Radical Anions and Lanthanide Complexes as NMR Shift Reagents

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Presented at the Fourth International Symposium on Magnetic Resonance
Israel, August, 1971

The negative ions of triphenylene and coronene give striking spectral simplifications in the NMR spectra of polyglycoldimethylethers (glymes) by virtue of reversible complexation, leading to isotropic Fermi contact shifts. In this aspect they resemble the lanthanide shift reagents, such as tris(dipivalomethanato)-europium and -praseodymium. The NMR spectra of glymes complexed with both types of shift reagents have been measured. Similarities but also differences were found, as manifested by measuring partially deuterated glymes. Information is obtained on the structure of the complexes and on the mechanisms of spin transfer from the radical center to the glymes.

1. INTRODUCTION

The proton NMR solvent shift for ethereal solutions of aromatic hydrocarbon radical anions is often considerably less than the value theoretically predicted for solutions of paramagnetic species (1-5). We observed striking examples of these effects for the sodium salts of triphenylene and coronene dissolved in tetrahydrofuran (THF) (3, 4). The downfield shift was clearly demonstrated by the addition of equimolar amounts of polyglycoldimethylether [glyme, general formula CH₃O(CH₂CH₂O)ₙCH₃] to these solutions; the peaks arising from the THF protons shifted to their theoretically predicted position, whereas the CH₂ peaks of the glymes were shifted by more than 4 ppm to low field in the case of sodium triphenylene and by 6-10 ppm in the case of sodium coronene. Moreover, the NMR patterns of the glymes transformed into a first-order spectrum.

In the latter aspect the two radical anions resemble the lanthanide shift reagents, such as tris(dipivalomethanato)europium (Eu(DPM)₃, (6)) and -praseodymium (Pr(DPM)₃, (7)). This prompted us to investigate the behavior of glymes in the presence of these reagents in order to compare the observed NMR patterns with those found in the presence of the radical anion salts. Differences but also some similarities were found. Experiments on partly deuterated glymes furnished information on the assignment of the CH₂ groups.

Our experiments shed light on the structure of the complexes in solution and on the mechanism of spin transfer from the paramagnetic center to the attached glyme.
molecules. The experiments were performed with a Varian DP-60 and a Varian A-60 spectrometer.

2. RESULTS AND DISCUSSION

(a) Alkali Coronene Glyme Complexes

The solvent protons of a solution of paramagnetic species undergo an upfield NMR shift due to the paramagnetic bulk susceptibility. However, in 1966, Jesse (1) found a downfield shift for the protons of 1,2-dimethoxyethane, in which negative ions of coronene were dissolved. 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. This downfield shift is very clearly demonstrated by the NMR spectra of complexes of alkali-coronene with glymes. As a typical example we have shown in Fig. 1 the NMR spectrum of the 1:1 complex of sodium coronene with glyme-5

![NMR Spectrum](image)

Fig. 1. $^1$H NMR spectrum (60 MHz) of the 1:1 complex of sodium coronene with glyme-5 in tetrahydrofuran at 120°C. Peak positions are given relative to TMS.

($n = 4$, the number following the glyme indicates the number of oxygen atoms in the glyme). At 120°C four absorption peaks are observed at 570, 530, 450 and 320 Hz downfield from the $\alpha$-THF peak (shown at 218 Hz downfield from Me$_4$Si). For a solution of glyme-5 in THF, only two glyme peaks are observed 5 and 21 Hz upfield from the $\alpha$-THF peak. The ratio of the integrated intensities for the glyme-5 complex (a total of 22 protons), at 120°C are 8:4:4:6. Similar spectra were recorded for other glyme complexes, e.g., with glyme-4 ($n = 3$) four absorption peaks were observed at 682, 620, 532 and 380 Hz downfield from $\alpha$-THF and with integrated intensity ratios of 4:4:4:6 (18 protons). From the spectra it is clear that the least shifted peak with intensity 6 can be ascribed to the two terminal CH$_3$ groups. The assignment of the CH$_2$ peaks is more difficult. Therefore it is necessary to study deuterated glymes. Thus far we succeeded in preparing (CH$_3$OCH$_2$CH$_2$OCD$_2$CH$_2$)$_2$O, (CH$_3$OCH$_2$CD$_2$OCH$_2$CH$_2$)$_2$O and CH$_3$OCH$_2$CD$_2$OCH$_2$CH$_2$OCH$_2$CH$_3$. The first two partially deuterated glyme-5 molecules complexed with the anion of coronene again produced NMR spectra consisting of four absorption peaks, but now with integrated intensity ratios of 4:4:4:6. Hence the CH$_2$ groups at the deuterated positions are shifted most. In order
to get a complete assignment of the spectrum, more work on partially deuterated glymes is in progress.

