$$H_3O^+ClO_4^- \downarrow + N(n\text{-}C_4H_9)_4^+ClO_4^- \longrightarrow H_2O + N(n\text{-}C_4H_9)_4^+H(ClO_4)_2^-$$

In terms of acid–base reactions, we conclude that water in dichloromethane is a weaker base with respect to perchloric acid than tetrabutylammonium perchlorate. For electrochemical studies in dichloromethane, we must consider that the strength of the perchloric acid is weakened in the presence of tetrabutylammonium perchlorate when this salt is used as supporting electrolyte.

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Anomalous Features of Nuclear Magnetic Resonance Spectra of Methyl and Methylene Halides Oriented in a Nematic Solvent. Unusual Ordering due to Specific Solute–Solvent Interaction

Sir:

In the present communication we wish to report the observation of unusual ordering of the solute molecule arising from specific solute–solvent interaction in the nematic phase, where separation of the spectral splitting increases when temperature is raised. This finding is expected to shed light on the elucidation of the nature of ordering of the solute molecule in the liquid-crystal solvent.

We have measured proton magnetic resonance spectra of CH_3X (X = I, Br, and CN) and CH_2X_2 (X = I and Cl) dissolved in the various nematic solvents I–V; (I, *p,p'*-ethoxyphenylazophenyl valerate; II, *p,p'*-ethoxyphenylazophenyl hexanoate; III, the mixture of 40 mol % I and 60 mol % II; IV, *p,p'*-ethoxyphenylazophenyl heptanoate; and V, *p,p'*-di-*n*-hexyloxyazoxybenzene). Spectra were obtained at 60 MHz (Jeolco 3H-60) and at 220 MHz (Varian HR-220) at various temperatures ranging from 30 to 110°.

Figure 1 shows an example of proton nmr spectra of 10% methyl iodide in III at various temperatures. With increasing temperature, the spacing of the triplet signal increased gradually. When the temperature is raised more (near the nematic–isotropic transition), the separation decreased rapidly in a normal way, leading to the appearance of isotropic spectrum. These unusual phenomena were found to be reversible with respect to raising and lowering the temperature. The unusual temperature dependency of the spectral splitting for methyl iodide was encountered for solvents I–IV, but not for V. In the mixed solvent III, this anomalous behavior is most conspicuous. Figures 2 and 3 present the temperature dependence of the degree of order, S_{zz}, which describes the average orientation of the molecular threefold axis (*z* axis) with respect to the applied magnetic field for CH_3I, CH_3Br, and CH_3CN in solvents III and V, respectively. Methyl iodide has the maximum value of S_{zz} at an appreciably high temperature (85–90°) in solvent III. Acetonitrile behaves in an almost ordinary manner in all the solvents;[1] the S_{zz} value increases linearly with decreasing temperature, although at lower temperatures this temperature dependency deviates slightly from linearity. Methyl bromide behaves in a manner similar to methyl iodide: the spectral splitting maintained almost constant separation in solvent III when the temperature was varied from 30 to 110°. The results obtained by the usual 60-MHz nmr spectrometer were reproduced by 220-MHz nmr with rapid sample spinning. The unusual phenomena were not affected significantly by variation of solute concentration or by addition of tetramethylsilane, a globular molecule.

For methylene halides, similar unusual but not so conspicuous observations as for the methyl halides were obtained in solvent III. The doublet separation for methylene iodide in III (10 mol %) increases until the temperature is raised from 30 to 50°, but above this temperature the separation decreases gradually in a normal manner. When the temperature was lowered, this unusual spectral change was reproduced. Methylene chloride, however, exhibits a normal trend for all the solvents (see Figure 4).

From these observations it could be said that the unusual temperature dependency of the spectral splitting of the oriented solute molecule is characteristic of iodide or bromide derivatives dissolved in the nematic solvent of azo compounds I–IV. These observations allow us to expect that the specific solute–solvent interaction in the nematic phase is responsible for the unusual alignment of the solute molecule.[2] The unusual observations presented above are not absolutely due to temperature inhomogeneity in the nmr probe. This is confirmed from the facts that this phenomenon is reversible with raising or lowering temperature, that it is not significantly affected by the solute concentration, and that it is always reproduced in 60-MHz nmr with no spinning and in the 220-MHz nmr with rapid spinning of the sample tube. It seems also unlikely that a "looser" nematic phase is produced at the lower temperature in which the isotropic motion of the solute molecule is partially allowed, resulting in the decrease in the S_{zz} value. The following mechanism is proposed to explain how the unusual temperature dependence of the spectral splitting occurs. We are now forced to assume that methyl iodide does not remain in a single mode of orientation, but in at least two modes of orientation[3] which are in an equilibrium state and have opposite directions of ordering. Temperature variation shifts this equilibrium, thus leading to the change in the apparent S_{zz} value. The smaller spacing of the spectral splitting at lower temperature possibly implies that methyl iodide tends to be aligned

