

Nuclear Magnetic Resonance and Electron Absorption Studies of Acenaphthylene Dianion. Ion-pair Structure and Charge Distribution

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The ^1H and ^{13}C n.m.r. chemical shifts of acenaphthylene dianion are studied by variation of cation, solvent, and temperature. For the description of the charge distribution, comparisons are also made with the neutral hydrocarbon, acenaphthylene. In the contact ion pair structure, the cations occupy non-equivalent positions relative to the dianion. The ability to undergo solvation also differs for the two cations. The Na and K salts exist solely as contact ion pairs under the investigated conditions. ^7Li N.m.r. and u.v.-visible spectroscopic characterization provide further evidence for the proposed ion pair structures. The comparatively small and variable ^{13}C chemical shift-charge correlation factor of the dinegative-uncharged compounds is discussed in view of a varying degree of diatropicity. The electronic structure of the dianion is best described in terms of a partly localized π -electronic system.

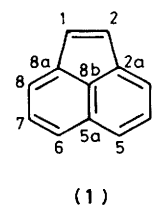
We have recently reported the results from n.m.r. investigations of the dianions of dibenzo[*b,f*]pentalene and *s*-indacene.¹ It was found that the ion pairing situation of these dilithium salts can be described as an equilibrium between contact ion pairs (c.i.p.s) and solvent-separated ion pairs (s.s.i.p.s), in accord with experience from a large number of monoanionic systems.² However, this description does not exclude the existence of more complicated structures in multiply charged systems, such as a dianion structure with one cation in a c.i.p. state and the other one in a solvated state, rapidly exchanging on the n.m.r. time scale.³

As earlier reported, it is important to know the actual ion pair structure if one intends to compare ^1H and ^{13}C n.m.r. chemical shifts with atomic charges from MO calculations.^{1,4} The reason is that cation-induced charge polarization can be significant in anionic systems.^{1,4,5}

The use of ^{13}C n.m.r. shieldings to probe the charge distribution qualitatively stems from the theory that the ^{13}C chemical shifts are dominated by the paramagnetic shielding.⁶ In a simplified treatment the shielding is determined by the electron density in the $2p$ orbitals, if other factors such as bond orders and energies for excitations of electrons are constant.⁷ The ^1H chemical shifts, on the other hand, depend mainly on diamagnetic contributions and anisotropy effects such as ring currents.^{6b,8} The polarization of electrons in the C-H bonds caused by electric fields (*e.g.* carbon and/or cation charges) can be included in the diamagnetic shielding term.^{6b,9}

There are several reasons for choosing the dianion of acenaphthylene (1^{2-}) as a model system. From CNDO calculations of (1^{2-}) a comparatively high charge is predicted at C-1 and -2, while most of the remaining charge is more uniformly spread at the peripheral C-3(-8) and C-5(-6). Hence, if the preferred cation positions in a c.i.p. structure are close to the high charge positions C-1 and -2, one would expect both cation and electron repulsive effects to be pronounced in this system.¹⁰ It is also of interest to investigate whether a delocalized peripheral ring current model is more attractive than a structure composed of conjugated subunits with or without anisotropic character.

In the present study the ^{13}C n.m.r. chemical shifts were measured in order to determine the ion pair structure and to provide information of the charge distribution at different conditions, *i.e.* various combinations of cation, solvent, and temperature. Complementary information was obtained from ^1H and ^7Li chemical shifts and electron absorption spectroscopy.



Experimental

Compounds and N.m.r. Techniques.—The ether solvents were refluxed over Na-K alloy and distilled prior to use. [$^2\text{H}_{18}$]Hexamethylphosphoric triamide ($[\text{H}_{18}]$ HMPA) was dried with molecular sieves. [$^2\text{H}_8$]Tetrahydrofuran ($[\text{H}_8]$ THF) was used without further purification. Acenaphthylene (1) (EGA Chemie) was recrystallized from methanol.