The NMR spectra of the coronene-glyme complexes reveal information on the structure of these complexes in solution. The difference in chemical shift for the various protons of the complexed glymes indicates that the glyme-coordinated alkali ion does not rotate randomly above the plane of the coronene molecule in the time scale of our experiments. The pattern of the NMR spectra suggest a ring-type conformation of the glyme around the alkali ion, the entire moiety symmetrically bound to the aromatic plane in a sandwich type fashion.

(b) Europium and Praseodymium Glyme Complexes

Large proton NMR shifts have recently been observed for many organic compounds in the presence of Eu(DPM)$_3$ and Pr(DPM)$_3$ (8). This urged us to investigate the behavior of glymes in the presence of these reagents in order to compare the observed

![NMR spectrum of a 1:2 mixture of Eu(DPM)$_3$ and glyme-4 at room temperature. Peak positions are given relative to TMS.](image)

Fig. 2. $^1$H NMR spectrum (60 MHz) of a 1:2 mixture of Eu(DPM)$_3$ and glyme-4 at room temperature. Peak positions are given relative to TMS.

NMR patterns with those found in the presence of coronene salts. In the actual experiments small quantities of glymes with $n$ ranging from 1 to 6 were added to a 0.15 $M$ solution of the lanthanide complex in CCl$_4$ and the NMR spectra recorded. Figures 2
and 3 show the NMR spectra of 1:2 mixtures of Eu(DPM)$_3$ with glyme-4 and glyme-5. For glyme-4 with three combinations of two CH$_2$ groups, two triplets and a singlet are found, for glyme-5 four triplets, arising from the four combinations of two CH$_2$ groups.

![NMR spectrum of Eu(DPM)$_3$ with glyme-5](image)

**Fig. 3.** $^1$H NMR spectrum (60 MHz) of a 1:2 mixture of Eu(DPM)$_3$ and glyme-5 at room temperature. Peak positions are given relative to TMS.

In addition, of course, to the CH$_3$ peak. Glyme-3 yields only two triplets, and for glyme-6 four well-resolved triplets and a singlet are observed, again apart from the CH$_3$ peak. These results show that the two CH$_2$ groups representing an NMR peak are not adjacent.
ones, but are equally far removed from the center of the molecule. In the case of glyme-4:

\[
\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3
\]

The C(1) protons give a singlet, while those on C(2) and C(3) produce triplets. Generally, the glymes with an odd number of oxygen atoms only give triplet CH\(_2\) peaks, while those with an even number can be identified by the singlet representing the protons of the two center CH\(_2\) groups.

![Graph showing proton NMR shifts of glyme-4 vs. the ratio of Eu(DPM)_3 to total glyme concentration at 40°C. Proton shifts are relative to those of pure glyme. \([\text{Eu(DPM)}_3] = 0.15 \text{ M in CCl}_4\).](image)

Similar NMR patterns are found with glyme adducts of Pr(DPM)_3 but, as reported for other compounds (6), the shifts are upfield and usually three times larger than those observed with Eu\(^{3+}\).

When 1:1 lanthanide-glyme mixtures are used the spectra show a sharp peak due to the two terminal CH\(_3\) groups, and a series of broad peaks each representing two CH\(_2\) groups, very similar to what has been observed for the glyme-coronene anion complexes. We believe that the interpretation given for the Eu/glyme NMR spectra also holds for the spectra of the gylmated radical anions. In the spectra of the latter complexes, however, the triplet fine structure is obscured by the larger line widths of the absorption peaks, as also occurs in the former complexes when the concentration of paramagnetic particles increases.

Figure 4 demonstrates for glyme-4, that the proton shifts are linearly related to the ratio of the Europium to total glyme concentration. This also means that in the 1:1 mixture essentially all of the glyme is bound to the Eu complex.

The NMR spectra of the partially deuterated glymes (see Section 2a) complexed with
Eu (or Pr) permit the complete assignment of the CH$_2$ peaks, since the presence of a CD$_2$ group removes a CH$_2$ peak in the spectrum or reduces its intensity by a factor of two, depending whether or not one or two CD$_2$ groups are present in the glymes and simultaneously removes the triplet fine structure of the adjacent CH$_2$ peak. In Figs. 2 and 3 the assignments are indicated.

The lanthanide-glyme NMR spectra indicate that the rare earth ion is bound to the oxygen atoms of the glyme in such a way that the complex retains twofold symmetry. If it would be bound asymmetrically, rapid exchange must occur between equivalent O atoms, so that on the average twofold symmetry in the complex exists. In a recent publication (9) we have shown that the lanthanide ion is most likely bound to the outer two oxygen atoms on one end of the glyme chain, exchanging rapidly, intra- or intermolecularly, to the two outer oxygen atoms at the other end of the chain.

