

EFFECT OF MEDIUM ON $^1\text{H-NMR}$ SPECTRA

Vojtěch BEKÁREK and Vilém ŠIMÁNEK

Palacký University, 771 46 Olomouc

Received May 16th, 1980

$^1\text{H-NMR}$ spectra of benzene, salicylaldehyde, 2-nitroniline, 4-nitroaniline and 4-aminotoluene have been measured in 13 solvents. The solvent-induced changes in chemical shifts of the proton signals of these compounds have been correlated with refractive index and relative permittivity (D) by the Rummens equation extended by the term $f(D) = ((D - 1)/(2D + 1))^2$.

Investigation of solvent effects on position of NMR signals provides information about (i) intermolecular interactions in solution – about structural and dynamic parameters of the solvation process and (ii) about structure of the solute. A number of methods based on quantum chemical and classic models were developed for evaluation of influence of medium on NMR chemical shifts. On the basis of critical analysis of these methods and a great number of studied systems Rummens¹ arrived at the conclusion concerning dependence of the solvent-induced shifts on the square of the Onsager solvent factor² $g_n = f(n^2) = (n^2 - 1)/(2n^2 + 1)$. In contrast to application of the first power³⁻⁵ or the fourth power^{6,7} of this solvent factor, the equation containing the square of this term applied also to chemical shift of the compound in gas phase. Validity of the Rummens equation:

$$\delta = c((n^2 - 1)/(2n^2 + 1))^2 \quad (1)$$

agrees with the theoretically derived² dependence of the van der Waals shielding constant on the square of electric field in the vicinity of the studied nucleus, changes of this electric field being presumed to be determined by the changes in the Onsager field due to changes of medium. The equation (1) was derived for evaluation of influence of non-polar solvents on chemical shifts of nuclei of non-polar compounds; application of this equation to evaluation of influence of polar solvents revealed no deviations.

We have measured chemical shift of 12 signals of the protons of aromatic compounds in non-polar and polar solvents for which only non-specific interactions with solutes can be presumed. As the correlation significance of these chemical shifts by Eq. (1) was low, we have correlated these experimental data by the Eq. (1) extended by a term involving relative permittivity. This modification is known in IR and electron spectroscopy, in this case, however, it was used with squared terms.

EXPERIMENTAL

The measurements were carried out with a Varian T-60 apparatus using 1% (v/v) solution (benzene) and 10 and 5% (w/v) solutions (salicylaldehyde, 2-nitroaniline, 4-nitrotoluene and 4-aminotoluene) and using tetramethylsilane as external standard. The chemical shifts were read by frequency counter, extrapolated to zero concentration, and corrected to magnetic susceptibility of the medium. Accuracy of the obtained chemical shifts is ± 0.02 ppm.

RESULTS AND DISCUSSION

Chemical shifts of the protons of the studied compounds are given in Table I. Values of chemical shift of benzene in gas phase and some solvents were taken from ref.¹. For evaluation of influence of medium on chemical shifts of these protons we used besides Eq. (1) also the equations containing – along with the Rummens term – the term with relative permittivity, too:

$$\delta = A + B((n^2 - 1)/(2n^2 + 1))^2 + C((D - 1)/(2D + 1))^2 \quad (2)$$

$$\delta = A + B((n^2 - 1)/(2n^2 + 1))^2 + C((D - 1)(n^2 - 1)/(2D + 1)(2n^2 + 1))^2 \quad (3)$$

