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On the Correlation Between Solvent Scales and Solvent-induced ^{13}C NMR Chemical Shifts of a Planar Lithium Carbanion. A Multivariate Data Analysis Using a Principal Component–Multiple Regression-like Formalism

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The solvent influence on the ^{13}C NMR chemical shifts of indenyllithium has been measured. A principal component data analysis showed that the shift matrix is described to 80–90 % by a two-component model. Only 58 % of the systematic variation in the shift data could be explained by the generally accepted solvent scales as shown by a partial least squares analysis. Although the π^* scale seems to be the most appropriate, no single scale has such high relevance in this complex solute–solvent system that it could be of a practical predictive utility. However, for subsets of the solvent matrix, single solvent parameter correlations can give acceptable results.

It is well known that the physico-chemical properties of a solute are influenced by the solvent and that the theories for the nature of these interactions are quite insufficient. This lack of an accurate theory is one of the reasons for the large number of empirical solvent "polarity" scales which appear in chemical literature.[1]

In order to describe kinetic, thermodynamic and spectroscopic data, single solvent scales as well as multiparameter equations have been applied.[1b,d,2–7] Multiple regression using a linear combination of two or several empirical scales usually gives better correlations than models with single scales but demands more data points (*i.e.* data from a large number of solvents) if any conclusions are to be reached from the regression coefficients. Furthermore, if the scales are highly correlated to each other, the ratio between the regression coefficients becomes very unreliable.[8,9] A way to overcome the latter problem is to use uncorrelated variables in the multiple regression analysis. These variables can be extracted from the correlated ones (*i.e.* the empirical solvent scales) with the aid of factor analysis[10] or principal component analysis.[11,12] The uncorrelated vectors are then successively calculated from the data set. The first vector describes the largest amount of variation in the data, while the second accounts for the largest possible amount in the remaining data, and so on. Several applications of factor analysis of solvent effects have recently appeared in the literature.[2c,10,12c,13]

The present work concerns the solvent effects on the ion pair structure and the charge distribution of indenyllithium (*I*) as reflected by the ^{13}C NMR chemical shifts. We have chosen this conjugated planar system as a suitable model because of its rigidity and stability, and also due to the high sensitivity of the ^{13}C chemical shifts of this anion towards changes in solvent, temperature and cation.[14,15] By going from a solvent with low solvating ability to one with high solvating ability, the external solvation of the ion pair will increase and/or the ion pair structure will be altered from a contact ion pair (c.i.p.) to a solvent separated ion pair (s.s.i.p.) and/or free ions.[14] The existence of an ion pair equilibrium (1)[16,17] has been shown in many investigations.[18–22]

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$$\underset{\text{c.i.p.}}{A^-C^+} \rightleftharpoons \underset{\text{s.s.i.p.}}{A^-||C^+} \rightleftharpoons \underset{\text{free ions}}{A^- + C^+} \quad (1)$$

Since the cation in *I* has its average position above the five-membered ring in the c.i.p. structure,[14a,15a] an increase in cation solvation causes a redistribution of negative charge to the six-membered ring. This change is a consequence of a decreased π-polarization of negative charge towards the five-membered ring when the cation becomes more solvated as indicated by the ^{13}C chemical shifts.[14,15a]

Although the theory for ^{13}C chemical shielding is quite intricate,[23] a simple correlation of 160 – 180 ppm/e$^-$ between changes in sp^2 carbon chemical shifts and π-electron density is often noticed.[24-27]

The dominating factor in the solvation of indenyllithium and similar systems, is the Coulombic forces between the cation and solvent dipoles.[19a,21] The theoretical basis for treating ion – solvent electrostatic interactions is the "sphere in continuum model",[28] developed by Born[29] and Bjerrum and Larsson.[30] In a simplified treatment of this model, the logarithm of the dissociation constant for the dissociation of the contact ion pairs into free ions, is linearly related to the inverse of the dielectric constant of the medium.[31]

However, this model has several defects. Since the medium is assumed to be structureless, coordination of ions and ion pairs with solvent molecules is neglected. This is a serious approximation, especially with small and highly polar solvent molecules. Aggregation effects and the size and the shape of the ions are other structural factors which are not accounted for. Furthermore, dielectric saturation of the solvent and charge density redistribution in ions and solvent molecules are ignored. In addition, hydrogen bonding with suitable solvent, π-complexing with aromatic solvents[32] *etc.*, may have importance in the solvation processes. Hence, the dielectric constant alone cannot be used to explain the observed induced changes in charge density and ion pair structure.[21,22]

In this work, we wish to present an empirical principal component (PC) model, which describes the ^{13}C chemical shifts of *I* as a function of the solvent. Our choice of solvents is determined by their inertness toward strong bases and by the solubility of the ion pair, but also by the existence of data in the empirical solvent matrix. The predominating factors causing ion pair solvation are discussed on the basis of the parameters in the PC model. We have also examined the correlation between the chemical shift data and the empirical solvent scales. This study was performed by the use of a partial least squares (PLS) data analysis, *i.e.* a method similar to PC analysis of the chemical shift data but including a multiple regression-like formalism. Finally, the PLS method was used to predict chemical shift differences of *I* in two additional solvents, not included in the initial data analyses.