(c) Shift Mechanisms

Usually two mechanisms are involved to explain the induced paramagnetic shifts, namely, the Fermi contact interaction dependent on covalent bonding and the dipolar interaction, dependent on distance, geometry and the anisotropy in the g tensor ("pseudo-contact shift") (10). For aromatic radical ions the g tensor is nearly isotropic; therefore the observed contact shifts can be ascribed exclusively to the Fermi contact interaction. This is certainly not the case for the lanthanide shift reagents. Generally, one assumes that for these ions the dipolar interaction is the predominant mechanism. This may be true for Pr$^{3+}$, for which the lowest term is $^3H_4$ (II), but not as pointed out by Weissman (12) for Eu$^{3+}$. For the latter ion the lowest term is $^7F_0$ (II), accordingly no g-tensor, contact or pseudo-contact shifts can exist. As Van Vleck and Frank (11) have shown, an effective magnetic moment arises here through the second-order paramagnetism, which is rather large for Eu$^{3+}$ by virtue of the nearby presence of the $^7F_1$ term lying 255 cm$^{-1}$ above $^7F_0$. This second-order paramagnetism induces a downfield shift, proportional to $\langle 1/r^3 \rangle$, where $r$ is the distance between Eu and the observed nucleus. It should be noted that there is no angular dependence in the expression for the second-order paramagnetism, as occurs in the formula for the pseudo-contact shift. Compared with Pr$^{3+}$, a contact or a pseudo-contact shift arises in the case of Eu$^{3+}$ only in second order.

The reported Eu shifts are downfield; just recently a few upfield shifts have also been observed (13). They may arise from the thermal population of the $^7F_1$ state instead of arising from a particular geometry of the molecule as has been suggested (13). Shift measurements as a function of the temperature may shed more light on the origin of these upfield shifts.

The NMR spectra of glyme-4 and glyme-5 complexed with Pr (DPM)$_3$ show that the shifts for the terminal and the penultimate CH$_2$ groups are only twice as large as those observed with Eu$^{3+}$, while the other CH$_2$ shifts are three times larger, with Pr than with Eu, a shift ratio that has also been observed for other compounds (9). This observation points to a Fermi contact shift on the protons which are close to the rare earth ion (cf. 2b), in addition to the second-order paramagnetic shift (Eu) and/or pseudo-contact shift (Eu, Pr). In the case of Eu$^{3+}$ the Fermi contact shift reinforces the downfield shift, whereas in the case of Pr$^{3+}$ it decreases the upfield shift. Hence the ratio of Pr to Eu shift will diminish for those protons which are subjected to a Fermi
contact interaction. Also the spectra of the glymated coronene complexes suggest that in the lanthanide complexes the Fermi contact shifts on nuclei closely situated to the paramagnetic center contribute significantly to the total contact shifts.

(d) Isotope Effect

An interesting isotope effect was observed in the NMR spectra of $d_2$-glyme-4 (CH$_3$OCH$_2$CD$_2$OCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_3$) complexed with Eu or Pr. The NMR spectrum with Pr is shown in Fig. 5. A doublet is observed for the two CH$_3$ groups with a separation of 19 Hz; for the C$_4$ protons (see figure) a narrow singlet for the CH$_2$ group adjacent to the CD$_2$ group; and a broad singlet (unresolved triplet structure) for the other CH$_3$ group, the separation is about 23 Hz, for the C$_3$ protons, a broad single peak with relative intensity 2 and for the C$_1$ protons, an unresolved $A_2B_2$ spectrum, with a separation between the two discernable main peaks of about 14 Hz. Apparently, the coordination of the glyme to the rare earth ion greatly modifies the chemical shift differences in the deuterated glyme molecule or an unequal bonding of Eu or Pr to —OCH$_2$CH$_2$O— and —OCH$_2$CD$_2$O— induces the chemical shift differences. This is another illustration of the usefulness of the lanthanide shift reagents to unravel geometric differences in structures of complicated molecules.

ACKNOWLEDGMENTS

One of the authors (de B.) enjoyed an enlightening discussion with Prof. Weissman about the spectroscopic properties of Eu. The partial support of this research by the National Institutes of Health (Grant No. G.M. 15965) and by the National Science Foundation (Grant No. G. P26350) is gratefully acknowledged.

REFERENCES

8. J. K. M. Sanders and D. H. Williams, J. Amer. Chem. Soc. 93, 641 (1971); in this paper a large list is given of papers dealing with lanthanide shift reagents.


