

Towards the Understanding of Aromatic Solvent Induced Chemical Shifts. A Multivariate Data Analysis of ^1H ASIS of Cyclic Ethers and Thioethers

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The ^1H aromatic solvent induced shifts (ASIS) of a variety of mostly ethereal solutes have been analyzed by means of a multivariate data analysis method. By the use of an internal reference, tetramethylsilane (TMS), the ASIS can be described by a single parameter model which explains 95 % of the variance. This model is related to the earlier proposed solvent clustering model, where the ASIS is expressed as a product of a site factor for the substrate and a solvent parameter. If externally referenced data are used, free from bulk susceptibility effects, a two-component model is needed. The major component values (93 % of the variance) are strongly correlated to the intrinsic medium effects on TMS. The minor component (6 % of the variance) corresponds to the specific ASIS found in the first analysis.

The quantitative and even qualitative understanding of aromatic solvent induced shifts (ASIS) is far from satisfying, yet numerous papers appear each year where this method is used empirically to yield structural information of certain solutes. The ^1H ASIS is thought to arise from the magnetic anisotropy of an aromatic solvent. By studying the ^1H NMR chemical shift differences of a solute in an "inert" reference solvent and in an aromatic solvent, subtle solute–solvent interactions can be revealed which can be hard to probe otherwise. These shift differentials appear in many cases to be characteristic of the position of the examined nucleus

with respect to a polar functional group in the solute.¹

Two different approaches have been presented to account quantitatively for these induced shifts. The original assumption was that a discrete 1:1 solute–solvent complex, which should possess a definite energy and geometry, is formed.² This approach was later criticized by Engler and Laszlo in favor of a "solvent clustering" model.³ This model considers the ASIS as a result of a slight organization of the solvent molecules in "the cage" around the polar site of the solute, and that the interactions must be very weak, in the order of RT. Hence, it was argued that the lifetime of these transient complexes must be very short on the NMR time scale and that the resultant ^1H spectrum will be a weighted average among all solute–solvent species involved.

In their study of ASIS of camphor, Engler and Laszlo proposed that the solvent shifts should be expressed as a product of two contributing factors:³

$$\text{ASIS} = \Delta_L = mS_L \quad (1)$$

The first factor m , the site factor, is a purely geometric term relating the various proton positions in camphor to the solvated polar carbonyl group. The second term S_L , the solvent parameter, was suggested as being composed of a "size" or molecular volume and an "electronic" contribution related to effects such as the group

Table 1. Solvent-induced chemical shifts (ASIS) relative to internal TMS in different aromatic solvents.

