Paramagnetic Solvent Nuclear Magnetic Resonance Shifts in Radical Anion Solutions. 2. Some Cation-Dependent Phenomena in Concentrated Solutions of Aromatic Hydrocarbon Radical Anions and Dianions

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The molar paramagnetic solvent shifts (MPSS's) of (biphenyl)⁻·Li⁺, (*p*-terphenyl)⁻·M⁺ (M = Li, Na), (naphthalene)⁻·M⁺ (M = Li, Na, K), (2-*tert*-butylnaphthalene)⁻·Li⁺, (2,6-di-*tert*-butylnaphthalene)⁻·Li⁺, (phenanthrene)⁻·M⁺ (M = Li, Na, K), (anthracene)⁻·M⁺ (M = Li, Na, K), (pyrene)⁻·M⁺ (M = Li, Na, K), (chrysene)⁻·M⁺ (M = Li, Na, K), (*cis*-stilbene)⁻·Li⁺, and (*trans*-stilbene)⁻·Li⁺ have been measured in tetrahydrofuran (THF) at 60 MHz and at 35 ± 1 °C. These parameters, which are more or less cation as well as anion dependent, may reflect structural properties of the ion-pair in solution such as covalency in the ion-pair bond or aggregation to diamagnetic species. The effect of alkyl substitution on the magnitude of the MPSS has been studied in the case of lithium naphthalene radical anion. A *tert*-butyl group in the 2-position has no effect on the molar shift. Two *tert*-butyl groups in the 2,6-positions, however, cause a dramatic drop in the magnitude of the MPSS. It has been shown that this change is due to extensive spin pairing. A double internal reference technique has been used in order to separate contributions due to the bulk paramagnetism and the contact shift. Contrary to previous belief that THF protons undergo only negative contact shifts, it was shown that they may undergo positive contact shifts as well. Thus the α protons of THF in the presence of lithium naphthalene radical anion exhibit a contact shift of −0.25 ppm/mol, whereas in the presence of lithium (*p*-biphenylyl)phenylketyl they exhibit a contact shift of 0.25 ppm/mol. These contact shifts correspond to coupling constants of the order of 10^{-3} G. Attention is called, however, to the possibility that in strongly cation-complexing agents such as glymes, the contact shift could correspond to a coupling constant of the order of 0.1 G. In such a case, line broadening in the ESR spectra could be caused by additional small splitting due to the interaction of the unpaired spin with the protons of the coordinated-to-cation ligands. The effect of adding poorly solvating cosolvents, Et_2O and Et_3N, on the structure of (naphthalene)⁻·M⁺ (M = Li, Na, K) has been studied. Three patterns of behavior have been observed. (1) The added cosolvent does not perturb the structure of the radical anion–cation pair. (2) A change occurs after the composition of the medium reaches a certain point, and the change varies gradually as the medium becomes enriched in cosolvent. (3) An abrupt change occurs at a *certain* composition of the medium. The above phenomena are strongly cation dependent. Dianions of polynuclear aromatic hydrocarbons, particularly those with angularly condensed rings, are chemically unstable in THF, causing cleavage of the ethereal solvent. Instability appears to depend markedly on the cation and increases in the order K, Na, Li.

Some time ago deBoer and co-workers[1] showed that the tetrahydrofuran (THF) solvent in solutions of sodium triphenylene radical anion and sodium coronene radical anion undergoes a paramagnetic NMR shift, which is linear with respect to the formal concentration of the radical anion. They also showed that the observed shift is a resultant of two components, one large and positive, due to the bulk paramagnetism of the solution, and a smaller negative component which was attributed to Fermi contact interaction between the unpaired spin and the magnetic nuclei of the solvent molecules. The linear relationship between solvent shift and concentration was shown to hold also for the lithium radical anions of biphenyl, naphthalene, phenanthrene,[2] stilbene, anthracene,[3] benzophenone, and fluorenone.[4] This linearity between solvent shift and concentration made possible the measurement of kinetics[2-4] and equilibria[3-6] by observing solvent shifts in the NMR.

Recently[7] we have provided experimental evidence that the straight lines that represent the shift vs. concentration relationship have slopes that differ from one radical anion–cation pair to another, regardless of the fact that the two pairs have a common anion and different cation or vice versa. Thus, we were led to suggest that the shift corresponding to a concentration of 1.0 M is a characteristic molecular parameter for a given anion–cation pair in a given solvent at a temperature.[7] The most obvious utilities of these parameters, which are called molar paramagnetic solvent shifts (MPSS's), are the following. (1) In measuring kinetics by following a solvent shift with respect to time, except in first-order kinetics, the resulting rate constants are based on concentration units of hertz/liter and not of moles/liter. Thus, the knowledge of MPSS is necessary in order to make the appropriate conversion. (2) The magnitude of the MPSS may reflect a number of properties of the radical anion–cation pair in the solvent under consideration, e.g., magnitude and sign of the contact shift or state of aggregation. All monomeric or unassociated radical anions in solution should have approximately equal MPSS's, if no contact interactions were operable. Therefore, in the absence of aggregation the "individuality" of the MPSS's should be attributed to the negative or positive contribution to the solvent shift, arising from the contact interaction between the unpaired electron of the anion and the solvent molecules. A major conclusion of the same work[7] was that the contact or any other microscopic magnetic interaction between the unpaired electron of the anion and the solvent molecules is transmitted through the mediation of the cation, which is bonded to both the anion and the solvent molecules. Under the above-mentioned conditions one can draw conclusions about covalency or ionicity in the radical anion–cation pair, because hyperfine interactions are present where covalency is also present.[8]

