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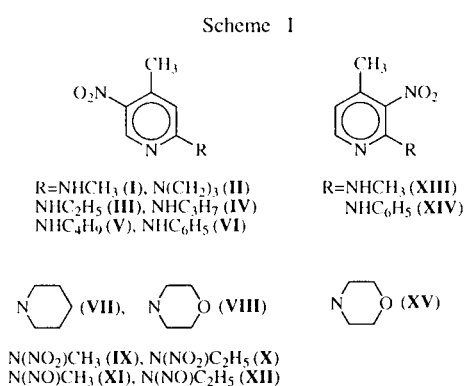
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The dipole moments of twelve 2-*N*-substituted amino-5-nitro-4-methylpyridines (**I-XII**) and three 2-*N*-substituted amino-3-nitro-4-methylpyridines (**XIII-XV**) were determined in benzene. The polar aspects of intramolecular charge-transfer and intramolecular hydrogen bonding were discussed. The interaction dipole moments,  $\mu_{\text{int}}$ , were calculated for 2-*N*-alkyl(or aryl)amino-5-nitro-4-methylpyridines. Increased alkylation of amino nitrogen brought about an intensified push-pull interaction between the amino and nitro groups. The solvent effects on the dipole moments of 2-*N*-methylamino-5-nitro-4-methyl- (**I**), 2-*N,N*-dimethylamino-5-nitro-4-methyl- (**II**) and 2-*N*-methylamino-3-nitro-4-methylpyridines (**XIII**) were different. Specific hydrogen bond solute-solvent interactions increased the charge-transfer effect in **I**, but it did not disrupt the intramolecular hydrogen bond in **XIII**.

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## Introduction.

An increased interest in the structure of aminopyridines, observed in recent years, is related to their potential use as non-linear optical materials. From this point of view, 2-amino-5-nitropyridines [1-5], in which interaction between the nitro and amino groups through the  $\pi$ -electron system is the main factor determining their electronic structure and conformation, are of interest. Equally interesting are 2-amino-3-nitropyridines where, besides strong conjugation, also the intramolecular hydrogen bond between the nitro and amino groups is an important structural element. In the present work, we have determined the dipole moments of a series of *N*-substituted 2-amino-5-nitro-4-methylpyridines (**I-XII**) and *N*-substituted 2-amino-3-nitro-4-methylpyridines (**XIII-XV**) (with substituents shown below, see Scheme 1) in benzene.



Molecules under consideration are "electronically non-rigid" and, because of this, their electronic properties should exhibit pronounced sensitivity to substitution and solvents. Changes in molecular structure and spectroscopic properties of aminopyridines caused by substitution in the pyridine ring were the subject of several recent

papers [6-11]. However, nothing is known about the influence of substitution of the nitrogen amino group on the molecular dipole moment and charge-transfer effect. The latter is discussed, in this work, in terms of the dipole moment of intramolecular interaction,  $\mu_{\text{int}}$ . We are also interested in solvent effects on electronic structure and stability of intramolecular hydrogen bond. In order to gain some insight into these effects, the dipole moments of **I**, **II** and **XIII** were determined in the solvents benzene, tetrachloroethylene, and dioxane. The influence of substitution and of the solvent on the polar properties has been corroborated by uv-visible and ir spectra in the region of the  $\tilde{\nu}(\text{NH})$  stretching vibrations.

## Results and discussion.

The experimental dipole moments of 2-amino-5-nitro-4-methylpyridines (**I-XII**) and 2-amino-3-nitro-4-methylpyridines (**XIII-XV**) in benzene are presented in Table 1.

Table 1

Dipole moments of 2-amino-5-nitro-4-methylpyridines (**I-XII**) and 2-amino-3-nitro-4-methylpyridines (**XIII-XV**) in benzene.

