orientation is partially allowed in the lower temperature, leading to the smaller value of S_{zz}.[6]

In a nematic solvent, the solute molecule orients in a configuration of minimum energy dictated by its shape (or size) and by dispersion forces.[7] On the basis of shape (or size), the observed trends for CH$_3$CN, CH$_3$I, and CH$_3$Br are not consistent. Perhaps dispersion forces play a role in unusual orientation of methyl iodide. A possible interpretation in favor of perpendicular orientation of methyl iodide at lower temperatures in I–IV is that the interaction between methyl iodide and the nitrogen lone pairs in the solvent molecules plays an important role. At elevated temperatures, this solvent–solute interaction is partially destroyed and the usual parallel orientation could be preferred. The usual temperature dependency at higher temperatures would be due to this. This type of solvent–solute interaction may not be available in the solvent V: the different behaviors of oriented solute molecules in solvents I–IV and V probably arise from the different functions of the azo and azoxy groups interacting with the solute molecule. The fact that unusual behavior of temperature dependency of S_{zz} value has never been encountered in solvent V implies that the perpendicular orientation of methyl iodide in V is quite unstable and that the parallel orientation predominates in the nematic phase.

The behavior of methyl bromide appears to be in accord with the above interpretation, because it is less polarized and less subjected to the dispersion interaction than methyl iodide. The observation for methylene halides may follow this interpretation. Acetonitrile, inert to the above type of specific interaction, thus behaves itself in a usual manner in all the solvents I–V.[8]

In summarizing the above discussion, we can conclude that the nature of the solute molecule, not the shape or size but polarity or polarizability, is markedly reflected in the temperature dependence of the S_{zz} value in the nematic phase of azo compounds. Further study on this problem might serve as an aid in the elucidation of the nature of solvent–solute interactions in nematic solvents.

(6) The magnitudes of the S_{zz} values for CH$_3$I and CH$_3$Br are substantially less in solvents I–IV than in V (Figure 3) in the whole temperature range. This appears to be partly due to more preferential contribution of the perpendicular orientation of CH$_3$I and CH$_3$Br in solvents I–IV than in solvent V.

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(8) The extent of the unusual ordering of the solute molecules (CH$_3$X and CH$_2$X$_2$) in solvents I–IV seems to fall in the order of X = I > Br > Cl > CN, the order of polarizability of the X atom or group.

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Received December 22, 1970

New Superior Paramagnetic Shift Reagents for Nuclear Magnetic Resonance Spectral Clarification

Sir:

The effects of paramagnetism on nuclear magnetic resonances have been studied since 1948—the very beginning of nmr spectroscopy.[1] Despite large observed frequency shifts caused by several paramagnetic chelates, much of the work to date has centered around the question of which metal will permit the observation of high-resolution nmr spectra of its complexes without objectionable peak broadening.[2–13] Hinckley[4] has reported on the ability of the dipyridine adduct of tris(2,2,6,6-tetramethyl-3,5-heptanedionato)europium(III), Eu(thd)$_3$(py)$_2$, to produce relatively large concentration-dependent paramagnetic shifts in cholesterol monohydrate without serious peak broadening. Sanders and Williams[5] subsequently reported that the coordinating effectiveness of the Eu was significantly improved by elimination of the pyridine using the unsolvated Eu(thd)$_3$ synthesized and characterized by Eisentraut and Sievers.[14–16]

However, despite the proven utility on specific classes of compounds, the effectiveness of the above chelates is drastically reduced when used with weak Lewis bases.[5] Moreover, the solubility of the thd chelates is relatively low in nonalcoholic solutions.[9] We wish to report our preliminary results using europium and praseodymium chelates that are vastly superior to the thd analogs, with respect to both solubility and Lewis acidity. The improvements are derived from the use of a partially fluorinated ligand, 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione, in Eu(fod)$_3$ and Pr(fod)$_3$[17] instead of thd. Substitution of fluorocarbon moieties in β-diketonate ligands increases the solubility of the metal complex, and the electron-withdrawing fluorines increase the residual acidity of the cation, making it a better coordination site for weak donors.