This paper is the continuation of our effort to understand the structure of the radical anions in solution at concentrations comparable to those of the preparative

(1) de Boer, E.; Grotens, M.; Smid, J. *J. Am. Chem. Soc.* 1970, *92*, 4742; *J. Chem. Soc. D* 1970, 1035.
(2) Screttas, C. G. *J. Chem. Soc., Chem. Commun.* 1972, 869.
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(5) Screttas, C. G.; Cazianis, C. T. *Tetrahedron* 1978, *34*, 933.
(6) Screttas, C. G.; Micha-Screttas, M. *J. Org. Chem.* 1978, *43*, 1064.
(7) Screttas, C. G.; Micha-Screttas, M. *J. Org. Chem.* 1981, *46*, 993.

(8) Owen, J.; Thornley, J. H. M. *Rep. Prog. Phys.* 1966, *29*, 675.

Table I. Molar Paramagnetic Solvent Shifts (in Hz/mol) of Aromatic Radical Anions in THF at 35 ± 1 °C and 60 MHz

entry	radical anion	$\Delta\nu_m^\alpha$	$\Delta\nu_m^\beta$	$\Delta\nu_m^{app}$	$10^2\Delta\Delta\nu_m^{\alpha\beta}$
1	(biphenyl)⁻·Li⁺	117	107		8.5
2	(p-terphenyl)⁻·Li⁺	162	150	93[a]	7.4
3	(p-terphenyl)⁻·Li⁺			162[b]	
4	(p-terphenyl)⁻·Na⁺	143	131	138[a]	8.4
5	(naphthalene)⁻·Li⁺	115	105		8.7
6	(naphthalene)⁻·Na⁺	113	105		7.0
7	(naphthalene)⁻·K⁺	145	136		6.2
8	(2-tert-butylnaphthalene)⁻·Li⁺	116	101		12.9
9	(2,6-di-tert-butylnaphthalene)⁻·Li⁺	62	54		12.0
10	(phenanthrene)⁻·Li⁺	114	118	24[a]	-3.4
11	(phenanthrene)⁻·Na⁺	124	122	123[a]	1.6
12	(phenanthrene)⁻·K⁺	140	138	127[a]	1.4
13	(anthracene)⁻·Li⁺	142	126	117	11.3
14	(anthracene)⁻·Na⁺	138	127	122[a]	8.0
15	(anthracene)⁻·K⁺	138	125	135	8.2
16	(pyrene)⁻·Li⁺	134	130	42[a]	3.0
17	(pyrene)⁻·Na⁺	129	125	71[a]	3.1
18	(pyrene)⁻·K⁺	131	130	121[a]	1.0
19	(chrysene)⁻·Li⁺	110	110	10[a]	0.0
20	(chrysene)⁻·Na⁺	120	118	88[a]	1.7
21	(chrysene)⁻·K⁺	119	116	124[a]	2.5
22	(cis-stilbene)⁻·Li⁺	156	139		10.9
23	(trans-stilbene)⁻·Li⁺	153	138	74[a]	9.8
24	(trans-stilbene)⁻·Li⁺			150[b]	
25	(trans-stilbene)⁻·Na⁺	144	127	96	11.8

[a] Prepared according to eq 2 at room temperature. [b] Prepared according to eq 2 at 0 °C. The indicated apparent molar shift is referred to the α-proton band of THF, and it should be compared with $\Delta\nu_m^\alpha$.

reactions. More specifically, it is intended (1) to report the molar paramagnetic solvent shifts of a number of aromatic hydrocarbon radical anions, (2) to discuss the possible implications of the MPSS's on the covalency in the anion–cation pair under our conditions, i.e., high concentrations, (3) to report the effect of added cosolvent on the structure of certain radical anion–cation pairs in THF, and (4) to communicate our results on the chemical instability of aromatic hydrocarbon dianions.

Table I summarizes the MPSS's of a number of aromatic hydrocarbon radical anions. These molar shifts are referred to THF solvent and were recorded at 60 MHz (at 35 °C) as described previously[7] and under the assumption that the concentration of the paramagnetic species in solution is equal to the formal concentration of the radical anion. In Table I are given the radical anion–cation pair, the MPSS referred to the α-proton band of THF, $\Delta\nu_m^\alpha$, and the MPSS with respect to the β proton band of THF, $\Delta\nu_m^\beta$. These molar shifts were measured on solutions of radical anions prepared by direct reaction of equivalent amounts of the aromatic hydrocarbon and the alkali metal, i.e., eq 1. The $\Delta\nu_m^{app}$ term denotes the molar shift referred

