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The Strange Behavior of Lithium Salt of Tetraphenylethylene Dianion

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Abstract: We examined the optical and ^{13}C NMR spectra of the disodium and dilithium salts of tetraphenylethylene dianion (T^{2-}) as well as the spectra of their mixtures. A strong band appearing in the spectrum of $T^{2-},2Li^+$ at 385 nm is not seen in the spectrum of $T^{2-},2Na^+$. The extinction coefficient of that band is unaffected by dilution of $T^{2-},2Li^+$ even when more than 50% of the salt is dissociated into $T^{2-},Li^+ + Li^+$. In the mixture of $T^{2-},2Na^+$ and $T^{2-},2Li^+$, the relative intensity of the 385-nm band varies with the ratio Na^+/Li^+, being ½ as intense for $Na^+/Li^+ = 1$ than for $T^{2-},2Li^+$. An appreciable upfield shift of the ethylenic ^{13}C is seen in the NMR spectrum when the hydrocarbon is reduced to its dianion, the shift being substantially greater for the dilithium than for the disodium salt. Mixture of the salts give only one NMR line for that carbon, indicating (in NMR time scale) a rapid exchange of the cations. A proposed tentative structure of these salts accounts for all the apparently inconsistent observations.

Striking differences in the optical spectra of the disodium and dilithium salts of tetraphenylethylene dianions ($T^{2-},2Na^+$ and $T^{2-},2Li^+$) were reported in our previous publication.[1] The spectrum of the disodium salt, shown in Figure 1, has a broad absorption with maximum at 485 nm ($\epsilon = 3.7 \times 10^4$). A similar absorption band appears at λ_{max} 495 nm ($\epsilon = 2.6 \times 10^4$) in the spectrum of the dilithium salt; however, as revealed by Figure 1, an additional strong peak at λ_{max} 385 nm ($\epsilon = 3.0 \times 10^4$) is seen in the spectrum of the latter salt.

The 385-nm absorption band of $T^{2-},2Li^+$ was tentatively ascribed to a charge-transfer transition;[1] however, we are exploring now an alternative explanation of this phenomenon. The intensity of the 385-nm band is clearly derived from the intensity of the 495-nm band, implying their common origin. Moreover, change of the solvent shifts both peaks, to the same degree; namely, the respective maxima are at 363 and 475 nm in dioxane, 355 and 463 nm in diethyl ether but the ratio $\epsilon_{max\ short\ wave}/\epsilon_{max\ long\ wave}$ is lower in dioxane and diethyl ether than in THF.

The present studies were initiated with the intention of gaining more information about this transition, and their results provided interesting insight into the structure of these salts. Investigation of optical spectra of analagous salts will be reported later.

NMR Studies of $T^{2-},2Na^+$ and $T^{2-},2Li^+$

The ^{13}C spectra of tetraphenylethylene (T) and of the disodium and dilithium salts of its dianion were obtained in deuterated THF by means of a Varian XL 100 NMR spectrometer equipped with a Fourier transform gear. The results are collected in Table I. The ethylenic and quaternary phenyl carbon nuclei were recognized by their long relaxation times and low intensity (¼ and ½, respectively, of the most abundant ortho and meta carbons), while the para carbon nuclei are again distinguished by their low intensity (equal to that of the quaternary ring carbons) but shorter relaxation time. The distinction between the most abundant meta and ortho carbons is made possible by the effect of negative charge on their position; the respective lines of the hydrocarbon and of the dianion salts virtually coincide for the meta carbons but are substantially separated for the ortho nuclei. The large upfield shift of the ethylenic line caused by the conversion of the hydrocarbon into dianion is the most striking result transpiring from the data collected in Table I. The line of the sodium salt is shifted by 43.42 ppm, and an even larger upfield shift by 52.66 ppm is observed for the lithium salt. This finding confirms the suggestion that the Li^+ cation in $T^{2-},2Li^+$ is placed closer to the dianion than the Na^+ in $T^{2-},2Na^+$. Interestingly, the