The n.m.r. samples of (1^{2-}) were prepared directly in the n.m.r. tubes by reduction of (1) with alkali metal. After addition of a small amount (*ca.* 15 mol-%) of cyclohexane, as internal reference, fresh pieces of metal were cut in the actual solvent and added to the argon-flushed solutions. The samples were then degassed by repeated freeze-pump-thaw cycles and sealed off from the vacuum line. An increase in the rate of formation of (1^{2-}) was achieved by placing the tube in an ultrasonic bath.¹¹ During the reduction process no signals of (1) or (1^{2-}) were seen due to fast electron exchange with the radical anion.^{12a} Within 0.5–1 h the highly resolved n.m.r. spectrum of the dianion appeared without any traces of impurities. The samples were found to be stable at room temperature for several months. The THF- $[\text{H}_{18}]$ HMPA samples were obtained by generation of (1^{2-}) in THF, followed by addition of degassed $[\text{H}_{18}]$ HMPA from a side-arm on the tube. Deuteriated HMPA was used since slower decomposition of (1^{2-}) was noticed in this medium compared with the situation in the protio-solvent.

All spectra were obtained on a Bruker WM 250 n.m.r. spectrometer, equipped with a B-VT 1000 temperature control unit. The chemical shifts were measured relative to the internal reference and adapted to the tetramethylsilane scale with δ_{H} (cyclohexane) 1.43 and δ_{C} (cyclohexane) 27.70 p.p.m. The ^7Li chemical shifts were referenced to external aqueous 1.0M-LiCl. If not stated otherwise, the temperature was 25 °C and the concentrations were in the range 0.05–0.21M.

The ^1H n.m.r. signals of (1) and (1^{2-}) and the ^{13}C n.m.r. signals of (1) have been assigned earlier.^{12–14} The signals of the

protonated carbons of (1^{2-}) were assigned by selective proton decoupling, while the signals of the nonprotonated carbons were assigned from their relative intensities. The assignments of (1^{2-}) are in agreement with the reported chemical shifts in an independent study.^{4b}

U.v.-Visible Techniques.—The samples for the electron absorption measurements were prepared in a small glass apparatus consisting of a cuvette and a side-arm. Acenaphthylene (1) (*ca.* 4 mg) was introduced into the side-arm, followed by the solvent (*ca.* 3 ml) and the metal flakes. After degassing, the apparatus was sealed off and placed in the ultrasonic bath. The reaction could be followed by transferring a small amount of the reaction solution to the cuvette and diluting the sample to the appropriate concentration by distillation of solvent from the side-arm into the cuvette. With this technique, where the dianion was prepared at comparatively high concentration (*ca.* 10mM) and subsequently diluted, the problems with small amounts of impurities could be eliminated (*e.g.* moisture and oxygen in the solvent and on the glass walls). Furthermore, the same sample could be used for concentration studies in the range 10^{-3} – 10^{-4} M (500–800 nm absorptions). The highest concentrations were determined by quenching the sample with water, followed by titration with HCl. The lower concentrations were estimated from the absorbance ratio Abs.(low concentration)/Abs.(high concentration). For the low-temperature measurements the glass apparatus was placed in a quartz vessel filled with methanol and solid CO_2 . The spectra were recorded in a Pye-Unicam SP 1750 u.v. spectrometer (range 300–700 nm) and repeated on a Beckman Acta CIII spectrometer in the range 500–800 nm.

Results and Discussion

Chemical Shift-Charge Density Correlations.—A previous ^{13}C n.m.r. investigation of (1) has suggested that this 12 π -electron system can be regarded as a naphthalene unit weakly coupled with a strongly localized double bond.¹⁴ Chemical reactivity of (1) and low-field absorptions of the 'naphthalene' protons compared with 1- and 2-H support this view (Table 1).¹⁵

The ^{13}C chemical shifts and the calculated π -charges or total charges (CNDO) of (1^{2-}) suggest that most of the charge is located at the protonated C-1(-2), -3(-8), and -5(-6) (Table 2).¹⁶ Furthermore, a noticeable positive charge is indicated for C-5a.

If only the increased charge on the carbons influences the ^1H chemical shifts, one would on the basis of the relationship 10.7 p.p.m. per electron (*i.e.* ^1H chemical shift *versus* π -electron density) expect the average ^1H chemical shift to be 4.8 p.p.m. in the dianion.^{6b,17} This chemical shift value is calculated with the two extra electrons at the protonated carbons. Cation-induced polarization of the electrons in the C-H bonds towards the carbons would cause the average ^1H signal to appear at somewhat lower field.⁹ However, one observes the average ^1H chemical shift being located upfield from the calculated value (δ 4.25–4.53) (Table 1). The 4-(7)-H signal is shifted 2.2 p.p.m. to higher field by going to the dianion, although no negative charge is predicted at this position by ^{13}C n.m.r. or MO data. The most obvious explanation to these findings is a decreased diatropicity going from the partly diatropic (1) to (1^{2-}). This is strengthened by the change of the ^{13}C chemical shifts, where the observed shift/charge ratio (K_c) of 114.2–124.3 p.p.m. per electron is considerably lower than the most quoted value of 160 p.p.m. per π -electron.^{6b,18,19} This latter correlation factor was originally derived from mono-

cyclic systems with purely diatropic character. Even lower values of K_c (0–103 p.p.m. per electron) can be observed in cases where paratropic dianions are compared with the corresponding neutral diatropic systems.^{4,20}

