trifluoromethyl as *ortho* substituent enables the boundaries between class A and class B behaviour to be defined, but the steric and hydrogen bond properties of the *ortho* substituent cannot be distinguished from each other.

In less favourable cases, non-bonding interactions between solvents and the *ortho* substituent affect the strength of the intermolecular hydrogen bond, as well as the extent of the amine-solvent association. The frequency shifts are anomalously small for these solvents. In addition, *N*-methyl-2-phenylaniline exhibits behaviour not fitting into any of the above categories.

The solvent shifts of N–H stretching frequencies clearly involve more factors than can be identified and measured at this time, and this study confirms our earlier conclusion that these shifts cannot be used to single out the intramolecular hydrogen bond term.