Compound	$\alpha\epsilon_1$	$\beta$	$\gamma n_1^2$	$\mu$ , D	$\mu_{\text{int}}$ , D
<b>I</b>	48.795	0.7647	0.8710	5.83±0.08	1.19
<b>II</b>	52.918	0.6519	0.7508	6.09±0.04	1.43
<b>III</b>	50.318	0.7540	0.6464	5.94±0.03	1.22
<b>IV</b>	52.099	0.7514	0.7108	6.04±0.01	1.34
<b>V</b>	52.929	0.9129	0.7935	6.08±0.02	1.39
<b>VI</b>	36.978	0.9612	1.4085	5.03±0.07	0.90
<b>VII</b>	57.258	0.7666	1.1588	6.31±0.01	1.54
<b>VIII</b>	32.261	0.8295	1.1914	4.70±0.03	-
<b>IX</b>	9.957	1.0318	0.5368	2.59±0.02	-
<b>X</b>	14.695	1.3145	0.6743	3.16±0.02	-
<b>XI</b>	3.544	0.9341	0.5149	1.47±0.02	-
<b>XII</b>	3.842	0.9521	0.5058	1.55±0.02	-
<b>XIII</b>	7.967	0.6236	0.5690	2.29±0.04	-
<b>XIV</b>	9.908	0.9864	1.2533	2.48±0.03	-
<b>XV</b>	13.881	0.8834	0.5859	3.08±0.05	-

Expected departures from the additive nature of the dipole moments in multiply substituted compounds may be due to many effects. An important contribution, though not the only one, is represented by electron density changes due to the conjugation of the substituents. Besides this effect, also the inductive effect, intramolecular hydrogen bonding, and certain changes in geometry brought about by steric effects may be significant. Algebraic difference between the experimental dipole moment and the moment calculated by vectorial summation of the dipole moments of monosubstituted derivatives is called the interaction dipole moment,  $\mu_{\text{int}}$ . To calculate the non-additive effect of the dipole moment in terms of  $\mu_{\text{int}}$  it is necessary to know the group dipole moments and the angle  $\Theta$  by which  $\mu(\text{NR}_1\text{R}_2)$  deviates from the ring plane. Two questions concerning the polarity of 2-*N*-substituted amino-5-nitropyridines are of importance. The first question concerns the effect of the extent of substitution of the amino group on its interaction with the nitro group. The second question is how the interaction is modified by the presence of other groups. To answer the first question, we calculated  $\mu_{\text{int}}$  in *N*-alkyl (or aryl) compounds, for which the dipole moments of the respective aminobenzenes are known. The dipole moments of *N*-methyl-, *N,N*-dimethyl-, *N*-ethyl- and *N*-propylaminobenzene are 1.68, 1.61, 1.69 and 1.66 D [12-14], respectively, while those of *N*-phenylpiperidine and diphenylamine are 1.74 D [15] and 1.05 [16], respectively. The angles  $\Theta$  in *N*-methylamino-, *N,N*-dimethylamino- and *N*-phenylaminobenzene are commonly accepted [17,18] to be 38.5°, 30° and 40°, respectively. An angle of  $\Theta = 30^\circ$  was postulated for the other *N*-alkylamino groups. We have made an assumption that the conjugation of the nitro group with the ring was weakened as a result of the "ortho" methyl effect. The dipole moment of such a nitro group is 3.90 D [19], while those of the methyl group and pyridine equal 0.36 and 2.18 D [19]. Thus, the expected dipole moments in compounds **I-VII** were calculated by vectorial summation according to equation 1:

$$\mu_{\text{calc}}^2 = \left( \mu_{\text{py}} + \mu_{\text{NR}_2} \cos \Theta \cos \alpha + \mu_{\text{CH}_3} + \mu_{\text{NO}_2} \cos \gamma \right)^2 + \left( \mu_{\text{NR}_2} \cos \Theta \sin \alpha + \mu_{\text{NO}_2} \sin \gamma \right)^2 + \left( \mu_{\text{NR}_2} \sin \Theta \right)^2 \quad (1)$$

where  $\alpha$  and  $\gamma$  are the angles between the group moments C-NR<sub>2</sub> and C-NO<sub>2</sub> and the C<sub>4</sub>-N axis of pyridine. Here it should be emphasized that  $\mu_{\text{calc}}$  is not very sensitive to the choice of  $\Theta$ ; reduction of  $\Theta$  to 0° changes  $\mu_{\text{calc}}$  within the range 0.1 ÷ 0.2 D.

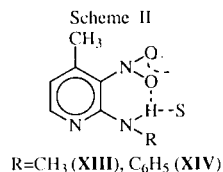
The values of  $\mu_{\text{int}}$  are collected in the last column of Table 1. As can be seen, the charge transfer effect in **VII** ( $\mu_{\text{int}} = 1.54$  D) is considerably greater than in **VI** ( $\mu_{\text{int}} = 0.90$  D). This is consistent with the electron-donating ability of the piperidino and phenylamino substituents. The alkylation effect of amino nitrogen is interesting.