It may be noticed that the low diatropicity of (1^{2-}) is not in agreement with a 14 π -electron peripheral ring current model. From reactivity data of acenaphthene and X-ray diffraction studies of organometallic complexes between $\text{Fe}(\text{CO})_{12}$ and (1^{2-}), the delocalization has been interpreted as a cyclopentadienyl anion (C-1, -2, -2a, -8a, -8b) and a heptatrienyl anion (C-3–5, -5a, -6–8).²¹ ^7Li N.m.r. of (1^{2-})- 2Li^+ has also supported a structure composed of these subunits.²²

The low K_c values may be ascribed to a reduced average excitation energy and consequently an increased paramagnetic shielding in the dianions. This may also be the explanation for the variation of K_c of (1^{2-}) with different combinations of cation, solvent, and temperature (Table 2). An even larger variation of K_c has recently been observed for the paratropic dianion of acepleiadylene by changing the cation from Li to K ($27 \rightarrow -1$ p.p.m. per electron).^{4b}

Another explanation to the variation of the K_c values may arise from the 'coupling' between the π - and the σ -electron densities.^{19b,23} A low K_c value could then indicate that some π -electron density is 'transformed' into σ charge (increased *p*-character), for instance by a certain degree of covalency of the carbon-alkali-metal bonds. In this context the one-bond C-H couplings are of interest since a cation-anion overlap would be expected to reduce the coupling constants, even under fast cation exchange conditions.²⁴ However, the $^1J_{\text{CH}}$ values of (1^{2-}) are typical for negatively charged sp^2 carbons, and do not indicate any carbon rehybridization (Table 2). Moreover, with a covalent contribution we would expect $^1J_{\text{CH}}$ to be smallest for the Li^+ salt. This is not in accord with the observations.

Furthermore, the high-field ^7Li chemical shifts of the (1^{2-})- 2Li^+ system are typical of an ionic structure (Table 1).²⁵

Hence, as indicated above, caution must be stressed when ^{13}C (and ^1H) chemical shift changes between neutral systems and dianions and between different ion pair structures of anions are interpreted in terms of charge density redistributions. Since there is a rough correlation between π -electron or total electron densities and ^{13}C n.m.r. data of (1) and (1^{2-}) ($\Delta\rho_\pi$ or $\Delta\rho_{\text{tot}}$ *versus* $\Delta\delta$ ^{13}C , Table 2), it may in this case be assumed that the different carbons are influenced in a similar extent by the anomaly which causes the low K_c values. The use of system-specific K_c values for the calculation of experimental charge patterns has earlier been recommended.^{14,4} Moreover, it seems reasonable to discuss the ^{13}C chemical shift changes of (1^{2-}) at different ion-pair conditions as electron redistributions, since in these cases the geometry of the carbon skeleton should remain unaltered.

Ion-pair Structures.—a *N.m.r. studies.* The c.i.p./s.s.i.p. ratio for a specific carbanionic system can be increased by: (a) higher temperature, as a consequence of a higher entropy in the c.i.p. system, (b) a larger cation, which reduces the cation-solvent interaction more than the cation-anion interaction, and (c) a solvent with less solvating ability.²

Several investigations have shown that variable-temperature ^{13}C n.m.r. measurements are useful for obtaining information about ion-pair equilibria.^{1a,5b-e} The change from s.s.i.p. to c.i.p. causes an electron redistribution in the anion towards the preferred cation position(s), which can be monitored with the chemical shifts.

