

## Carbon-13 Contact Solvent Shifts in Radical Anion Solutions. Mechanism of Spin Density Transfer to Solvent

Constantinos G. Screttas and Maria Micha-Screttas

The National Hellenic Research Foundation, Athens 501/1, Greece

Radical anion solutions in tetrahydrofuran exhibit negative  $^{13}\text{C}$  contact solvent shifts for both types of carbon; the phenomenon is strongly cation dependent, indicating that spin delocalisation takes place in the ternary complex  $(\text{ArH})^{\cdot-}\text{M}^+(\text{R}_2\text{O})_n$  through the mediation of the cation.

Radical anions in ethereal solvents induce a finite spin density in the nuclei of the ether molecules,<sup>1-3</sup> a fact which has not attracted proper attention owing to the relatively small number of reports on this subject, and to somewhat indirect experimental evidence. We now report direct evidence for spin density delocalisation from radical anions to solvent molecules, based on  $^{13}\text{C}$  contact shift measurements. This work is of relevance to problems such as (i) why the pairing theorem appears to break down,<sup>4</sup> (ii) why crown ethers or strongly cation-complexing ligands apparently fail to produce 'naked' radical anions,<sup>1-3,5</sup> and (iii) the perturbation of e.s.r. spectra caused by strongly cation-complexing agents.

We measured<sup>2</sup> solvent shifts in the n.m.r. spectrum of concentrated (0.2–1.0 M) solutions of radical anions in tetrahydrofuran (THF). In all cases studied the signals for both types of carbon in the THF molecule were shifted to lower fields from the resonance positions of neat solvent, see Table 1. As is shown in Figure 1 this shift is linearly dependent on the concentration of the paramagnetic solute. Assuming that the concentration of the paramagnetic species is equal to the formal concentration of the radical anion, we determined the molar  $^{13}\text{C}$  contact solvent shifts,  $\Delta\delta_m(\text{C}^\alpha)$  and  $\Delta\delta_m(\text{C}^\beta)$ , see Table 1. The negative shifts imply that both types of carbon atom of THF acquire positive spin density by the Fermi contact interaction.<sup>6</sup>

Proton<sup>2</sup> and carbon-13 solvent shifts contrast in that the  $^{13}\text{C}$  contact shift seems to overwhelm the respective bulk paramagnetic solvent shift whereas, for proton solvent shifts, the reverse occurs. We measured the bulk paramagnetic shift for the lithium dihydronaphthylidene radical anion by employing a double-reference technique, namely internal cyclohexane and the  $\alpha$ -carbon of THF. Unlike the THF carbons, the cyclohexane carbon was shifted to higher fields to the extent of 0.5 p.p.m./mol. It appears reasonable to assume that cyclohexane 'feels' merely, or at least mainly, the bulk paramagnetic shift, owing to (almost complete?) lack of complexation between the ion pair and the hydrocarbon. We conclude, then, that in order to obtain the actual values of molar contact shifts one has to add *ca.* 0.5 p.p.m./mol to the values given in Table 1.

The  $\Delta\delta_m(\text{C}^\beta)$  values in Table 1 are cation-dependent, compare *e.g.* 1–3. This cation dependency could mean either

