

# Solvent Effect on Electronic and Vibrational Spectra of *N*-Methyl-2-nitroaniline and *N*-Methyl-4-nitroaniline\*

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*Dedicated to Professor Š. Toma in honour of his 60th birthday*

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Medium effect on the long-wave absorption maximum (vapour state and 35 solvents) and N—H stretching vibration (26 solvents) of the title compounds was measured and analyzed by the Reichardt, Taft—Kamlet, and Pytela methods, and by the methods of Onsanger's and Born's functions of relative permittivity and refractive index. Except the Reichardt method the applicability of the methods is satisfactory. Performed analysis points to the effect of only nonspecific interactions on the electronic spectrum of *N*-methyl-2-nitroaniline, effects of acidity and basicity of solvents being meaningless. The N—H stretching vibration of *N*-methyl-2-nitroaniline is affected by refractive index of medium only.

The problematics of the evaluation of the medium effect on chemical properties and processes has been studied extensively over the past three decades by empirical methods. These studies have resulted in a great number of papers containing new experimental data on medium effect on various equilibrium, kinetic, and spectral properties and new proposed methods for evaluation of medium effect (for review see *e.g.* [1—5]). Both the types of papers contain usually testing of various methods of solvent effect evaluation and conclusions on the solute and processes studied.

For the further development of the problematics it seems reasonable at present to obtain new experimental data on the medium effect on chemical properties in broad sets of solvents mutually differing in their basic properties and in vapour state if possible, to test existing recommended methods of evaluation of medium effects with these data and to make conclusions on the solute studied.

## EXPERIMENTAL

The solvents were purified by distillation and fractions boiling at the tabulated temperatures were used for the measurements. *N*-Methyl-2-nitroaniline and *N*-methyl-4-nitroaniline were products of Janssen Chemica and were used without further purification. Electronic spectra were measured on a Pye—Unicam 8750

UV VIS spectrometer using fused silica cells 5 mm optical pathway except for diiodomethane and carbon disulfide solutions (1 mm). Infrared spectra were measured on FT—IR spectrometer Genesis (Pye—Unicam) using 0.6 mm KBr cells.

## RESULTS AND DISCUSSION

Wavenumbers ( $\bar{\nu}$ ) of absorption maxima of electronic spectra of *N*-methyl-2-nitroaniline (C-1—C-2 band) and of *N*-methyl-4-nitroaniline (C-1—C-4 band) measured in vapour state and 35 solvents and wavenumbers of stretching vibrations of N—H bond of the compounds measured in 26 solvents are given in Table 1. Some of the data were taken from the papers by *Yokoyama* [6] and *Dyall and Kemp* [7] (data designated by *a* and *b* in the table).

The solvents for the study were elected with an effort to comprise a broad scale of their basic properties. Moreover, the election was affected by possible optical interference of the solvents and the solutes studied, and by resistance of the cells used.

The total solvent set used (see Table 1) may be divided into four subsets: solvents (1—14) capable of only nonspecific interactions with solute, aliphatic aprotic solvents capable to act as electron donor for hydrogen bonding with solute (15—27), amphiprotic solvents capable to act as both electron and proton

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Table 1. Solvent Effect on Electronic and Vibrational Spectra of *N*-Methyl-2-nitroaniline and *N*-Methyl-4-nitroaniline