By lowering the temperature, the resonances of C-1(-2) and -3(8) of (1^{2-})- 2Li^+ undergo upfield shifts, while a downfield

Table 1. ^1H N.m.r. chemical shifts of acenaphthylene (1) and acenaphthylene dianion (1^{2-}). ^7Li n.m.r. chemical shifts of $(1^{2-})\text{-}2\text{Li}^+$ ^a

| Compound | Cation | Solvent | 1-,2-H | 3-,8-H | 4-,7-H | 5-,6-H | Average | $\delta(^7\text{Li})$ |
|------------|--------|--|--------|--------|--------|---------------------|---------|-----------------------|
| (1) | | THF | 7.04 | 7.65 | 7.50 | 7.78 | 7.49 | |
| (1^{2-}) | Li | Et ₂ O | 4.49 | 4.63 | 5.29 | 3.70 ^b | 4.53 | -3.38 |
| | | 2-MeTHF | 4.36 | 4.54 | 5.20 | 3.64 ^b | 4.44 | |
| | | [² H ₈]THF | (-0.1) | (-0.1) | (-0.1) | (-0.1) ^c | | |
| | | | 4.30 | 4.52 | 5.18 | 3.61 | 4.40 | |
| | Na | THF-[² H ₁₈]HMPA | 4.26 | 4.44 | 5.07 | 3.5 ^b | 4.32 | -2.75 |
| | | | (-0.2) | (-0.2) | (-0.2) | (-0.2) | | |
| | K | [² H ₈]THF | 4.49 | 4.46 | 5.04 | 3.34 | 4.33 | |
| | | | (0.0) | (-0.2) | (-0.3) | (-0.4) | | |
| | | THF | 4.45 | 4.42 | 4.92 | 3.21 | 4.25 | |
| | | | | (0.0) | (-0.2) | (-0.4) | (-0.5) | |

^a ^1H Chemical shifts are measured relative to internal cyclohexane and referenced to Me₄Si with δ_{H} (cyclohexane) 1.43 on the Me₄Si scale. ^7Li Chemical shifts are determined relative to external aqueous 1.0M-LiCl, with a negative sign for an upfield shift. ^b The signal of 5-(6)-H was hidden by a solvent peak and localized by selective ^1H decoupling while observing the ^{13}C n.m.r. resonance of C-5(-6). ^c Values in parentheses refer to differences in chemical shifts from $(1^{2-})\text{-}2\text{Li}^+$ in Et₂O.

Table 2. ^{13}C N.m.r. chemical shifts and CNDO data of acenaphthylene (1) and acenaphthylene dianion (1^{2-}) ^a

| Compd. | Cation | Solvent | T/°C | C-1, -2 | C-3, -8 | C-4, -7 | C-5, -6 | C-2a, -8a | C-5a | C-8b | K _c (p.p.m. per e ⁻) |
|------------|---|--|-------|---------|-------------------|-------------------|-------------------|-----------|---------|---------------------|---|
| (1) | | THF | 25 | 129.9 | 124.7 | 128.3 | 127.8 | 140.7 | 129.1 | 129.3 | |
| (1^{2-}) | Li | Et ₂ O | 25 | 84.2 | 96.6 | 129.0 | 85.3 | 124.1 | 148.3 | 135.6 | 119.5 |
| | | | | (-45.7) | (-28.1) | (+0.7) | (-42.5) | (-16.6) | (+19.2) | (+6.3) ^b | |
| | | 2-MeTHF | -33 | 82.3 | 95.8 | 129.0 | 85.9 | 124.0 | 148.1 | 135.7 | 121.7 |
| | | | 25 | 82.5 | 96.0 | 129.0 | 85.4 | 124.3 | 148.8 | 136.3 | 120.9 |
| | | | | (157) | 155 | 144 | 153) ^c | | | | |
| | | | -40 | 80.9 | 95.6 | 129.3 | 86.2 | 124.6 | 148.7 | 136.3 | 121.5 |
| | THF | 25 | 81.0 | 95.8 | 128.4 | 85.3 | 124.7 | 148.8 | 137.1 | 122.5 | |
| | | | (156) | 154 | 143 | 153) ^c | | | | | |
| | Na | THF-[² H ₁₈]HMPA | -35 | 78.7 | 95.4 | 128.1 | 86.1 | 124.9 | 148.4 | 137.9 | 124.3 |
| | | | 25 | 83.0 | 96.6 | 127.7 | 84.1 | 125.0 | 149.6 | 137.8 | 120.5 |
| | | THF | 25 | 86.1 | 97.0 | 126.8 | 82.6 | 123.4 | 149.3 | 137.7 | 121.2 |
| | K | THF | -36 | 85.5 | 96.6 | 127.1 | 83.3 | 123.3 | 149.1 | 137.2 | 121.7 |
| 25 | | | 89.5 | 98.0 | 127.3 | 83.0 | 125.0 | 150.3 | 139.5 | 112.9 | |
| | | (154) | 153 | 143 | 151) ^c | | | | | | |
| -33 | | 89.1 | 97.9 | 127.1 | 82.9 | 124.8 | 150.0 | 139.3 | 114.2 | | |
| CNDO data | | $\rho_{\pi}(1^{2-})$ | | 1.28 | 1.27 | 0.99 | 1.38 | 1.09 | 0.88 | 1.11 | |
| | $\Delta\rho_{\pi}(1) \rightarrow (1^{2-})$ | | | -0.24 | -0.33 | +0.04 | -0.43 | -0.08 | +0.11 | -0.04 | |
| | $\rho_{\text{tot}}(1^{2-})$ | | | 4.15 | 4.16 | 3.99 | 4.22 | 4.06 | 3.93 | 4.04 | |
| | $\Delta\rho_{\text{tot}}(1) \rightarrow (1^{2-})$ | | | -0.14 | -0.20 | +0.03 | -0.25 | -0.05 | +0.06 | -0.04 | |