$$ArH + M \rightarrow ArH^-\cdot M^+ \qquad (1)$$

$$ArH^{2-}M_2^{2+} + ArH \rightarrow 2ArH^-\cdot M^+ \qquad (2)$$
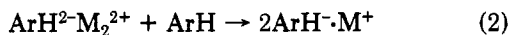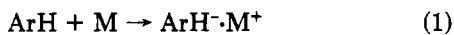
to the α-proton band of THF, with the solution of the radical anion having been prepared by inverse disproportionation of the relevant dianion and the neutral hydrocarbon, i.e., eq 2. In the last column of Table I is given the percent difference between $\Delta\nu_m^\alpha$ and $\Delta\nu_m^\beta$, $10^2\Delta\Delta\nu_m^{\alpha\beta}$. In most cases the two molar shifts $\Delta\nu_m^\alpha$ and $\Delta\nu_m^\beta$ for a given anion–cation pair are not equal. For example, in entry 1 of Table I the percent difference between the two MPSS's of lithium biphenyl radical anion is $10^2\Delta\Delta\nu_m^{\alpha\beta}$ = 8.5. The reason for the inequality between the two shifts has been already discussed.[7] As in the case of the ketyl anions,[7] usually $\Delta\nu_m^\alpha$ is larger than $\Delta\nu_m^\beta$. There are, however, exceptions to this rule, e.g., lithium phenanthrene radical anion (entry 10), where $\Delta\Delta\nu_m^{\alpha\beta}$ = -3.4, but the difference becomes positive again in sodium and potassium

phenanthrene radical anions (entries 11 and 12). We notice that, generally, the MPSS's are more or less anion as well as cation dependent. Bearing in mind that the MPSS's were determined by assuming that the concentration of the paramagnetic species is equal to the formal concentration of the radical anion–cation pair, one can attribute the observed differences in the $\Delta\nu_m^\alpha$ (or $\Delta\nu_m^\beta$) values to either a different degree of aggregation (to diamagnetic species) of the radical anion–cation pairs or, in case of lack of aggregation, to the different magnitude of the contact shift. If the latter alternative were true,[9] then the observed differences could reflect differences in the ionic character of the bond in the anion–cation pairs. A small $\Delta\nu_m^\alpha$ value could imply a large covalent character of the ion pair and vice versa, and this under the condition that comparisons are made between pairs which exhibit contact shifts of negative sign. The following specific points can be made on the basis of the information given in Table I. The lithium radical anions of cis- and trans-stilbenes exhibit identical molar shifts (entries 22 and 23). Obviously, during the preparation of the cis-stilbene radical anion isomerization took place.[10] Introducing a tert-butyl group in the 2-position of naphthalene has no effect upon the magnitude of the MPSS (compare entries 5 and 8). A dramatic decrease in the MPSS is observed, however, when a second tert-butyl group was introduced in the 6-position of naphthalene (compare entries 5 and 9). This marked change of MPSS could mean either that the lithium di-tert-butylnaphthalene radical anion pair is more covalent than Li⁺C₁₀H₈⁻· or that the drastic reduction of the electron affinity in 2,6-di-tert-butylnaphthalene[11] results in an instability of the radical anion, which, in turn, leads to spin-paired species. Fortunately, there was a way of distinguishing between these two possibilities. By measurement of the bulk paramagnetism of solutions of lithium

(9) The linearity between $\Delta\nu$ and C guarantees, at least, that the number of free spins in solution is proportional to the formal concentration of the radical anion pair.

(10) Sorensen, S.; Levin, G.; Szwarc, M. *J. Am. Chem. Soc.* **1975**, *97*, 2341.

(11) Lawler, R. G.; Tabit, C. T. *J. Am. Chem. Soc.* **1969**, *91*, 5671.
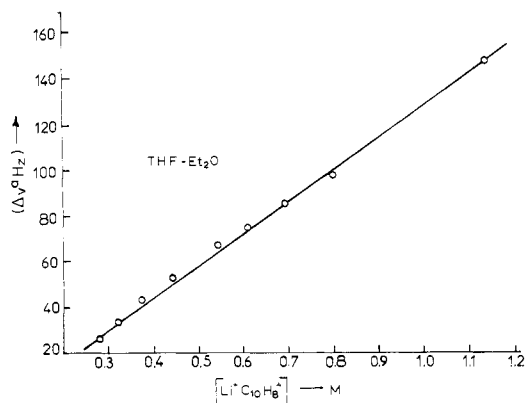
Figure 1. Shift (induced to the α-proton band of THF) vs. concentration relationship for $\text{Li}^+\text{C}_{10}\text{H}_8^-$ in mixtures of THF and Et_2O. Points were obtained by adding 0.20, 0.30, 0.40, 0.50, 0.70, 0.90, and 1.10 mL of Et_2O to 0.50 mL of 1.18 M $\text{Li}^+\text{C}_{10}\text{H}_8^-$ in THF.