EXPERIMENTAL

Solvent purification and sample preparation. Anisole was refluxed over Na and distilled. The remaining ethers were refluxed over an Na/K alloy and finally distilled. All ethers were stored over Na-wire. The remaining solvents were refluxed over CaH_2, distilled, and stored over molecular sieves, except for dimethylsulfoxide which only was treated with molecular sieves.

I was obtained by adding an equivalent amount of n-BuLi (90 % in c-hexane) to a cooled solution of indene in the actual solvent. However, the anion could not be prepared directly in dimethyl formamide (DMF) or acetonitrile (AcN) because of the high reactivity of these solvents towards n-BuLi. Therefore *I* was prepared in diethylether (DEE) followed by evaporation of the ether by a stream of argon and finally addition of DMF or AcN. All work was performed under argon atmosphere.

NMR measurements and signal assignments. All spectra were obtained at 62.89 MHz on a Bruker WM-250 NMR spectrometer. The chemical shifts were measured relatively internal c-hexane,[33] and adapted to the TMS scale using δ (c-hexane)= 27.7 ppm. (Table 1.) The probe temperature was 25 ± 1 °C.

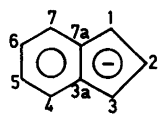
The assignment of the NMR signals of *I* in the solvents 3, 5, 6 and 9 has earlier been reported.[14a,34] In the remaining solvents, the signals of *I* were assigned by comparing the signal intensities and by the aid of standard decoupling techniques.

Before the PLS analysis was performed using all solvents, we found it necessary to undertake a concentration study of *I*. A comparison between the measured shift data and the calculated ones for anisole and dioxane might be erroneous since the ^{13}C shift values were obtained at much lower concentration of *I*. Three representative solvents were used in the investigation of the solvent dependence, TEA, THF, HMPA. The concentrations varied in the range of 0.04 – 1 M exept for TEA where solubility restrictions only allowed a maximum concentration of 0.4 M (Table 1). Only very small differences were observed by varying the concentration. This means that, if existent,[19b] stacking of

Table 1. ^{13}C NMR chemical shifts of indenyllithium (*I*) in various solvents.[a,b]

No.	Solvent[c]	Conc. (M)	C-1,3	C-2	C-3a,7a	C-4,7	C-5,6	$\Delta\delta_{av.}$
1	TEA	0.04	92.71	114.58	126.60	121.16	117.53	
		0.26	92.72	114.55	126.57	121.20	117.51	
		0.40	92.71	114.54	126.56	121.18	117.49	
2	i-Pr_2O	0.22	92.72	114.69	126.57	121.37	117.48	
			(0.00)	(0.14)	(0.00)	(0.17)	(−0.03)	0.05
3	Et_2O	0.27	92.13	115.42	128.14	120.66	116.13	
			(−0.59)	(0.87)	(1.57)	(−0.54)	(−1.38)	−0.11
4	THP[d]	0.23	91.69	115.38	128.78	120.30	115.24	
			(−1.03)	(0.83)	(2.21)	(−0.90)	(−2.27)	−0.35
5	DME	0.26	92.09	115.71	129.13	120.11	114.36	
			(−0.63)	(1.16)	(2.56)	(−1.09)	(−3.15)	−0.38
6	THF	0.04	91.66	115.55	129.72	119.76	114.25	
		0.25	91.68	115.59	129.76	119.66	114.06	
			(−1.04)	(1.04)	(3.19)	(−1.54)	(−3.45)	−0.52
		0.40	91.70	115.63	129.80	119.63	114.00	
		1.0	91.70	115.61	129.68	119.55	113.88	
7	AcN	0.20	93.60	118.5[e]	130.86	119.00	112.49	
			(0.88)	(4.0)	(4.29)	(−2.20)	(−5.02)	−0.01
8	Pyridine	0.26	94.83	119.43	132.16	119.87	112.82	
			(2.11)	(4.88)	(5.59)	(−1.33)	(−4.69)	0.92
9	DMSO	0.28	94.12	118.93	130.81	118.79	111.71	
			(1.40)	(4.38)	(4.24)	(−2.41)	(−5.80)	−0.08
10	DMF	0.20	93.60	118.48	131.40	118.48	111.19	
			(0.88)	(3.93)	(4.83)	(−2.72)	(−6.32)	−0.30
11	HMPA	0.05	93.29	118.02	131.37	118.15	110.19	
		0.20	93.24	117.98	131.33	118.15	110.19	
			(0.52)	(3.43)	(4.76)	(−3.05)	(−7.32)	−0.75
		1.0	93.27	118.04	131.31	118.15	110.27	
12	Anisole	0.07	93.09	115.65	127.60	121.3[e]	117.36	
			(0.37)	(1.10)	(1.03)	(0.1)	(−0.15)	0.4
13	Dioxane	0.05	92.01	115.59	130.44	119.86	114.52	
			(−0.71)	(1.04)	(3.87)	(−1.34)	(−2.99)	−0.14

