A CONTRIBUTION TO STUDY OF HYDROGEN BOND AND SOLVATION OF *o*-NITROANILINE

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IR spectra of fourteen 4- and 5-substituted 2-nitroanilines have been measured in pyridine, and those of their N-monodeuterated analogues have been measured in tetrachloromethane. Wave numbers of valence vibrations of N—H and N—D bonds have been correlated with the respective Hammett substitution constants. The correlations obtained indicate existence of intramolecular hydrogen bond between nitro group and one of the hydrogen atoms of the amino group of 2-nitroaniline both in tetrachloromethane and pyridine media. From the concentration and temperature dependences of intensities of the absorption bands thermodynamic characteristics have been determined for association of 2-nitroaniline with acetonitrile and dimethyl sulphoxide.

2-Nitroaniline and its N- and ring substituted derivatives were thoroughly investigated[1-18]. The aim of most of the papers was solution of the problem of existence of intramolecular hydrogen bond between amino resp. imino group in derivatives of 2-nitroaniline, investigation of influence of medium on spectral characteristics, investigation of influence of ring substituents and sterical interactions of *ortho* groups. The NHD group of 2-nitroaniline-d$_1$ showed two equally intensive absorption bands in both v(N—H) and v(N—D) regions of IR spectrum: the bands were ascribed to valence vibrations of N—H resp. N—D bond in *cis* or *trans* position with respect to nitro group[5,6]. It was a matter of controversy[7,12,18] to what extent the difference between wave numbers of these absorption bands (31 and 14 cm^{-1} in the cases of v(N—H) and v(N—D), respectively) was caused by hydrogen bond between the hydrogen of *cis* N—H resp. N—D group and nitro group.

In connection with studies of polar effects of substituents on PMR chemical shifts and wave numbers of valence and deformation vibrations of the groups having a hydrogen atom bonded by a hydrogen bond it was shown that these spectral characteristics can be correlated with polar substituent constants by means of a two-parameter equation containing, besides a term characterizing the substituent influence on the proton-donor group, also a term characterizing influence of the same substituent on the proton-acceptor group[17,19,20].

The aim of this work was to evaluate the influence of substituents of benzene ring on wave numbers of valence vibrations of N—H and N—D bonds in a series of 4- and 5-substituted 2-nitroanilines-d$_1$ in tetrachloromethane medium, evaluate the influence of these substituents on position of absorption bands in v(N—H) region of the same set of 2-nitroanilines in pyridine, and evaluate the solvation of 2-nitroaniline by acetonitrile and dimethyl sulphoxide from temperature and concentration dependences of the IR spectra.

EXPERIMENTAL

The same set of fourteen 2-nitroanilines was used as that in the previous work[17]. The deuteration was carried out by two crystallizations of the nitroanilines from a mixture of methanol-d$_1$ and deuterium oxide. The IR spectra were measured with a UR-20 (Zeiss, Jena) apparatus in 15 mm cells of NaCl. Temperature of the solutions was maintained within the limits $\pm 0.2°C$. The solvents used were of IR spectra purity grade.

RESULTS AND DISCUSSION

The measured wave numbers of valence vibrations of N—H and N—D bonds are given in Table I. From the Table it can be seen that, in the case of monodeuterio derivatives, IR spectrum contains absorption bands due to valence vibrations of N—H and N—D bonds *cis* and *trans* with respect to nitro group. However, whereas in the given set of compounds the position of the band situated at higher wave numbers changed within 10 cm^{-1} about the value 3481 cm^{-1} without being markedly affected by the ring substituents, the band at lower wave numbers was sensitive to polar effects of the substituents (especially marked in the case of 5-dimethylamino and 5-nitro derivatives) in the sense of substituent effects on the strength of hydrogen bond[19] and hence on $v(N—H)$, too. Absorption bands $v(N—D)$ at lower wave numbers behaved similarly, again showing marked dependence on the polar in-

TABLE I

Wave Numbers of Valence Vibrations of N—H and N—D bonds (cm^{-1}) of 4- and 5-Substituted 2-Nitroanilines-d$_1$ in Tetrachloromethane (A) and Substituted 2-Nitroanilines in Pyridine (B)

