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Solvatochromism of Heteroaromatic Compounds: XXVI.[1] Solvent Effect on the Solvatochromic Parameters of IR Bands of *N*-Methylanilines and Related Hydrogen Bond Donors

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Abstract—Formation of a hydrogen bond between molecules of a proton donor (phenol, pyrrole, *N*-methylanilines) and a solvent decreases the sensitivity of the XH stretching frequency to the polarity/polarizability of solvents. A change in the bond configuration in the amine moiety of *N*-methylaniline and related compounds upon formation of a solvation H complex is manifested in that the absolute terms of the solvatochromic equations for inert and protophilic media are different. The spectroscopic effect from the geometric reorganization of molecules is determined by their structure and the capability to act as hydrogen bond donors. Multicentered hydrogen bond with π bases affects the geometry of the amine fragment of N-substituted anilines to a lesser extent than does two-centered H bond with onium bases.

As demonstrated in basic papers [2, 3], the general (π*, β) Kamlet–Taft parameters describing the polarity/polarizability of a solvent (π*) and its capability to act as a hydrogen-bond acceptor in an H complex with a solute (β) are applicable to correlations between the positions of IR bands of solutes and the solvent properties. In particular, the following solvatochromic equation was obtained for solutions of phenol in binary mixtures of CCl_4 with proton acceptors [3]:

$$\Delta\nu_{OH} = -34.5 + 512\beta + 313\xi, \quad (1)$$
$$r\ 0.989,\ n\ 43.$$

Here $\Delta\nu_{OH}$ is the difference between the frequencies (ν_{OH}) of the stretching vibrations of the OH bond of the nonspecifically solvated molecule and its H complex; and ξ is the group parameters determining the relative degree of covalence of the coordination bond. The absolute term in Eq. (1) is essentially nonzero, which is apparently due to different dependences of ν_{OH} of a molecule and its solvation H complex on the π* of the solvent.

In the previous paper [1] we considered separately the effects exerted on te ν_{OH} of phenol by nonspecific and specific solvation. Regression analysis showed that the effect is described by two solvatochromic equations, different for inert [Eq. (2)] and protophilic [Eq. (3)] solvents.

$$\nu_{OH} = (3617 \pm 1) - (34 \pm 2)\pi^*, \quad (2)$$
$$r\ 0.986,\ sd\ 3,\ n\ 10,$$
$$\nu_{OH} = (3616 \pm 13) - (18 \pm 16)\pi^* - (455 \pm 16)\beta - (423 \pm 31)\xi, \quad (3)$$
$$R\ 0.975,\ sd\ 13,\ n\ 27.$$

Comparison of the parameters of these equations shows that, in inert and protophilic media, indeed, the regression coefficients (*s*) at the parameter π* are somewhat different; the difference is more pronounced in the IR spectra of 4-nitrophenol and 2,6-dibromo-4-nitrophenol [1]. A trend toward a decrease in *s* in the case of inert solvents was also found for compounds with a chelate ring with an increase in the strength of the intramolecular hydrogen bond OH···X (NO_2, Hlg) in the series 2,6-dichlorophenol, 2,6-dibromo-4-nitrophenol, 2-nitrophenol [1]. For the latter compound, s even changes sign. This can be interpreted as a consequence of a change in the sign of the derivative of the dipole moment of the OH bond with respect to the vibration coordinate [1, 4]. It is unclear whether the dependence of *s* on the kind of the solvent is characteristic of phenols only or of other hydrogen

[1] For communication XXV, see [1].

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bond donors as well. To clarify this question, we examined in this study the solvatochromism of the IR bands of some aromatic amines. Analysis of their solvatochromic behavior is complicated by possible changes in the configuration of bonds in the amine moiety upon formation of an H complex. In particular, IR and quantum-chemical studies [5, 6] showed that, in going from the gas phase and inert solvent to aprotic protophilic solvents, the bond angle in the amino group of 1- and 2-amino-9,10-anthraquinones tends to increase. In this connection, the position of the maximum of the NH stretching band (ν_{NH}) should additionally vary depending on the extent of nonplanarity of the NHR fragment. In particular, in inert solvents ν_{NH} in planar pyrrole is 3500 cm^{-1} [7]; in alkylarylamines, 3420–3450 cm^{-1}; and in alkylamines, 3310–3350 cm^{-1} [8]. The main goal of this study was to find how changes in the bond configuration in aromatic amines affect the solvatochromic parameters of the IR bands in aprotic protophilic solvents.