2,6-di-*tert*-butylnaphthalene and of lithium naphthalene radical anion under identical conditions with a Gouy balance, it was found that the disubstituted radical anion solution exhibited only 60% of the paramagnetism that was shown by the solution of $\text{Li}^+\text{C}_{10}\text{H}_8^-$. This finding leads to the conclusion that the observed small shift is due to extensive spin pairing, which leads to diamagnetic species.
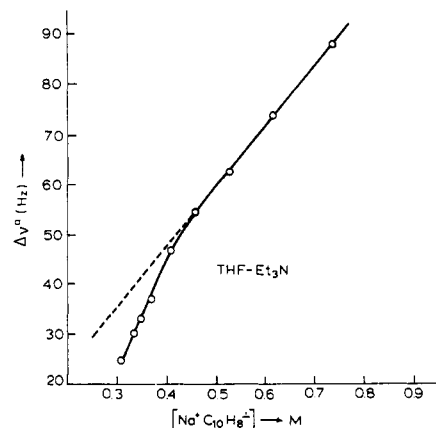
Assuming that the observed solvent shift, $\Delta\nu_{obsd}$, is related to the shift due to the bulk paramagnetism, $\Delta\nu_{bulk}$, and the shift caused by the contact mechanism, $\Delta\nu_{contact}$, through the eq 3, we attempted to separate the two con-

$$\Delta\nu_{obsd} = \Delta\nu_{bulk} + (\pm\Delta\nu_{contact}) \qquad (3)$$
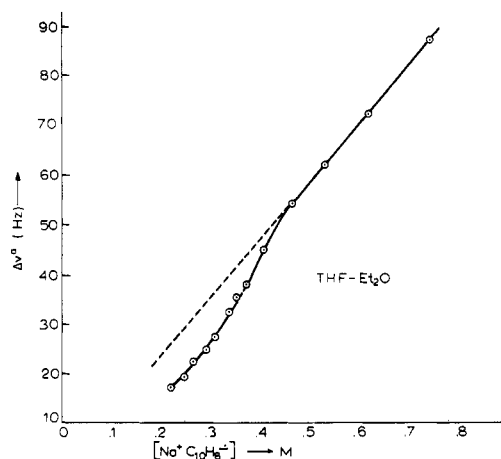
tributions. We reasoned that on addition of an internal marker, such as cyclohexane, to a solution of a radical anion in THF, the cyclohexane would feed the bulk paramagnetism solely (or at least mainly) because of the lack of complexation between the radical anion pair (or the cation) and the cyclohexane.[12] Indeed, the shift $\Delta\nu^\alpha$, which is the largest, was found to be significantly smaller in one case and significantly larger in another. Thus the occurrence of positive as well as negative[1] contact shifts was revealed. A 0.927 M solution of $\text{Li}^+\text{C}_{10}\text{H}_8^-$ in THF, containing approximately 20% of cyclohexane, exhibited the following (80 MHz) shifts at 35 °C: $\Delta\nu^\alpha = 158.5$ Hz, whereas the shift referred to cyclohexane was $\Delta\nu^{c\text{-hex}} = 170.6$ Hz.[13] The shift $\Delta\nu^{c\text{-hex}}$ is linear with respect to concentration of the radical anion in solutions of THF–cyclohexane (80–20% v/v), and a molar shift ($\Delta\nu_m^{c\text{-hex}}$) of 187 Hz/mol (80 MHz) has been obtained. The $\Delta\nu_m^\alpha$ under the same conditions was 168 Hz/mol. If we assume that $\Delta\nu_m^{c\text{-hex}} = \Delta\nu_{bulk}$, then from eq 3 we obtain the shift due to contact interactions: $\Delta\nu^\alpha_{contact} = 168 - 187 = -19$ Hz/mol. By the same method it was found that a solution of lithium (p-biphenylyl)phenylketyl in THF induces a contact shift of the α protons of THF of 20 Hz/mol. If our experimental method is sound, then the estimated contact shift is very small. Namely, it corresponds to a coupling constant of the order of 10^{-3} G, and the perturbation which can be caused by this effect in the ESR spectra is outside the resolving power of the present-day ESR spectrometers. However, in solvents of great solvating power such as glymes, contact shifts of the order of 10 ppm/mol have been reported,[1] and they correspond to coupling constants

Figure 2. Relationship of shift vs. concentration (see caption for Figure 1) for $\text{Na}^+\text{C}_{10}\text{H}_8^-$ in mixtures of THF and Et_3N. Points were obtained by diluting 0.50 mL of 0.74 M of $\text{Na}^+\text{C}_{10}\text{H}_8^-$ in THF with 0.10, 0.20, 0.30, 0.40, 0.50, 0.55, 0.60, and 0.70 mL of Et_3N.
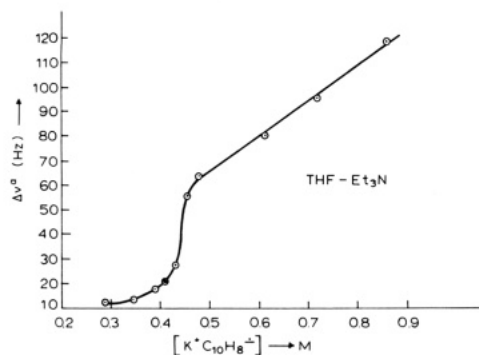

Figure 3. Relationship of shift vs. concentration (see caption for Figure 1) for sodium naphthalene radical anion in mixtures of THF and Et_2O. The points were obtained by diluting 0.50 mL of 0.74 M sodium naphthalene radical anion in THF with 0.10, 0.20, 0.30, 0.40, 0.50, 0.55, 0.60, 0.70, 0.80, 0.90, 1.00, and 1.20 mL of Et_2O.

of the order of 0.1 G.[14] Therefore, we call attention to the possibility that perturbation of ESR spectra caused by adding glymes might be due to additional small splitting arising from interaction of the odd electron with the protons of the complexed to glyme cation.