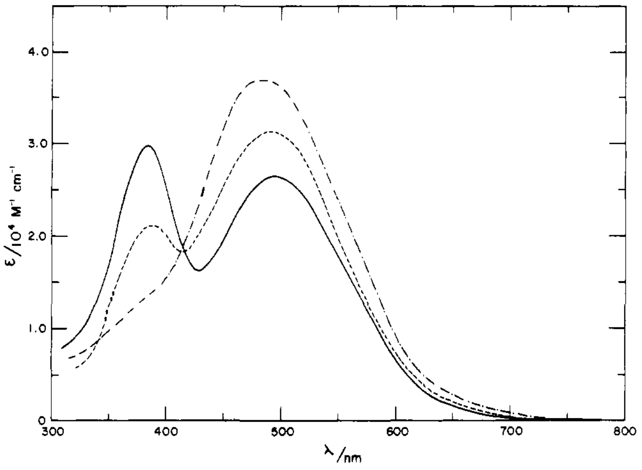

Figure 1. The spectrum of $T^{2-},2Na^+$ (- · · · -); of $T^{2-},2Li^+$ (solid line); and of T^{2-},Na^+,Li^+ or an equimolar mixture $T^{2-},2Na^+$ + $T^{2-},2Li^+$ (dashed line) in THF. Note the isosbestic point.

conversion of the hydrocarbon into dianion shifts downfield the resonance of the quaternary ring carbon, while the resonances of the ortho and of the para carbons are slightly shifted upfield.

Pursuing this line of investigation, we examined the NMR spectra of solutions of T^{2-} ions simultaneously coupled with Li^+ and Na^+ cations. Three types of ionic aggregates, $T^{2-},2Li^+$, $T^{2-},2Na^+$, and T^{2-},Na^+,Li^+, may be present in such solutions. In the absence of *inter*molecular exchange, $T^{2-},2Li^+$ should produce a line at 62.40 ppm, while $T^{2-},2Na^+$ would give rise to a line at 71.54 ppm (see Table I). The mixed aggregate could produce a line placed between the other two, provided that the *intra*molecular exchange is fast, or it could contribute to the lines of $T^{2-},2Li^+$ and $T^{2-},2Na^+$ if the *intra*molecular exchange is slow and each ethylenic carbon is permanently associated with its cation. The results show that only one sharp NMR line is formed between 62.40 and 71.54 ppm; it is located at the middle point of this interval when the ratio $Na^+/Li^+ = 1$, and it shifts linearly from one extreme to the other with increasing mole fraction of Li^+. Similarly, only intermediate lines were seen in other parts of the spectrum where the resonance frequencies of the lithium and sodium salts do not coincide. These results demonstrate that the cations are rapidly exchanged through *inter*molecular as well as through *intra*molecular reactions, e.g., $T^{2-},2Na^+ + T^{2-},2Li^+ \rightleftarrows 2T^{2-},Na^+,Li^+$ and $T^{2-},Na^+,Li^+ \rightleftarrows T^{2-},Li^+,Na^+$.

Optical Spectra of T^{2-} Salts

The NMR evidence reviewed in the preceding section strengthens the notion that in the respective salts the Li^+ cations are closer to the T^{2-} dianions than the Na^+ ions. It might be expected that the intensity of the 385-nm band should be twice as strong for $T^{2-},2Li^+$ than for the half-dissociated T^{2-},Li^+, provided that both Li^+ ions of the former aggregate are equally effective in the transition. Examination of the spectra of THF solutions of $T^{2-},2Li^+$ showed that the relative intensities of the 385- and 495-nm bands are unaffected by dilution from 5×10^{-3} M to less than 10^{-5} M, although the dissociation of $T^{2-},2Li^+$ into $T^{2-},Li^+ + Li^+$, which is negligible at the higher concentration (~3%), becomes appreciable (>50%) at the highest dilution.[1] It seems, therefore, that the two Li^+ of the $T^{2-},2Li^+$ are not equivalent within the *short time of light absorption* (10^{-14}–10^{-15} s); i.e., whenever one is strongly bound the other is loose, and only the former is effective in inducing the new transition. Nevertheless, since the two Li^+ ions rapidly exchange their relative positions in respect to T^{2-}, they give rise to only one resonance line of the ethylenic ^{13}C atoms in the *longer* NMR time scale.

Table I. ^{13}C NMR spectra of T, $T^{2-},2Na^+$, and $T^{2-},2Li^+$ [a]

Carbon atom	T	$T^{2-},2Na^+$	$T^{2-},2Li^+$
p-C (Phenyl)	100.15	84.26	84.66
m-C (Phenyl)	105.33	105.72	104.93
o-C (Phenyl)	101.55	93.40	94.99
q-C (Phenyl)	117.65	124.01	123.21
Ethylenic C	115.06	71.54	62.40

[a] In ppm downfield from the most upfield placed line of the deuterated THF.