Phenol (I). Along with the facts noted above, we should note low quality of one-parameter (2) and multiparameter (3) correlations between the ν_{OH} of phenol and Kamlet–Taft empirical solvatochromic parameters. This, along with the error in determination of the position of the maximum for broad IR bands, may be caused by the fact that the solvatochromic parameters estimated from the UV spectra are applied here to the ground state spectra. This inconsistency stimulated us to study in more detail how the coefficient *s* varies in going from inert to protophilic solvents. To this end, we analyzed the data obtained for binary mixtures of an inert solvent and an ether. The inert solvent (CCl_4, hexane, cyclohexane, tetrachloroethylene, dichloromethane; data from [9, 10] was the major component determining the macroscopic properties of these mixtures. The effect of ether solvents (hydrogen bond acceptors, group parameter ξ 0.2) on ν_{OH} of phenol in an inert solvent is described by the following system of equations (for mixtures of CCl_4 with some solvents, the following data were additionally obtained: CCl_4/anisole 3450, CCl_4/dioxane 3378, CCl_4/dibutyl ether 3332, CCl_4/THF 3325 cm^{-1}).

Hexane (π^* –0.08):
$$\nu_{OH} = (3544 \pm 18) - (374 \pm 48)\beta,$$
$$r\ 0.977,\ sd\ 17,\ n\ 5,$$

Cyclohexane (π^* 0.00):
$$\nu_{OH} = (3544 \pm 16) - (386 \pm 41)\beta,$$
$$r\ 0.983,\ sd\ 15,\ n\ 5,$$

Tetrachloroethylene (π^* 0.28):
$$\nu_{OH} = (3538 \pm 15) - (398 \pm 38)\beta,$$
$$r\ 0.986,\ sd\ 14,\ n\ 5,$$

Carbon tetrachloride (π^* 0.28):
$$\nu_{OH} = (3540 \pm 11) - (423 \pm 29)\beta,$$
$$r\ 0.986,\ sd\ 11,\ n\ 8,$$

Dichloromethane (π^* 0.82):
$$\nu_{OH} = (3533 \pm 23) - (489 \pm 60)\beta,$$
$$r\ 0.978,\ sd\ 21,\ n\ 5.$$

The absolute term (ν^0_{OH}) of these partial equations corresponds to the state of the OH bond in a hypothetical nonspecifically solvated complex of phenol with a proton acceptor for which the general parameter β is 0 and the group parameter ξ is 0.2. Therefore, the ν^0_{OH} values for this narrow group of proton acceptors are lower than ν^0_{OH} in general equation (3). Regression analysis shows that, in a binary solvent mixture, the sensitivity of ν^0_{OH} of solvation complexes to the polarity/polarizability of its major component is also lower compared to the nonspecifically solvated molecule [cf. Eqs. (2) and (4)]:

$$\nu^0_{OH} = (3543 \pm 1) - (13 \pm 2)\pi^*, \quad (4)$$
$$r\ 0.980,\ sd\ 1,\ n\ 5.$$

Furthermore, the above system of equations shows that the regression coefficient (*b*) at β is not constant and depends on the properties of the inert medium surrounding the H complex, regularly increasing as π^* grows. It can be readily shown using the relationship between *b* and π^* that the angular coefficient characterizing the specific solvating effect in a purely protophilic medium [Eq. (3)] corresponds to the middle of the range of π^* (as a rule, for aprotic protophilic solvents $0.14 \le \pi^* \le 1.01$ [3]). Hence, the regression coefficient *b* determining the specific solvatochromic effect in protophilic solvents has a value averaged over the whole solvent set. Therefore, on the one hand, when applying the Kamlet–Taft parameters to the solvatochromism of the IR bands of H complexes, high correlation factors should hardly be expected [except for the case of $b \ne f(\pi^*)$]; on the other hand, to make the solvatochromic equations suitable for quantitative estimations, the parameter π^* of a protophilic medium should be varied in a maximum possible range, or an increased number of solvents with π^* ~0.55 should be used.