TABLE I

Influence of medium on ¹H-NMR spectra of the studied compounds

| solvent | Ben- zene | 2-Nitroaniline | | | Salicyl- aldehyde | | 4-Nitrotoluene | | | 4-Aminotoluene | | |
|---------------------|-------------------|----------------|------|------|----------------------|-------|-----------------|------|------|-----------------|------|------|
| | | H-6 | H-5 | H-3 | CHO | OH | CH ₃ | H-2 | H-3 | CH ₃ | H-3 | H-2 |
| Gas phase | 6.82 ^a | — | — | — | — | — | — | — | — | — | — | — |
| Perfluorohexane | 6.90 | — | — | — | 9.50 | 10.68 | — | — | — | — | — | — |
| n-Pentane | 7.01 | 6.49 | 7.00 | 7.85 | 9.62 | 10.78 | 2.22 | 7.02 | 7.87 | 1.97 | 6.22 | 6.64 |
| n-Hexane | 7.02 | 6.50 | 7.20 | 7.86 | 9.63 | 10.79 | — | 7.03 | 7.88 | 2.01 | 6.25 | 6.66 |
| n-Heptane | 7.04 ^a | 6.52 | 7.04 | 7.88 | 9.65 | 10.80 | — | 7.03 | 7.88 | — | 6.24 | 6.66 |
| Cyclohexane | 7.04 | 6.53 | 7.05 | 7.88 | 9.65 | 10.83 | — | 7.03 | 7.88 | — | 6.22 | 6.66 |
| Tetrachloromethane | 7.22 | 6.74 | 7.24 | 8.04 | 9.84 | 10.86 | 2.42 | 7.24 | 8.06 | 2.16 | 6.37 | 6.79 |
| Tetrachloroethylene | 7.16 | 6.37 | 7.16 | 8.00 | 9.74 | 10.86 | 2.33 | 7.15 | 7.97 | 2.10 | 6.45 | 6.89 |
| Trichloroethylene | 7.20 | 6.70 | 7.23 | 7.98 | 9.81 | — | 2.33 | 7.17 | 7.98 | 2.10 | 6.37 | 6.79 |
| Carbon disulphide | 7.32 ^a | 6.86 | 7.37 | 8.07 | 9.92 | 10.94 | 2.55 | 7.36 | 8.08 | 2.27 | 6.46 | 6.91 |
| Dichloromethane | 7.30 | 6.92 | 7.39 | 8.07 | 9.85 | 10.92 | 2.40 | 7.25 | 8.01 | 2.19 | 6.52 | 6.92 |
| 1,2-Dichloroethane | 7.33 | 6.92 | 7.38 | 8.07 | 9.88 | 10.95 | 2.43 | 7.30 | 8.06 | 2.18 | 6.52 | 6.90 |
| Dibromomethane | 7.37 | 6.96 | 7.40 | 8.08 | 9.93 | 10.97 | 2.50 | 7.37 | 8.14 | 2.22 | 6.54 | 6.92 |
| Diiodomethane | 7.54 | 7.14 | 7.62 | 8.20 | 10.17 | 10.99 | 2.73 | 7.62 | 8.32 | 2.42 | 6.70 | 7.05 |

^a Taken from ref.¹.

$$\delta = A + B((n^2 - 1)/(2n^2 + 1))^2 + C(((D - 1)/(D + 2) - (n^2 - 1)/(n^2 + 2))(2n^2 + 1)/(n^2 + 2))^2. \quad (4)$$

The parameters A, B, C only depend on solute and solvation process. The Eq. (2) with linear terms is known in IR spectroscopy as the Buckingham⁸ or Pullin⁹ equation and in electron spectroscopy as the Mattaga or Lippert equation¹⁰⁻¹³. The terms of Eq. (3) in the first power are also members of the Buckingham expansion⁸, the product term of this equation being decisive for evaluation of influence of medium on position of IR spectral lines^{14,15} and — in some cases — on position of electronic spectral lines¹⁶, a significant dependence being also found¹⁶ between this term and the Taft-Kamlet solvent parameters π^* . The Eq. (4) containing again the first power of the solvent terms represents the used form of the Bakhshiev equation¹⁷. This equation was recommended¹⁸ as the most suitable of the equations suggested for evaluation of solvent effects on position of lines in electronic spectra.

Correlation analysis of experimental data showed that relative permittivity of medium has a significant effect on the solvent-induced changes in chemical shifts. Out of Eqs (2)–(4) the Eq. (2) showed the best applicability for correlation of experimental data, but the correlation characteristics (R and F) for Eqs (3) and (4) were

