Line-breadth Variations in the Electron Spin Resonance Spectra of Lithium–Naphthalene Ion-pairs

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THE electron spin resonance spectrum of naphthalene anion, prepared by reduction with lithium in 2-methyltetrahydrofuran, shows hyperfine splitting from the ^7Li nucleus of spin $\frac{3}{2}$, indicating the formation of ion-pairs. In contrast to the case when naphthalene is reduced with sodium in this solvent, there is no evidence for dissociated naphthalene anions.[1] The spectrum exhibits an unusual dependence of line-breadth on the nuclear spin states. Low-field, central, and high-field regions of a typical spectrum are shown in the Figure.

The general theories of relaxation in free radicals show that line-breadth variations of the type apparently observed here occur if the predominant relaxation mechanism is through the anisotropy of the g- and hyperfine tensors.[2] If

this type of system support the latter assumption.[1,4] If the opposite sign is assumed for the spin density at the lithium nucleus then the signs of some of the line-breadth coefficients determined from the comparison are reversed. It appears
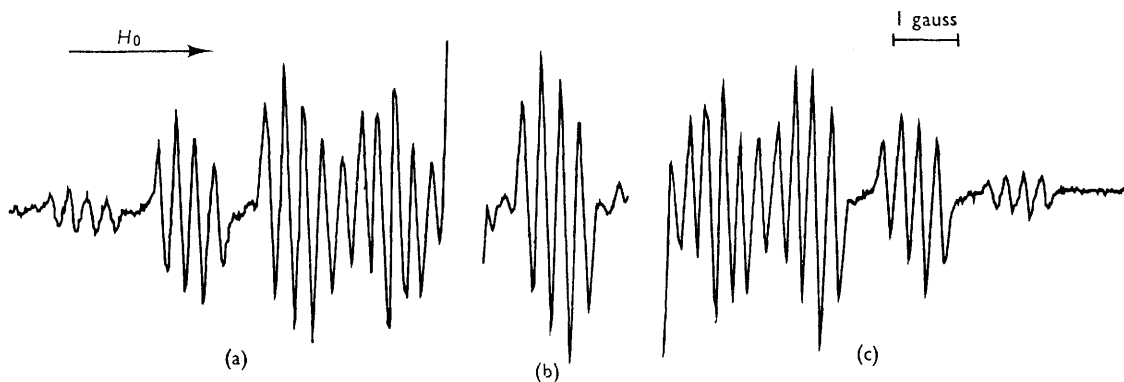
FIGURE

Low-field (a), *central* (b) *and high-field* (c) *regions of the e.s.r. spectrum of lithium–naphthalene ion-pairs at* 22°c. *The* [7]Li *hyperfine coupling constant is* 0·28 *gauss. Amplifier gain* ×012 *for* (b).

this mechanism is operative in the present case, then, because the differences in line-breadth are quite small, and because there is only one nucleus of spin greater than $\frac{1}{2}$, the breadth of the ith line, which may be a resultant of degenerate transitions, should be given[2] by Equation 1.

from the Table that Equation 1 describes the line-breadth variations quite well, which is surprising, since the anisotropy of the lithium hyperfine coupling, and of the g-tensor, would be expected to be small.

Two features of the line-breadth coefficients

$$\left\langle \frac{1}{T_2} \right\rangle_i = A + \sum_\nu B_\nu M_\nu(i) + \sum_\nu C_\nu M_\nu(i)^2 + \sum_{\nu \neq \mu} D_{\nu\mu} M_\nu(i) M_\mu(i) \tag{1}$$

Here the $M_\nu(i)$ are the resultant nuclear spin quantum numbers, for the νth group of symmetrically equivalent nuclei, corresponding to the ith line. In what follows, the lines in the spectrum are labelled with the M_ν as $(M_\alpha,\ M_\beta,\ M_{\text{Li}})$, corresponding to the α-protons, the β-protons, and the [7]Li nucleus respectively.