^a ^{13}C Chemical shifts are measured relative to internal cyclohexane and adapted to the Me₄Si scale with δ_{C} (cyclohexane) 27.70 p.p.m. ^b Values in parentheses refer to differences in chemical shifts from the neutral compound (1). ^c One-bond C-H coupling constants (Hz).

shift takes place for C-5(-6) (Table 2, Figure 1).^{*} However, since the average carbon signal also is shifted somewhat upfield, we shall restrict the interpretation to an increased π - (or total) electron density at C-1(-2) at the expense of the electron density at C-5(-6). A similar chemical shift rearrangement is observed for the Na salt although the shift changes are smaller. With K⁺ as counterion all the chemical shifts appear slightly upfield when the temperature is lowered, but also in this case the C-1(-2) are the most influenced positions. From the minor

temperature effects on the chemical shifts it may be concluded that the Na and K salts predominantly exist as c.i.p.s (*i.e.* flat temperature curves), while the larger effects on the Li salt suggest significant changes in cation solvation and accompanying changes in cation-anion distances (Table 2, Figure 1).

The increased (cation) solvation of $(1^{2-})\text{-}2\text{Li}^+$, which is caused by a change of the ether solvent (*i.e.* Et₂O \rightarrow 2-MeTHF \rightarrow THF), also results in upfield shifts of C-1(-2). However, in these cases the downfield shifts are not observed for C-5(-6) but instead for the quaternary carbons and in particular C-8b (Table 2). These shifts, induced by variations of cation, temperature, and solvent, imply preferred cation positions at C-5(-6) and/or C-8b in discrete c.i.p. structures. This proposal is based on a decreased charge polarization towards these positions in the anion when the ion-pair solvation is increased. However, there are several observations which interfere with this model of the c.i.p. (a) Both ^{13}C

^{*} In this context one may notice that the intrinsic temperature effect on the ^{13}C chemical shifts of (1^{2-}) in the interval -40 to +25 °C should be less than 0.4 p.p.m. which is the largest change observed for $(1^{2-})\text{-}2\text{K}^+$ in THF. The intrinsic temperature shift in other systems (*e.g.* dibenzo[*b,f*]pentalene dianion) has been found to be considerably smaller as judged from constant chemical shifts in the c.i.p. situation.^{1a}

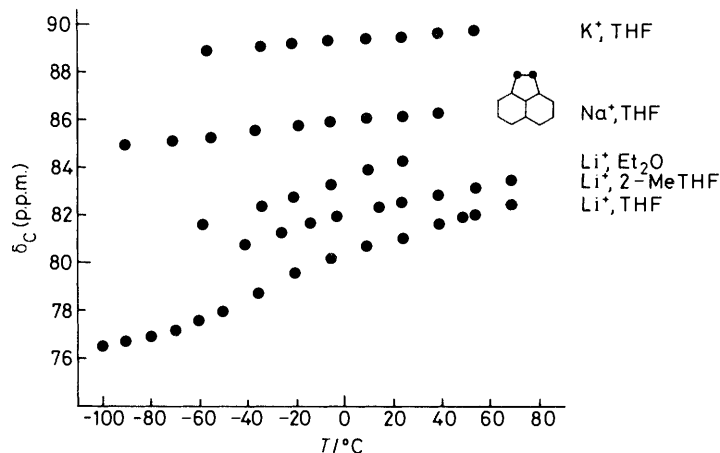


Figure 1. Variable-temperature ^{13}C n.m.r. chemical shifts (C-1, -2) of acenaphthylene dianion