The effect of added poorly solvating cosolvents, i.e., diethyl ether and triethylamine, on the structure of naphthalene radical anion in THF has been studied. Three patterns of behavior hae been encountered which obviously depend very strongly on the cation. (1) Addition of the cosolvent did not perturb the linearity in the $\Delta\nu$ vs. concentration relationship, e.g., lithium naphthalene radical anion in THF–Et_2O (Figure 1). (2) A significant deviation from linearity appears after the solvent reaches a certain composition. Beyond this point the $\Delta\nu$ vs. C relationship becomes concave, e.g., sodium naphthalene radical anion in THF–Et_2O (Figure 3). (3) An abrupt change occurs in the $\Delta\nu$ vs. C relation, e.g., in $\text{K}^+\text{C}_{10}\text{H}_8^-$ in THF–Et_3N (Figure 4). We notice that this break occurs at different cosolvent/solvent ratios, depending on whether the cosolvent is diethyl ether (Figure 5) or triethylamine (Figure

(12) This argument is based on the conclusion[7] that hyperfine interactions between odd electron and solvent molecules are transmitted through the mediation of the cation.

(13) This shift is the resonance frequency difference of cyclohexane in the radical anion solution and the resonance frequency of cyclohexane in THF (20:80 v/v).

(14) For the expression relating NMR contact shift and the relevant coupling constant see e.g. Eaton, D. R.; Phillips, W. D. *Adv. Magn. Reson.* **1965**, *1*, 115. The expression reduces to a_i^{1H} (in gauss) $= -1.39 \ (\pm\delta_c^i;$ in ppm/mol) $\times 10^{-2} \ (T = 308.16$ K).

Figure 4. Relationship of shift vs. concentration (see caption for Figure 1) for potassium naphthalene radical anion in THF–Et$_3$N. The points were obtained by diluting 0.50 mL of 0.86 M potassium naphthalene radical anion in THF with 0.10, 0.20, 0.40, 0.45, 0.50, 0.55, 0.60, 0.80, 1.00, and 1.20 mL of Et$_3$N.
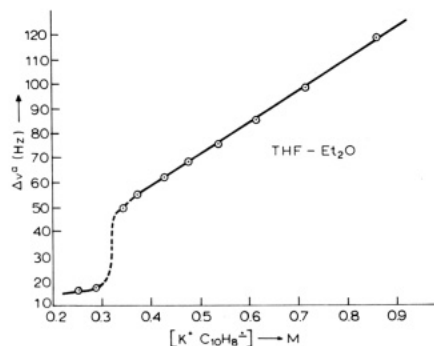
Figure 5. Relationship of shift vs. concentration (see caption for Figure 1) for potassium naphthalene radical anion in THF–Et$_2$O. The points were obtained by diluting 0.50 mL of 0.86 M potassium naphthalene radical anion in THF with 0.10, 0.20, 0.30, 0.40, 0.50, 0.65, 0.80, 1.00, and 1.20 mL of Et$_2$O.

4). Roughly, the respective breaks occur when 60 molecules of Et$_2$O or 40 molecules of Et$_3$N correspond to 100 molecules of the solvent system. We interpret these abrupt changes in the $\Delta\nu$ vs. C relationship as arising from structural changes of the radical anion–cation pair. The latter change can be caused either by the perturbation of THF's "solvent structure" by the added cosolvent or, more probably, by displacement of THF molecules at the solvation or coordination sphere of the cation by the cosolvent molecules. It should be noted that these phenomena are strongly cation dependent. Namely, with lithium as the counterion Et$_2$O does not seem capable of inducing any structural changes for Li$^+$C$_{10}$H$_8^-$· in THF. With sodium as the counterion the added cosolvent Et$_2$O or Et$_3$N does cause structural changes in Na$^+$C$_{10}$H$_8^-$·, and both cosolvents appear to be equally effective in bringing about structural changes in Na$^+$C$_{10}$H$_8^-$· (compare Figures 2 and 3). With potassium as the counterion the structural changes become even more pronounced. In this case Et$_3$N appears to be more structurally destructive than Et$_2$O, because it takes fewer Et$_3$N molecules than Et$_2$O molecules in order to bring about the abrupt change (compare Figures 4 and 5). It appears probable that lack of perturbation in the case of Li$^+$C$_{10}$H$_8^-$· is due to the inability of Et$_2$O molecules to displace THF molecules at the solvation sphere of the lithium cation. In the case of Na$^+$C$_{10}$H$_8^-$· and K$^+$C$_{10}$H$_8^-$· the cosolvent molecules can probably compete successfully against THF for coordination sites in the sodium and potassium cations.

