

E.S.R. Spectroscopic Investigations on Tight Ion Pairs in the Lithium Salt of the Benzene Radical Anion

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The occurrence of resolved splittings due to the ${}^7\text{Li}$ nucleus in the e.s.r. spectrum of the lithium salt of the benzene radical anion in 2-methyltetrahydrofuran (MTHF) provides fundamental information about the ion pair structure and a rationalization of the e.s.r. line broadening effects.

Although the benzene radical anion ($\text{bz}^{\cdot-}$) has been extensively studied by e.s.r. spectroscopy, the detailed interpretation of the observed e.s.r. spectra is still a matter of dispute. It has not been shown experimentally whether the occurrence of broad e.s.r. lines is due to a dynamic Jahn-Teller effect^{1,2} or to unresolved alkali metal coupling constants.^{3,4} The present communication provides a solution to this problem, since it reports the successful preparation of the lithium salt of $\text{bz}^{\cdot-}$ ($\text{bz}^{\cdot-}\text{Li}^+$) in 2-methyltetrahydrofuran (MTHF) whose e.s.r. spectrum exhibits a fully resolved splitting due to the ${}^7\text{Li}$ nucleus.

Clearly, the lithium salt of $\text{bz}^{\cdot-}$ cannot be prepared in MTHF by simply bringing a solution of the neutral species into contact with the lithium metal. It is generated by a recently described technique, in which an electron transfer from a stable carbanion to a neutral species is induced photochemically.⁵ In a typical experiment, the lithium salt of the fluorenyl anion⁶ (approx. 0.05 M) in a mixture of MTHF-benzene (approx. 10:1) was irradiated with the visible spectrum ($\lambda > 300$ nm) of a high pressure mercury lamp (1000 W) within the cavity of an e.s.r. spectrometer. After a short irradiation time, a well resolved e.s.r. spectrum (Figure 1), attributed to $\text{bz}^{\cdot-}\text{Li}^+$ (see below), was observed in the temperature range 220–190 K. The light induced generation of $\text{bz}^{\cdot-}\text{Li}^+$ can be rationalized by the photo-oxidation of fluorenyl anion followed by the capture of the ejected electron by benzene.

Analysis of the e.s.r. spectrum at 220 K yields coupling constants of 0.375 mT and 0.169 mT, due to a set of six equivalent protons and to a ${}^7\text{Li}$ nucleus, respectively. The proton coupling constant is close to that observed for the

protons of $\text{bz}^{\cdot-}$ in 1,2-dimethoxyethane (DME).^{7†} The coupling constant of the ${}^7\text{Li}$ nucleus increases significantly on lowering the temperature (0.179 mT at 190 K).

This is the first report of a resolved alkali metal coupling constant in the e.s.r. spectrum of $\text{bz}^{\cdot-}$. Two factors seem to be responsible for this result: (i) the use of MTHF as a solvent of low cation solvating power, which is certainly of prime importance; and (ii) the occurrence of a relatively large Li coupling constant probably owing to the high magnetic moment of the ${}^7\text{Li}$ nucleus. Indeed, comparison of the observed coupling constant ($a_{\text{Li}} = 0.169$ mT) with the coupling constant of the free Li atom ($a^\circ = 14.36$ mT) indicates a rather small spin density in the 2s orbital of the Li cation ($\rho_s = a_{\text{Li}}/a^\circ = 0.012$).⁸ Since the magnetic moment of the potassium nucleus is significantly smaller it is not surprising that in the case of the K salt of $\text{bz}^{\cdot-}$ (in MTHF) a resolved coupling constant was not observed by us. The preparation of sodium and caesium salts of $\text{bz}^{\cdot-}$ has so far failed.

In view of the problems mentioned earlier, the e.s.r. data of $\text{bz}^{\cdot-}\text{Li}^+$ in MTHF lead to the following considerations: (i) $\text{bz}^{\cdot-}\text{Li}^+$ exists in MTHF as a contact ion pair. It is important to mention that the tight ion pairing does not reduce the D_{6h} symmetry of the molecule. Such a possibility has been discussed in the literature.⁴ (ii) The negative temperature coefficient of the ${}^7\text{Li}$ coupling constant indicates a negative

† The lithium salt of $\text{bz}^{\cdot-}$ was prepared in DME by the same technique used in MTHF. The e.s.r. spectrum shows only one proton coupling constant (0.378 mT) of six equivalent protons.

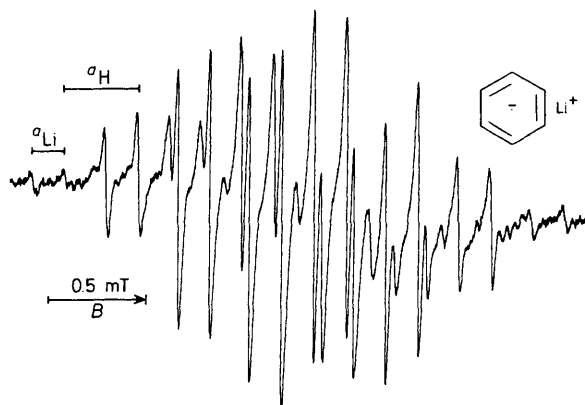


Figure 1. E.s.r. spectrum of $\text{bz}^{\bullet-}\text{Li}^+$ in MTHF at 220 K.

spin density on the ^7Li nucleus.⁸ One would thus expect spin polarization effects to be the dominant mechanism for creating unpaired spin density on the lithium nucleus. The dominance of such a mechanism over a direct spin transfer mechanism suggests an ion pair structure with localization of the lithium cation on the six-fold rotation axis of $\text{bz}^{\bullet-}$. (iii) The e.s.r. line-width in the spectrum of the contact ion pair of

$\text{bz}^{\bullet-}\text{Li}^+$ (in MTHF) is at least 2–3 times smaller than the line-width which occurs if a resolved alkali metal splitting is absent† (e.g., $\text{bz}^{\bullet-}\text{Li}$ in DME). It can therefore be assumed that in the latter case unresolved alkali metal coupling constants contribute significantly to the e.s.r. line-width. This finding should be taken into consideration when estimating a dynamic Jahn–Teller effect in $\text{bz}^{\bullet-}$ by the observed e.s.r. line broadening.^{1,2}

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