Aromatic solvents	Δ_{int}^a Hz							
1 H	1.0	14.5	23.8	-1.0	12.0	13.6	17.8	1.6
	1.1	23.3	22.0	22.0	4.2	2.0	14.5	11.0
	-3.5	17.0	22.5	3.5	-2.8	19.6	14.1	5.3
	9.6							
2 CH ₃	5.5	15.0	25.4	-2.0	10.5	12.9	18.9	2.5
	3.8	24.7	23.2	18.5	3.2	3.0	12.9	12.0
	-1.1	15.5	23.5	4.8	-0.2	17.9	14.1	4.5
	8.7							
3 1,4-(CH ₃) ₂	-0.3	14.6	21.0	-0.5	8.0	12.9	—	3.0
	3.8	22.7	20.6	17.2	4.6	3.7	11.4	12.5
	0.7	16.3	17.7	3.5	1.4	17.9	14.1	4.0
	9.7							
4 1,3-(CH ₃) ₂	0.0	15.5	22.5	0.5	9.0	12.7	19.0	3.4
	3.5	21.5	19.0	18.0	6.2	2.0	11.7	12.7
	0.6	16.9	—	6.9	1.8	17.7	14.2	4.0
	9.1							
5 1,3,5-(CH ₃) ₃	1.0	14.5	23.5	-2.5	5.0	15.6	—	5.0
	5.0	22.4	20.2	17.7	6.5	2.7	11.1	10.6
	0.8	16.7	19.7	7.0	2.6	16.8	13.2	4.2
	8.3							
6 Br	-6.2	7.7	14.5	-3.2	-1.5	7.7	10.0	0.4
	0.8	11.6	10.3	13.4	2.4	2.5	8.4	4.5
	-1.9	8.2	12.2	2.5	0.5	13.0	10.0	-0.4
	3.5							
7 Cl	-7.0	5.8	14.0	-3.5	2.8	7.8	10.0	0.4
	2.0	12.8	12.0	13.7	2.2	0.5	9.4	5.3
	-2.5	8.0	12.6	2.1	-0.1	12.9	10.0	0.2
	3.9							
8 1,2-(Cl) ₂	-8.3	1.8	7.8	-6.0	-4.5	4.3	5.2	0.7
	0.0	5.7	4.2	8.0	0.3	-1.0	5.2	-2.0
	-2.8	3.0	7.4	1.5	-0.1	10.0	8.0	-0.3
	3.5							
9 1-Cl,2-CH ₃	-2.4	9.6	14.0	-2.7	4.0	9.5	11.8	2.0
	2.6	14.7	14.0	13.5	3.2	1.0	8.6	6.4
	-0.2	10.0	—	3.3	1.0	13.7	11.0	-1.3
	3.0							
10 1-CH ₃ ,2-NO ₂	-6.3	-2.3	2.0	-5.0	-7.2	-0.7	—	-0.5
	0.8	1.8	2.0	5.0	-0.3	0.0	2.8	-0.8
	-2.8	-1.7	2.7	0.0	0.0	8.3	5.2	-3.7
	4.7							
11 NO ₂	-13.5	-8.5	-3.5	-8.5	-11.0	-2.2	-2.5	-3.0
	-0.9	-1.3	-2.0	4.0	-2.3	-1.5	3.4	-3.2
	-5.3	-4.3	-1.7	-2.1	-2.5	4.8	2.9	-5.1
	-2.9							

12 CHO	-9.6	0.0	5.6	-2.5	-3.0	1.7	3.0	-1.6
	-0.9	5.5	4.4	11.0	1.7	-2.0	6.4	-1.0
	-5.8	-1.0	3.5	-0.1	-1.3	9.7	7.1	-3.2
	1.2							
13 CN	-15.2	-5.5	0.3	-6.5	-3.8	-2.1	-0.8	-2.2
	-0.9	1.7	0.3	5.5	-1.3	-1.8	4.2	-0.6
	-5.5	-3.5	0.5	-1.0	-1.3	6.7	5.2	-4.9
	-1.0							
14 COCH ₃	-10.2	2.7	—	-4.0	0.0	2.5	—	-0.7
	0.8	6.0	5.5	9.0	1.7	2.5	7.7	—
	-2.0	3.1	—	0.8	0.7	10.0	7.5	1.2
	1.6							
15 COCl	-9.8	-1.0	2.6	-4.0	-5.0	-0.1	2.8	-1.4
	—	—	—	7.3	0.0	-3.2	4.1	0.3
	—	—	—	—	-1.7	7.7	6.6	0.7
	4.8							

^a ASIS values listed according to the numbering given in Fig. 1.

dipole moment of the aromatic substituent.

Although the solvation theory is the most accepted ASIS model at present, it neither accounts for induced shifts in molecules having an electric quadrupole moment but no dipole moment, nor does it explain why nonpolar solutes show significant ASIS.⁴ A variety of other models have been offered throughout the years. These alternative models, as well as the clustering model, have recently been reviewed and criticized, but no realistic alternative was presented.⁵

It is somewhat puzzling that although the clustering model was presented more than ten years ago, only limited attempts have been undertaken to confirm the generality of this model to other solutes than camphor.^{6,17}

In this paper we report a study on the ¹H ASIS of a variety of mostly ethereal solutes (Fig. 1) to test whether models, such as the clustering model, have a more general validity. The ¹H shift data were analyzed by a multivariate method in an effort to separate specific and general medium effects on the solute. The referencing problem will be discussed in view of the aim of the ASIS investigations.

