

A ^{13}C NMR Spin-Lattice Relaxation Study of the Ion Pairing and Aggregation of Lithium Indenide

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The ^{13}C spin-lattice relaxation times of lithium indenide in a variety of solvent systems have been compared, in a multivariate fashion, with the changes in ^{13}C NMR chemical shift. Generally, lithium indenide tumbles slower in ethereal solvents that favour contact ion pairs, compared with solvents, such as dimethyl sulphoxide or *N,N*-dimethylformamide, in which solvent-separated ion pairs are suggested. Intermolecular aggregation of lithium indenide is only observed in higher dialkyl ethers. Although lithium indenide is highly solvated in bis(2-methoxyethyl) ether and 1,2-bis(2-methoxyethoxy)ethane, the T_1 values suggest appreciable motional restriction caused by intermolecular association between ion pairs.

The structure and aggregation of organolithium compounds have lately been the subject of considerable debate.¹ Alkyl lithium compounds have been described in detail, since slow-exchange conditions make it possible, using NMR and carbon–lithium couplings, to determine the state of aggregation.² However, in delocalized systems, in which the lithium interaction is essentially electrostatic, fast-exchange conditions exclude this possibility. Aggregation of organoalkali-metal compounds has mainly been studied by cryoscopy³ and X-ray crystallography,⁴ however, both these techniques have their limitations. Cryoscopy has the disadvantage that the degree of aggregation can be determined only at a given low temperature since it is well established that ion pairing and aggregation change with temperature. X-Ray characterization is limited to such systems from which crystals can be obtained. Most of the isolated salts studied so far have been *N,N,N',N'*-tetramethyl-1,2-ethylenediamine (TMEDA)-complexed salts.⁴ Structural suggestions from solid-state data are often in conflict with those from solution data i.e. where high resolution NMR⁵ or other spectrophotometric techniques have been used.^{4,6}

Information about anion–cation interactions in solution is of special relevance to synthetic organic chemistry. A change in aggregation may, in the first instance, alter the reactivity and a significant change in the charge distribution may also influence the regioselectivity in many bond-forming reactions.

Most NMR studies dealing with ion pairing or aggregation of delocalized carbanions are based on ^{13}C shift differences induced by changes in the solvent, temperature or alkali-metal counterion.⁵ The results from these studies usually conform nicely with those from spectrophotometric studies,⁶ i.e. using methods with totally different time-scales. The induced chemical shifts of the delocalized car-

banions are usually interpreted as reflecting equilibrium changes between a contact ion-pair state (CIP) and a solvent-separated ion-pair state (SSIP). Lithium-shift studies provide additional support for this model.⁷

We have already shown the potential of using ^{13}C spin-lattice relaxation times as a probe for the aggregation of lithium salts of delocalized carbanions such as lithium indenide.^{5f} The advantage of this technique is that the induced shifts and T_1 can be measured simultaneously under various ion-pair conditions. The basic diffusion models suggest that rotational diffusion is correlated with the molecular volume of the species;⁸ for isotropic bodies this volume can be approximated by the molecular weight.

In earlier ion-pair studies based on induced NMR chemical shifts we have used a multivariate approach based on principal component data analysis to extract the information content.^{5a,b} Since the indenide system has been well characterized by a variety of spectroscopic techniques,^{4,7} it was a natural choice as a model for a delocalized carbanion system. The indenide anion is conformationally rigid and it is one of the few systems for which both X-ray and solution data suggest the same preferred cation position, i.e. above the five-membered ring. In an earlier report we compared the T_1 ratios for the protonated C4–C7 carbons of indene and indenide in tetrahydrofuran (THF),^{5f} and it was found that the indenide carbon T_1 s were approximately three times shorter than those for the indene reference molecule. Since essentially isotropic diffusion can be assumed, this value indicates extensive solute–solute or, more likely, solute–solvent interactions provided that the microviscosity factor of the two species is not significantly different. This study is now extended to include a variety of solvent systems and the T_1 values of the protonated sp^2 carbons of indane are used as reference values. In this way effects due to proton exchange can be neglected. Such exchange

processes might be present for the indene–indenide system under highly polar conditions.

As a comparison with the T_1 ratios, the solvent-induced ^{13}C NMR chemical-shift changes are reported for the indenide anion. The solvent systems used include some of the most common aprotic solvents as well as cation-chelating agents such as TMEDA.

