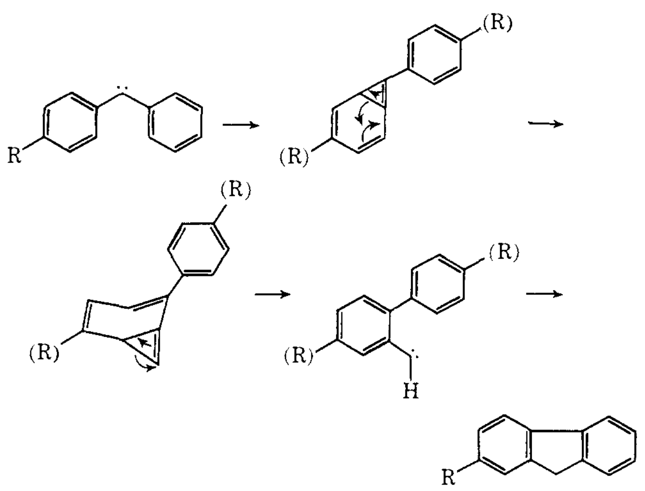
analysis of the crude reaction product showed no detectable quantity (<1%) of the 3 isomer. Thus, apparently all of the fluorene arises by the ring expansion–contraction mechanism![13]

In the suggested mechanism, ring contraction of phenylcycloheptatrienylidene was particularly surprising since cycloheptatrienylidene generated in solution does not show typical carbene properties.[6] Furthermore, Hedaya[15] has found that the sodium salt of tropone tosylhydrazone, when pyrolyzed at 900°, gives no fulvenallene, a product that would be expected[2] if cycloheptatrienylidene contracted to phenylcarbene. In contrast, 2-methylcycloheptatrienylidene generated in these laboratories at 350° gives 10–15% styrene—thus requiring contraction—and Cais[16] and his group have found that reaction of phenyltropylium fluoroborate with diisopropylamine gave products that may have arisen from ring contraction of complexed cycloheptatrienylidene.

It was, therefore, imperative that the proposed intermediate phenylcycloheptatrienylidene be generated under our pyrolysis conditions. Moreover, it became even more important when it was realized that a vinylcyclopropene → vinylcyclopropene rearrangement, as shown in Scheme III, could be envisaged which would by-pass the expanded carbene while retaining the requirements for the exclusive formation of 2-methylfluorene (**5b**).

Scheme III



The sodium salt of 2-phenyltropone tosylhydrazone was synthesized and subjected to reaction conditions. In addition to the above mentioned diphenylheptafulvalene, fluorene was formed in 10–15% yield.

The formation of fluorene from phenylcycloheptatrienylidene thus requires the intermediacy of phenylcycloheptatrienylidene (but not as the sole source of fluorene) in these pyrolyses. Its intermediacy is further supported by the structures of the other two products mentioned before, triphenylheptafulvene and diphenylheptafulvalene.

Other multiple carbene rearrangements are presently under intensive investigation.

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[13] In like manner, pyrolysis of *p*-methoxydiphenyldiazomethane gave 2-methoxyfluorene (mp 108°, lit. 109°).[14] Moreover, preliminary results indicate that pyrolysis of *p*-phenylphenyldiazomethane gives fluorene. This observation suggests a series of ring expansions and contractions involving several intermediate carbenes. Both M. Jones, Jr., of Princeton University and E. Hedaya of Union Carbide have advised us of similar multiple carbene rearrangements of *p*- and *m*-tolylcarbenes yielding benzocyclobutene and styrene.

[14] G. W. Gray, J. B. Hartley, and A. Ibbotson, *J. Chem. Soc.*, 2686 (1955).

[15] Private communication from E. Hedaya.

[16] P. Ashkenasi, S. Lupan, A. Scharz, and M. Cais, *Tetrahedron Lett.*, 817 (1969).

[17] National Science Foundation Trainee, 1965–1969.