Pyrrole (II). The solvatochromism of the IR band of pyrrole, corresponding to the stretching vibrations of its NH bond, has been fairly extensively studied [7, 11–14]. In an inert medium (including the gas phase), it is described by one-parameter equation (5):

$$\nu_{NH} = (3503 \pm 1) - (25 \pm 2)\pi^*, \quad (5)$$
$$r\ 0.994,\ sd\ 2,\ n\ 4.$$

In aprotic protophilic solvents, the position of the IR absorption maximum of pyrrole, as in the case of phenols, mainly correlates with the parameters β and ξ (Fig. 1). However, in contrast to the case of phenols [1], aromatic solvents (π bases) in the case of pyrrole belong to the group with ξ 0.1. Taking into account this fact, we also found for pyrrole a two-parameter solvatochromic equation common for all types of aprotic protophilic solvents:

$$\nu_{NH} = (3507 \pm 9) - (237 \pm 13)\beta - (229 \pm 11)\xi, \quad (6)$$

$$R\ 0.989,\ sd\ 10,\ n\ 21.$$

Note that the dependence of the ν_{NH} of pyrrole on π* is insignificant.

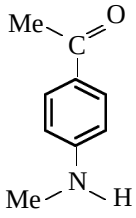
A similar result (ξ 0.1) in the series of π bases follows from the IR spectra of pyrrole in binary mixtures of CCl_4 with aprotic protophilic solvents [14]:

$$\nu_{NH} = (3505 \pm 8) - (229 \pm 15)\beta - (182 \pm 12)\xi, \quad (7)$$

$$R\ 0.980,\ sd\ 12,\ n\ 13.$$

Thus, similarly to the case of phenols, hydrogen bonding of pyrrole with solvent molecules decreases the sensitivity of the ν_{NH} frequency to the solvent polarity/polarizability. It should be noted also that the absolute terms in Eqs. (5) and (6) coincide, i.e., there are no effects going beyond those involved in the Kamlet–Taft parameter scale.

N-Methylanilines. In going from pyrrole, in which the bond configuration at the N atom is fixed, to *N*-methylanilines, some details of the solvatochromic behavior change. In particular, it was noted in [17] that in 4-substituted anilines the medium affects the absolute term in the corresponding solvatochromic equations {data for 4-acetyl-*N*-methylaniline (**III**) are given as example [17]}.



III

Inert medium (0.28 ≤ π ≤ 0.81)*:

$$\nu_{NH} = 3465 - 31\pi^*,$$

$$r\ 0.979,\ sd\ 1.2,\ n\ 4,$$

Aliphatic protophilic medium (ξ 0.0) (0.55 ≤ π ≤ 0.92)*:

$$\nu_{NH} = 3513 - 27\pi^* - 207\beta,$$

$$R\ 0.994,\ sd\ 4.2,\ n\ 6.$$

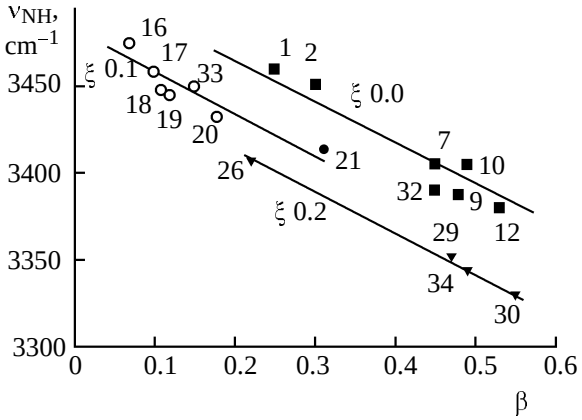
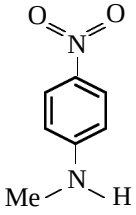


Fig. 1. Graphic analysis of the solvatochromism of the IR band of pyrrole NH stretching vibrations in aprotic protophilic solvents (data from [7, 11, 12]). The solvent numbering is given in Table 1; (32) 3-pentanone, (33) anisole (band corresponding to the NH···π complex), and (34) diisopropyl ether. Dark marks denote onium bases.

The difference (48 cm^{-1}) between the absolute terms in these equations was attributed in [17] to a change in the properties of the NH bond in going from a nonspecifically solvated molecule to an H complex. If this is the case, then it is unclear why this factor is not manifested in the IR spectra of pyrrole or phenols. As already noted, there is another viewpoint according to which the extent of sp^3 hybridization of the nitrogen atom in anilines and related compounds decreases upon formation of a solvation H complex [5, 6]. In this case, the solvent effect will depend not only on the extent of nonplanarity of the NHR fragment of aniline molecules, but also on the degree of deformation of the nitrogen pyramid in the proton-donor component of a solvation H complex.

Published data [16–18] for *N*-methyl-4-nitroaniline **IV** show that the above features of the IR solvatochromism are manifested in this compound also.