Increase in alkylation increases the charge transfer degree and the electronic interaction between the NR<sub>1</sub>R<sub>1</sub> and nitro groups. It is worth noting that the longest wavelength  $\pi \rightarrow \pi^*$  band corresponding to the intramolecular charge-transfer transition (IMCT) displays a bathochromic shift due to alkylation. Moreover, there is a satisfactory correlation ( $R = 0.94$ ) between  $\mu_{\text{int}}$  and the wavenumber  $\tilde{\nu}$  (benzene solution) in this group of similar chromophores:

$$\mu_{\text{int}} = 7.56 - 2.20 \cdot 10^{-4} \tilde{\nu} \quad (2)$$

The interaction dipole moment in morpholino derivative **VIII** has not been calculated because the values of  $\mu$  and  $\Theta$  in *N*-phenylmorpholine are not known. The wavenumber of IMCT transition in **VIII** is 28,060 cm<sup>-1</sup>. According to equation 2, it gives  $\mu_{\text{int}} = 1.38$  D. The alkylation effect in 2-*N*-substituted amino-5-nitropyridines is not surprising, as a similar effect is also observed for 4-nitroaminobenzenes. The dipole moments of *para* NH<sub>2</sub>, NHCH<sub>3</sub>, N(CH<sub>3</sub>)<sub>2</sub>, NC<sub>5</sub>H<sub>10</sub> and N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> substituted nitrobenzenes are 6.27, 6.74, 6.89, 6.80 and 7.16 D [16], respectively. Rationalizing the intramolecular charge transfer interaction on the basis of non-additivity of  $\mu$ , we obtain the following values of  $\mu_{\text{int}}$  for the above series: 1.17, 1.36, 1.48, 1.27 and 1.56 D, respectively ( $\mu$  and  $\Theta$  for aminobenzene and *N,N*-diethylaminobenzene are taken as 1.53 D [17] and 48.5° [13] and 1.81 D [18] and 30°). This is the polar increment. According to the X-ray diffraction results [20-21], alkylation is responsible for intensification of charge transfer and increase of planarity of the molecule. At the same time, comparison of  $\mu_{\text{int}}$  for respective 4-nitroaminobenzenes and for our compounds points to a similar effect of charge transfer. Thus, conjugation of the amino group with the heterocyclic nitrogen does not weaken the push character of the amino group or the whole aminopyridine moiety. As seen from Table 1, the dipole moments of *N*-nitroso and *N*-nitramino derivatives (**IX-XII**) are much lower in comparison with *N*-alkyl (or aryl) derivatives. This may signify that the conjugation of both groups is weakened as a result of reduction of their electron donating abilities. However, a quantitative assessment of this effect in terms of  $\mu_{\text{int}}$  is difficult because the dipole moments and  $\theta$  of respective *N*-nitro- and *N*-nitrosoaminobenzenes are not known. The dipole moment of an alkyl nitramino group is of the order 4.4 ÷ 4.8 D [22]. Assuming the dipole moment of this magnitude to lie in the ring plane, we obtain the final dipole moments of **IX** and **X** in the range of 2.8 - 3.1 D, similar to the experimental values. Different character of aryl-bounded nitrogen in nitramino and amino groups was demonstrated by <sup>15</sup>N nmr spectroscopy [8]. The crystallographic structure of 4-nitro-*N*-methyl-nitraminobenzene [23] shows that the N(NO<sub>2</sub>)CH<sub>3</sub> group is deflected by an angle of 72° towards the ring plane and interacts with it only by inductive effect.

The dipole moments of 2-*N*-substituted amino-3-nitro-4-methylpyridines (**XIII**-**XV**) in benzene are presented in Table I. An important structural element of **XIII** and **XIV** is the intramolecular hydrogen bond between the amino and nitro groups.



Formation of a quasi-aromatic system with intramolecular hydrogen bonding and broadening of the chromophore due to a planar configuration is proven by a bathochromic shift of the IMCT band in **XIII** and **XIV** compared with the **I** and **VI** analogs. The shifts are 4490 and 4160 cm<sup>-1</sup>, respectively. However, the dipole moment of such systems does not lend much support to a possible intramolecular interaction. The formation of a quasi-aromatic chelate ring leads not only to a change of molecular conformation, but also, as a result of conjugation, to a redistribution of the charge within the chelate ring. Therefore, often no changes or even reduction of polarity in relation to *para*-isomers, methyl analogs or dipole moments calculated with an assumption of free rotation are observed [24-26]. The dipole moment of **XIII**, calculated according to equation (1) is 2.47 D, somewhat higher than the experimental value.