STATISTICAL ANALYSIS

The data analysis of the two sets of ASIS data (internally or externally referenced data) is per-

formed by the use of principal component (PC) models. Since a complete description of the used data analysis package SIMCA has been reported earlier,⁷ the presentation will be limited to a summary.

The ASIS of 12 solutes measured in 15 solvents are entered into a data matrix, X , in such a way that every solute is represented by as many columns in the matrix as the number of measured positions (Table 1). Each solvent will thus be represented by a row of ASIS values. The data matrix X is then modelled as:

$$X = x_{ik} = \bar{x}_i + \sum_{a=1}^A b_{ia} t_{ak} + e_{ik} \quad (2)$$

with variables i , *e.g.* measured ASIS at the various positions and objects k , *e.g.* the different solvents. The \bar{x}_i term is the variable mean, b_{ia} is the loading equivalent to the regression coefficient and t_{ak} constitutes the component value for a solvent k . In comparison with eqn. (1), the solvent clustering model, the b_{ia} value corresponds to the site factor m , and the t_{ak} expresses the solvent effects S_L . It should be mentioned that the PC method calculates the b_{ia} values so that the sum of squares of b_{ia} is equal to 1. This means that only the relative values of b_{ia} are relevant.

The b and t values are obtained by minimizing the sum of the squared residuals, e_{ik} . The number of product terms *i.e.* the degree of parameteriza-

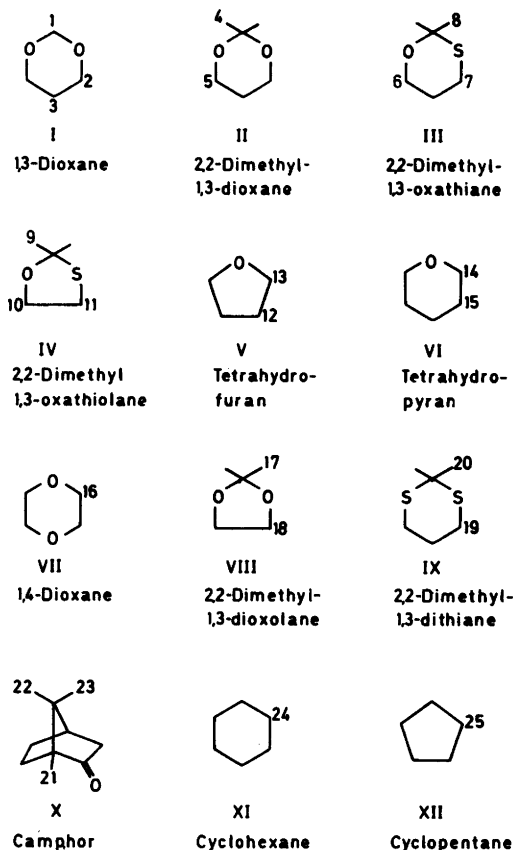


Fig. 1. Solutes used in the ASIS study. Arabic numbers refer to measured positions.

tion, A , is estimated by a cross-validation procedure.⁸ The average value, \bar{x}_i , of each descriptor is estimated (constitutes a model with $A=0$) and the residuals, $\bar{x}_i - x_{ik}$, are calculated. The sum of squares of these residuals are recognized as the total variation of the data set. Systematic information in the residuals is then accounted for by repeatedly adding product terms, $b_{ia}f_{ak}$ until only non-systematic noise remains.

The residuals after the last significant component are used to confirm the predictive ability of the model. The total sum of squares of the residuals, e_{ik} , is compared with the sum of squares of residuals for $A=0$, which gives the information content in the data expressed as percent (%) variation explained. In the same way the information content of each solvent or solute

can be estimated by calculating the sum of squares for that row/column (using a correctly parameterized model) compared with the sum of squares for that row/column for a model with $A=0$.

The ^1H chemical shifts were not scaled in this study.