| Medium                           | Spectrum   |                    |   |                     |
|----------------------------------|--|--------------------|---|---------------------|
|                                  | Electronic<br>$\bar{\nu} \cdot 10^{-3}/\text{cm}^{-1}$ |                    | Vibrational<br>$\bar{\nu}/\text{cm}^{-1}$ |                     |
|                                  | Derivative   |                    | Derivative                                |                     |
|                                  | 2-nitro  | 4-nitro            | 2-nitro                                   | 4-nitro             |
| 1 Vapour state                   | 26.21  | 32.55              | —   | —                   |
| 2 Perfluorohexane                | 25.23  | 30.39              | 3408.6                                    | —                   |
| 3 Pentane                        | 24.77 <sup>a</sup>                                     | 29.70 <sup>a</sup> | 3401.3                                    | —                   |
| 4 Hexane                         | 24.75 <sup>a</sup>                                     | 29.57 <sup>a</sup> | 3401.0                                    | 3461.9              |
| 5 Heptane                        | 24.71 <sup>a</sup>                                     | 29.48 <sup>a</sup> | 3399.0 <sup>b</sup>                       | 3460.0 <sup>b</sup> |
| 6 Cyclohexane                    | 24.62 <sup>a</sup>                                     | 29.22 <sup>a</sup> | 3399.2                                    | 3457.4              |
| 7 Tetrachloroethylene            | 24.08  | 28.60              | 3399.0                                    | 3455.2              |
| 8 Carbon tetrachloride           | 24.11 <sup>a</sup>                                     | 28.54 <sup>a</sup> | 3400.5 <sup>b</sup>                       | 3457.0 <sup>b</sup> |
| 9 Trichloroethylene              | 23.80 <sup>a</sup>                                     | 27.62 <sup>a</sup> | 3400.9                                    | 3453.7              |
| 10 Carbon disulfide              | 23.70  | 27.25              | 3394.1                                    | 3444.3              |
| 11 Methylene chloride            | 23.36 <sup>a</sup>                                     | 26.69 <sup>a</sup> | 3402.5                                    | 3444.7              |
| 12 1,2-Dichloroethane            | 23.35 <sup>a</sup>                                     | 26.67 <sup>a</sup> | 3400.5                                    | 3437.2              |
| 13 Methylene bromide             | 23.00  | 26.14              | 3396.6                                    | 3433.5              |
| 14 Methylene iodide              | 22.64  | 25.48              | 3388.7                                    | 3419.9              |
| 15 Diethyl ether                 | 23.99  | 27.34              | 3402.7                                    | 3360.4              |
| 16 Triethylamine                 | 24.00  | 27.32              | 3401.8                                    | 3315.6              |
| 17 Nitromethane                  | 23.06  | 25.93              | 3404.7                                    | 3431.0              |
| 18 Acetonitrile                  | —  | —                  | 3403.0                                    | 3396.6              |
| 19 Ethyl acetate                 | 23.75 <sup>a</sup>                                     | 26.20              | 3400.0                                    | 3395.2              |
| 20 Acetone                       | 23.41  | 26.20              | 3400.0                                    | 3395.2              |
| 21 Tetrahydrofuran               | 23.69 <sup>a</sup>                                     | 27.03 <sup>a</sup> | 3400.9                                    | 3346.5              |
| 22 1,2-Dimethoxyethane           | —  | —                  | 3403.6                                    | 3362.0              |
| 23 <i>N,N</i> -Dimethylformamide | 23.08 <sup>a</sup>                                     | 25.48 <sup>a</sup> | —   | —                   |
| 24 <i>N</i> -Methylpyrrolidone   | 23.06 <sup>a</sup>                                     | 25.39 <sup>a</sup> | —   | —                   |
| 25 Pyridine                      | —  | —                  | 3400.5 <sup>b</sup>                       | 3269.0 <sup>b</sup> |
| 26 Triethyl phosphate            | 23.40 <sup>a</sup>                                     | 25.85 <sup>a</sup> | —   | —                   |
| 27 Dimethyl sulfoxide            | 22.87 <sup>a</sup>                                     | 25.06 <sup>a</sup> | 3398.0 <sup>b</sup>                       | 3282.0 <sup>b</sup> |
| 28 Water                         | 22.73  | 23.92              | —   | —                   |
| 29 Methanol                      | 23.54 <sup>a</sup>                                     | 25.98 <sup>a</sup> | —   | —                   |
| 30 Ethanol                       | 23.67 <sup>a</sup>                                     | 26.09 <sup>a</sup> | —   | —                   |
| 31 Propan-1-ol                   | 23.71 <sup>a</sup>                                     | 25.97 <sup>a</sup> | —   | —                   |
| 32 Butan-1-ol                    | 23.75 <sup>a</sup>                                     | 26.01 <sup>a</sup> | —   | —                   |
| 33 Propan-2-ol                   | 23.70 <sup>a</sup>                                     | 25.93 <sup>a</sup> | —   | —                   |
| 34 Butan-2-ol                    | 23.67 <sup>a</sup>                                     | 25.86 <sup>a</sup> | —   | —                   |
| 35 Ethylene glycol               | 22.96 <sup>a</sup>                                     | 25.30 <sup>a</sup> | —   | —                   |
| 36 Benzyl alcohol                | 22.92 <sup>a</sup>                                     | 25.38 <sup>a</sup> | —   | —                   |
| 37 Benzene                       | 23.67 <sup>a</sup>                                     | 27.32 <sup>a</sup> | 3400.0 <sup>b</sup>                       | 3423.0 <sup>b</sup> |
| 38 Toluene                       | 23.76 <sup>a</sup>                                     | 27.36 <sup>a</sup> | —   | —                   |
| 39 Chlorobenzene                 | 23.48 <sup>a</sup>                                     | 27.36 <sup>a</sup> | 3398.0 <sup>b</sup>                       | 3431.0 <sup>b</sup> |
| 40 Nitrobenzene                  | —  | —                  | 3399.7                                    | 3421.8              |

a) The values taken from [6]; b) from [7].

donors in hydrogen bonding with solute (28—36), and aromatic solvents (36—40).