Dielectric measurements were carried out in benzene, which interacts specifically with the NH group. To investigate the influence of specific solute-solvent interactions on the polarity of aminonitropyridines, the dipole moments of representative derivatives **I**, **II** and **XIII** were measured in tetrachloroethylene and dioxane, in addition to benzene. The results are presented in Table 2.

moment increment as compared to the moment in tetrachloroethylene and benzene, is 0.49 and 0.36 D. The enhancement of the effective dipole moment is brought about by specific HB interaction of the solvent towards the NH group. The dipole moments correlate with parameters  $\beta$  (hydrogen-accepting ability) of the solvent [27], which for tetrachloroethylene, benzene and dioxane equals 0.00, 0.10 and 0.37, respectively. The high solvent sensitivity of the dipole moments of 2-*N*-methylamino-5-nitro-6-methylpyridine in different solvents has been already established [28]. Nevertheless, to confirm the specific role of the N-H... solvent interactions, its spectra in the region of the  $\tilde{\nu}(\text{NH})$  stretching vibrations were measured. The  $\tilde{\nu}(\text{NH})$  bands for **I** in tetrachloroethylene, benzene and dioxane are observed at 3469(3445), 3437 and 3363 cm<sup>-1</sup>, respectively. The shift of the  $\tilde{\nu}(\text{NH})$  band to lower frequencies increases with increasing effective dipole moment. The doublet structure of the  $\tilde{\nu}(\text{NH})$  band in tetrachloroethylene (3469 and 3445 cm<sup>-1</sup>) most likely arises from the presence of *syn*- and *anti*-conformers in an equilibrium mixture. The band observed at lower frequency could correspond to the *syn*-conformer, which in this nonpolar solvent is stabilized by the N-H...N<sub>ar</sub> hydrogen bond. The ir spectra of **I** obtained in poly(chlorotrifluoroethylene) oil and in potassium bromide disk show a single band at 3241 and 3244 cm<sup>-1</sup>, respectively and conspicuous is a large low-frequency shift in comparison with solutions. The solid phase effect is due to the engagement of the NH group in intermolecular hydrogen bond towards the nitro group of the neighboring molecule. The N-H...NO<sub>2</sub> chains are a typical feature of non-centrosymmetric crystal lattice of 2-amino-5-nitropyridines [1].

The dipole moment of **XIII** is practically independent of the solvent. This invariability and absence of the "dioxane effect" ( $\mu$  in benzene and dioxane is 2.29 and 2.34 D) is a proof of high stability of hydrogen-bonded chelate system.

Table 2

Dipole moments of selected 2-amino-5-nitro-4-methylpyridines (**I** and **II**) and of 2-*N*-methylamino-3-nitro-4-methylpyridine (**XIII**) in various solvents.

Compound	Benzene <sup>a</sup>				Tetrachloroethylene					Dioxane			
	$\mu$ , D	$\alpha\epsilon_1$	$\beta$	$\gamma n_1^2$	$\mu$ , D	$\alpha\epsilon_1$	$\beta$	$\gamma n_1^2$	$\mu$ , D	$\alpha\epsilon_1$	$\beta$	$\gamma n_1^2$	$\mu$ , D
<b>I</b>	5.83±0.08	40.708	-0.2485	0.7294	5.70±0.06	56.247	0.3410	1.2876	6.19±0.04	57.218	0.2989	1.3288	6.24(5)±0.03
<b>II</b>	6.09±0.04	45.475	-0.3425	0.6255	6.04±0.04	8.566	0.3478	0.9100	2.34±0.02				
<b>XIII</b>	2.29±0.04	6.921	-0.2901	0.5766	2.28±0.03								

<sup>a</sup> The values of coefficients  $\alpha\epsilon_1$ ,  $\beta$  and  $\gamma n_1^2$  are shown in Table I.

As it can be seen from Table 2, the dipole moment of **II** depends only slightly on the solvent. It can be assumed that, as with other solvents of similar polarity and in absence of any specific hydrogen bond interactions, the solvent stabilization of polar charge transfer structure in **II** is similar in the solvents under study. Small increase in  $\mu$  (**II**) may be fully explained in terms of the polarity/polarizability parameter  $\pi^*$  [27] of the solvent.