Results and discussion

The ratio between the average ^{13}C T_1 value (C4–C7) of indane and the corresponding value of lithium indenide is given in Table 1 as a function of the solvent. As mentioned in the earlier study, both solute–solute interactions, such as

sandwich-like stacking of the planar anions, and solute–solvent interactions have to be considered. If the solvent interaction with the ion pair, i.e. for aprotic solvents in which mainly solvent–cation interactions occur, is long-lived on the rotational correlation time scale, shorter T_1 values will be observed for the carbanion carbons as the size of the complex increases. The observed T_1 is a weighted average of the T_1 value of the various complexes. The existence of minute concentrations of highly aggregated complexes may therefore yield significantly shorter observed T_1 values. When calculating the mass of the complex, different solvent coordination numbers were tested. Since the intercept at unit T_1 ratio must be close to the molecular weight of the free indenide anion (M_w 115) more

Table 1. ^{13}C NMR chemical shifts and T_1 values of lithium indenide in various solvents.

Solvent	NMR descriptors ^{a,b}							\bar{T}_1/\bar{T}_1^d
	M^c	$C_{1,3}$	C_2	$C_{4,7}$	$C_{5,6}$	$C_{3a,7a}$	δ	
1 DEE	344	92.2 (35.9)	115.3 (12.8)	120.7 (7.4)	116.2 (11.9)	128.1	114.4 (17.6)	4.01
2 DEE–TMEDA	238	91.8 (35.8)	114.9 (12.7)	120.7 (6.9)	115.9 (11.7)	127.6	114.1 (17.4)	3.39
3 THF	338	91.6 (37.8)	115.5 (14.1)	119.7 (9.9)	114.7 (14.9)	129.6	114.1 (19.9)	2.93
4 THF–TMEDA	238	91.8 (36.5)	115.3 (13.0)	120.6 (7.7)	115.2 (13.1)	128.3	114.1 (18.3)	2.89
5 DME	257	92.1 (36.8)	115.6 (13.3)	120.3 (8.6)	114.8 (14.1)	128.9	114.2 (18.9)	2.69
6 DME–TMEDA	238	92.0 (36.0)	115.2 (12.8)	120.7 (7.3)	115.6 (12.4)	128.0	114.2 (17.7)	3.24
7 2–MTHF	380	91.9 (36.5)	115.5 (12.9)	120.5 (7.9)	115.6 (12.8)	128.4	114.3 (18.1)	4.31
8 THP	380	91.8 (37.0)	115.4 (13.5)	120.4 (8.4)	115.3 (13.4)	128.8	114.2 (18.7)	4.20
9 IBF	500	90.9 (37.7)	114.7 (13.9)	119.1 (9.5)	113.6 (15.0)	128.6	113.2 (19.8)	6.09
10 DPE	428	92.8 (35.5)	115.4 (12.9)	121.7 (6.6)	117.6 (10.7)	128.3	115.1 (16.9)	10.88
11 DBE	512	92.9 (35.3)	115.4 (12.8)	121.6 (6.6)	117.6 (10.8)	128.2	115.1 (16.9)	10.84
12 DMEU	115	92.8 (38.0)	117.6 (13.2)	117.7 (13.1)	110.2 (20.6)	130.8	113.4 (22.4)	2.39
13 DMF	115	92.3 (37.6)	117.1 (12.8)	117.2 (12.7)	109.9 (20.0)	129.9	112.9 (21.9)	1.66
14 GLYME–2	242	93.1 (37.7)	117.7 (13.1)	118.5 (12.3)	111.1 (19.7)	130.8	113.9 (21.8)	7.60
15 GLYME–3	282	92.8 (37.7)	117.3 (13.2)	118.5 (12.0)	111.3 (19.2)	130.5	113.7 (21.6)	7.58
16 DMSO	115	94.3 (36.7)	119.1 (11.9)	118.9 (12.1)	111.8 (19.2)	131.0	114.6 (21.1)	1.75

^aChemical shifts are reported relative to SiMe_4 , see the Experimental. ^bValues in parentheses refer to the ^{13}C chemical-shift difference between the actual position and $C_{3a,7a}$. ^cThe mass was calculated as the mass of lithium indenide and a given number of solvent molecules, see the text. ^dThe T_1 ratio was measured as the average T_1 for the protonated sp^2 carbons in indane divided by the average T_1 for the corresponding carbons in lithium indenide.