Especially in the case of medium effect on electronic spectra the media used cover total scales of the principal medium characteristics. Thus *e.g.* in the case of the deformational polarizability characterized by Onsanger's function of refractive index the common region used to be 0.18 (hexane) to 0.24 (bromobenzene) while in the present study it is from 0.00 (vapour state) over 0.134 (C<sub>6</sub>F<sub>14</sub>), 0.260 (CS<sub>2</sub>) to 0.287 (CH<sub>2</sub>I<sub>2</sub>).

For the evaluation of the medium effect on the

spectral characteristics studied the following methods and thus correlational equations were applied.

1. Method of *Reichardt* [1] with only one characteristics of medium  $E_T^N(30)$  (normalized transition electron energy of 2,6-diphenyl-4-(2,4,6-triphenylpyridin-2-yl)phenoxide with respect to tetramethylsilane as the medium)

$$\{\bar{\nu}\} = A + e \cdot E_T^N(30) \quad (1)$$

2. Method of *Taft—Kamlet* [2] with solvent characteristics  $\pi^*$  (polarity—polarizability),  $\alpha$  (acidity), and

Table 2. Results of Correlation of Experimental Data by Eqns (1–5)

| Method      | Electronic spectrum |          |                 |          | Infrared spectrum |          |          |       |
|-------------|---------------------|----------|-----------------|----------|-------------------|----------|----------|-------|
|             | Derivative          |          |                 |          |                   |          |          |       |
|             | 2-nitro-            |          | 4-nitro-        |          | 2-nitro-          |          | 4-nitro- |       |
| <i>N</i>    | <i>R</i>            | <i>N</i> | <i>R</i>        | <i>N</i> | <i>R</i>          | <i>N</i> | <i>R</i> |       |
| Reichardt   | 32                  | 0.615    | 32              | 0.810    | 21                | 0.403    | 21       | 0.03  |
| Taft—Kamlet | 36 <sup>a</sup>     | 0.992    | 33 <sup>a</sup> | 0.992    | 22                | 0.543    | 20       | 0.919 |
| Pytela      | 26                  | 0.970    | 26              | 0.969    | 16                | 0.787    | 15       | 0.932 |
| Onsanger    | 24 <sup>a</sup>     | 0.977    | 14 <sup>a</sup> | 0.980    | 12                | 0.949    | 13       | 0.942 |
|             |                     |          |                 |          | 21                | 0.920    |          |       |
| Cross-term  | 24 <sup>a</sup>     | 0.990    | 14 <sup>a</sup> | 0.998    | 13                | 0.690    | 13       | 0.922 |

a) Including vapour state. *N* – number of solvents, *R* – correlation coefficient.

$\beta$  (basicity); *A* means wavenumber of solute obtained in cyclohexane

$$\{\bar{\nu}\} = A + s \cdot \pi^* + b \cdot \beta + a \cdot \alpha \quad (2)$$

3. Method of Pytela [3] with characteristics PP (polarity—polarizability), PA (polarity—acidity), and PB (polarity—basicity)

$$\{\bar{\nu}\} = A + p \cdot PP + a \cdot PA + b \cdot PB \quad (3)$$

4. Method of Onsanger's functions of relative permittivity ( $\epsilon_r$ ) and refractive index [5] (*n*). In IR spectroscopy is the equation known as the Buckingham equation, in electronic spectroscopy as the Bayliss equation

$$\{\bar{\nu}\} = A + B \cdot [(\epsilon_r - 1)/(2\epsilon_r + 1)] + C \cdot [(n^2 - 1)/(2n^2 + 1)] \quad (4)$$

5. Method of cross-term of Born's functions of relative permittivity and refractive index [5]

$$\{\bar{\nu}\} = A + B \cdot [(\epsilon_r - 1)(n^2 - 1)/(\epsilon_r \cdot n^2)] \quad (5)$$

Characteristics of the correlations – number of experimental data and correlation coefficient – are in brief given in Table 2. It is apparent from the table that the method of Reichardt failed in all the cases. It corresponds with the known facts that the Reichardt solvent characteristics do not evaluate the effects of deformational polarizability and basicity of solvents and these effects are significant in the studied systems. Electronic transition energy of the Reichardt polarity indicator (2,6-diphenyl-4-(2,4,6-triphenylpyridinio)phenoxide) and other betaines is quite independent of medium basicity and the effect of medium orientational polarizability highly prevails over the medium deformational polarizability. Accurate comparison of the efficiency of the other four methods is difficult because different numbers of solvents were used, and moreover the correlations ob-

tained with sets containing vapour state should be more efficient (if vapour state characteristics is right). Similarly as with many other solvent effects on electronic spectra [5] the cross-term of the Born functions is more effective than the two-parametric equation with terms of relative permittivity and refractive index.