Substituent	A			B			
	$v(N—H)$	$v(N—D)$		$2\delta(NH_2) + v(N—H)$			$v(N—H)$
H	3 449·1	3 479·9	2 552·2	2 566·3	3 174	3 303	3 469
5-N(CH$_3$)$_2$	3 427·8	3 484·0	2 538·0	2 570·1	3 172	3 301	3 458
5-OCH$_3$	3 435·0	3 486·1	2 541·3	2 571·7	3 174	3 302	3 462
4-OCH$_3$	3 447·0	3 476·5	2 549·5	2 562·3	3 172	3 300	3 469
4-OC$_2$H$_5$	3 446·3	3 476·6	2 549·2	2 563·3	3 173	3 302	3 467
4-CH$_3$	3 447·2	3 477·1	2 549·2	2 563·0	3 174	3 301	3 470
4-F	3 449·8	3 479·8	2 552·6	2 566·7	3 174	3 307	3 468
4-Cl	3 449·3	3 483·5	2 550·0	2 569·2	3 173	3 301	3 467
4-Br	3 448·6	3 483·4	2 549·3	2 569·2	3 172	3 301	3 467
4-I	3 447·3	3 483·4	2 551·8	2 569·1	3 173	3 301	3 467
5-Cl	3 445·3	3 484·7	2 546·4	2 569·9	3 175	3 300	3 464
5-NO$_2$	3 451·0	3 483·0	2 550·0	2 570·3	3 172	3 303	3 469
4-NO$_2$	3 440·3	3 482·0	2 545·4	2 569·2	3 170	3 301	3 455
4-COOH	—	—	—	—	3 173	3 305	3 463

fluence of ring substituents on both NHD and NO_2 groups. We have evaluated quantitatively the substituent effects on wave numbers of these valence vibrations with the use of the two-parameter equation[17] *(1)*, where *a*, *b*

$$v = v_0 + a\sigma_1 + b\sigma_2 \tag{1}$$

and v_0 are constants calculated from experimental data by the least squares method, and σ_1 and σ_2 are substituent constants with respect to NHD and NO_2 groups, respectively. For correlation of the $v(\text{N—H})$ and $v(\text{N—D})$ values measured in tetrachloromethane we have used σ_1^- and σ_2 or σ_2^+ substituent constants. The equations obtained have the following form:

$$v(\text{N—H}) = 3443.5 - 12.89\sigma_1^- + 20.97\sigma_2 , \quad R = 0.941 , \quad s = 2.25 , \tag{2}$$

$$v(\text{N—H}) = 3444.5 - 16.64\sigma_1^- + 23.46\sigma_2 , \quad R = 0.976 . \quad s = 1.56 , \tag{3}$$

$$v(\text{N—H}) = 3446.7 - 11.39\sigma_1^- + 12.85\sigma_2^+ , \quad R = 0.989 , \quad s = 1.07 , \tag{4}$$

$$v(\text{N—D}) = 2548.2 - 11.3\sigma_1^- + 14.5\sigma_2 , \quad R = 0.906 , \quad s = 1.98 . \tag{5}$$

The Eqs *(2)* to *(4)* refer to the wave numbers of valence vibrations of N—H bond. For Eq. *(2)* all data were used, whereas 4-alkoxy derivatives were omitted in calculation of Eq. *(3)*. Neither were these derivatives considered in calculation of Eq. *(4)*, in which case σ_2^+ substituent constants were used for the correlation. 4-Alkoxy derivatives make the correlation worse, which is probably due to some other influence of these substituents on $v(\text{N—H})$ and $v(\text{N—D})$; these marked effects are specific for IR spectroscopy and cause the correlation of IR data with polar substituent constants to have usually worse regression characteristics. In the case of the both alkoxy derivatives this effect probably also lowers the wave numbers of valence vibrations of the both free N—H and N—D groups. The good applicability of Eq. *(1)* for correlation of $v(\text{N—H})$ and $v(\text{N—D})$ and the sign of the constants *a* and *b* $(a < 0 < b)$[17,19] prove that out of the two absorption bands both in $v(\text{N—H})$ and $v(\text{N—D})$ regions that one at lower wave number corresponds to the valence vibration of N—H resp. N—D bond in the *cis* position to the nitro group to which the hydrogen resp. deuterium atom is bonded by intramolecular hydrogen bond. The band at higher wave numbers is due to valence vibration of the free N—H resp. N—D bond.