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(1) In order to substantiate further this unusual behavior, we measured ^{13}C nmr spectra of 50% enriched $^{13}CH_3I$ and $^{13}CH_3CN$ dissolved in solvent III at 15.1 MHz on a Jeolco 3H-60 spectrometer [for a detailed description of the ^{13}C nmr of oriented molecules in the nematic solvent, see I. Morishima, A. Mizuno, and T. Yonezawa, *Chem. Phys. Lett.*, 7, 633 (1970)]. The spectral splitting in the quartet pattern also exhibited unusual temperature dependency as in the proton nmr spectra for $^{13}CH_3I$ but not for $^{13}CH_3CN$.

(2) ^{13}C chemical shift of $^{13}CH_3I$ in solvent III is almost equal to that in the solvent V and in neat liquid, indicating that CH_3I does not exist as quaternary ion forming at nitrogen atom of the solvent molecule.

(3) Nonunique ordering of the solute molecule in liquid-crystal solvents has recently been detected by nmr [T. Yonezawa, I. Morishima, K. Deguchi, and H. Kato, *J. Chem. Phys.*, **51**, 5731 (1969)] and by epr [G. Havach, P. Ferruti, D. Gill, and M. P. Klein, *J. Amer. Chem. Soc.*, **91**, 7526 (1969)].

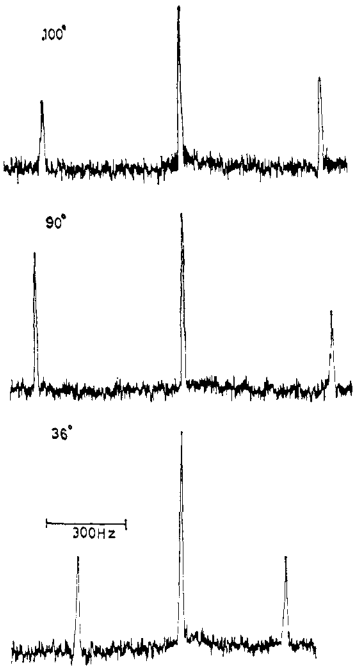

Figure 1. Proton nmr spectra of methyl iodide dissolved (10 mol%) in the mixed solvent III at various temperatures (at 60 MHz).

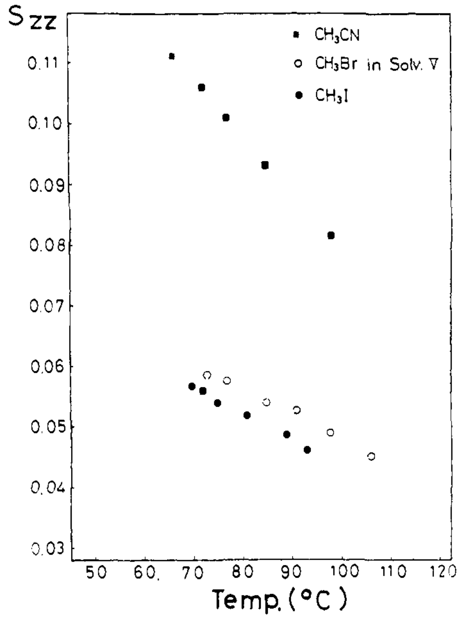

Figure 2. Temperature dependences of S_{zz} value for CH_3I (●), CH_3Br (○), and CH_3CN (■) in the solvent V. All the solute concentrations were *ca.* 10 mol%.

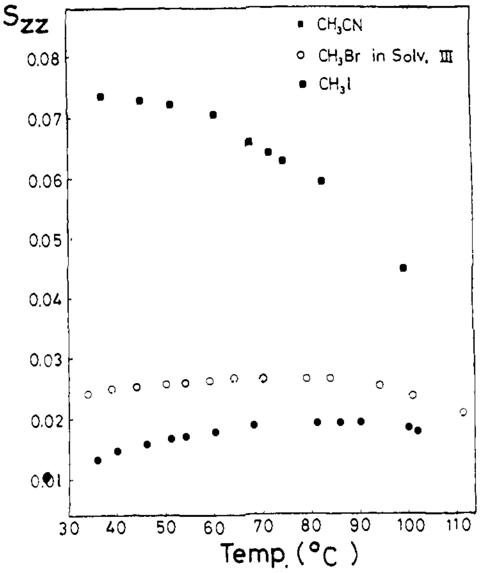

Figure 3. Temperature dependences of S_{zz} value for CH_3I (●), CH_3Br (○), and CH_3CN (■) in the solvent III. All the solute concentrations were *ca.* 10 mol%.