RESULTS AND DISCUSSION

In an ASIS study, the solute is dissolved in two different media, an "inert" solvent (I) and an aromatic solvent (A). The chemical shift difference is:

$$\text{ASIS} = \Delta = \delta_x^I - \delta_x^A \quad (3)$$

where the δ_x 's are the chemical shifts relative to a suitable reference. The choice of "inert" solvent and shift reference is, however, far from trivial. Much of the confusion around the ASIS phenomenon can be ascribed to the referencing procedure.

The choice of inert solvent will in most cases be a compromise between the practical solubility of the solutes in the medium and the desire to use a truly inert solvent. An ideal inert solvent should possess a dielectric constant as near unity as possible, since polar solutes are submitted to a reaction field effect which increases with the dielectric constant of the medium.¹ Due to solute solubility limitations we have chosen carbon tetrachloride as inert solvent in this study. Moreover, it is one of the more widely used solvents in ASIS studies and a far better choice than, for instance, chloroform, which is also commonly used. It should be noted that the magnitudes of ASIS reported here are sufficiently large to make our results virtually unaffected by the choice of inert solvent. For camphor, the chemical shift difference measured in carbon tetrachloride and in the more inert cyclohexane is in the order of 1 Hz.³

The choice of referencing method is a more delicate problem. The most common procedure is the use of an internal standard such as TMS, cyclohexane or the hydrocarbon analog to the solute studied. It is known, however, that intrinsic medium shifts on the reference can vary substantially which makes many internal standards less suitable.^{5,9,17} A way to circumvent this

problem is the use of an intramolecular standard.³ In this case ASIS is defined as:

$$\text{ASIS} = \Delta_L = \Delta_{xm}^{\text{pos1}} - \Delta_{xm}^{\text{pos2}} \quad (4)$$

where $\Delta_{xm}^{\text{pos1}}$ is the solute medium shift for position 1 and $\Delta_{xm}^{\text{pos2}}$ is the medium shift for the proton signal used as the intramolecular reference. The advantage of this method is the elimination of the overall medium effect. In the study of ASIS of camphor, which formed the basis for the clustering model, this Δ -difference method was used.³ The most unaffected proton signal, the 10-methyl protons, was used as internal reference. Virtually the same result was then obtained using the hydrocarbon analog, camphane, as internal reference. The disadvantage with intramolecular standard is the necessity to have at least two moieties in the solute whose induced shifts can be measured. This method is also questionable when comparing different solutes, since in such cases the reference positions in each solute must be truly unaffected by the specific ASIS, Δ_L .

The most obvious solution to the referencing problem would be the use of an external reference. This would circumvent medium effects on the reference. To obtain reference independent ASIS one needs to eliminate bulk susceptibility effects, either by the use of a spherical inner capillary cell,¹⁰ or by measuring the shifts on two NMR instruments with different field geometry.¹¹ Earlier reported intrinsic medium shifts, obtained by various methods for the elimination of bulk effects, show some discrepancies.^{9,12,13} A correct determination of bulk effects is essential for the use of the external referencing procedure. Otherwise significant errors will occur in the ASIS values.

Several other modified referencing methods have been proposed but they have not gained as wide popularity as those mentioned above.^{5,13}

In the initial analysis we used an internal reference. TMS, and the ASIS can then be defined as:

$$\Delta = \Delta_{rm} - \Delta_{xm} \quad (5)$$

where Δ_{rm} is the difference in intrinsic medium effect on the reference and Δ_{xm} is the difference in intrinsic medium effect on the solute. Defined in this way, the observed ASIS is the difference in

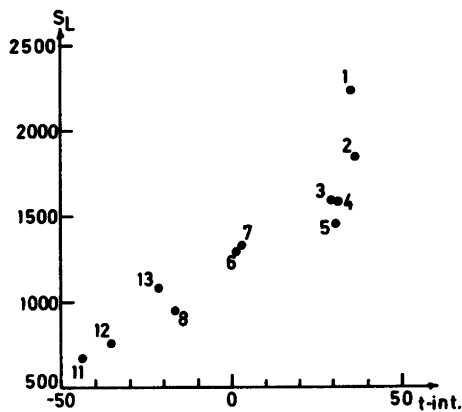


Fig. 2. A plot of the component values t against the solvent parameter S_L .³ Component values from eqn. (2), $A=1$, using internally referenced ASIS.

specific interaction (solvent clustering) on the reference and the solute, and in addition the difference in overall solvent effect (non-specific interaction) on the reference and the solute. Included in the Δ_{xm} term will then be any specific interaction as the ASIS defined by Laszlo (Δ_L). Bulk susceptibility effects can, of course, be ignored when using an internal standard.