chemical shifts and π -charge calculations indicate that a substantial part of the charge is located at C-1(-2). (b) X-Ray crystallography of the TMEDA-complexed $(1^{2-})-2\text{Li}^+$ has shown that the two Li-TMEDA fragments are co-ordinated to both sides of the five-membered carbon ring.²⁶ (c) Li salts of carbanions normally exist as c.i.p.s in poorly solvating media such as Et_2O and 2-MeTHF.^{5a-f,27} (d) There are better agreements between calculated π -charge distributions (free anion) and ^{13}C n.m.r. data of the c.i.p.s $(1^{2-})-2\text{Na}^+$ and $(1^{2-})-2\text{K}^+$ compared with the correlations for the more solvated Li salt [cf. C-1(-2) and C-5(-6)]. (e) The ^7Li n.m.r. chemical shift of $(1^{2-})-2\text{Li}^+$ in THF appears somewhat upfield from the chemical shift in Et_2O . If the average Li^+ position is in the shielding region above the plane of the dianion, which seems reasonable, there should be a reversed condition since Li^+ is more solvated in THF.^{22,28}

The explanation which unifies all these observations is a discrete structure for the Li salt in which one of the Li ions is tightly bound to the five-membered ring or C-1(-2), while the other one is located at the C-5(-6) position in a more easily solvated state (Figure 2). The effect of a lowered temperature or a better solvating medium is an increased solvation of the latter cation with subsequent reduction of its charge-polarizing ability. By changing the ion pair conditions mentioned above, the solvation of the cation at the five-membered ring is mainly unaltered, and π -charge is consequently redistributed towards this part of the dianion.

A plausible explanation for the chemical shift behaviour of the Na and K salts is then the existence of a structure with both cations in c.i.p. states at the cyclopentadienyl [or C-1(-2)] and heptatrienyl [or C-5(-6)] substructures, respectively. The decreased polarizing ability of the larger cations provides an explanation why better chemical shift-charge correlations are obtained in these cases, compared with the situation for the Li salt.

The ^{13}C chemical-shift dependence on temperature noticed for the Li salt in 2-MeTHF and Et_2O can be rationalized as a greater tendency for a c.i.p. with a small cation to respond to changes in 'external' solvation of the ion pair.^{5f,27b} Moreover, the ^7Li chemical shift 'discrepancy' can be understood from the fact that the average Li^+ position is expected to be closer to the cyclopentadienyl anion fragment using THF instead of Et_2O . Hence, due to the diatropicity of such a fragment, an increased shielding is expected in THF.

The information about the ion-pair structures obtained from ^1H chemical shifts is more limited. However, the upfield

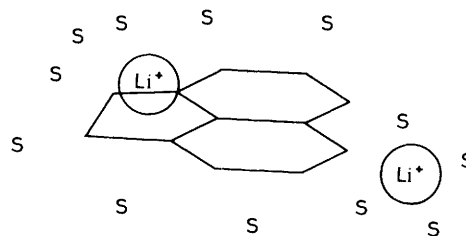


Figure 2.

shifts of $(1^{2-})-2\text{Li}^+$ observed when using better solvating media (*i.e.* $\text{Et}_2\text{O} \rightarrow 2\text{-MeTHF} \rightarrow \text{THF}$) are in agreement with the ^{13}C chemical shift observations, *i.e.* increased polarization of charge towards C-1(-2), and with the reduced direct cationic field effect (Table 1). This latter contribution is most pronounced for 5(-6)-H. With a change of cation from Li to the larger Na and K cations, the decreased polarization of the C-H bond electrons is expected to affect the chemical shifts of 1(-2)-H more than of 5(-6)-H if the Li cation at the five-membered ring is in a c.i.p. state while the other is more solvated. When the effects of the charge density redistributions, as indicated by the ^{13}C n.m.r. data [*i.e.* downfield shift of C-1(-2) and upfield shift of C-5(-6)] are added to these increased shieldings, the ^1H chemical shifts indeed behave in the expected way (Table 1).