The fod chelates were prepared by the method of Springer, Meek, and Sievers.[18] Ethyl propionate and di-*n*-butyl ether were studied with various metal chelates, and these investigations have confirmed the improved performance of Eu(fod)$_3$ and Pr(fod)$_3$ relative to any of the other complexes heretofore examined.

With a Varian HA-60-IL spectrometer, the nmr spectra were obtained at 60 MHz with CCl$_4$ solutions containing 0.1 mmol of ethyl propionate and of di-*n*-butyl ether. Figures 1 and 2 show the effect of adding Eu(fod)$_3$ to the ester and the ether, respectively. As can be seen from the spectra of di-*n*-butyl ether, the

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(17) fod represents the anion of 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl 4,6-octanedione; Eu(fod)$_3$, Pr(fod)$_3$, Eu(thd)$_3$, and Pr(thd)$_3$ are available commercially from Norell Chemical Co., Landing, N. J.

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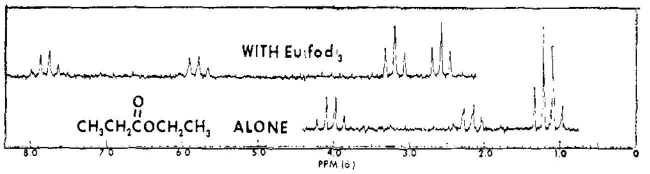

Figure 1. Spectra (60 MHz) of ethyl propionate (10 mg, 1×10^{-4} mol) in 0.5 ml of CCl_4: lower trace, without Eu(fod)$_3$; upper trace, with Eu(fod)$_3$ added (25 mg, 2.5×10^{-5} mol). TMS used as internal reference.

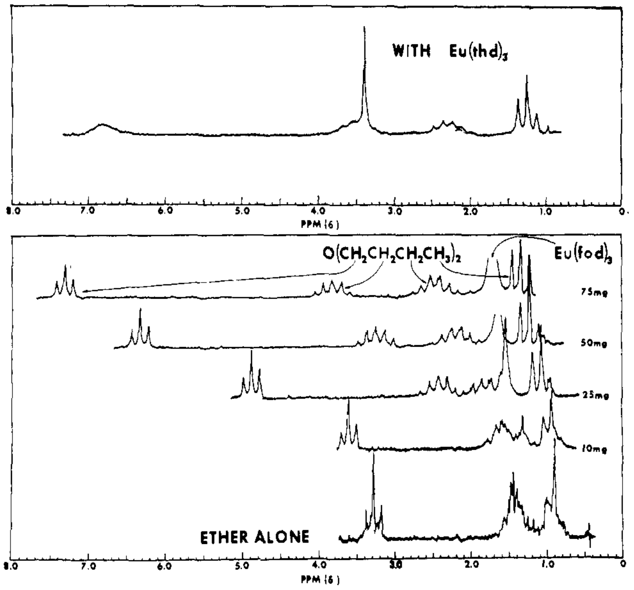

Figure 2. Spectra (60 MHz) of di-*n*-butyl ether (13 mg, 1.0×10^{-4} mol) in 0.5 ml of CCl_4 containing 0–75 mg (7.5×10^{-5} mol) of Eu(fod)$_3$: top trace, spectrum of CCl_4 solution (0.5 ml), 1×10^{-4} *M* in ether and saturated in Eu(thd)$_3$.

use of this reagent greatly simplifies and clarifies the spectrum. It is worth noting that Eu(thd)$_3$ was quite ineffective by comparison, owing to its poorer Lewis acidity and much lower solubility. In fact, upon adding Eu(thd)$_3$ to the ether solution, the latter was heated in order to dissolve as much of the Eu complex as possible. The shifts, therefore, induced in the ether (Figure 2, top) are the maximum obtainable with Eu(thd)$_3$. In the case of the ester, methyl group assignments in the untreated spectrum were confirmed by double-irradiation experiments on a shifted spectrum. As with Eu(thd)$_3$, these shifted spectra reflect rapid exchange between complexed and uncomplexed ester (or ether).