[a] The chemical shifts were measured relatively internal c-hexane and adapted to the TMS scale using δ (c-hexane) = 27.7 ppm. [b] Values within parenthesis refer to differences in chemical shifts from TEA. [c] 1 = triethylamine, 2-diisopropyl ether, 3 = diethyl ether, 4 = tetrahydropyran, 5 = 1,2-dimethoxyethane, 6 = tetrahydrofuran, 7 = acetonitrile, 9-dimethylsulfoxide, 10 = *N*,*N*-dimethylformamide, 11 = hexamethylphosphoric triamide. [d] Measured relatively the methylene carbon in n-butane, with $\delta(-CH_2-) = 25.67$ ppm on the TMS scale. [e] Center of a solvent signal.



ion pairs is not reflected in the observed ^{13}C chemical shifts.

METHODS AND RESULTS

Solvent descriptors and ^{13}C chemical shift variables. Our choice of empirical solvent scales (Table 2) is mainly limited by the existence of at least eight data values per scale. In our data matrix, which is formed by eleven solvents and twelve solvent parameters, there are fourteen missing data values. We have tried to include solvent properties with expected relevance for the solvation process and thus tried to avoid parameters such as boiling points, molecular weights, viscosities, *etc.*

Although the dielectric constant, the dipole moment and the refractive index are bulk properties not representing the microscopic region, they have been included in the data analysis. Attempts to

Table 2. Empirical solvent scales.

No.	Symbol, name	Method, system	Solvents	Ref.
1	B	Difference in the IR stretching wave numbers of the free and hydrogen bonded OH-group in C_6H_5OH in CCl_4. Some LFER extensions are made, using data from similar measurements on CH_3OH and CH_3OD	All	35
2	pK_{HB}	^{19}F NMR of *p*-FC_6H_4OH in CCl_4 using *p*-$FC_6H_4OCH_3$ as an internal reference. The formation constant for the hydrogen-bonded complex *p*-FC_6H_4OH...Base is calculated. LFER extensions are applied, using calorimetric and IR data, and measurements on other alcohols.	No. 5 missing data	36
3	$\Delta\nu_D$	Difference in IR adsorption (wave number) of the OD-group in CH_3OD in pure solvent relative to that in benzene	No. 11 missing data	37
4	DN	Calorimetrically measured ΔH of the reaction $SbCl_5$ + Levis base with 1,2-dichloroethane as reference solvent	Nos. 2,4,12 missing data	38
5	$\Delta\nu_A$	Difference in the IR wave number of the C=O absorption in $C_6H_5COCH_3$, in the pure solvent relative to that in benzene	Nos. 8,10,11 missing data	37
6	AN	^{31}P NMR of $(C_2H_5)_3PO$ in pure solvents with hexane as reference solvent	Nos. 1,2,4,12 missing data	38
7	$E_T(30)$	UV/visible absorption spectroscopy. Exitation energy of a pyridinum-*N*-phenoxide betaine dye in pure solvents	No. 4 missing data	1b,c,39
8	π^*	UV/visible absorption spectroscopy. The wave numbers of seven indicators (*e.g.* 4-nitroanisole, *N,N*-diethyl-3-nitroaniline *etc.*) in pure solvents are forming a primary data set, which is extended using LFER and data from other indicators. Combinations of solvents and indicators with possible hydrogen bonding interacions are avoided	All	40
9	lg *P*	The logarithm of the octanol-water partition coefficient	Nos. 2,4,5 missing data	41
10	ε	Dielectric constant	All	standard handbooks
11	μ	Dipole moment	All	standard handbooks
12	n_D	Refractive index	All	standard handbooks

correlate these bulk solvent properties to solvation processes are frequently made.[1e]

The first four scales (Table 2) can be considered as representing solvent basicity, the next two scales as representing solvent acidity and the remaining ones as measures of "polarity".

The trend in the ^{13}C NMR chemical shifts by charging solvents, starting from TEA, is a decreased shielding in the five-membered ring and an increased shielding in the C4–C7 positions (Table 1). This trend is supposed to reflect changes in π-electron distribution caused by a varying cationic field. This proposal is supported by the observation that the average chemical shift ($\Sigma\Delta\delta/n$) is almost constant for most ethers, in spite of significant shift changes at individual positions.[25b] However, a deviating behaviour is noticed for some solvents, especially the anisotropic ones.