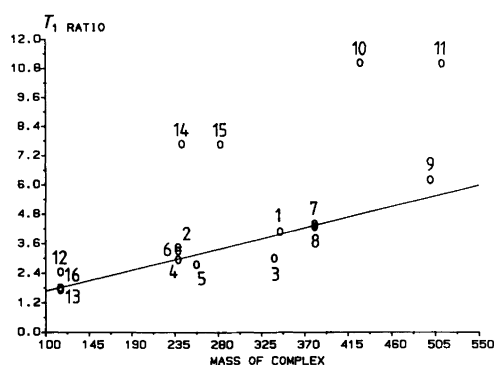


Fig. 1. T_1 Ratio vs. mass of complex.

than two or three solvent heteroatom coordination sites could be excluded as being present in the complex. In fact, the best fit to experimental data was obtained when a model was used in which the lithium cation is coordinated to three heteroatom sites (Fig. 1). In the case of TMEDA-complexed ion pairs, steric hindrance excludes the possibility of more than one chelating molecule per lithium cation.⁹ For the 1,2-dimethoxyethane (DME)-lithium indenide system the average mass includes an average coordination of 1.5 solvent molecules. For systems expected to be under SSIP conditions, the molecular weight was set equal to that of the indenide anion.

Our solvation model is consistent with the results from an earlier reported NMR study of lithium fluorene,¹⁰ a system with strong similarities to the indenide system. In that study the lithium salts in THF or DME were isolated and dried under vacuum. After the salts had been dissolved in benzene, the upper coordination limit was determined by simple integration. The number of solvent molecules associated with lithium fluorene was determined to be 3 for the THF complexed salt but 1.3 for DME.¹⁰ In this context, it should be remembered that the coordination

number of lithium is governed primarily by steric factors. The suggested solvent coordination model for a CIP should be considered as an upper limit since inorganic lithium salts dissolved in THF have been shown to be associated with up to four THF molecules.¹¹

As seen from Table 1, the smallest T_1 ratio is observed in the systems in which SSIP conditions are expected to be fulfilled i.e. solvents numbered 12, 13 and 16. Although these values appear in a rather narrow range, the trend in the data reflects the molecular weight of the solvent. Hence, even in an SSIP some electrostatic interaction seems to exist between the anion and the solvated cation; an interaction with a sufficiently long lifetime to affect slightly the rotational motion of the indenide anion. The average size of the complex, as defined from the NMR time scale, seems to be considerably smaller than for a CIP. From Fig. 1 we can also exclude the possibility that in these solvent systems significant intermolecular aggregation, such as stacking, takes place.

The most noticeable deviation from a straight line is observed for the higher dialkyl ether systems for which the T_1 ratio is close to 11. The most likely explanation for such a large T_1 ratio is a significant amount of intermolecular aggregation. Solubility is also strongly limited in these solvents in contrast with that found in diethyl ether (DEE). Although only a limited concentration interval can be studied in these solvents a slight concentration dependence of T_1 can be observed. In a better solvating medium such as THF, T_1 is independent of concentration below 1 M (Table 2).

The T_1 ratios obtained in bis(2-methoxyethyl) ether (GLYME-2) and 1,2-bis(2-methoxyethoxy)ethane (GLYME-3) are also unexpectedly large. Glyme-solvated alkali-metal salts of lithium fluorene are known to exist mainly in SSIPs in more polar ethers, but the concentration of CIPs is still appreciable.⁹ In the less delocalized lithium indenide system, the equilibrium is shifted further towards

Table 2. Concentration dependence of ^{13}C NMR chemical shifts and T_1 values of lithium indenide in tetrahydrofuran and dibutyl ether.

Solvent	Conc/M	$C_{1,3}$	C_2	$C_{4,7}$	$C_{5,6}$	$C_{3a,7a}$	δ	\bar{T}_1/\bar{T}_1
THF	2.0	91.8 (37.8)	115.7 (13.9)	119.9 (10.2)	114.5 (15.1)	129.6	114.2 (20.0)	5.30
	1.0	91.8 (37.8)	115.7 (13.9)	119.9 (10.2)	114.5 (15.1)	129.6	114.2 (20.0)	3.74
	0.5	91.7 (38.0)	115.6 (14.1)	119.8 (9.9)	114.3 (15.4)	129.7	114.1 (20.1)	2.93
	0.25	91.7 (38.0)	115.6 (14.1)	119.8 (9.9)	114.3 (15.4)	129.7	114.1 (20.1)	3.15
DBE	0.21	93.0 (35.3)	115.6 (12.7)	121.6 (6.7)	117.3 (11.0)	128.3	115.1 (17.0)	10.20
	0.15	93.0 (35.4)	115.8 (12.6)	121.6 (6.8)	117.3 (11.1)	128.4	115.2 (17.0)	9.20
	0.11	93.0 (35.4)	115.8 (12.6)	121.6 (6.8)	117.2 (11.2)	128.4	115.2 (17.0)	8.48