Table II. Effect of Tetraglyme Addition to $T^{2-},2Li^+$ in THF

[Tetraglyme], M	*R*	K_G, M^{-1}	K_{GG}, M^{-2}
1.13	0.15	0.13	0.115
1.83	0.22	0.12	0.065
3.23	0.45	0.14	0.045

We also investigated the spectra of THF solution of $T^{2-},2Na^+$ ($\sim 1 \times 10^{-2}$ M) to which increasing amounts of LiCl were added. The addition of the THF soluble LiCl leads to the precipitation of the THF insoluble NaCl and to a gradual replacement of Na^+ ions by Li^+ in the T^{2-} salt. This leads to continuous spectral changes; the absorbance at 485 nm decreases, and the new 385-nm band grows, reaching its final intensity when *all* the Na^+'s are replaced by Li^+. Further addition of LiCl does not affect the spectrum any more. For the sake of illustration, we showed in Figure 1 the absorption spectrum of the salt containing equal proportion of Li^+ and Na^+ ions. The 385-nm band is only *half* as intense as in $T^{2-},2Li^+$, and significantly, an isosbestic point is seen at ~420 nm. Both observations imply that Li^+ does not preferentially occupy the "tight" position in the aggregate, but apparently these cations exchange their position in respect to the ethylenic carbon atoms, and at any time either one or the other is tightly bound to T^{2-}. This does not preclude the "tight" Na^+ to be located further from C^- than the "tight" Li^+. The characteristic spectrum of the lithium salt is converted into the one-band spectrum of the sodium salt when an excess of Na^+,BPh_4^- is added to the THF solution of $T^{2-},2Li^+$.

It is well known[2] that glymes, like tetraglyme, convert tight alkali aggregates into loose ones. The effect of tetraglyme addition to $T^{2-},2Li^+$ in THF was investigated, and the addition led to a gradual decrease in the intensity of the 385-nm band. It is reasonable to assume that the ratio $R = [\mathrm{od}\ (385)_O - \mathrm{od}\ (385)_G]/[\mathrm{od}\ (385)_G - \mathrm{od}\ (385)_\infty]$ gives the proportion of the glymated to the nonglymated aggregates. Here the subscripts O, G, and ∞ refer to the spectra observed in the absence of the glyme, in its presence, and at complete conversion of the tight to the loose pairs, while $[T^{2-},2Li^+]$ was kept constant. The equilibrium constant of the reactions

$$T^{2-},2Li^+ + G \rightleftarrows T^{2-},Li^+G,Li^+ \qquad K_G$$

and

$$T^{2-},2Li^+ + 2G \rightleftarrows T^{2-},(Li^+G)_2 \qquad K_{GG}$$

are given by $R/[G]$ and $R/[G]^2$, respectively. As shown by the data summarized in Table II, K_G is constant implying that only one molecule of the glyme is needed to convert the species absorbing at 385 nm into the one which does not absorb at this wavelength.

These results may be rationalized if one notes that a high concentration of the glyme is needed (~1 M) to convert about 15% of the absorbing species into the nonabsorbing. We can argue that, at these high concentrations of the glyme, one Li^+ cation is already "glymated", and the other Li^+ cation of the resulting aggregate, $T^{2-},Li^+(Li^+,G)$, is then permanently and tightly bound to T^{2-}. Further addition of the glyme leads to the reaction

$$T^{2-},Li^+(Li^+,G) + G \rightleftarrows T^{2-},(Li^+G)_2$$

justifying our findings.