The ambition of this work is to derive a solvent scale which can be useful as a guide for the generation of delocalized anions. Hence, we want to exclude superimposed solvent–anion interactions. Therefore, in addition to a matrix formed by the relative chemical shift differentials referenced to internal cyclohexane, we have also analyzed a similar matrix where the $C_{5,6}$ chemical shift value was taken as an intramolecular reference (Table 3). Numerous studies in this field have confirmed that for aprotic *n*-electron donor solvents, the dominant role for the physical and chemical properties of organoalkali species can be ascribed to specific cationic solvation.[19,21] A more "polar" solvent would solvate the cation more effectively, producing an increase in the average interionic distance due to the weakening of the Coulombic attractions between anion and cation. Thus, an increased cation solvation will be the major cause for the generation of delocalized anion structures. The concentrations of *I* in the solvents 1–11 were 0.2–0.3 M, except for anisole and dioxane where, due to the limited solubility, the concentrations were 0.07 and 0.05 M, respectively. The low solubility made us exclude these two solvents in the first analysis, but they were used as test solvents for chemical shift predictions in the partial least squares analysis.

Data analysis. For a data matrix with variables i, *e.g.* chemical shifts, and objects *k*, *e.g.* solvents, the data y_{ik} can be described by the model

$$y_{ik} = \alpha_i + \sum_{a=1}^{A} \beta_{ia}\theta_{ak} + \varepsilon_{ik} \qquad (2)$$

where α_i is the variable mean, β_{ia} the loadings (corresponding to regression coefficients) and θ_{ak} are the component values corresponding to the solvent scales. The term ε_{ik} contains the remaining data variation *i.e.* model errors, and errors of measurements.

We have used the SIMCA program package for this principal component (PC) analysis. The rank of the matrix, A, is determined on a statistical basis using a cross–validation (CV) procedure.[42] A complete description of the data program package has earlier been reported.[12,43]

Initially a PC analysis was performed on the data matrix containing the ^{13}C chemical shift differentials referenced to cyclohexane, *i.e.* five variables measured in eleven solvents. A two-component model

Table 3. The ^{13}C NMR chemical shift differences between the $C_{5,6}$ signal and the four remaining signals of indenyllithium (I).

No.	Solvent	C-1,3–C-5,6	C-2–C-5,6	C-3a,7a–C-5,6	C-4,5–C-5,6
1	TEA	−24.79	−2.96	9.06	3.69
2	i-Pr_2O	−24.76	−2.79	9.09	3.89
3	Et_2O	−24.00	−0.71	12.01	4.53
4	THP	−23.55	0.14	13.54	5.06
5	DME	−22.27	1.35	14.77	5.75
6	THF	−22.38	1.53	15.70	5.60
7	AcN	−18.89	6.01	18.37	6.51
8	Pyridine	−17.99	6.61	19.34	7.05
9	DMSO	−17.59	7.22	19.10	7.08
10	DMF	−17.59	7.29	20.21	7.29
11	HMPA	−16.95	7.79	21.14	7.96
12	Anisole	−24.27	−1.71	10.24	3.94
13	Dioxane	−22.51	1.07	15.92	5.34

Table 4. Solvent θ values and F test values from principal component (PC) analysis of ^{13}C chemical shift data of indenyllithium (*I*).

No.	Solvent	Intermolecular chemical shift reference[a] θ_1	θ_2	F[c]	Intramolecular chemical shift reference[b] θ_1	θ_2	F^d
1	TEA	5.32	−0.70	1.0	9.80	−0.80	0.60
2	i-Pr_2O	5.28	−0.81	0.85	9.63	−0.82	0.45
3	Et_2O	3.19	0.00	0.34	6.08	0.22	0.94
4	THP	2.30	0.81	0.90	4.30	0.83	0.49
5	DME	1.27	0.83	0.33	2.08	0.62	1.0
6	THF	0.78	1.43	1.5	1.47	1.27	0.42
7	AcN	−2.73	−0.47	0.45	−4.69	−0.28	3.1
8	Pyridine	−3.58	−2.17	2.6	−6.15	−0.25	0.12
9	DMSO	−3.54	−0.58	1.4	−6.55	−0.85	0.48
10	DMF	−3.94	0.31	0.20	−7.33	−0.06	0.12
11	HMPA	−4.34	1.36	1.4	−8.64	0.13	3.3

[a] The chemical shifts are measured using c-hexane as reference compound. [b] The chemical shifts are referenced to the $C_{5,6}$ NMR signal of *I*. [c] *F*-test value, used in assigning the solvents to the class described by the PC model. The F values are compared to the critical value $F_{crit} = 3.0$ at the 95 % confidence level. (Degrees of freedom = 3.24). [d] $F_{crit} = 3.6$ (D.F. = 2.16).

($A = 2$) was found to be adequate by CV, accounting for 79 % of the original data standard deviation.

If the residual variance of one object (solvent) is compared with the total residual variance by means of an *F-test*, one gets a measure of how well the object is represented by the model (Table 4). It is found that pyridine is a "borderline" solvent. This is in accordance with the deviating behaviour noticed above for the anisotropic solvents. As the next step, the PC analysis was repeated using the four chemical shift variables earlier mentioned, *i.e.* having the $C_{5,6}$ carbon as an intramolecular reference. Again, a two-component model was obtained which described 94 % of the standard deviation of the four variables. This model has a reduced standard deviation compared with the model resulting from the first analysis. However, it should be noted that there is a good correlation between the θ scales of the models (Table 4).