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Effect of Ion-Pair Solvation on the Paramagnetic Solvent Shift of Aromatic Radical Anion Solutions. Spin Density on Solvating Molecules

Sir:

Theory predicts that the solvent protons of a solution of paramagnetic species undergo an upfield nmr shift due to the paramagnetic bulk susceptibility. The magnitude of this shift for cylindrical sample tubes is, according to Langevin, given by

$$\delta_s \text{ (ppm)} = -\frac{2}{3}\pi 10^3 \frac{N\beta_e^2}{kT}c$$

N being Avogadro's number, β_e the Bohr magneton, and c the concentration in mol/l.[1]

The expression has often been utilized to determine the concentration of paramagnetic species from the observed solvent shift, and as long as no scalar interactions with the solvent molecules exist, the procedure appears to be reliable.[2] However, recent reports indicate that the molar solvent shift of ethereal solutions of certain radical anion salts is considerably smaller than the theoretically predicted value.[3] Apparently the solvent protons are also subjected to a downfield shift, due to specific ion pair solvation, which brings them in close proximity to the unpaired electron.

We were able to confirm this hypothesis and clearly demonstrate the downfield shift by investigating the nmr spectra of complexes of triphenylenesodium with glyme-5 (tetraethylene glycol dimethyl ether). Solutions of triphenylene in THF, stirred on a sodium mirror, are quantitatively converted to the radical anion salt $Tp\cdot^-,Na^+$. Addition of glyme-5 to this salt in a 1:1 ratio (excess glyme-5 must be avoided) yields the glyme-separated ion pair $Tp\cdot^-,G5,Na^+$. Optical and esr data show that between concentrations of 0.1 and 1 M essentially all of the glyme-5 is bound to $Tp\cdot^-,Na^+$, the complexation constant at 25° being higher than 10^4 M^{-1}. The proton nmr spectra were recorded on a Varian DP60 spectrometer.

The observed solvent shifts δ_s of THF solutions of $Tp\cdot^-,Na^+$ and $Tp\cdot^-,G5,Na^+$ (relative to a THF solution of the nonreduced hydrocarbon) are plotted in Figure 1 *vs.* the radical anion concentration. While

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[1] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw Hill, New York, N. Y., 1959, p 20.

[2] E. de Boer and C. MacLean, *J. Chem. Phys.*, **44**, 1334 (1966); E. de Boer and H. v. Willigen, *Prog. Nucl. Magn. Resonance Spectrosc.*, **2**, 157 (1967); A. Calder, A. R. Forrester, J. W. Emsley, G. R. Luckhurst, and R. A. Storey, *Mol. Phys.*, **18**, 481 (1970).

[3] G. W. Canters, Ph.D. Thesis, University of Nijmegen, The Netherlands, 1969; R. E. Jesse, Ph.D. Thesis, University of Amsterdam, The Netherlands, 1966.

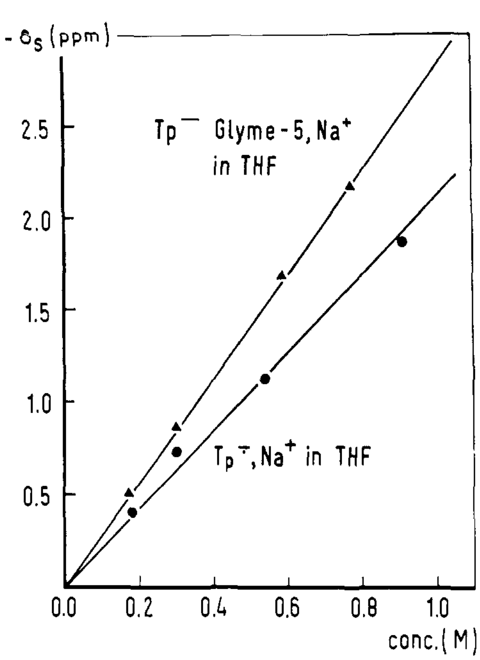

Figure 1. Plots of solvent shifts, δ_s, for the α protons of THF, *vs.* the concentrations of triphenylene$\cdot^-$,Na$^+$ (Tp$\cdot^-$,Na$^+$) and its complex with glyme-5 (Tp$\cdot^-$,G5,Na$^+$) in mol/l. at 33°.