Further support for a model with a successive cation solvation in $(1^{2-})-2\text{Li}^+$ in ether solvents is gained from ^{13}C , ^1H , and ^7Li n.m.r. measurements of the Li salt using a mixture of THF and $[\text{H}_{18}]\text{HMPA}$. With the addition of $[\text{H}_{18}]\text{HMPA}$ to a THF solution one expects the ion-pair equilibrium to be shifted towards s.s.i.p.s, where *both* cations are extensively solvated. In comparison with the ^{13}C chemical shifts of $(1^{2-})-2\text{Li}^+$ in neat THF, the $[\text{H}_{18}]\text{HMPA}$ medium [ratio $(1^{2-}) : \text{HMPA} = 1 : 4$]* causes downfield shifts of C-1(-2) and upfield shifts of C-5(-6) (Table 2). This electron redistribution is in accord with a decreased π -polarizing ability of the cation located in the five-membered ring region.

Since the average ^{13}C chemical shift of the protonated carbons is shifted slightly downfield with the addition of HMPA, the corresponding upfield shift of the average ^1H signal can be understood from a decreased cationic field at the C-H bonds, which strengthens the idea of an equilibrium shift towards s.s.i.p. (Table 1). The individual ^1H shieldings are also consistent with the superimposed effects of the reduced cationic field and the change in charge densities as indicated by ^{13}C n.m.r. Moreover, it may be noticed that the ^7Li resonance is shifted downfield by the addition of HMPA. This low-field shift is expected when the average Li position is more remote from the dianion system.

b Electron absorption studies. Ion-pairing investigations of carbanionic systems have shown that the electron absorption spectra of s.s.i.p.s are largely unaffected by the cation.^{9a,27a,c-h} However, for c.i.p.s the perturbation of the MO energy levels increases with a decrease in cationic radius.^{9a,27a,c-h} This condition results in a greater stabilization of the ground state than of the first excited state.²⁹

The u.v.-visible spectra of (1^{2-}) in the range 300–800 nm are characterized by a strong absorption band at *ca.* 373–380 nm and weaker absorptions at *ca.* 579–649 nm (Table 3,

* When more than 4–6 equiv. of $[\text{H}_{18}]\text{HMPA}$ were added to a THF sample of $(1^{2-})-2\text{Li}^+$, a low-quality spectrum was obtained mainly due to radical formation caused by residual oxygen in the HMPA. Therefore, the results are reported from a sample of $\text{THF} : [\text{H}_{18}]\text{HMPA} : (1^{2-}) = 100 : 4 : 1$.

Table 3. Absorption maxima (nm) of acenaphthylene dianion at 25 °C

| Cation | Solvent | $\lambda_{\text{max.}}/\text{nm}$ | | |
|--------|-------------------|-----------------------------------|---------|----------------------------|
| | | 373—375 | 579—581 | |
| Li | Et ₂ O | 373—375 | 579—581 | |
| Li | THF | 379—380 | 582—584 | $\approx 627^a$ |
| Na | THF | 375—376 | 620—623 | $\approx 578\text{—}585^a$ |
| K | THF | 378—380 | 645—649 | $\approx 598\text{—}600^a$ |

^a Shoulder on the main absorption.

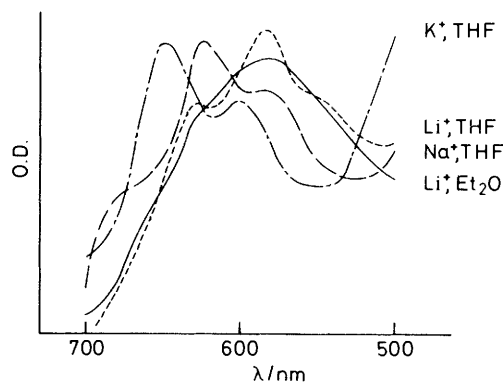
Figure 3). A PPP type of calculation has assigned these absorptions to ground state \rightarrow second excited state and ground state \rightarrow first excited state transitions, respectively.³⁰ Hence, we will restrict our discussions to the latter excitation which shows a large cation dependence.