IV

Inert medium:

$$\nu_{NH} = (3471 \pm 2) - (38 \pm 4)\pi^*, \quad (8)$$

$$r\ 0.989,\ sd\ 2,\ n\ 4,$$

Protophilic medium (onium bases):

$$\nu_{NH} = (3521 \pm 8) - (19 \pm 9)\pi^* - (272 \pm 11)\beta - (106 \pm 11)\xi, \quad (9)$$

$$R\ 0.984,\ sd\ 6,\ n\ 16.$$

Table 1. Solvatochromism of the NH stretching bands in the IR spectra of *N*-methylaniline (**V**) and *N*,*N*-dimethyl-4-nitrophenylhydrazine (**VI**) in aprotic protophilic solvents

No.	Solvent	Kamlet–Taft parameters[a]			ν, cm^{-1}	
		π*	β	ξ	**V**	**VI**
1	Nitromethane	0.85	0.25	0.0	3422	3302
2	Nitrobenzene	1.01	0.30	0.0	3428[b]	3299
3	Ethyl chloro-acetate	0.70	0.35	0.0	3419	–
4	Propylene carbonate	0.83	0.40	0.0	3414	–
5	Benzaldehyde	0.92	0.44	0.0	3414	3274
6	Butyl acetate	0.50	0.45	0.0	3414	3280
7	Ethyl acetate	0.55	0.45	0.0	3413	3284
8	Butanone	0.67	0.48	0.0	3407	3279
9	Acetone	0.71	0.48	0.0	3399[b]	3274
10	Acetophenone	0.90	0.49	0.0	3408	3276
11	Butyrolactone	0.87	0.49	0.0	–	3268
12	Cyclohexanone	0.76	0.53	0.0	3390	3268
13	1-Methyl-2-pyrrolidone	0.92	0.77	0.0	3347	3225
14	Iodobenzene	0.81	0.05	0.1[c]	3425	–
15	Bromobenzene	0.79	0.06	0.1[c]	–	3290
16	Chlorobenzene	0.71	0.07	0.1[c]	3435[b]	3293
17	Benzene	0.59	0.10	0.1[c]	3430	3288
18	Toluene	0.54	0.11	0.1[c]	3426	3287
19	*p*-Xylene	0.43	0.12	0.1[c]	3422[b]	3280
20	*N*,*N*-Dimethyl-aniline	0.90	0.18[d]	0.1[c]	3414	–
21	Acetonitrile	0.75	0.31	0.1	3411[b]	–
22	Propionitrile	0.71	0.37	0.1	3408	–
23	Benzonitrile	0.90	0.37	0.1	3414	3284
24	Diphenyl ether	0.66	0.13	0.2	3426	3287
25	Phenetole	0.69	0.20	0.2	3422	–
26	Anisole	0.73	0.22	0.2	3420	3276
27	Dioxane	0.55	0.37	0.2	3404	3252
28	1,2-Dimethoxy-ethane	0.53	0.41	0.2	3392	3260
29	Diethyl ether	0.27	0.47	0.2	3389[b]	–
30	THF	0.58	0.55	0.2	3380	3240
31	Pyridine	0.87	0.64	0.6	3315[b]	3186

[a] Solvatochromic parameters from [3, 15]. [b] Values from [16]. [c] Taken on the basis of data on ν_{NH} of pyrrole in aromatic solvents and acetonitrile (Fig. 1). [d] From the data for phenols [1].

The ν_{NH} values for **IV** in aromatic protophilic solvents that are weak π bases do not obey Eq. (8). This means that their molecules form with **IV** a solvation complex with an NH···π hydrogen bond. Being protophilic, these solvents exert an abnormally strong effect on the NH stretching frequency in **IV** compared to pyrrole (cf. Figs. 1, 2). Nevertheless, it appears possible to combine these solvents with onium bases if a constant correction δ_{Ph} 45 cm^{-1} is added to ν_{NH} measured in aromatic solvents. Then, solvatochromic equation (9) takes the following general form:

$$\nu_{NH} = (3519 \pm 7) - (14 \pm 9)\pi^* - (276 \pm 8)\beta - (104 \pm 11)\xi, \quad (10)$$

$$R\ 0.988,\ sd\ 7,\ n\ 19.$$

Comparison of the absolute terms and regression coefficients *s* in Eqs. (8) and (10) allows two conclusions. The difference between the absolute terms ($\Delta\nu_0$) is close to δ_{Ph}: 48 ± 9 cm^{-1}. Hence, formation of weak multicentered solvation complexes with an NH···π bond only slightly affects the extent of nonplanarity of the NHMe fragment in *N*-methyl-4-nitroaniline, i.e., such complexes of this proton donor are similar to the solvation complexes of pyrrole and phenols. The trend in variation of the regression coefficient *s* depending on the solvent is for **IV** the same as for pyrrole.