According to a cross-validation procedure,^{7,8} one significant component explains 95 % of the variance of the experimental data. The standard deviation after applying the one component model is 1.3 Hz, *i.e.* approximately the same as the experimental error. Thus this model explains all systematic shift variation in the data. As shown in Fig. 2, the component values, t , are correlated to the solvent parameter, S_L ($r=0.92$, $n=11$), given by Laszlo.³ This solvent parameter was derived from the ASIS of camphor using the 10-methyl protons as intramolecular reference. The obtained correlation indicates that the differences in overall nonspecific solvent effects between the solutes used in this study and TMS are small.¹⁷ The 10-methyl protons are, as expected, poorly described by this PC model. Only 18 % of the variance is accounted for, *i.e.* the ASIS effect in this position is not very significant, as mentioned by Laszlo. The observed deviations observed in Fig. 2 can be ascribed to the different referencing procedures used. Measured in this way, the non-polar solutes, cyclopentane and cyclohexane, as well as the non-dipolar 1,4-

Table 2. The loadings b obtained from the two principal components data analysis.

Position ^a	$b(\text{int})^b$	$b_1(\text{ext})^c$	$b_2(\text{ext})^c$
1	-0.20	-0.21	-0.04
2	-0.29	-0.21	-0.23
3	-0.34	-0.22	-0.35
4	-0.07	-0.19	0.23
5	-0.24	-0.22	-0.11
6	-0.22	-0.20	-0.10
7	-0.27	-0.21	-0.20
8	-0.07	-0.18	0.22
9	-0.06	-0.18	0.25
10	-0.33	-0.23	-0.29
11	-0.31	-0.23	-0.25
12	-0.20	-0.21	-0.03
13	-0.09	-0.19	0.20
14	-0.06	-0.18	0.24
15	-0.13	-0.20	0.11
16	-0.20	-0.21	-0.03
17	-0.06	-0.17	0.24
18	-0.29	-0.21	-0.22
19	-0.30	-0.21	-0.26
20	-0.09	-0.18	0.18
21	-0.03	-0.17	0.31
22	-0.17	-0.20	0.03
23	-0.14	-0.19	0.09
24	0.11	-0.19	0.14
25	-0.12	-0.19	0.12

^a Position numbers according to Fig. 1. ^b b -Values using internally referenced shifts, eqn. (2), $A=1$. ^c b -Values using reference-independent shifts, eqn. (2), $A=2$.

dioxane will show small but significant ASIS. This observation supports the earlier suggestions that TMS has a slight tendency to interact with aromatic solvents.^{9,17}

In Table 2 the loadings, b , are listed according to eqn. (2). The b -values correspond to the site factors, m , introduced earlier. As expected, systematic intramolecular differences between the "site" factors b are noticed. The b -values of the 2-methyl groups are the smallest in magnitude and almost the same for all solutes, the non-polar solutes have intermediate b -values, while all methylene protons have large b -values. Hence, the observed ASIS can be modelled as a product of a t -value specific for the solvent and a b -value dependence on the solute and the position within the solute.

The problem associated with the use of an internal reference, *i.e.* that it does not provide a

fixed zero, has been realized earlier,⁵ but this fact is usually ignored. Therefore, as a complement to the data analysis based on shift data referenced to internal TMS we also performed a PC analysis on reference independent ¹H data, where bulk susceptibility effects on the reference were eliminated (see Experimental). The ASIS data defined in this way were described by two PC components, explaining 99 % of the variance (S.D. 1.2 Hz). The major component, t_1 , which accounts for 93 %, is strongly correlated to the intrinsic medium shifts of TMS reported by Maciel⁹ ($r=-0.98$ $n=7$, Fig. 3). The constancy of the b_1 -values obtained for all positions means that all positions are affected in the same way and this supports the conclusion that the first component can be considered as an overall medium effect. The second component, t_2 -values, is related to the t -values in the former analysis using TMS as internal standard ($r=-0.93$ $n=15$, Fig. 4). The b_2 -values show the same behaviour as the b -values in the earlier analysis.