In pyridine solution the bands in the region about 3170 and 3300 cm^{-1} are due to the Fermi resonance between $v(\text{N—H})$ and overtone $2\delta_{\text{NH}_2}$, and they do not show to be markedly affected by the polar character of substituent. On the contrary, the absorption bands in the region about 3460 cm^{-1} remind one of the behaviour

of $v(\text{N—H})$ of an NH group bonded by intramolecular hydrogen bond. Again Eq. (1) was used for correlation of $v(\text{N—H})$ of this vibration with the substituent constants to give Eq. (6).

$$v(\text{N—H}) = 3467 - 15\cdot3\sigma_1^- + 13\cdot3\sigma_2 , \quad R = 0\cdot897 . \quad s = 2\cdot11 . \tag{6}$$

This correlation, which can be called satisfactory, shows that one of the amino hydrogen atoms of 2-nitroaniline is bonded by intramolecular hydrogen bond to nitro group even in pyridine medium, and solvation is limited to only one amino hydrogen atom. Dimethyl sulphoxide is similar to pyridine in its effect on $v(\text{N—H})$ spectral region (Fig. 1). Increasing dimethyl sulphoxide content in solution of 2-nitroaniline in tetrachloromethane again causes formation of three new absorption bands. Two of them are due to the Fermi resonance $v(\text{N—H}) + 2\delta(\text{NH}_2)$, and the third one at the highest wave number is due to valence vibration of N—H bond of the NH group bonded to nitro group by intramolecular hydrogen bond.

We have used the intensity changes of all the absorption bands of the region above 3100 cm^{-1}, caused by various concentrations of components of the system 2-nitroaniline–tetrachloromethane–dimethyl sulphoxide resp. 2-nitroaniline–tetrachloromethane–acetonitrile and by various temperatures, to evaluate quantitatively the association of 2-nitroaniline with dimethyl sulphoxide resp. acetonitrile. IR spectra have been measured of the system having the molar concentration ratios of proton-acceptor to 2-nitroaniline 2, 4, 8, 16, 32 at 20, 40, and 60°C. As there is a more or less marked overlap of the absorption bands of the free and bonded forms in this region (Fig. 1), Ketelaar transformation[22] has been used for calculation of equilibrium constants. The following thermodynamic characteristics have been found for the association of 2-nitroaniline with dimethyl sulphoxide resp. acetonitrile: $K_{20} = 12\cdot4$ resp. $1\cdot4 \text{ kmol}^{-1} \text{ m}^3$, $-\Delta H = 4\cdot4 \pm 0\cdot4 \text{ kcal}/\text{mol}$
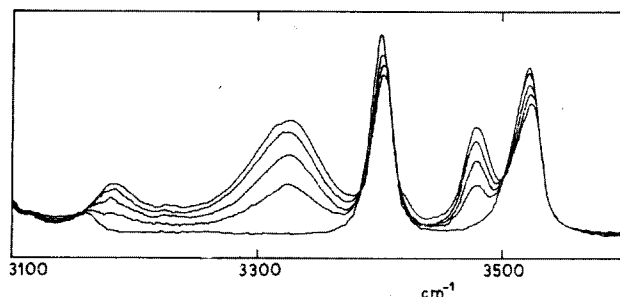

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IR Spectrum of 2-Nitroaniline in Tetrachloromethane with Various Additions of Dimethyl Sulphoxide

resp. 3.1 ± 0.2 kcal/mol, and $-\Delta S = 9.0 \pm 2.0$ resp. 9.0 ± 2.0 cal mol^{-1} grad^{-1}.

The present work and the published IR studies of solvation of other amines[8,15,24] indicate that the solvation degree due to formation of hydrogen bond in the given medium must be taken into account when evaluating the relations between structure and the measured quantity. Especially those quantities are meant which depend markedly on the existence of hydrogen bond as *e.g.* PMR chemical shifts eventually also the ionization constants. In the case of PMR chemical shifts hydrogen bond acts as an amplifier of structural effects on chemical shifts of a series of acidic groups[19]. However, if only a part of the protons of the group studied is bound to solvent molecules by hydrogen bond, then this amplification of structural effects appears to be smaller, because both the protons of the free and bound form are manifested by a single signal in PMR spectrum, position of the signal being the weighted mean of the signal positions of the protons in the both states. Also the far smaller influence of substituents on PMR chemical shifts of the NH_2 protons of substituted 2-nitro-anilines (as compared with substituted anilines measured also in dimethyl sulpho-xide[21,23]) can be ascribed to solvation of only one hydrogen atom of amino-group of 2-nitroaniline by dimethyl sulphoxide.

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