To make sure that the effect exerted by π bases on the ν_{NH} frequency in *N*-methylanilines is regular, we studied in detail the solvatochromism of the ν_{NH} band in the simplest representative of these compounds, *N*-methylaniline. Previously [16, 18] *N*-methylaniline **V** was used as a reference in construction of the Bellamy dependences and in solution of certain special problems by IR spectroscopy. We considered the results obtained in a large number of aprotic protophilic solvents of diverse chemical structures (Table 1). We found that, for a large set of hydrogen bond acceptors, no common linear (with respect to parameters) solvatochromic equation can be found even for onium bases. A satisfactory result can be obtained only after exclusion of the weakest hydrogen bond acceptors (nitromethane, β 0.25, ξ 0.0; diphenyl ether, β 0.13, ξ 0.2) from the groups with ξ = const:

$$\nu_{NH} = (3485 \pm 7) - (12 \pm 7)\pi^* - (152 \pm 10)\beta - (103 \pm 9)\xi, \quad (11)$$

$$R\ 0.953,\ sd\ 6,\ n\ 21.$$

Further analysis of the solvatochromism of the IR band of **V** was performed using as spectral characteristic the quantity $\nu'_{NH} = \nu_{NH} + 12\pi^* + 103\xi$, where ν_{NH} is the observed frequency. Figure 3 presenting the correlation of ν'_{NH} with β shows that the points corresponding to nitromethane and diphenyl ether and to π bases deviate from regression line (11) toward smaller ν'_{NH}. In the case of π bases, the deviations

may also be due to the fact that *N*-methylaniline, being a weak hydrogen bond donor, does not specifically interact with these compounds.

In inert solvents, the solvatochromism of the NH stretching band in **V** (data from [16, 18]: heptane 3446, cyclohexane 3441, carbon tetrachloride 3440, 1-chlorobutane 3435, 1,2-dichloroethane 3427, dichloromethane 3428 cm^{-1}) is described by Eq. (12):

$$\nu_{NH} = (3444 \pm 1) - (20 \pm 2)\pi^*, \quad (12)$$

$$r\ 0972,\ sd\ 2,\ n\ 6.$$

We found that aromatic solvents that are π bases do not obey this equation, i.e., these solvents, as in the case of *N*-methyl-4-nitroaniline, form with *N*-methylaniline only solvation H complexes.

Taking into account this fact and assuming for π bases δ_{Ph} 30 cm^{-1}, we obtained a general solvatochromic equation (13) for aprotic protophilic solvents:

$$\nu_{NH} = (3489 \pm 5) - (12 \pm 6)\pi^* - (160 \pm 6)\beta - (103 \pm 9)\xi, \quad (13)$$

$$R\ 0.972,\ sd\ 6,\ n\ 27.$$

Its parameters are the same as in Eq. (11), and

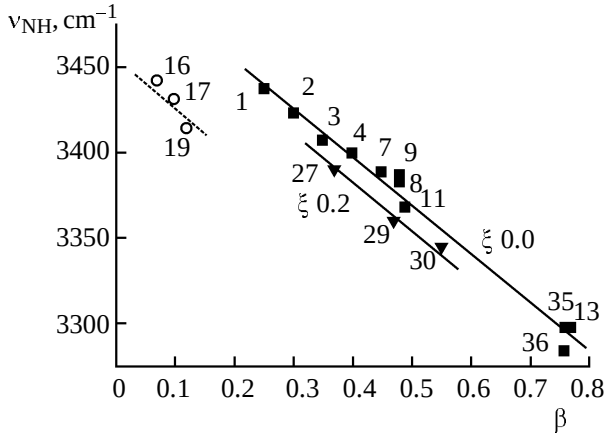


Fig. 2. Graphic analysis of the solvatochromism of the IR band of *N*-methyl-4-nitroaniline NH stretching vibrations in aprotic protophilic solvents (frequencies taken from [16–18]). The solvent numbering is given in Table 1; (35) *N*,*N*-dimethylacetamide and (36) DMSO. Dark marks denote onium bases.