In order to gain some information concerning the structure of the species formed after the abrupt break in the $\Delta\nu$ vs. C line, we carbonated a solution of K$^+$C$_{10}$H$_8^-$· after adding Et$_3$N to make a 50:50 (v/v) THF–Et$_3$N
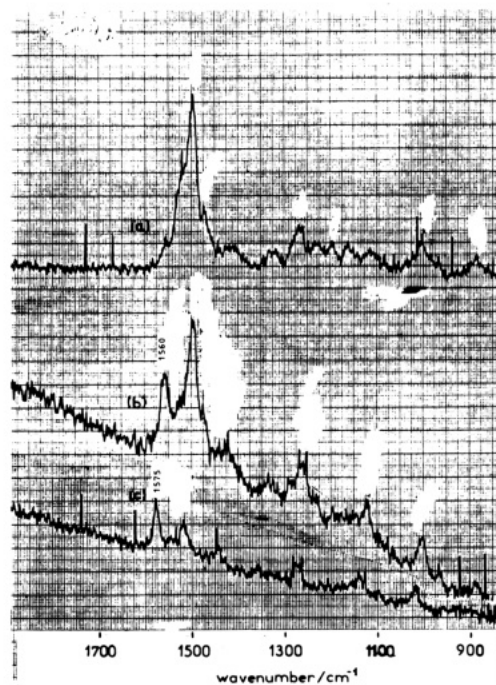
Figure 6. Laser Raman spectra of (a) potassium naphthalene radical anion in THF, (b) the same anion–cation pair in THF–Et$_3$N (50:50 v/v); the band at 1560 cm^{-1} is attributed to the dianion, and (c) dipotassium naphthalene dianion in THF–Et$_3$N (50:50 v/v).

Table II. Chemical Stability of Aromatic Hydrocarbon Dianions Determined by Double Titration Using Ethylene Bromide

entry	dianion	non-active alkalinity, % of total	$\Delta\nu_m^\alpha - \Delta\nu_m^{app}$, Hz/mol
1	(chrysene)$^{2-}$K$_2^{2+}$	2.0	5
2	(chrysene)$^{2-}$Na$_2^{2+}$	8.2	32
3	(chrysene)$^{2-}$Li$_2^{2+}$	37.6	100
4	(pyrene)$^{2-}$Li$_2^{2+}$	34.3	92
5	(phenanthrene)$^{2-}$Li$_2^{2+}$	32.4	90
6	(*p*-terphenyl)$^{2-}$Li$_2^{2+}$	22.0	69
7	(stilbene)$^{2-}$Li$_2^{2+}$	14.0	79
8	(anthracene)$^{2-}$K$_2^{2+}$	1.0	3
9	(anthracene)$^{2-}$Na$_2^{2+}$	4.6	16
10	(anthracene)$^{2-}$Li$_2^{2+}$	7.8	25

mixture. The isolated carboxylic acid from the carbonation mixture exhibited an NMR spectrum identical with that derived by carbonation of K$^+$C$_{10}$H$_8^-$· in pure THF. This probably indicates that the abrupt drop of paramagnetism on adding Et$_3$N is due to disproportionation.[15] This conclusion seems to be supported by the laser Raman spectroscopic evidence given in Figure 6 (see the figure caption).

Measurements of the molar shifts of solutions of radical anions prepared by inverse disproportionation of the relevant dianion and the neutral hydrocarbon[16] (eq 2) afforded the values denoted in Table I by $\Delta\nu_m^{app}$. These values, which correspond to the α-proton band of THF, in most cases, are not equal to the corresponding $\Delta\nu_m^\alpha$

(15) Either naphthalene radical anion or naphthalene dianion on carbonation afford the same product. See, e.g.: Coates, G. E.; Green, M. L. H.; Wade, K. "Organometallic Chemistry"; Methuen: London, 1967; p 57.

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values, as they should (perhaps) be. For example, a large discrepancy is observed in the case of the lithium *trans*-stilbene radical anion, for which $\Delta\nu_m{}^\alpha = 153$ Hz/mol and $\Delta\nu_m{}^{app} = 74$ Hz/mol (entry 23, Table I). In order to investigate the cause of this discrepancy, we carried out double titrations on solutions of the dianions. The titrations showed that, in most cases, there was a considerable percentage of "nonactive alkalinity" (see Table II). The molar shifts can be used here in conjunction with the double-titration data to draw conclusions about the chemical stability of dianions. In entries 1–3 of Table II are given the nonactive alkalinities of solutions of (chrysene)$^{2-}$M$_2{}^{2+}$ (M = K, Na, Li) in THF. This nonactive alkalinity is obviously produced by solvent cleavage during preparation of the dianions, i.e., 24 h at room temperature at concentrations of 0.5–1.0 M. It can be seen that the nonactive alkalinity increases as the positive ion changes from potassium to sodium to lithium, and with latter it becomes rather large. In the fourth column of Table II are given the respective ($\Delta\nu_m{}^\alpha - \Delta\nu_m{}^{app}$) differences (see also Table I). These differences seem to correlate with the nonactive alkalinities. An analogous behavior is exhibited by anthracene dianion (entries 8–10, Table II). Namely, the dianion appears to become more unstable as the counterion changes from K$^+$ to Na$^+$ to Li$^+$. However, in this case anthracene dianion appears to be considerably more stable than chrysene dianion. Comparing the stabilities of the two isomeric dianions (lithium phenanthrene dianion and lithium anthracene dianion, entries 5 and 10 of Table II), we can see that the phenanthrene dianion is less stable. From this information the following points seem to emerge. Dianion stability appears to be a cation–dependent property and increases with increasing electropositivity of alkali metal from which the cation is derived. Dianions derived from polynuclear aromatic hydrocarbons with angularly condensed rings are less stable than those derived from linear polynuclear hydrocarbons (compare chrysene, pyrene, and phenanthrene with anthracene, entries 3–5 and 10 of Table II).