The evaluation of solvent effect on *N*-methyl-4-nitroaniline by the Pytela method carried out with some subsets of the total solvent set attracts attention. The correlation equations for total solvent set of 26 solvents and for the subsets formed from it had the following forms:

Total solvent set: solvents 4, 5, 6, 8, 10, 11, 12, 15, 16, 17, 19, 20, 21, 23, 27, 28, 29, 30, 32, 33, 34, 35, 37, 38, 39

$$\{\bar{\nu}\} = 29.18 - 0.923PA - 2.17PB - 2.14PP \quad (6)$$

$$R = 0.969 \quad \sigma = 0.36$$

Solvents 4, 5, 6, 8, 10, 11, 12, 15, 16, 17, 19, 20, 23, 27, 37, 38, 39

$$\{\bar{\nu}\} = 28.88 + 6.10PA - 1.38PB - 4.81PP \quad (7)$$

$$R = 0.979 \quad \sigma = 0.29$$

Solvents 4, 5, 6, 8, 10, 11, 12, 15, 16, 17, 19, 20, 23, 27

$$\{\bar{\nu}\} = 28.75 + 8.4PA - 0.79PB - 6.04PP \quad (8)$$

$$R = 0.981 \quad \sigma = 0.31$$

Solvents 4, 5, 6, 8, 10, 11, 12

$$\{\bar{\nu}\} = 29.40 + 2.04PA + 1.77PB - 6.11PP \quad (9)$$

$$R = 0.990 \quad \sigma = 0.25$$

In eqn (9) regression parameters at PA and PB and

in eqn (8) also at PB are under significance level.

Two main conflicts of these results are considered to be as follows:

1. Effect of the polarity—acidity term is negative in the case of total set, when amphiprotic solvents were considered (eqn (6)) and strongly positive in the case of only aprotic solvents (eqns (7, 8)).

2. In the case when only aprotic aliphatic solvents were considered (eqn (8)) the effect of polarity—basicity term is insignificant in spite of the presence of basic solvents as dimethyl sulfoxide, triethylamine, and *N,N*-dimethylformamide in the set. Similar problem was met in the case of the evaluation of solvent effect on the N—H stretching vibration of *N*-methyl-4-nitroaniline.

More interesting are the results of the evaluation of solvent effect on both the electronic and vibrational spectra of the 2-nitro derivative. Thus in the case of IR spectrum a satisfactory dependence on Onsanger's refractive index function has been found only; the methods of Taft—Kamlet and Pytela quite failed. The correlation equation has the form (20 aliphatic, aprotic solvents)

$$\{\bar{\nu}_{\text{N-H}}\} = (3423 \pm 2.5) - (110.9 \pm 11.8) \cdot \left[ \frac{(n^2 - 1)}{(2n^2 + 1)} \right] \quad (10)$$

$$R = 0.911 \quad \sigma = 1.7$$

The dependence of the stretching vibration of the N—H bond in the 2-nitro derivative on the refractive index of medium only even in the case of highly basic solvents such as dimethyl sulfoxide, pyridine, and triethylamine may be ascribed to the intramolecular hydrogen bond between NH and NO<sub>2</sub> groups of the compound which is stable even in these basic solvents.

As it is apparent from Table 2 all the methods except that of Reichardt have been found as suitable for the evaluation of the solvent effect on electronic spectrum of *N*-methyl-2-nitroaniline. Of high significance seems to be the conclusion of both Taft—Kamlet and Pytela methods that effect of basicity and especially acidity is not significant in the case of C-1—C-2 band position of the compound, in spite of the application of highly electron-donor and proton-donor solvents.

Thus the correlation equations have the form for total and partial solvent sets

$$\{\bar{\nu}\} = (24.55 \pm 0.02) - (1.63 \pm 0.04) \cdot \pi^* \quad (11)$$

36 solvents

$$R = 0.992 \quad \sigma = 0.10$$

$$= (24.56 \pm 0.03) - (1.62 \pm 0.04) \cdot \pi^* \quad (12)$$

27 aprotic solvents

$$R = 0.992 \quad \sigma = 0.10$$

Similarly without a significant effect are PA and PB solvent parameters obtained by Pytela. The solvent effect of all the solvents is well described by the equations

$$J = (24.64 \pm 0.06) + (0.07 \pm 0.16)\text{PA} - (0.05 \pm 0.17)\text{PB} - (2.01 \pm 0.19)\text{PP} \quad (13)$$

$$R = 0.970 \quad \sigma = 0.14$$

and simply

$$\{\bar{\nu}\} = (24.63 \pm 0.06) - (2.02 \pm 0.10)\text{PP} \quad (14)$$

$$R = 0.970 \quad \sigma = 0.13$$

The electronic spectroscopy of *N*-methyl-4-nitroaniline seems thus to be the unique method of the direct determination of pure polarity—polarizability effect of amphiprotic solvents.

Obtained results of the evaluation of solvent effect on two properties of two compounds show that the problematics of medium effect in chemistry has not yet been definitively solved up-to-now and that surprising results may be still met.

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