nitromethane and diphenyl ether show deviations from this equation also. Apparently, in solvation H complexes of *N*-methylaniline with these weak onium bases, the geometric reorganization of the hydrogen bond donor is incomplete. The difference between the

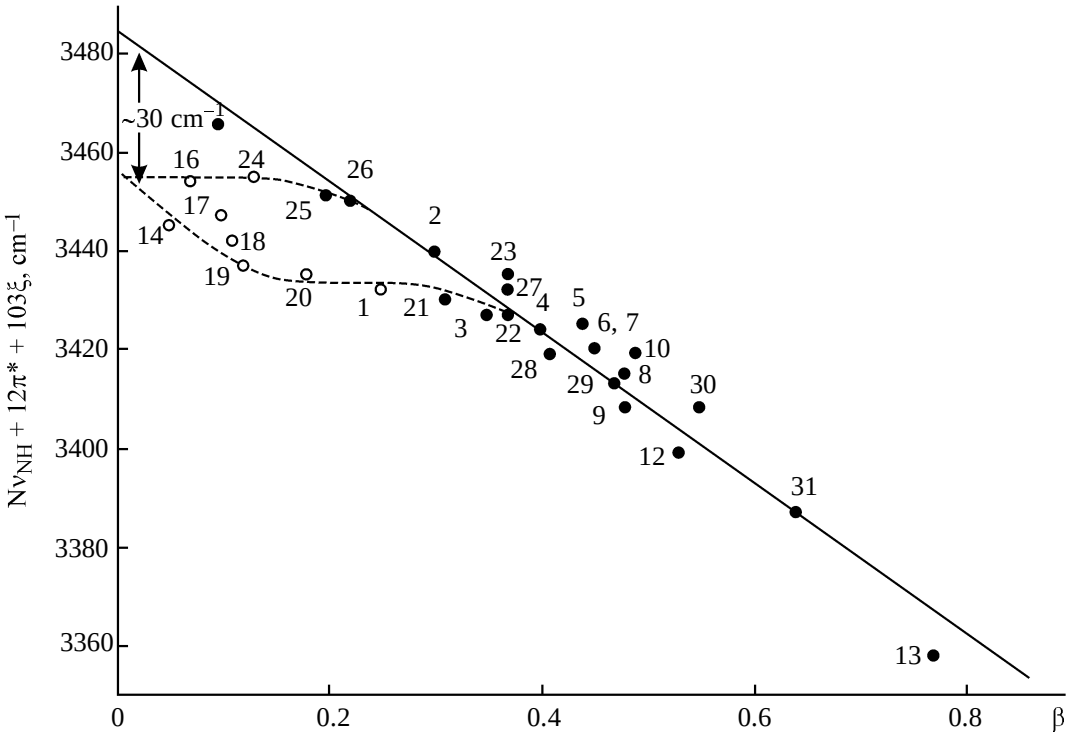


Fig. 3. Solvatochromism of the NH stretching vibration band of *N*-methylaniline in aprotic protophilic solvents. The solvent numbering is given in Table 1. Hollow circles denote π bases, nitromethane, and diphenyl ether.

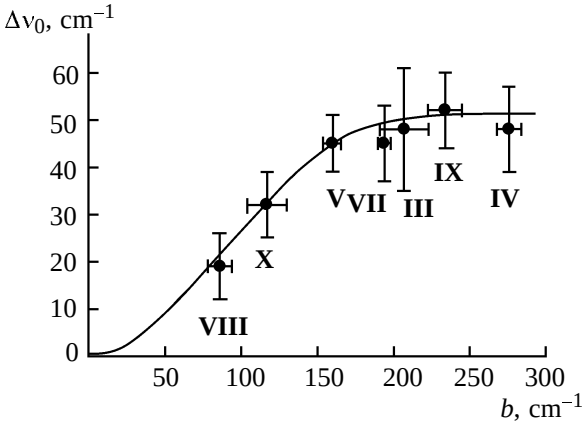


Fig. 4. Correlation between the spectroscopic effect $\Delta\nu_0$ from geometric reorganization of the *N*-methylaniline molecules and their capability to act as hydrogen-bond donors (*b*).

absolute terms of the solvatochromic equations for the molecule and solvation H complexes of **V** is 45 cm^{-1} and, in contrast to **IV**, appreciably exceeds the correction factor δ_{Ph}.