The Structure of T^{2-},$2Li^+$ Aggregate

All of the observations reported here may be accounted for by the following tentative structure of $Li^+,Ph_2\bar{C}-\bar{C}Ph_2,Li^+$. The two $\bar{C}Ph_2$ groups are lying in two mutually perpendicular planes and one Li^+ cation is located close to the negatively charged C–C framework, while the other, being fully solvated by THF, is placed further away. However, the two cations continually exchange their state, the process could be described as a reaction, tight Li^+ + solvated Li^+ $\rightleftarrows$ solvated Li^+ + tight Li^+. Coulombic repulsion between these cations probably is responsible for this behavior of that salt, keeping one cation away as the other is placed near to the C–C center. Thus, at any time, only one Li^+ is tightly bound, but they become equivalent if the observation is extended over a longer time period. Their equivalence is shown, therefore, in NMR results but not in electronic spectra. The 385 nm band arises from the absorption by the very tight $-\bar{C}(Ph)_2Li^+$ pair, its tightness being due to the vicinity of the second $\bar{C}$ center, whereas the loose, solvent separated pair $-\bar{C}(Ph)_2||Li^+$ absorbs at 495 nm. The closeness of the two $\bar{C}$ centers prevents both Li^+ cations to be simultaneously tightly bonded. The absorption of loose pairs is often indistinguishable from that of free ions; therefore the spectrum of $Li^+,\bar{C}(Ph)_2\cdot\bar{C}(Ph)_2||Li^+$ is virtually identical with that of $Li^+,\bar{C}(Ph)_2\cdot\bar{C}(Ph)_2$. The very large degree of tightness of the $Li^+,\bar{C}(Ph)_2-$ is due to the smallness of Li^+, but it requires also the presence of a closely located second $\bar{C}$ center because $Li^+,\bar{C}(Ph)_2\cdot CH_2CH_2\cdot\bar{C}(Ph)_2,Li^+$ absorbs only at ~490 nm, i.e., both Li^+ are fully solvated. Both sodium cations are fully solvated in $Na^+||\bar{C}(Ph)_2\bar{C}(Ph)_2||Na^+$ since the spectrum of that salt shows only one absorption band at 485 nm.

This example strikingly illustrates how much may be learned about the intricate structure of ionic aggregates from their spectroscopic studies.

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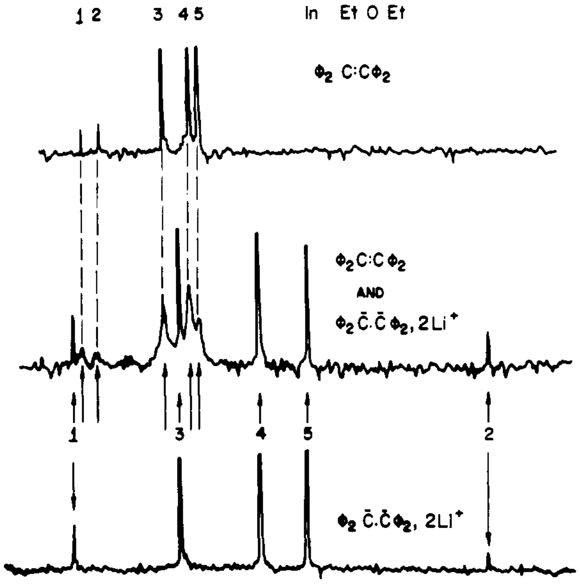

Figure 2. The ^{13}C NMR spectra of $Ph_2C:CPh_2$ (0.05 M), of a mixture of $Ph_2C:CPh_2$ (0.07 M) and its dilithium salt, $Ph_2\bar{C}\cdot\bar{C}Ph_2,2Li^+$ (0.02 M) and of the dilithium salt only (0.02 M) in diethyl ether. The long arrows point to the hydrocarbon lines and the short ones to the lines of the salt. The numbers refer to the quaternary carbons of the phenyl groups (1), the ethylenic carbons (2) and the meta, ortho, and para carbons (3, 4, and 5), respectively.

Appendix

The pronounced difference in the ^{13}C NMR spectra of tetraphenylethylene and the lithium salt of its dianion prompt us to investigate the ^{13}C NMR spectrum of their mixture in diethyl ether and in benzene. The results obtained in diethyl ether ([T] = 0.07 M, $[T^{2-},2Li^+]$ = 0.02 M) are shown in Figure 2. Both sets of lines, those of T and the other of $T^{2-},2Li^+$, appear in the spectrum of the mixture, implying a very slow, if any, two-electron transfer, $T + T^{2-},2Li^+ \rightleftarrows T^{2-},2Li^+ + T$. Interestingly, the lines of T, but not those of $T^{2-},2Li^+$, are broadened. Apparently T, but not $T^{2-},2Li^+$, exchanges with the minute amount of $T\cdot^-,Li^+$ present in the solution. The concentration of the radical anions is unknown, because no ESR signal could be observed.

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