Recently an ASIS study of p - X - benzaldehydes in a variety of alkylated benzenes was reported.¹⁷ Poor correlations were found for the ASIS of the formyl protons in these aldehydes and the deviations were of a magnitude (6–30 Hz) that was difficult to explain in terms of solute–solvent interactions. The authors then suggested that the only "logical conclusion" is that the general solution of the ASIS is a sum of two terms, one factorable into solute and solvent parameters and the other dependent on the solvent. The first term was assigned to the intrinsic ASIS of the studied position (mS_L) and the second to the intrinsic medium effect on the TMS protons used as internal reference.

The models derived in this study are in agreement with their findings. We also show that this approach can be extended to a large number of rather non-polar solutes but more important, to a more complete set of aromatic solvents.

CONCLUSION

We can conclude from the two performed analyses that a general medium effect is the major contribution to the difference between internally and externally referenced ASIS. It is also obvious that the overall medium effects on the solutes used in this study and TMS roughly

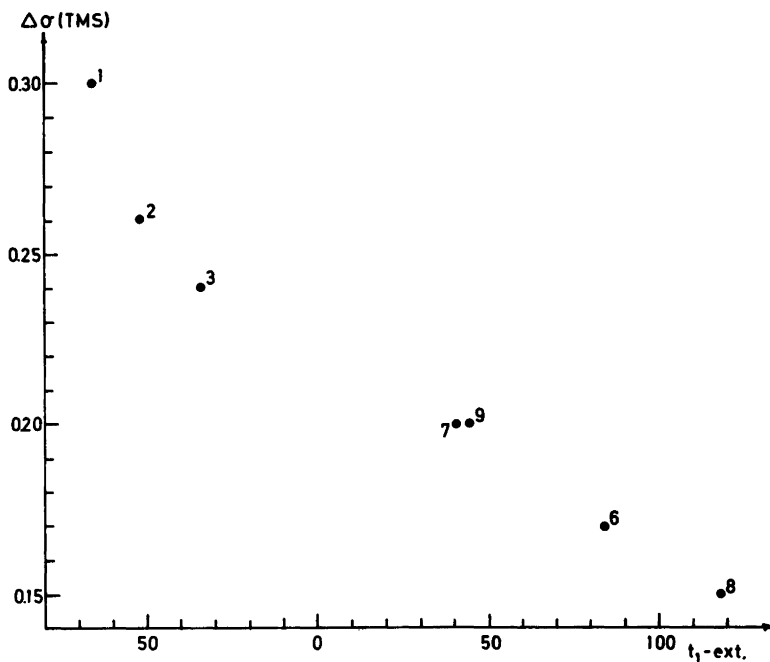


Fig. 3. A plot of the major component t_1 against the intrinsic medium shift on TMS.⁹ Component values from eqn. (2), $A=2$, using reference-independent data.

cancel, leaving the "specific" interaction as defined by Laszlo³ as the remaining contribution when internal TMS is used. Our results also support the opinion that the choice of internal reference can be critical for the ASIS magni-

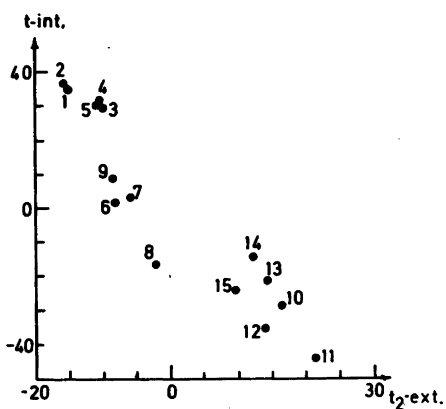


Fig. 4. A plot of the component values t using internally referenced data against the minor component t_2 using reference-independent data.

tudes. In comparative studies, the use of internal reference should be limited to such solutes where the differences in overall solvation is negligible or constant. The reported results are in favor of the solvent clustering model where the "specific" ASIS is a product of a substrate specific site factor and a solvent parameter.