TABLE II
Results of regression analysis of experimental data by Eq. (2)

| Compound | | A | B | C | R | F | $r(\delta \sim f^2(n^2))$ | $r(\delta \sim f^2(D))$ |
|-----------------|---------------|-------|------|------|-------|-----|---------------------------|-------------------------|
| Benzene | | 6.77 | 6.52 | 1.46 | 0.985 | 181 | 0.906 | 0.821 |
| 2-Nitroaniline | H-6 | 6.15 | 8.07 | 2.25 | 0.977 | 93 | 0.770 | 0.829 |
| | H-5 | 6.68 | 8.11 | 1.84 | 0.978 | 100 | 0.813 | 0.791 |
| | H-3 | 7.68 | 4.88 | 0.91 | 0.954 | 46 | 0.826 | 0.733 |
| Salicylaldehyde | CHO | 9.32 | 8.05 | 1.07 | 0.977 | 103 | 0.916 | 0.713 |
| | OH | 10.65 | 3.33 | 0.77 | 0.979 | 103 | 0.853 | 0.811 |
| 4-Nitrotoluene | CH_3 | 1.92 | 8.42 | 0.69 | 0.953 | 29 | 0.909 | 0.405 |
| | H-2 | 6.65 | 9.34 | 1.19 | 0.970 | 71 | 0.893 | 0.662 |
| | H-3 | 7.61 | 6.91 | 0.79 | 0.950 | 41 | 0.887 | 0.624 |
| 4-Aminotoluene | CH_3 | 1.75 | 6.84 | 0.70 | 0.965 | 48 | 0.908 | 0.555 |
| | H-2 | 6.42 | 5.96 | 1.14 | 0.956 | 48 | 0.823 | 0.740 |
| | H-3 | 5.97 | 5.21 | 1.46 | 0.968 | 68 | 0.797 | 0.791 |

only slightly lower. Therefore, Table II only gives the regression analysis results obtained by correlation of data by Eq. (2). The correlation coefficients of the double correlation R are above 0.95 in all the cases, and the significance level of the Fisher F criterion is within the limits 0.025–0.01. Correlation coefficients of partial correlation of the chemical shifts with individual terms of Eq. (2) $r(\delta \sim f^2(n^2))$ and $r(1 \sim f^2(D))$ show a significant contribution of the both terms on the overall correlation, the former coefficient $r(\delta \sim f^2(n^2))$ being simultaneously the correlation coefficient of the dependence of chemical shift of the studied protons on the refractive index of solvent according to the Rummens equation (1). From the results in Table II it follows that the extension of the Rummens equation by the term $(D - 1)/(2D + 1)$ considerably improves the correlation.

In contrast to the ^{13}C -NMR studies of aliphatic compounds^{19–21}, the results obtained allow no conclusions to be drawn with respect to relation of structure and magnitude of the solvent-induced shifts. In the case of 2-nitroaniline the H–3 proton shows the lowest sensitivity to influence of medium (about one half, as compared to that of H–5 and H–6). This lowest sensitivity of this hydrogen to influence of medium shows that differences in chemical shifts of these protons of 2-nitroaniline observed on transition from solvents in tetrachloromethane to those in dimethyl sulphoxide need not be due to breakage of intramolecular hydrogen bond between amino and nitro groups by action of dimethyl sulphoxide²².

In the mentioned studies the problem is frequently discussed concerning applicability of carbon disulphide and other solvents containing multiple bonds for a potential contribution of diamagnetic anisotropy to the overall shielding constant^{23–28}. Our results and those by Rummens²⁹ and Tiffon¹⁹ show that carbon disulphide (similar to tri- and tetrachloroethylene) exhibits no significant contribution of diamagnetic anisotropy to the overall shielding constant, and the mentioned solvents are suitable for these solvent studies.

The chemical shift found in tetrachloromethane showed the largest systematic deviations from the calculated values, which is similar to the solvent effects found in IR and electronic spectroscopy. These deviations are ascribed, to a certain extent, to specific interactions of tetrachloromethane and double bonds, which is manifested by the additional thermodynamic functions of the systems of tetrachloromethane with aromatic compounds³⁰.

Furthermore, our results show that the Taft and Kamlet empirical solvent factors π^* will not be suitable for evaluation of the solvent effects on position of ^1H -NMR signals, which was presumed in refs^{31,32}. In our previous study¹⁶ it was shown that these solvent factors π^* correlate significantly with the product term $(D - 1)(n^2 - 1)/(2D + 1)(2n^2 + 1)$. However, regression analysis of our experimental data by Eq. (3) showed that the both terms of this equation are significant for evaluation of solvent effects, which also follows from the different magnitude of the constants B and C in Eq. (2).

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Translated by J. Panchartek.