We also studied the solvatochromism of the NH stretching band in *N*,*N*-dimethyl-4-nitrophenylhydrazine **VI**. The IR data for **VI** in protophilic solvents are given in Table 1. These data show that the general solvatochromic equation for **VI** has a low correlation coefficient. Consideration of only onium bases leads to the following correlation:

$$\nu_{NH} = (3333 \pm 5) - (125 \pm 10)\beta - (121 \pm 10)\xi, \quad (14)$$

$$R\ 0.949,\ sd\ 6,\ n\ 18.$$

The ν_{NH} frequencies of **VI** in aromatic solvents, as in the case of the compounds described above, obey this relationship upon introducing a fixed correction δ_{Ph} 25 cm^{-1}. Then the solvatochromic equation becomes as follows:

$$\nu_{NH} = (3336 \pm 3) - (130 \pm 7)\beta - (121 \pm 10)\xi, \quad (15)$$

$$R\ 0.962,\ sd\ 6,\ n\ 23.$$

The polarity of an inert solvent has virtually no effect on ν_{NH} (cm^{-1}) of **VI**: 3289 in CCl_4, 3287 in 1-chlorobutane, 3286 in trichloroethylene, 3288 in 1,2-dibromoethane, and 3288 in 1,2-dichloroethane (dilute solution). Therefore, there is no correlation between ν_{NH} and π^* [Eq. (16)]. Nevertheless, judging from ν^0_{NH}, we can state that the correction factor δ_{Ph} for *N*,*N*-dimethyl-4-nitrophenylhydrazine is also considerably lower than $\Delta\nu_0$.

$$\nu_{NH} = (3289 \pm 3) - (4 \pm 4)\pi^*, \quad (16)$$

$$r\ 0.491,\ sd\ 2,\ n\ 5.$$

In other words, as expected, the correction factor δ_{Ph} depends on the structure of the proton donor, on the kind of the hydrogen bond with solvent molecules (multicentered or two-centered), and, apparently, on the affinity for hydrogen bonding of the subunit of the solvation complex.

Correlation between the capability of *N*-methylanilines to act as hydrogen-bond donors and the spectroscopic effect from reorganization of the NHMe fragment in their molecules. As a quantitative measure characterizing a hydrogen bond donor from the above series, we can take the regression coefficient *b*. Its value is mean for the chosen set of protophilic solvents and is independent of their chemical structure. To find a relationship between $\Delta\nu_0$ (difference between the absolute terms in the solvatochromic equations in the protophilic and inert media) and *b*, we used published data on the solvent effect on the ν_{NH} frequency in the IR spectra of 4-cyano-*N*-methylaniline **VII**, 4-carboxymethyl-*N*-methylaniline **VIII**, 4-bromo-*N*-methylaniline **IX**, and 2-phenyl-*N*-methylaniline **X**. The IR spectra of **X** in protophilic solvents show a superposition of the absorption bands of the nonspecifically solvated molecule (MH) and solvation H complex (MH·S), existing in a dynamic equilibrium MH + S $\rightleftarrows$ MH·S [19]. Processing of the avaiable data [19] shows that π bases do not form solvation H complexes with 2-phenyl-*N*-methylaniline, probably because of steric factors. This allowed us to obtain for this compound a solvatochromic equation under conditions of nonspecific solvation using data for not only inert but also protophilic solvents (Table 2).

The quantitative data on the solvatochromism of the IR band for *N*-methylanilines **III**–**V** and **VII**–**X** are given in Table 2, and the correlation between $\Delta\nu_0$ and **b** is shown in Fig. 4. It is seen that the plot is S-shaped, suggesting that the spectroscopic effect from the reorganization of the NHMe fragment significantly varies only in the series of relatively weak hydrogen bond donors. As *b* increases, this effect flattens out, apparently because the NHMe fragment in H complexes formed by such molecules takes the configuration favorable for specific interactions.

Thus, data on the solvatochromism of the XH stretching bands in the IR spectra of phenols, 4-nitro-*N*-methylaniline, *N*-methylaniline, *N*,*N*-dimethyl-4-nitrophenylhydrazine, and pyrrole, when considered in combination for a broad set of aprotic protophilic solvents, allow a conclusion that a decrease in the nonspecific solvatochromic effect ($s\pi^*$) upon hydro-

Table 2. Quantitative characteristics of the solvatochromism of the NH stretching vibration bands in the IR spectra of *N*-methylanilines **III**–**V** and **VII**–**X** in inert and protophilic media