The given interpretation of the solvent parameter, S_L ,³ as composed of a molecular volume and an electronic effect seems reasonable.¹⁷ Considering the importance of the electronic effect, the alkylbenzenes do have very similar t -values and this observation is also valid within the halobenzenes and acceptor-type aromatics (Table 3). Hence, the same grouping of the solvents is found in this study as in our study of substituent chemical shifts of monosubstituted benzenes.¹⁴

The obvious choice of reference, to qualitatively and quantitatively understand solvent effects such as the ASIS phenomenon, would be to use a reference independent method. However, the use of an external reference cannot be expected to gain a wide popularity in practical work, since

Table 3. Component values t from the two principal components data analysis.

Aromatic solvent		$t(\text{int})^a$	$t_1(\text{ext})^b$	$t_2(\text{ext})^b$
1	H	-34.9	-65.2	-15.1
2	CH ₃	-36.3	-51.9	-15.8
3	1,4-(CH ₃) ₂	-29.4	-34.0	-10.0
4	1,3-(CH ₃) ₂	-31.8	-39.5	-10.5
5	1,3,5-(CH ₃) ₃	-30.7	-26.9	-10.8
6	Br	-1.6	84.1	-8.3
7	Cl	-3.0	40.7	-6.0
8	1,2-(Cl) ₂	16.7	118.1	-2.1
9	1-Cl,2-CH ₃	-8.9	44.9	-8.6
10	1-CH ₃ ,2-NO ₂	28.7	-3.3	16.3
11	NO ₂	44.1	-21.6	21.2
12	CN	35.3	22.1	13.7
13	CHO	21.4	-60.7	14.3
14	COCH ₃	14.3	-29.9	12.1
15	COCl	24.1	21.2	9.5

^a t -Values using internally referenced shifts, eqn. (2), $A=1$. ^b t -Values using reference-independent shifts, eqn. (2), $A=0$.

the major structural information of ASIS lies in the minor second component. Therefore, if the aim of the work is to find structural information, and the solutes are structurally similar, we would recommend the use of an intramolecular reference if possible. For quantitative structural investigations, when the non-specific solute-solvent interaction do not vary substantially between the solutes studied, the use of an internal reference such as TMS or cyclohexane can be adequate.

The use of data analytical methods such as the PC data analysis technique is, of course, strongly recommended whatever the aim of the investigation is. Handling problems of this kind, where one has a desire to evaluate independent effects, the PC-method is ideal since, by definition, the obtained effects or component values will be truly orthogonal. Moreover, the PC model has an attractive form similar to many physical or semi-empirical models such as the mentioned solvent clustering model, Hammett equations *etc.*^{15,16}

EXPERIMENTAL

¹H NMR spectra were recorded on a 60 MHz Perkin Elmer R-10 NMR spectrometer. Carbon tetrachloride was used as "inert" solvent in all measurements. The aromatic solvents were all commercially available and of high purity. Our

efforts to minimize solute-solvent peak overlap partly determined the selection of aromatic solvents.

The synthesis of the heterocyclic solutes has earlier been published by one of us.⁴ The remaining solutes were all commercial reagents (E. Merck AG, *p.a.*). The solute concentrations were 2 % (w/v). All NMR spectra were measured at 306.4 K.

The ASIS values are given as (CCl₄)-(aromatic solvent) using TMS as an internal standard. Reference-independent values were obtained as earlier reported,¹² having a 4 % TMS solution in the outer tube and neat TMS in an inner capillary. Bulk susceptibility effects were eliminated by having a spherical interphase between sample and reference. The reliability of the method was tested by interchanging the sample and reference standard. With such a procedure, the difference between observed and true shifts was shown to be <1 Hz at 60 MHz.

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