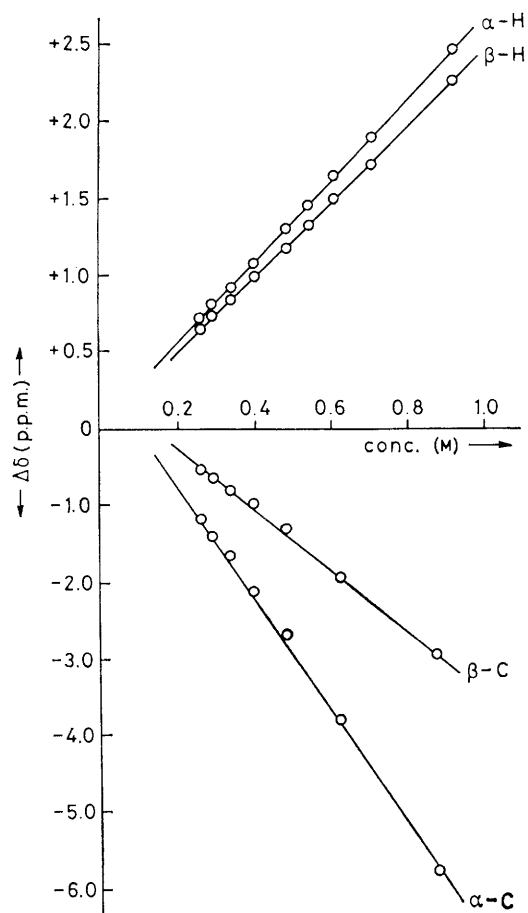


Figure 1. Solvent-nuclei shifts induced by sodium *p*-biphenylphenylketyl in THF.

that the aggregation of radical anions to form diamagnetic species is a cation-dependent property of theirs, or, in the case of lack of aggregation, that the amount of spin transferred to the nuclei of the solvent molecules is cation-

Table 1. Molar carbon-13 contact solvent (THF) shifts in radical anion solutions and relevant h.f.s.c.'s.<sup>a</sup>

Entry	Radical anion	$\Delta\delta_m(\text{C}^\alpha)$	h.f.s.c. $\times 10^4$	$\Delta\delta_m(\text{C}^\beta)$	h.f.s.c. $\times 10^4$	$\Delta\delta_m(\text{C}^\alpha)/\Delta\delta_m(\text{C}^\beta)$
1	(naphthalene) $^{\cdot-}\text{Li}^+$	-16.23	+0.059	-15.45	+0.056	1.05
2	(naphthalene) $^{\cdot-}\text{Na}^+$	-7.21	+0.027	-5.89	+0.022	1.21
3	(naphthalene) $^{\cdot-}\text{K}^+$	-9.88	+0.036	-8.31	+0.031	1.19
4	(anthracene) $^{\cdot-}\text{Li}^+$	-10.09	+0.037	-9.81	+0.036	1.03
5	(anthracene) $^{\cdot-}\text{Na}^+$	-7.87	+0.029	-7.28	+0.027	1.08
6	(anthracene) $^{\cdot-}\text{K}^+$	-6.62	+0.025	-5.48	+0.021	1.21
7	( <i>p</i> -biphenylphenyl ketone) $^{\cdot-}\text{Li}^+$	-7.35	+0.027	-2.65	+0.011	2.77
8	( <i>p</i> -biphenylphenyl ketone) $^{\cdot-}\text{Na}^+$	-6.46	+0.024	-3.24	+0.013	1.99
9	( <i>p</i> -biphenylphenyl ketone) $^{\cdot-}\text{K}^+$	-5.47	+0.021	-2.87	+0.012	1.91

<sup>a</sup> Carbon-13 h.f.s.c.'s were calculated using the molar shifts increased by 0.5 p.p.m./mol, see the text. Contact solvent shifts in p.p.m./mol, h.f.s.c.'s in teslas (1T =  $10^4$  gauss). Temperature = 35 °C.

dependent. One explanation of this could be the observation that the shift attenuates at the  $\beta$  carbon. In addition, the rate of attenuation [expressed by the ratio  $\Delta\delta_m(C^\alpha)/\Delta\delta_m(C^\beta)$  of the two molar shifts] is also cation dependent, see Table 1. Obviously, this ratio should be independent of the extent of aggregation (if any) of the radical anions. We can safely conclude then that the extent of spin density transfer to solvent is cation-dependent, or in other words hyperfine interactions between anion and solvent molecules arise through the mediation of the cation. This conclusion has been stated earlier,<sup>2</sup> but on the basis of somewhat ambiguous evidence.