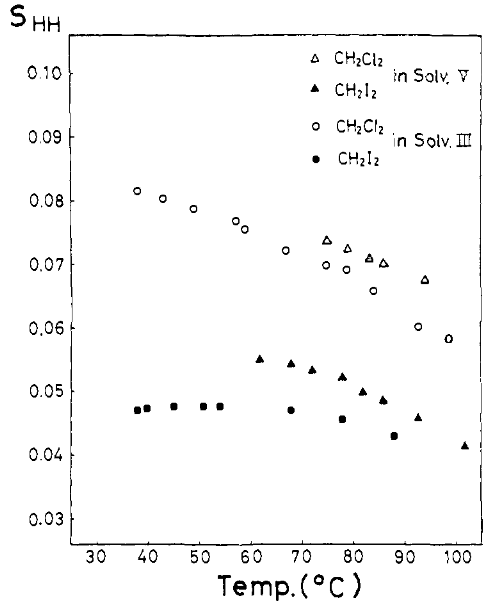

Figure 4. Temperature dependences of the absolute S_{HH} value for CH_2I_2 (●) and CH_2Cl_2 (○) in the solvent III and CH_2I_2 (▲) and CH_2Cl_2 (△) in the solvent V. All the solute concentrations were *ca.* 10 mol %. S_{HH} shows the parameter which describes the average orientation of the interproton axis in CH_2X_2.

partially with its C_{3v} axis directed perpendicular to the applied magnetic field ("the perpendicular orientation"), while at higher temperatures methyl iodide possesses a higher degree of order with the threefold axis parallel to the magnetic field, the direction of the optical axis of the solvent molecule ("the parallel orientation"). In the parallel orientation which is normally encountered,[4] the H-H direct coupling constant in the CH_3X molecule is positive.[5] The increase in contribution of the perpendicular orientation which corresponds to the negative value of the H-H direct coupling constant reduces the apparent value of the H-H direct coupling constant and results in the appearance of the reduced spectral splitting at lower temperature. On the basis of the observed trends only, however, one cannot determine which orientation, perpendicular or parallel, contributes dominantly, because the sign of the observed S_{zz} value is not known. Therefore, we have determined the sign of the S_{zz} value from spectral analysis of a ^{13}C-enriched sample of methyl iodide.[1] Since a positive sign of the indirect coupling constant J_{CH} is well accepted, the sign of the S_{zz} value which is commonly related to the H-H and ^{13}C-H direct coupling constants is easily determined.[1] The positive value of S_{zz} thus determined implies the predominant contribution of the parallel orientation. It then follows that the perpendicular

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(4) Perpendicular orientation has been obtained for acetylene dissolved in solvent V: G. Englert, A. Saupe, and J. P. Weber, *Z. Naturforsch. A*, **23**, 152 (1968).

(5) G. P. Ceasar, C. S. Yannoni, and B. P. Dailey, *J. Chem. Phys.*, **50**, 373 (1969).

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_3CN, CH_3I, and CH_3Br 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.

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(6) The magnitudes of the S_{zz} values for CH_3I and CH_3Br 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_3I and CH_3Br in solvents I–IV than in solvent V.

(7) A. Saupe, *Mol. Cryst.*, **1**, 527 (1966); J. Nehring and A. Saupe, *Mol. Cryst. Liq. Cryst.*, **8**, 403 (1969); C. S. Yannoni, *J. Amer. Chem. Soc.*, **92**, 5237 (1970).

(8) The extent of the unusual ordering of the solute molecules (CH_3X and CH_2X_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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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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(15) K. J. Eisentraut and R. E. Sievers, U. S. Patents 3,429,904 and 3,453,319 (1969).

(16) $Eu(thd)_3$ represents tris(2,2,6,6-tetramethyl-3,5-heptanedionato)-europium(III) and is also sometimes abbreviated $Eu(DPM)_3$.

(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.

(18) C. S. Springer, D. W. Meek, and R. E. Sievers, *Inorg. Chem.*, **6**, 1105 (1967).