The absorptions of $(1^{2-})\text{-}2\text{Na}^+$ and $(1^{2-})\text{-}2\text{K}^+$ in THF are consistent with a c.i.p. structure of these salts, since $\lambda_{\text{max.}}$ of $(1^{2-})\text{-}2\text{Na}^+$ occurs at appreciably shorter wavelength than $\lambda_{\text{max.}}$ for the K salt ($\Delta\lambda_{\text{max.}}$ ca. 25 nm). A c.i.p. structure is also indicated for $(1^{2-})\text{-}2\text{Li}^+$ in THF and Et₂O, where $\lambda_{\text{max.}}$ differs by ca. 38 and ca. 41 nm, respectively, from $\lambda_{\text{max.}}$ of the Na salt. Lowering the temperature to -65°C causes no significant changes in the spectra of $(1^{2-})\text{-}2\text{Na}^+$ and $(1^{2-})\text{-}2\text{K}^+$, except for a small shift (ca. 5 nm) of $\lambda_{\text{max.}}$ towards shorter wavelength. The spectrum of $(1^{2-})\text{-}2\text{Li}^+$ in Et₂O at -65°C has identical curvature with the spectrum of the Li salt in THF at $+25^\circ\text{C}$, but with $\lambda_{\text{max.}}$ at ca. 576 nm and the shoulder at ca. 620 nm. For $(1^{2-})\text{-}2\text{Li}^+$ in THF, the spectrum is better resolved at low temperature, now forming two absorption peaks at ca. 578 and ca. 625 nm. However, the intensity ratio between the two peaks at -65°C seems to be the same as between the main band and the shoulder at $+25^\circ\text{C}$, which denotes approximately the same ion-pair structure(s) in this temperature interval.

The broad absorption bands of the different species prevent further analysis, but some conclusions may be drawn: (a) $(1^{2-})\text{-}2\text{Na}^+$, 2K^+ exist as c.i.p.s in THF, without any significant temperature effects on the structure. (b) $(1^{2-})\text{-}2\text{Li}^+$ in THF and Et₂O can be classified as c.i.p.s on the average due to absorption maxima at shorter wavelengths compared with the Na and K salts. However, the somewhat different shapes of the curves, especially for the THF solution at low temperature, may be interpreted in terms of the proposed structure with one 'tight' and one more solvated cation, as emerged from the n.m.r. studies. Furthermore, the differences in $\lambda_{\text{max.}}$ between $(1^{2-})\text{-}2\text{Li}^+$ and $(1^{2-})\text{-}2\text{Na}^+$, 2K^+ (Li \rightarrow Na ca. 40 nm, Li \rightarrow K ca. 65 nm) are unusually large in comparison with other carbanionic systems. It is tempting to compare these results with those of the tetraphenylethylene dianion in THF, where the change of cation from Na to Li caused an extra absorption at ca. 100 nm shorter wavelength in the optical spectrum.³ This was explained by a structure of the Li salt with only one Li⁺ 'tightly' bound to the highly charged two-carbon centre, the other one being solvated. However, in the Na salt both cations were assumed to be tightly associated with the dianion.

Finally, we wish to mention that no concentration effects were observed in the electron absorption spectra or in the n.m.r. spectra, in the ranges $10^{-3}\text{--}10^{-4}$ and 0.05—0.21M, respectively. Hence, we feel that the comparison of the results from the two techniques is justified, which is also strengthened by the overall agreement.

Conclusions.—(a) The combined results of ¹H, ⁷Li, and ¹³C n.m.r. and optical spectroscopy provide evidence for a

**Figure 3.** Visible absorption spectra of acenaphthylene dianion at 25 °C

structure of $(1^{2-})\text{-}2\text{Li}^+$ in ether solvents with one cation in a c.i.p. situation above the five-membered ring and the other more easily solvated cation preferably located near C-5(-6). The degree of solvation depends on solvent and temperature. However, in the strongly solvating medium THF + [²H₁₈]-HMPA both cations are appreciably solvated. A pronounced c.i.p. structure, with both cations desolvated, is found for $(1^{2-})\text{-}2\text{Na}^+$ or 2K^+ in THF at ambient temperature.

(b) The ion-pair structure is shown to have a marked influence on the n.m.r. and electron absorption properties of (1^{2-}) , where merely the change of cation from Li to K causes ca. 9 p.p.m. decreased shielding of C-1(-2) and ca. 65 nm red shift of the long-wavelength absorption maximum. This demonstrates the importance of considering the ion-pair situation and the cationic fields when spectroscopic data are compared with theoretical charge parameters.

(c) The K_c value for the system $(1)\text{-}(1^{2-})$ varies in the range 114—124 p.p.m. per electron, depending on the ion-pair structure of $(1^{2-})\text{-}2\text{M}^+$. These low K_c values are in agreement with a lowered diatropicity when (1) is transformed into (1^{2-}) . Furthermore, the variation of K_c with ion-pair structure suggests the K salt of (1^{2-}) to be less diatropic compared with the Li salt. A structure of (1^{2-}) composed of a cyclopentadienyl and a heptatrienyl anion better explains our observations compared with a peripheral diatropic ring current structure.

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