Partial least squares analysis (PLS). A PC analysis of physicochemical data, followed by a multiple regression (MR) analysis of the latent variables θ_{ak} and biological activity data as dependent variables, has been shown to be a useful approach to multivariate data analysis problems.[44] One of the advantages of this analysis method lies in the fact that the problem using correlated variables and a limited object−variable ratio (at least 3−4 to avoid chance correlation[9]) can be eliminated.

In the PLS method, the PC analysis and the MR analysis are accomplished in one step. The method has all the advantages of an ordinary PC-MR routine, combined with a better predictive and classifying ability.[45]

The data set is divided into two blocks, one *y*-block containing the dependent variables, *e.g.* chemical shift differences, and one *x*-block containing the independent variables, *e.g.* solvent scales. The two blocks are described by one PC-like model each, (3) and (4), *cf.* eqn. (2).

$$y_{ik} = \alpha_i + \sum_{a=1}^{A} \gamma_{ia}\eta_{ak} + \varepsilon_{ik} \quad (3)$$

$$x_{jk} = \alpha_j + \sum_{a=1}^{A} \gamma_{ja}\xi_{ak} + \varepsilon_{jk} \quad (4)$$

The two blocks are related to each other by means of the latent variables η and ξ (5), where ρ is the least square regression coefficient.

$$\eta_{ak} = \rho_a\xi_{ak} + e_{ak} \quad (5)$$

This relationship is utilized in the PLS prediction model (6).

$$y_{pred.,ik} = \alpha_i + \sum_{a=1}^{A} \gamma_{ia}\rho_a\xi_{ak} \quad (6)$$

The relevance of each *x*-variable in describing the data variation of the matrix *Y* is expressed in its γ value.

Before the PLS analysis was performed, the missing values in the solvent matrix were calculated by

Table 5. Solvent component values and F-test values from partial least squares (PLS) analysis of the empirical solvent data and the chemical shift data of indenyllithium (*I*).

No.	Solvent	η^a	ξ^b	F^c
1	TEA	+9.79	+3.34	0.66
2	i-Pr_2O	+9.61	+2.59	2.3
3	Et_2O	+6.08	+2.81	0.20
4	THP	+4.31	+1.57	0.15
5	DME	+2.09	+1.03	0.13
6	THF	+1.50	+0.93	0.47
7	AcN	−4.70	−2.00	0.06
8	Pyridine	−6.15	−0.83	3.5
9	DMSO	−6.57	−4.47	4.5
10	DMF	−7.33	−2.79	0.03
11	HMPA	−8.63	−2.19	2.2

[a] Principal component of the chemical shift data. (*Cf.* θ_1 in Table 1). [b] Principal component of the empirical solvent data. [c] *F*-test value, used in assigning the solvents to the class described by the ξ model. The *F* values are compared to the critical value $F_{crit}=3.0$ (D.F. 3.27).

Table 6. γ values of the empirical solvent scales from the partial least squares analysis of chemical shift data of indenyllithium (*I*)[a].

	B	pK_{HB}	$\Delta\nu_D$	DN	$\Delta\nu_A$	AN
γ	−0.036	0.26	0.042	−0.089	0.34	0.33
	$E_T(30)$	π^*	lg*P*	ε	μ	n_D
γ	0.37	0.40	−0.31	0.34	0.38	0.25

[a] A value close to unity indicates a high relevance for the solvent scale in describing the ^{13}C chemical shift data.

Table 7. Partial least squares prediction shift data of indenyllithium (*I*) in anisole and dioxane.

No.	Solvent	η	ξ	$Y_{1,pred}$[a]	$Y_{2,pred}$	$Y_{3,pred}$	$Y_{4,pred}$
12	Anisole	+3.2	+1.3	−22.4	0.95	13.8	5.2
13	Dioxane	+3.5	+1.4	−22.6	0.65	13.5	5.1

[a] $y_{i,pred}$ represents the predicted chemical shift data (referenced to $C_{5,6}$) of *I*. (*Cf.* the measured values in Table 3.)

means of a PC model. The SIMCA program tolerates missing data in the matrix. Hence a PC model can be determined using an iterative procedure. A significant two-component model resulted from the SIMCA study of the solvent matrix. The first component dealt mostly with scales Nos. 5−11, while the second component was associated to Nos. 1−4. The refractive index was poorly described.