Comp. no.	Medium	ν_0, cm^{-1}	$-s$, cm^{-1}	$-b$, cm^{-1}	$-e$, cm^{-1}	R	sd	n	$\Delta\nu_0$, cm^{-1}	$-\delta_{Ph}$, cm^{-1}
III	NS	3465 ± 3	31 ± 5	–	–	0.979	2	4[b]	–	–
	SS (NH···X)	3513 ± 10	27 ± 19	207 ± 16	–	0.988	4	6[b]	48 ± 13	–
IV	NS	3471 ± 2	38 ± 4	–	–	0.989	2	4[c]	–	–
	SS (NH···X)	3521 ± 8	19 ± 9	272 ± 11	106 ± 11	0.984	6	16[c]	–	–
	SS (NH···X + NH···π)	3519 ± 7	14 ± 9	276 ± 8	104 ± 11	0.988	7	19[c]	48 ± 9	45
V	NS	3444 ± 1	20 ± 2	3	–	0.972	2	6[d]	–	–
	SS (NH···X)	3485 ± 7	12 ± 7	152 ± 10	103 ± 9	0.953	6	21[d]	–	–
	SS (NH···X + NH···π)	3489 ± 5	12 ± 6	160 ± 6	103 ± 9	0.972	6	27[d]	45 ± 6	30
VII	NS	3464 ± 5	30 ± 9	–	–	0.913	4	4[b]	–	–
	SS (NH···X)	3509 ± 3	37 ± 5	194 ± 4	–	0.999	1	6[b]	45 ± 8	–
VIII	NS	3415 ± 2	19 ± 3	–	–	0.981	1	4[b]	–	–
	SS (NH···X)	3434 ± 3	23 ± 9	86 ± 8	–	0.986	2	6[b]	19 ± 7	–
IX	NS	3448 (heptane)[e]	–	–	–	–	–	–	–	–
	SS (NH···X)	3498 ± 13	–	229 ± 25	84 ± 20	0.964	10	6[e]	–	–
	SS (NH···X + NH···π)	3500 ± 4	–	234 ± 11	83 ± 14	0.988	7	9[e]	52 ± 8	40
X	NS[f]	3441 ± 1	11 ± 1	–	–	0.939	1	9[g]	–	–
	SS (NH···X)	3473 ± 6	–	117 ± 13	101 ± 11	0.970	5	8[g]	32 ± 7	–

[a] (NS) Nonspecifically solvating medium and (SS) medium specifically solvating by NH···X or NH···π hydrogen bonding. [b] Experimental data from [17] were used. [c] Calculated from the mean values of ν_{NH} from [16–18]. [d] The ν_{NH} frequencies are given in Table 1 and in the text. [e] According to [16]. [f] Taking into account the ν_{NH} frequencies in protophilic solvents, corresponding to the nonspecifically solvated molecule. [g] The ν_{NH} frequencies were taken from [19].

gen bonding of a solute with a solvent is, most probably, a regular trend for this type of proton donors. The fact that the ν_{NH} frequencies in solvation complexes of 4-substituted anilines with π bases are lower than those expected from the solvatochromic parameters of aromatic solvents is associated with the weaker effect of the multicentered hydrogen bond NH···π on the geometry of the NHR fragment, compared to the effect exerted by the two-centered bond NH···X.

EXPERIMENTAL

The IR spectra of phenol, *N*-methylaniline, and *N*,*N*-dimethyl-4-nitrophenylhydrazine in a wide set of aprotic protophilic and aprotic inert solvents were recorded on a Specord IR-75 spectrophotometer. *N*-Methylaniline was distilled just before use. The purity of the proton donors and solvents was checked by GLC and IR spectroscopy.

***N*,*N*-Dimethyl-4-nitrophenylhydrazine.** Iodomethane, 7.10 g, was added to a stirred solution of 3.83 g of *p*-nitrophenylhydrazine and 1.00 g of NaOH in 30 ml of DMSO. The mixture was stirred for 40 h and poured into water; the precipitate was filtered off, washed with water to neutral reaction, and dried. Yield 3.00 g (66%), mp 89–91°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.58 s (6H, CH_3), 4.99 s (1H, NH), 6.84 d (2H, $H^{2,6}$, *J* 9.2), 8.11 d (2H, $H^{3,5}$, *J* 9.2). Calculated, %: C 53.03; H 6.12; N 23.19; O 17.66. $C_8H_{11}N_3O_2$. Calculated, %: C 53.11; H 6.18; N 23.22; O 17.63.

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