We noticed that in the case of, e.g., (phenanthrene)$^{2-}$Li$_2{}^{2+}$ $\Delta\nu_m{}^{app}$ is about 20% of the $\Delta\nu_m{}^\alpha$ value, although the active alkalinity is 70% of the total alkalinity. In order to account for this discrepancy, we carbonated an aliquot of the supposed lithium phenanthrene dianion. From the carbonation mixture was isolated a mixture of carboxylic acids, which on the basis of NMR analysis contained the (CH$_2$)$_n$CO$_2$H group. A hydrolyzed aliquot of the same dianion solution afforded a mixture of dihydrophenanthrenes containing the (CH$_2$)$_n$CH$_3$ group. These results point to the conclusion that the solution contained species bearing the functional group (CH$_2$)$_n$Li.

Recently, the reduction of pyrene by sodium metal in THF-d_8 at room temperature to the relevant tetraanion has been reported.[17] The authors[17] did not observe any decay of the tetraanion by solvent cleavage. This appears to be in contrast to our findings. Indeed, during conversion of pyrene to the corresponding tetraanion, it must go through the relevant dianion. The only explanation for lack of attack of the solvent we can offer is that either the unstable dianion is transformed rapidly enough to the respective radical trianion and to tetraanion or, less probably, the THF solvent cleavage exhibits a marked deuterium isotope effect.

The behavior of the lithium dianions of chrysene, pyrene, and phenanthrene is reminiscent of the analogous property of the covalent organolithium reagent to cleave
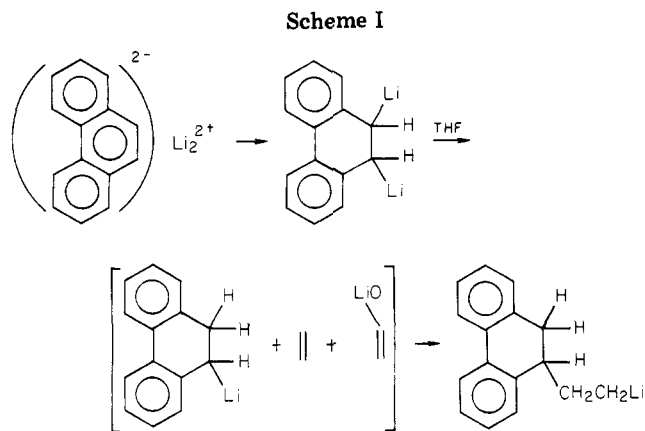
Scheme I

THF[18] and to incorporate the ethylene produced from the THF cleavage.[19] We propose the following scheme which, it is felt, can explain the observed chemistry. It is based on the reasonable assumption that angularly condensed polynuclear aromatic hydrocarbons can form π as well as σ complexes, the latter through their K region(s). According to the proposed scheme (Scheme I), e.g., the originally formed true phenanthrene dianion isomerizes to the respective "σ complex", 9,10-dilithio-9,10-dihydrophenanthrene. The latter species is a geminal dibenzylic-type organolithium compound. It is known[20] that even benzylic organolithium exhibit to a certain extent covalency in their C–M bonds, and that covalency should increase as M changes from K to Na to Li. Such species, then, could cleave THF with production of ethylene and the enolate of the acetaldehyde.[18] It must be stressed that the latter mode of THF cleavage is entirely different from that of THF cleavage by radical anions. Radical anions seem to cleave THF by a reductive ring-opening mechanism.[21]

We prepared (stilbene)$^{2-}$Li$_2{}^{2+}$ at 0 °C and used it to make lithium stilbene radical anion according to eq 2. From this sample a molar shift referred to the α-proton band of THF of 150 Hz/mol was obtained (entry 24, Table I). Comparing this value with the $\Delta\nu_m{}^\alpha$ value of 153 Hz/mol (entry 23, Table I), we can see that at ice-bath temperatures lithium stilbene dianion appears to be stable. Similar results were obtained with lithium *p*-terphenyl dianion (see entries 2 and 3, Table I). These results clearly indicate that dianions of aromatic hydrocarbons should be prepared at subzero temperatures in order to avoid contamination of the dianion by solvent-cleavage product.[22] It is also expected that dianions of aromatic hydrocarbons will be considerably less stable in 1,2-dimethoxyethane than they are in THF.

Concluding Remarks

Useful information concerning structure and reactivity of radical anions and dianions, at concentrations comparable to those of the preparative reactions, has been obtained from paramagnetic solvent NMR shift measure-

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(22) Müllen, K. *Helv. Chim. Acta* **1978**, *61*, 2307. This author has employed a low temperature (–80 °C) for the preparation of the pyrene–dilithium compound. Although the reason for this precaution was not explained, it seems likely that the author had observed the instability of the pyrene dianion.

ments. The fact that radical anions might have a concentration-dependent structure justifies the search for information under the above-mentioned conditions. It is felt that this information is more realistic and directly applicable by the organic chemist who deals with the chemistry of radical anions. Although solutions of radical anions may contain a plethora of species which differ in the degree of association, the magnetic state, the ion-pair situation, etc., our results, in certain instances, reveal that the situation is astonishingly simple. For example, the abrupt break in the $\Delta\nu$ vs. C curve in Figure 4 hardly suggests the existence of more than one thermodynamically distinct species, under those conditions.