Figures 3 and 4 demonstrate an essentially linear dependence of the paramagnetic shifts on added Eu(fod)$_3$ at lower concentrations, but with both compounds a point was reached where further addition of metal complex caused no further spectral shifts. This information at high Eu-to-ligand ratios is of great importance for both theoretical and practical reasons. It indicates quite clearly that the shift is due to bonding of the organic donor groups with the coordinatively unsaturated europium chelate and that the spectrum is now essentially that of a coordinated ligand rather than that of the average of the free ligand and complexed ligand.

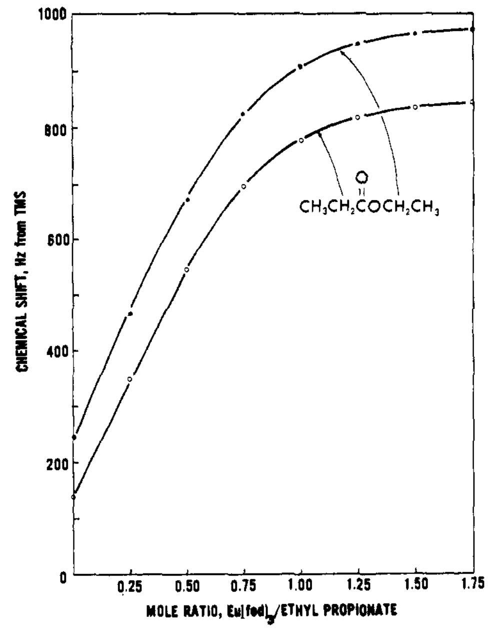

Figure 3. Induced contact shifts of methylene resonances of ethyl propionate as a function of added Eu(fod)$_3$. Points represent stepwise addition of 25 mg of Eu(fod)$_3$ to a solution containing 10 mg of the ester in 0.5 ml of CCl_4. Shifts are in hertz from TMS (internal).

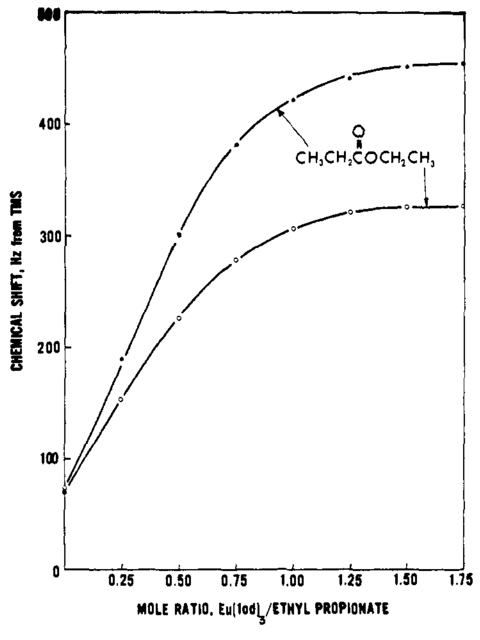

Figure 4. Induced contact shifts of methyl resonances of ethyl propionate as a function of added Eu(fod)$_3$. Same conditions as in Figure 3.

On the more practical side, the use of highly soluble fod complexes permits high enough Eu-to-organic-donor ratios that a constant value can be assigned to a given compound. This can be extremely helpful in compound identification, but it was previously impossible with the less soluble Eu(thd)$_3$ complex. As Demarco, *et al.*,[9] observed, the solubility of this chelate is exceeded before a high enough ratio of Eu(thd)$_3$ to ligand can be achieved, and even the use of a CAT did not permit these workers to overcome the problem by reducing the ligand concentration. To establish with certainty the identity of compounds with similar spectra, one need only add a large excess of Eu(fod)$_3$ and observe the spectrum of the resulting complexed ligands. This procedure should work for any complex with a reasonably large formation constant. This constant can often be determined from data of the type shown in Figures 3 and 4. The large molar ratio of $Eu(fod)_3$ needed to reach this saturation point is indicative of the low basicity of these organic compounds and the extreme solubility of the fod complex. In the case of the ether, 2.0 mol equiv of the chelate was required to achieve complete coordination of the ether. This represents a solubility of over 200 mg of the europium complex in a 0.5-ml CCl_4 solution of the ether. Consequently, an important function of the fod ligand is to impart extremely high solubility to the resulting complex, enabling the attainment of larger induced shifts.