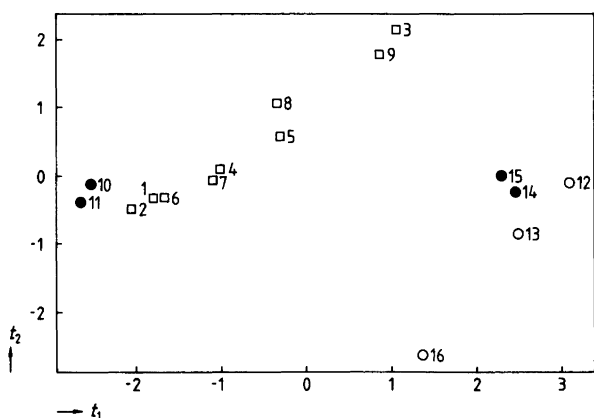


Fig. 2. First vs. second principal component including only shift data. Numbers refer to the solvent systems listed in Table 1.

CIP. Hence, the most likely explanation for the short T_1 values is that these externally solvated CIPs are intermolecularly aggregated, with the solvent molecules acting as links between the CIPs.

It may also be of interest to compare the T_1 data with the corresponding ^{13}C chemical shifts using multivariate principal component data analysis. A shift matrix composed of autoscaled ^{13}C shifts relative an intramolecular reference (C-3a, -7a) was analysed initially. Fig. 2 shows a plot of the two relevant components which in total explain 95% of the variance in the shift data. Two major groupings are seen, one group containing mostly ether- and ether/TMEDA-complexed CIPs, while the other group contains more highly solvated SSIPs. The major component t_1 is strongly correlated to the major component or solvent scale found in an earlier study of solvated lithium indenide.^{5a} For the six solvents in common the same trend of increasing cation solvation is observed, i.e. $1 < 8 < 5 < 3 < 16 < 13$. As mentioned earlier, this major component was found to be correlated to a more conventional solvent scale, π^* , thus the extension of the CIP class model in Fig. 2 is largely accounted for by varying external cation solvation as reflected in the π^* values of the solvents. However, the shift data contain additional information as manifested by the grouping of the solvent systems. This is in perfect agreement with our earlier proposal that no single solvent scale could account for the shift variation and that solvents tend to fall into two groups, one group containing mainly ether- or amine-solvated CIPs and the other group containing good cation-solvating solvents, including solvents with π -electrons. The generality of this pattern is thus confirmed. A closer examination of Fig. 2 indicates that both the higher dialkyl ethers, 10 and 11, as well as both glymes, 14 and 15, seem to deviate somewhat from the class model extensions, although the number of objects in each class is too small to confirm this statistically. If relevant, this condition is not unexpected since aggregation or stacking of the π -systems can cause changes in ring currents at the measured nuclei.

An interesting point from this plot is that the positions representing systems in which TMEDA is added are much closer in space than the points where only the pure ether solvents are used. This strengthens the earlier proposal that TMEDA is a strongly chelating agent and that the methyl groups prevent further interaction with the solvent.⁹ This condition is also supported by the similar T_1 ratios for the TMEDA-complexed ion pairs. The similar T_1 values also support the initial assumption that the rotational motion is approximately similar for the indenide and indane systems.

In Fig. 3 we have added the T_1 ratio values as a variable and, although the ratio varies significantly, the main class-structure pattern seems to be retained. The higher dialkyl ethers (10, 11) and the glymes (14, 15) are clearly displaced from the CIP and the SSIP class structure. DME seems to have less solvating power than THF toward lithium salts, while, as has been shown earlier, DME is more effective than THF toward sodium salts.¹² Solvation of the small lithium cation reduces the mobility of the DME molecules and decreases the entropy of the total system by forcing DME to acquire an energetically unfavourable conformation.