The PLS analysis of empirical solvent data in the *x*-matrix and chemical shifts relative to the $C_{5,6}$ signal in the *y*-matrix yielded a one-component model, explaining 58 % of the residual standard deviation in the *y*-matrix (Table 5). In this analysis the RSD in the *x*-data was reduced by 23 %. The γ values of the *x*-variables indicates that solvent scales Nos. 5−8, 10 and 11 are the most important when representing the *y*-block data, although of limited relevance (Table 6). In the second step, the *x*-variable data for anisole and dioxane were included followed by calculation of their η, ξ and *y*-values (Table 7). A comparison between the experimental shift data in the two solvents with those calculated (Tables 3, 7) shows an acceptable prediction.

Summary of results. A. The chemical shift matrix *y* is described to 80 or 94 % of the SD (5 and 4 variables, respectively) by a PC model.

B. The same chemical shift matrix *y* (4 variables) is described only to 58 % by a correlation model

with various solvent scales included as independent variables in a PLS model. Hence about 30 % of the systematic variation in y is not modelled by a relation with the solvent scale matrix x.

DISCUSSION

As mentioned earlier, it is well established that solvent coordination to the cation is of a major importance for the solvation and structure of the ion-pair. Moreover, it has been found from NMR studies, as well as from spectrophotometric studies, that the spectrum of the solvent-separated structures is mainly unaffected by a solvent change.[21] This means that solvent effects that are not affecting the anion – cation distance are of minor importance for the carbon shieldings, *i.e.* effects like solvent anisotropy, van der Waals and electric field contributions, acting on the anion.

It could possibly be argued that a ^{7}Li NMR study would be more appropriate than the present one to probe cation solvation. However, attempts to use ^{7}Li chemical shifts in this sense have been somewhat unsuccessful.[46] This can in fact be expected, since the very similar magnitude of the diamagnetic and paramagnetic screening constants for ^{7}Li allows for ring currents and other anisotropy effects to exercise a major influence on the chemical shifts.[46]

From above, one would intuitively expect some correlation between solvent basicity scales, *i.e.* Nos. 1 – 4, and the principal component(s) of the shift matrix. However, for the complete solvent matrix this is not observed, instead θ_1 which is the dominating "effect", has a moderate correlation to the "acicity" or "polarity" scales. Using the θ_1 values 1.7 and 8.0 for dioxane and anisole, respectively, the best fit to θ_1 is found for π^*, $r = 0.86$, $n = 13$. If anisole is excluded, the correlation is improved, $r = 0.96$, $n = 12$ (Fig. 1).

Future studies of other carbanions will show if the θ_1 scale has a wider generality. It can be mentioned that an identical trend, as the one indicated by our θ_1 values, has been found in an electron absorption study of 1,3-diphenylbut-1-enyllithium. The s.s.i.p. – c.i.p. ratio increased by going from from i-$Pr_2O \approx Et_2O$, dioxane, THP, THF $\approx$ DME, DMSO, HMPA.[22] The second component, θ_2, does not show any acceptable correlation to any of the empirical solvent scales, and can be considered as specific for the complex system at hand.

Another conclusion that can be reached from this study is that ion pair solvation cannot successfully be explained by a single solvent effect (θ's) nor a solvent scale derived in structurally different systems, at least not for such a variety of solvents. It has been suggested that the Brønsted pK_a values should be of utility when studying the solva-

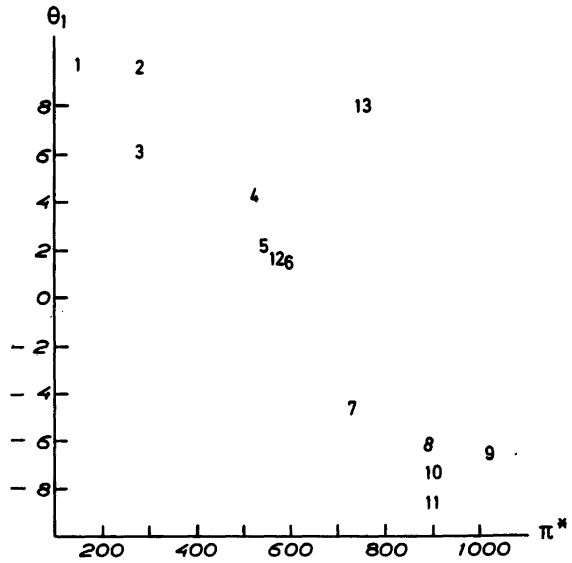


Fig. 1. Solvent θ_1 values from principal component analysis of ^{13}C NMR data of indenyllithium (*I*) are plotted against solvent π^* from solvatochromic shift data.

tion effects in various ethers.[18b] An acceptable correlation was indeed found in the ethereal subset between the θ_1 scale and a basicity scale, the pK_a scale of Arnett and Wu.[47] For the ethers 2,3,4,6,12,13 a correlation coefficient $r=0.77$ was achieved. This correlation was improved by excluding anisole, $r=0.93$.

Although *I* exists as a c.i.p. or tight ion pair in Et_2O the chemical shifts in TEA and i-Pr_2O are even more extreme. The most obvious explanation is that a different degree of "external" solvation causes a difference in the "effective" cation radius, *i.e.* a smaller positive sphere polarizes the π-cloud more strongly. Beyond cation solvation, other effects could influence the cation–anion distance such as anion solvation, π-cloud interactions and steric effects, especially when using other solvents than the saturated ethers.