The Table shows the results of fitting the relative breadths of the $(M_\alpha,\ 0,\ M_{\text{Li}})$ lines, as measured from their relative amplitudes on the first derivative spectrum,[3] to Equation 1. The line-breadth coefficients were determined from the two low-field quartets and from the reference line, and then used to predict the remaining line-breadths. It was assumed that the spin densities at the protons are negative, which is beyond dispute, and that the spin density at the lithium nucleus is positive. All the theoretical discussions of the mechanism of metal hyperfine splitting in

determined from the above comparison indicate that anisotropy of the g- and hyperfine tensors is *not* the relevant relaxation mechanism. Firstly, C_α is found to be negative, which cannot be, if it contains the inner product of the α-proton dipolar hyperfine tensor with itself.[2] Secondly, the coefficient $D_{\alpha\text{Li}}$ is found to be positive if the isotropic proton and lithium couplings are assumed to have opposite signs. The sign of $D_{\alpha\text{Li}}$ is determined by the sign of the inner product of the α-proton and lithium dipolar hyperfine tensors.[2] We estimate the sign of this inner product to be negative. This conclusion is based on expected values for the α-proton tensor elements,[5] and two types of estimate of the lithium tensor elements. The first of these assumed cylindrical symmetry for the tensor, as predicted classically for point dipoles at large separation; the second assumed the relative

magnitudes of the tensor elements to be approximated by the sum of the classical interactions of a point dipole, for the lithium nucleus, with a series of point dipoles, representing the $2p$-orbital spin populations in the anion. This model takes into account the possibility of an anomalous

averaging over all the accessible relative orientations of the two ions.[1] This could arise if the ion-pairs were particularly strongly associated or if there was equilibrium between ion-pairs of different types. So far as it can be followed, the lithium hyperfine splitting decreases smoothly as

TABLE

Comparison of observed line-breadths with those calculated with Equation (1)

Line $(M_\alpha, M_\beta, M_{Li})$	Observed relative breadth[b]	Standard deviation[d]	Calculated breadth (Equation 1)	Deviation[e]
$(-2, 0, +3/2)$[a]	1·077[c]	0·046	1·070	$-0·007$
$(-2, 0, +1/2)$	0·894[c]	0·022	0·898	0·004
$(-2, 0, -1/2)$	0·959[c]	0·035	0·960	0·001
$(-2, 0, -3/2)$	1·256[c]	0·042	1·256	0·000
$(-1, 0, +3/2)$	1·165[c]	0·027	1·174	0·009
$(-1, 0, +1/2)$	0·968[c]	0·009	0·962	$-0·006$
$(-1, 0, -1/2)$	0·986[c]	0·010	0·984	$-0·002$
$(-1, 0, -3/2)$	1·243[c]	0·030	1·240	$-0·003$
$(\ 0, 0, +3/2)$	1·225	0·026	1·252	0·027
$(\ 0, 0, +1/2)$	1·000[c]	—	1·000	—
$(\ 0, 0, -1/2)$	0·996	0·005	0·982	$-0·014$
$(\ 0, 0, -3/2)$	1·203	0·029	1·198	$-0·005$
$(+1, 0, +3/2)$	1·233	0·039	1·304	0·071
$(+1, 0, +1/2)$	0·986	0·015	1·012	0·026
$(+1, 0, -1/2)$	0·951	0·011	0·954	0·003
$(+1, 0, -3/2)$	1·143	0·027	1·130	$-0·013$
$(+2, 0, +3/2)$	1·238	0·061	1·330	0·092
$(+2, 0, +1/2)$	0·975	0·027	0·998	0·023
$(+2, 0, -1/2)$	0·865	0·031	0·900	0·035
$(+2, 0, -3/2)$	1·078	0·040	1·036	$-0·042$

[a] Low field.
[b] Mean from six spectra, taken from three samples, with field swept in forward and reverse directions.
[c] Used to determine line-breadth coefficients.
[d] Mean standard deviation, 0·028.
[e] Mean deviation for calculated line-breadths (14 lines), 0·032.

effect arising from negative spin populations at the 9- and 10-positions. All the estimates led to the conclusion that $D_{\alpha Li}$ should be negative, and there is no suggestion that a proper calculation would lead to the opposite result.

The strongest line-breadth dependence is on M_{Li}^2. This suggests that the relaxation mechanism arises through there being insufficiently rapid

the temperature is lowered, so there is no justification in this case for interpreting the observations in terms of only two types of ion-pair.[6]

Further analysis of these observations, and discussion of the implications with regard to the general patterns of behaviour of this type of associated system, will be published in due course.

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