Experimental Section

A Varian A60A NMR spectrometer was used for the solvent shift measurements. Details of the method have been given elsewhere.[7] In certain instances a Varian FT-80 spectrometer was employed (see the preceding discussion). The great stability of this instrument makes the use of external markers unnecessary. In order to obtain a lock, C_6D_6 was sealed in thin-walled capillaries. Under these conditions the THF proton bands exhibited resonances centered at 502.4 ± 0.3 and 355.6 ± 0.3 Hz from the "zero" of the instrument. The indicated values were obtained from a set of seven NMR tube–capillary pairs. Paramagnetic solvent shifts were measured relative to the THF bands in the absence of any paramagnetic solute, namely, by subtracting the resonance frequency of the α-proton band of THF, in the paramagnetic solution, from 502.5 Hz and the resonance frequency of the β THF band from 355.5 Hz. In the cases where a double internal reference was used, i.e., THF and cyclohexane, the solvent shifts were referred to the relevant resonance bands in 80:20 (v/v) THF–cyclohexane, in the absence of any solute. The centers of these bands were 500.3 (α-proton band of THF), 353.3 (β protons of THF), and 327.2 Hz (cyclohexane) downfield from the "zero" of the instrument. Bulk paramagnetism was measured with a Gouy balance. The Raman spectra were recorded on a Jobin-Yvon Ramanor Model HG-2S spectrometer. The exciting radiation was provided by a Spectra Physics Model 165-03 argon laser. The aromatic hydrocarbons were commercial products of 99% purity or better, and they were used without further purification. Tetrahydrofuran was purified as described previously.[6] Diethyl ether and triethylamine were distilled from lithium aluminum hydride under argon shortly before use. Solutions of radical anions were prepared by stirring strictly equivalent amounts of the hydrocarbon and the metal in THF for 16–24 h under an atmosphere of pure argon and using a glass-coated stirring bar. Solutions of the radical anions were standardized as previously described.[7] Aromatic hydrocarbon dianions were prepared in 0.5–1.0 M solutions in THF by following the method for preparing

the radical anions. Double titrations of dianion solutions were carried out by using ethylene bromide.[3]

Carbonation of "Lithium Phenanthrene Dianion". Phenanthrene (1.78 g, 10 mmol), lithium chips (0.140 g), and THF (18 mL), were stirred under argon for 18 h at room temperature. The reaction mixture was diluted with 10 mL of anhydrous THF and carbonated. From the carbonation mixture was isolated an acid fraction which weighed 1.5 g and was a glassy solid. The NMR spectrum of this material exhibited the following resonances in parts per million downfield from Me_4Si: 1.17, (br s), 3.23 (br s), 3.63 (br s), 4.25 (br s), 5.10 (sharp s). The number of aliphatic plus olefinic protons was nearly equal to the number of aromatic ones. The neutral fraction from the carbonation mixture (0.70 g) exhibited resonances in the aliphatic region the NMR spectrum, namely: 0.88 (diffuse t), 1.23 (br s), 2.70 (br s), 3.35 (diffuse t).

Carbonation of Potassium Naphthalene Radical Anion in THF–Et$_3$N. A solution of potassium naphthalene radical anion prepared from 2.6 g (ca. 20 mmol) of naphthalene, 0.79 g (ca. 20 mol) of potassium, and 20 mL of THF was diluted with 20 mL of anhydrous triethylamine and carbonated. From the carbonation mixture by a conventional workup was isolated 2.0 g of an acid. This acid exhibited an NMR spectrum identical with that obtained by carbonation of $K^+C_{10}H_8^-$· in pure THF, namely: 4.33 (unsym d), 6.22 (unsym br d), 6.95–7.45 (unsym br m).

β-Lactam Synthesis Using Organoiron Intermediates. Preparation of 3-Carbomethoxycarbapenam

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Claisen rearrangement of the vinyl allyl ether derived from methyl pyruvate diallyl ketal provides a convenient route to methyl 2-oxo-5-hexenoate (3). Exchange complexation with η-C$_5$H$_5$Fe(CO)$_2$(isobutylene)PF$_6$ in methylene chloride gives the olefin complex 4, and this is transformed to the pyrroline complex 5 on exposure to ammonia. Reduction of this substance with sodium borohydride yields a mixture of stereoisomeric pyrrolidine complexes 6-c,t. This is converted to a mixture of stereoisomeric chelate complexes 10 and thence by oxidation with silver oxide or air to the stereoisomeric 3-carbomethoxycarbapenams 11a,b.

Current interest in fused ring β-lactams, especially those of the carbapenem[1] class, led us to examine methods for

the synthesis of the parent saturated ring system using organoiron intermediates based on the η-C$_5$H$_5$Fe(CO)$_2$