An equally important function of the fod ligand is to produce a species with relatively high Lewis acidity. Feibush, *et al.*,[19] have made extensive studies of the interactions of various weak donor organic ligands with many different coordinatively unsaturated lanthanide chelates. In these experiments the metal chelates were dissolved in nonpolar liquid stationary phases in gas chromatographic columns, and various organic donors were passed through the columns. The interactions were much greater (from relative retention volume data) with columns containing lanthanide–fod complexes than those with thd, providing clear independent experimental evidence for the greater Lewis acidity of the former.

It should also be mentioned that the chemistry of both the thd and fod complexes is not as straightforward as one might assume.[20-23] Everyone usually writes the formulas as simply $M(thd)_3$ and $M(fod)_3$ when in fact such simple unsolvated species may not exist as such. In the crystalline state the thd chelate of praseodymium is a dimer, $(thd)_2Pr(thd)_2Pr(thd)_2$, in which each of the metal atoms is surrounded by seven oxygens.[22] A single-crystal X-ray study has revealed that one of the oxygen atoms of each of the two bridging chelate rings is shared equally between Pr atoms. Some of the lanthanide–thd chelates have been isolated as hydrates,[23] but they do not undergo hydration as rapidly as the fod complexes.[18] A structure determination of the hydrated praseodymium complex has shown that it is a dimer with the formula, $(fod)_2Pr(fod)_2(H_2O)Pr(fod)_2 \cdot H_2O$.[23] Bridging of the two Pr atoms is provided by two carbonyl oxygen atoms as well as one molecule of water. The other water is apparently hydrogen bonded to two perfluoropropyl side chains in the ligand shell and is not bonded to the metal ion. This illustrates that two basically different types of interactions are operative with the same ligand; consequently perhaps even in solution similar complications can occur with organic donors when lanthanide chelates are used as shift reagents. In this complex each Pr is surrounded by eight oxygen atoms, again illustrating the variable coordination number of the lanthanides.

The anhydrous fod complexes pick up 1 mol of water per metal when allowed to stand unprotected in a moist atmosphere. Therefore it is recommended that fod samples be stored over P_4O_{10} in a vacuum desiccator before use as shift reagents. In the present study, after the chelate samples were removed from the desiccator, no special care was taken to exclude moisture or to dry the solvents because we wanted to test the efficacy of the complexes under conditions of practical routine use. Since water acts as a competing donor, it may be necessary in special cases to exclude water insofar as is possible when very poor donors are under study.

We have examined several of the hundreds of lanthanide chelates synthesized in our laboratories and, while other complexes also produce shifts, the fod chelates of Eu(III) and Pr(III) are superior to all of the complexes so far studied.

Acknowledgment. We wish to thank Dr. K. J. Eisentraut, Col. J. W. Connolly, and Dr. Charles S. Springer, Jr., for synthesizing some of the samples used in this study.

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Received December 31, 1970

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Solid-State Photochemistry of Ammonium Azides

Sir:

Modern theories of solid-state physics and chemistry have been applied to explain the mode of photochemical decomposition of certain solid inorganic ionic azides, and the mechanism is based on thermodynamic, kinetic, and spectroscopic evidence.[1,2] This investigation deals with the photolyses of ammonium azides underneath the surface of liquid cyclohexane at 2537 Å. The purpose of the hydrocarbon was to scavenge the reactive free radicals and intermediates produced on the surface of the solid azide during photolysis.

Freshly sublimed and powdered ammonium[3] or cyclohexylammonium[4] azides, covered by purified cyclohexane[5] (analyzed by uv, vpc, and mass spectroscopy) and under dry nitrogen or argon, in quartz vessels (50% or more transmission of uv at wavelengths longer than 2000 Å) were irradiated at 30° with a low-pressure mercury lamp (G. E. Germicidal G30T8, 30 W) having maximum emission at 2537 Å. The 1849-Å Hg emission is eliminated effectively by the Vycor lamp envelope (0% transmission < 2200 Å for a new lamp). The products and relative yields are given in Table I.

In Table I, the extent of reaction depends on time and preparation batch, but the relative ratios of products are about the same for reactions proceeding 11–31% of completion. The product ratio varies noticeably at

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