To conclude, the present study confirms the complexity of the ion-pair system when it concerns the solvation of the ion pair(s). Reasonable correlations to singel solvent scales are obtained only on subsets of the original solvent matrix, which could indicate that, apart from cation solvation, solvent effects exercised on the anion also affect the anion–cation distance and thus the reflected π-polarization. These latter interactions are probably governed by other solvent characteristics than those valid for the cation solvation process and are more important for the non-etheral solvents.

Finally, we note that modern data analytic methods such as PC–CV and PLS give direct possibilities to find the systematic behaviour in multivariate data sets and to relate data sets to each other. This direct approach gives results which are easier to interpret than those obtained using indirectly derived solvent scales (and other empirical "substituent" scales) of dubious relevance for a given problem.

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REFERENCES

1. For reviews see: a. Griffiths, T. R. and Pugh, D. C. *Coord. Chem. Rev. 29* (1979) 129; b. Reichardt, C. *Angew. Chem. Int. Ed. Engl. 18* (1979) 98; c. *Ibid. 4* (1965) 29; d. Koppel, I. A. and Palm, V. A. In Chapman, N. B. and Shorter, J., Eds., *Linear Free Energy Relationships*, Plenum, London 1972, Chapter 5, p. 203; e. Rao, C, N. R., Singh, S. and Senthilnathan, V. P. *Chem. Soc. Rev. 5* (1976) 297.
2. a. Fawcett, W. R. and Krygowski, T. M. *Aust. J. Chem. 28* (1975) 2115; b. *J. Am. Chem. Soc. 97* (1975) 2143; c. *Can. J. Chem. 54* (1976) 3283.
3. Chapman, N. B., Dack, M. R. J. and Shorter, J. *J. Chem. Soc. B* (1971) 834.
4. Drago, R. S. and Wayland, B. B. *J. Chem. Soc. 87* (1965) 3571.
5. Fowler, F. W., Katritzky, A. R. and Rutherford, R. J. D. *J. Chem. Soc. B* (1971) 460.
6. Dougherty, R. C. *Tetrahedron Lett.* (1975) 385.
7. Kamlet, M. J., Solomonovici, A. and Taft, R. W. *J. Am. Chem. Soc. 101* (1979) 3734 and earlier papers in these series.
8. a. Clementi, S., Fringuelli, F., Linda, P. and Savelli, G. *Gazz. Chim. Ital. 105* (1975) 281; b. Clementi, S. and Fringuelli, F. *Anal. Chim. Acta 103* (1978) 477.
9. For a statistical approach to LFER, see: Wold, S. and Sjöström, M. In Shorter, J. and Chapman, N. B., Eds., *Correlation Analysis in Chemistry: Recent Advances*, Plenum, New York 1978, Chapter 1, p. 1.
10. a. Weiner, P. H., Malinowski, E. R. and Levinstone, A. R. *J. Phys. Chem. 74* (1970) 4537; b. Malinowski, E. R. and Howery, D. G. *Factor Analysis in Chemistry*, Wiley-Interscience, New York 1980.
11. Kruskal, J. *Factor Analysis and Principal Component Analysis, the Bilinear Methods in Encyclopedia of Statistics*, The Free Press, New York 1978.
12. a. Wold, S. *Pattern Recognition 8* (1976) 127; b. Wold, S. and Sjöström, M. In Kowalski, B. R., Ed., *Chemometrics: Theory and Application, Am. Chem. Soc. Symp. Ser. 52* (1977) 243; c. Sjöström, M. and Wold, S. *J. Chem. Soc. Perkin Trans. 2* (1979) 1274.
13. Chastrette, M. *Tetrahedron 35* (1979) 1441.
14. a. Edlund, U. *Org. Magn. Reson. 9* (1977) 593; b. *Ibid. 12* (1979) 661.
15. a. Van Der Giessen, J., Gooijer, C., MacLean, C. and Velthorst, N. H. *Chem. Phys. Lett. 55* (1978) 33; b. Gooijer, C. and Velthorst, N. H. *Org. Magn. Reson. 12* (1979) 684.
16. Winstein, S., Clippinger, E., Fainberg, A. H. and Robinson, G. C. *J. Am. Chem. Soc. 76* (1954) 2597.