In conclusion, the monomeric structure of lithium indenide has been demonstrated both under CIP and SSIP conditions. Appreciable intermolecular aggregation is observed only in the less polar alkyl ethers. Glyme-solvated CIPs also seem to deviate in behaviour, presumably through the formation of anisotropic aggregates where lithium indenide species are linked by solvent molecules. From our spin-lattice relaxation study it is also found that the solvent association to molecules is long-lived on the rotational-correlation time-scale in externally solvated CIP. The rotational motion of the indenide anion under SSIP conditions is considerably less affected by the interaction to the solvated counterion. In general, chemical shifts and T_1 values reflect the same solvation process, except in the polyethers and the higher alkyl ethers.

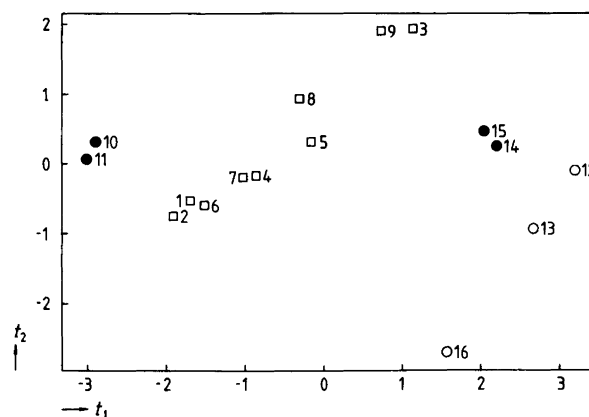


Fig. 3. First vs. second principal component including both chemical-shift and T_1 data. Numbers refer to the solvent systems listed in Table 1.

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

$$y_{ik} = \alpha_i + \sum_{a=1}^A \beta_{ia} t_{ak} + \varepsilon_{ik}$$

Where α_i is the variable mean, β_{ia} the loadings (corresponding to regression coefficients) and t_{ak} are the scores or 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 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.¹³ A complete description of the data program package has been reported.¹⁴

Initially the PC analysis was performed on the data matrix containing only the ¹³C chemical shifts. Data were autoscaled, that is all variables were given the same variance equal to one. An even better model, that accounted for 95% of the original data standard deviation using a two-component model, was found if $C_{3a,7a}$ was used as an internal reference, and the variables used were the shift differences relative to this position (Fig. 2).

If the T_1 ratio was used as an additional variable, a two-component model was obtained that accounted for 99% of the variance in the data (Fig. 3).

Experimental

Lithium salts in the solvents **1–11** were generated from indene and concentrated butyllithium in 10 mm NMR tubes oven-dried, purged with Ar and sealed with rubber septa. All solvents were carefully dried as reported in the earlier study.^{5a} At 0°C butyllithium was added to a 0.5 M solution of indene/indane, respectively. When cation-chelating additives were used, 2 equiv. were added at 0°C. Because of solubility limitations, the maximum concentration in solvents **10** and **11** was only 0.22 M. In solvents **12–16**, anions were prepared by solvent exchange from a solution of indenide anion in DEE. 2.5 M Butyllithium was added to the indene in DEE and lithium indenide was precipitated by the addition of hexane. The solvent was removed by syringe and the salt was washed twice with hexane and dried under high vacuum at room temperature in order to remove residual solvent. At 0°C the actual solvents and indane were added and the sample was sonicated in an ultrasonic bath in order to dissolve all the solid material. The solvents used were: DEE (diethyl ether), TMEDA (N,N,N',N' -tetramethyl-1,2-ethylenediamine, THF (tetrahydrofuran), DME (dimethoxyethane), 2-MTHF (2-methyltetrahydrofuran), THP (tetrahydropyran), IBF (octahydroisobenzofuran), DPE (dipropyl ether), DBE (dibutyl ether), DMEU (N,N -dimethylethyleneurea), DMF (N,N -dimethylformamide), GLYME-2 [bis(2-methoxyethyl) ether], GLYME-3 [1,2-bis(2-methoxyethoxy)ethane], and DMSO (dimethyl sulphoxide).

¹³C NMR spectra were obtained on Bruker WM-250 spectrometer at 62.89 MHz. T_1 Measurements were obtained using fast inversion recovery with delay list cycling with an accuracy of > 10% depending on the concentration. The chemical shifts were measured relative to internal cyclohexane, and converted into the SiMe₄ scale using $\delta(\text{cyclohexane}) = 27.7$.

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