linear relationships are obtained for both systems, the molar solvent shift for Tp$\cdot^-$,Na$^+$ (2.10 ppm) is 20% lower than the theoretical value of 2.57 ppm at 33°. When glyme is added, the THF is replaced as coordination sphere around the alkali ion. The THF molecules are now further removed from the unpaired electron, thereby preventing a downfield contact shift of its protons. On the other hand, all the glyme molecules are now close to the unpaired electron. The effect of this on the nmr spectrum of these molecules can be seen in Figure 2, showing the respective spectra of the systems glyme-5, Tp$\cdot^-$,G5,Na$^+$, and fluorenyl$^-$,G5,Na$^+$, all in THF. While in the latter system a diamagnetic upfield shift of 0.85 ppm is found for the CH_2 glyme protons,[4] complexation with Tp$\cdot^-$,Na$^+$ results in a downfield shift of 3.60 ppm (both with respect to the CH_2 protons of glyme-5 in pure THF, and in the case of Tp$\cdot^-$,G5,Na$^+$, corrected for the upfield paramagnetic bulk susceptibility shift). Apparently, the glyme protons have acquired positive spin density, causing a strong downfield Fermi contact shift. Such a shift has recently been observed for tetraalkylammonium ion pairs of anionic paramagnetic transition metal complexes, although in most of these systems dipolar interactions are responsible for the observed downfield shifts.[5] Such interactions are very small in systems of aromatic radical anions.

The actual contact shift for the CH_2 glyme protons is even larger, since it is partially compensated for by a diamagnetic upfield shift due to the aromatic ring currents. If we assume the latter shift to be comparable to that found for the fluorenyl system, the contact shift will come to 4.45 ppm, from which a coupling constant of 62 mG can be calculated. This value increases with temperature, but drops rapidly above 80° because the glyme complex dissociates into Tp$\cdot^-$,Na$^+$ and free glyme.

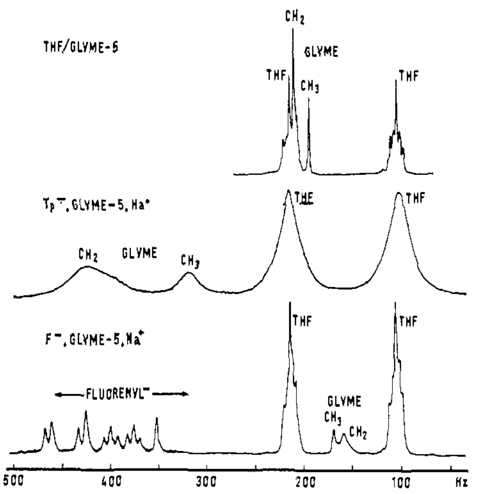

Figure 2. Proton nmr spectra of glyme-5 and its 1:1 complexes with triphenylene$\cdot^-$,Na$^+$ (at 33°) and fluorenyl$^-$,Na$^+$ (at −50°, where all glyme-5 is complexed to the salt) in THF. Concentrations are 0.3 *M*. The α-THF peaks were all "lined up" at 215 Hz downfield from TMS, which is the chemical shift for these protons in pure THF. This procedure automatically corrects for the bulk susceptibility change in the paramagnetic system.

The results demonstrate that the smaller solvent shifts in systems such as Tp$\cdot^-$,Na$^+$–THF are most likely caused by a Fermi contact shift on the protons of that fraction of solvent molecules which is specifically coordinated to the ion pairs. This makes a concentration determination based on the theoretical value of the molar solvent shift unreliable. However, the linearity between δ_s and c is maintained, and the fraction of paramagnetic species can still be obtained from the ratio δ_s/δ_s^0, where δ_s^0 now refers to the maximum solvent shift corresponding to quantitative reduction.

The observed downfield shifts of the glyme protons depend on the type of radical anion and are much smaller for the systems naphthalene$\cdot^-$,G5,Na$^+$ and anthracene$\cdot^-$,G5,Na$^+$. We suspect that the size of the radical anion and the spin distribution play an important role. Indeed, some preliminary data on the glyme complexes of the coronene radical salt show considerably larger downfield shifts than those found with triphenylene.

Finally, one can utilize the observed contact shifts to study other solvation equilibria. For example, addition of $NaBPh_4$ to Tp$\cdot^-$,G5,Na$^+$ causes the glyme protons to shift back upfield due to the reaction Tp$\cdot^-$,G5,Na$^+$ + Na$^+$,BPh_4^- $\leftrightarrows$ Tp$\cdot^-$,Na$^+$ + Na$^+$,G5,BPh_4^-. Such measurements will in turn yield quantitative information on equilibria of the type $NaBPh_4$ + G5 $\leftrightarrows$ Na$^+$,G5,BPh_4^-. These data are not easily obtainable for inorganic salts because optical or nmr spectra of the two types of ion pairs are very similar.

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