A substantially different solvent effect is observed for compound **I**. The "dioxane effect," defined as the dipole

We can state that even in hydrogen-accepting dioxane, the intramolecular hydrogen bond is not interrupted. A similar conclusion was drawn previously in relation to 2-nitroanilines [28] and 2-*N*-methylamino-3-nitro-6-methylpyridine [29] in weakly basic solvents. A single symmetrical  $\tilde{\nu}(\text{NH})$  band of hydrogen-bonded group occurs at 3430, 3430 and 3405 cm<sup>-1</sup> in tetrachloroethylene, benzene and dioxane solutions, respectively. However, the half-width of this band in dioxane (80 cm<sup>-1</sup>) is twice higher than in tetrachloroethylene and benzene. The shift of the

order  $\sim 30 \text{ cm}^{-1}$  as well as the band-broadening indicate the formation of a bifurcated hydrogen bond in dioxane solution according to Scheme II. In the spectrum of **XIII** in poly-(chlorotrifluoroethylene) oil and potassium bromide disk the  $\nu(\text{NH})$  band is observed at  $3408 \text{ cm}^{-1}$ .

In summary, the interaction dipole moments in 2-*N*-alkyl (or aryl) amino-5-nitro-4-methylpyridines (**I-VIII**) confirm a high intramolecular charge-transfer effect and conjugation of the  $\text{NR}_1\text{R}_2$  group increases with its alkylation. On the other hand, the interaction of the nitro and  $\text{NR}_1\text{R}_2$  groups is only slightly modified by the presence of the pyridine system. The electronic properties of *N*-nitramino and *N*-nitrosoamino groups are quite different from those of *N*-alkyl (or aryl) amino groups and their interaction with the nitro group seems to be clearly weakened. Polarities of 2-*N*-monoalkylamino-5-nitropyridines are strongly dependent on the solvent. Increase of hydrogen-accepting ability of the solvent amplifies the charge-transfer (CT) effect. The CT increment is caused mainly by specific hydrogen bond interactions with the NH group. In compounds with a 2-*N*-monoalkylamino-3-nitro moiety, a stable intramolecular hydrogen bond is formed. The solvent effect is only slightly pronounced in the case when bifurcated hydrogen bond with the solvent molecule occurs.

#### EXPERIMENTAL

Electric permittivity ( $\epsilon$ ) was measured on a dipole meter DM 01 (WTW) at 2 MHz. The dielectric capacity was determined with an accuracy of  $\Delta C/C \leq 1 \times 10^{-4}$ . The density ( $d$ ) was determined pycnometrically with an accuracy of  $\pm 1 \times 10^{-4} \text{ g/cm}^3$ , and the refractive index ( $n$ ) for the D sodium line was measured using an Abbe' refractometer with an accuracy  $\pm 4 \times 10^{-5}$ . The concentrations of solutions, limited by rather low solubility of compounds, were within the range of the molar fractions  $1 \times 10^{-3}$  -  $6 \times 10^{-3}$ . All the measurements were performed at  $25 \pm 0.02^\circ\text{C}$ .

The dipole molar polarization at infinite dilution was calculated according to Hedestrand's [30] equation:

$$P = \frac{3M_1}{d_1} \left( \frac{\alpha\epsilon_1}{(\epsilon_1 + 2)^2} - \frac{\gamma n_1^2}{(n_1^2 + 2)^2} \right) + \frac{M_2 - M_1\beta}{d_1} \left( \frac{\epsilon_1 - 1}{\epsilon_1 + 2} - \frac{n_1^2 - 1}{n_1^2 + 2} \right) \quad (3)$$

where the coefficients  $\alpha$ ,  $\beta$  and  $\gamma$  are defined as follows:

$$\epsilon_{12} = \epsilon_1 (1 + \alpha x_2); \quad d_{12} = d_1 (1 + \beta x_2); \quad n_{12}^2 = n_1^2 (1 + \gamma x_2)$$

The subscripts 1, 2 and 12 refer to the solvent, solute and solution, respectively;  $x_2$  is the molar fraction of the solute. Average deviation of the dipole moment from the mean value was in the range 0.02 - 0.04 D and was a little higher for compounds of the lowest solubility.

The IR spectra of solutions were recorded on an FT-IR Nicolet 205 spectrophotometer in potassium bromide cells and on an FT-IR Bruker 113 spectrophotometer in potassium bromide disks and in mineral oil (nujol). All UV-visible spectra were obtained on a Specord M-40 instrument.

Aminonitropyridines were synthesized and purified according to literature methods [31, 32]. The solvents were purified by standard methods [33] and were dried over sodium or molecular sieves of the type 4Å.

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