The present, as well as earlier,<sup>1-3,5</sup> experimental evidence points to the conclusion that the 'ion pair' picture of a radical anion in ethereal solvents needs some extension to include the solvent molecules. Perhaps, a better picture of a radical anion in solution could be the ternary complex (anion)-(cation)-(solvent molecules co-ordinated to cation). Given that transmission of spin density usually requires covalent bonds,<sup>7</sup> we are forced to consider that even in the case of cation complexation by glymes<sup>1,5</sup> or crown ethers<sup>2,3,5</sup> the bonding between anion and cation retains a certain amount of covalency. Otherwise, the contact shift of the glyme protons,<sup>1</sup> or the non-zero metal splitting<sup>5</sup> would not arise. In solvents like THF rapid exchange, on the n.m.r. time scale, of solvent molecules takes place between complexed and uncomplexed sites. Thus all THF molecules receive an average spin density. This, in turn, implies that the condition of spin averaging<sup>6</sup> is met, and one can use these shifts to calculate the relevant h.f.s.c's. In Table 1 are given the calculated <sup>13</sup>C h.f.s.c's, which correspond to the molar contact shifts. Obviously the calculated h.f.s.c's are too small to cause significant perturbation of the e.s.r. spectra. If one bears in mind, however, that a 1.0 M solution of radical anion in THF contains 10 mol of THF per mol of radical anion, then the total 'splitting' of THF is  $10 \times 2 [a(^{13}C^\alpha) + a(^{13}C^\beta)]$ . This number in the case of THF containing lithium dihydronaphthylide becomes substantial, i.e.  $2.3 \times 10^{-4}$  T. Assuming that a McConnell-type relationship holds for the present case, then a substantial amount of spin density could be expected<sup>†</sup> to be transferred from the anion

<sup>†</sup> A reliable  $Q$  value for the THF 'radical anion,' which is needed for the calculation of spin densities, is not available.

to solvent. We presume that this is one of the reasons that the pairing theorem appears to break down.<sup>4</sup> Cosolvent proton contact shifts of the order of 10 p.p.m./mol have been reported.<sup>1</sup> These correspond to h.f.s.c's of the order of  $0.1 \times 10^{-4}$  T, well within the resolving power of present-day e.s.r. spectrometers.

The spin density transfer mechanism from anion to solvent should include the following two steps: (i) transfer from anion to metal and (ii) transfer from metal to solvent molecules. The mechanism of the first step has been thoroughly reviewed.<sup>8</sup> A number of mechanisms for spin density transfer through  $\sigma$ -frameworks<sup>9</sup> or saturated chains<sup>10</sup> are available. On the basis of these, as well as the non-alternation of the shift sign, we assume that  $\sigma$ -delocalisation occurs through covalent bonds, rather than by spin polarisation, in the second step. The role of the cation is to provide orbitals of the correct symmetry to delocalise the spin from the anion to co-ordinated solvent molecules. Rapid exchange, on the n.m.r. time scale, of solvent molecules between complexed and uncomplexed sites, results in an average spin density transfer to *all* solvent molecules.

Received, 2nd April 1982; Com. 373

## References

- 1 E. deBoer, A. M. Grotens, and J. Smid, *Chem. Comm.*, 1970, 1035; *J. Am. Chem. Soc.*, 1970, **92**, 4742.
- 2 C. G. Screttas and M. Micha-Screttas, *J. Org. Chem.*, 1981, **46**, 993.
- 3 P. Belser, G. Desbiolles, U. Ochsenbein, and A. von Zelewsky, *Helv. Chim. Acta*, 1980, **63**, 523.
- 4 J. R. Bolton, in 'Radical Ions,' eds. E. T. Kaiser and L. Kevan, Interscience, New York, 1968, ch. 1.
- 5 B. J. Herold, M. Celina, R. L. R. Lazana, and H. M. Novais, *Tetrahedron*, 1977, **33**, 517.
- 6 D. R. Eaton and W. D. RPhillips, *Adv. Magn. Reson.*, 1965, **1**, 103.
- 7 J. Owen and J. H. Thornley, *Rep. Prog. Phys.*, 1966, **29**, 675.
- 8 J. L. Sommerdijk and E. deBoer, in 'Ions and Ion Pairs in Organic Reactions,' ed. M. Szwarc, Wiley-Interscience, New York, 1972, vol. 1, ch. 8.
- 9 D. Doddrell and J. D. Roberts, *J. Am. Chem. Soc.*, 1970, **92**, 6839.
- 10 R. W. Kreilick, *Adv. Magn. Reson.*, 1973, **6**, 141.