17. Sadek, H. and Fuoss, R. M. *J. Am. Chem. Soc. 76* (1954) 5905.
18. For reviews see: a. Szwarc, M., Ed., *Ions and Ion Pairs in Organic Reactions*, Wiley-Interscience, New York 1972, Vol. 1; 1974, Vol. 2; b. Hogen-Esch, T. E. *Adv. Phys. Org. Chem. 15* (1977) 153.
19. a. Hogen-Esch, T. E. and Smid, J. *J. Am. Chem. Soc. 88* (1966) 307; b. *Ibid. 89* (1967) 2764.
20. a. Hirota, N. *J. Am. Chem. Soc. 90* (1968) 3603; b. Hirota, N., Carraway, R. and Schook, W. *Ibid. 90* (1968) 3611.
21. Chan, L. L. and Smid, J. *J. Am. Chem. Soc. 90* (1968) 4654.
22. Burley, J. W. and Young, R. N. *J. Chem. Soc. B* (1971) 1018.
23. Ditchfield, R. and Ellis, P. D. In Levy, G. C., Ed., *Topics in Carbon-13 NMR Spectroscopy*, Wiley-Interscience, New York 1974, Vol. 1, Chapter 1, p. 1.
24. Spiesecke, H. and Schneider, W. G. *Tetrahedron Lett.* (1961) 468.
25. a. O'Brien, D. H., Hart, A. J. and Russell, C. R. *J. Am. Chem. Soc. 97* (1975) 4410; b. *Ibid. 98* (1976) 7427.
26. Farnum, D. G. *Adv. Phys. Org. Chem. 11* (1975) 123.
27. Lauterbur, P. C. *Tetrahedron Lett.* (1961) 274.
28. For a review see: Szwarc, M., Ed., *Carbanions, Living Polymers and Electron Transfer Processes*, Interscience, New York 1968, Chapter 5, p. 212.
29. Born, M. *Z. Phys. 1* (1920) 45.
30. a. Bjerrum, N. *K. Dan. Vidensk. Selsk., Mat.-Fys. Medd. 7* (1926) No. 9; b. Bjerrum, N. and Larsson, E. *Z. Phys. Chem. 127* (1927) 358.
31. a. Denison, J. T. and Ramsey, J. B. *J. Am. Chem. Soc. 77* (1955) 2615; b. Inami, Y. H., Bodenseh, H. K. and Ramsey, J. B. *Ibid. 83* (1961) 4745.
32. Colter, A. K. and Hui, S. H. *J. Org. Chem. 33* (1968) 1935.
33. a. Ziessow, D. and Carroll, M. *Ber. Bunsenges. Phys. Chem. 76* (1972) 61; b. Bacon, M. R. and Maciel, G. E. *J. Am. Chem. Soc. 95* (1973) 2413.
34. Taylor, G. A. and Rakita, P. E. *Org. Magn. Reson. 6* (1974) 664.
35. Koppel, I. A. and Paju, A. I. *Reakts. Sposobn. Org. Soedin. 11* (1974) 121.
36. a. Gurka, D. and Taft, R. W. *J. Am. Chem. Soc. 91* (1969) 4794; b. Taft, R. W., Gurka, D., Joris, L., Schleyer, P. von R. and Rakshys, J. W. *Ibid. 91* (1969) 4801.
37. Kagiya, T., Sumida, Y. and Inoue, T. *Bull. Chem. Soc. Jpn. 41* (1968) 767.
38. a. Mayer, U., Gutman, V. and Gerger, W. *Monatsh. Chem. 106* (1975) 1235; b. Gutman, V. *Electrochim. Acta 21* (1976) 661; c. Mayer, U., Gerger, W. and Gutman, V. *Monatsh. Chem. 108* (1977) 489.
39. Dimroth, K., Reichardt, C., Siepmann, T. and Bohlmann, F. Justus *Liebigs Ann. Chem. 661* (1963) 1.
40. a. Kamlet, M. J., Abboud, J. L. and Taft, R. W. *J. Am. Chem. Soc. 99* (1977) 6027; b. Kamlet, M. J. and Taft, R. W. *J. Chem. Soc. Perkin Trans. 2* (1979) 337.
41. a. Leo, A., Hansch, C. and Elkins, D. *Chem. Rev. 71* (1971) 525; b. *Data from Pomona College Medicinal Chemistry Project Data Bank*, Claremont, California.
42. Wold, S. *Tecnometrics 20* (1978) 397.
43. Wold, S. *SIMCA-2T Program Package*, Research Group for Chemometrics, Department of Chemistry, Umeå University, Umeå, Sweden 1980.
44. Dunn III, W. J., Wold, S. and Martin, Y. C. *J. Med. Chem. 21* (1978) 922.
45. Wold, S., Wold, H., Dunn III, W. J. and Ruhe, A. *Report UMINF-83.80*, Institutions of Information Processing and Chemistry, Umeå University, Umeå, Sweden 1980.
46. a. Maciel, G. E., Hancock, J. K., Lafferty, L. F., Mueller, P. A. and Musker, W. K. *Inorg. Chem. 5* (1966) 554; b. Cahen, Y. M., Handy, P. R., Roach, E. T. and Popov, A. I. *J. Phys. Chem. 79* (1975) 80.
47. a. Arnett, E. M. and Wu, C. Y. *J. Am. Chem. Soc. 84* (1962) 1680; b. *Ibid. 84* (1962) 1684.

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