considerable attention recently,[13-16] but most of the discussion has centered around angles of 180° *vs.* 120°. There is mounting evidence[17-20] that angles in the 160° range are quite prevalent in metal nitrosyls. Intermediate angles such as these are obviously not easily rationalized; it may be that better overlap between the metal and ligand orbitals can be achieved through moderate bending.

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On the Action of Europium Shift Reagents

Sir:

Since the discovery by Hinckley[1] of the large shifts in nuclear magnetic resonances produced by interaction with compounds of trivalent europium, many studies which exploit the effect for determination of structure have been carried out. This communication is intended to remind people of the analysis carried out by Van Vleck[2] about 40 years ago of the paramagnetisms of Eu^{3+} and to emphasize its bearing on interpretation of the phenomena observed with the shift reagents.

At room temperature Eu^{3+} is found in its lowest electronic state, $^7F_0$, and its first excited state at 200 cm^{-1}, $^7F_1$, with approximately equal occupation probabilities. The lowest state, $^7F_0$, is nondegenerate and has no Zeeman splitting. Hence the interactions usually cited—contact and pseudocontact—cannot operate in the lowest state. In the excited state $^7F_1$, where the crystal-field splittings are much smaller than kT, the pseudocontact and contact interactions may contribute to the shifts. The dominant contribution from the $^7F_0$ ground state is undoubtedly related to the second-order paramagnetism.

The static susceptibility of Eu^{3+} should be almost independent of temperature below ~100°K. At these temperatures, a shift independent of temperature is expected. It should have the $\langle r^{-3} \rangle$ dependence on distance exhibited by the pseudocontact shift. I would expect that, because of the very small crystal-field splittings of the excited state whose admixture produces the second-order paramagnetism, the temperature-independent part of the shift would be almost isotropic.

It is unfortunate that only meager data concerning the magnetic properties of the various rare earth ions in the compounds used as shift reagents are available. Their acquisition will probably enhance the usefulness of the method.

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A Simple Protecting Group Protection–Purification "Handle" for Polynucleotide Synthesis. I

Sir:

In recent years chemical reactions have been carried out on polymer supports by a number of investigators with the objective of simplifying the procedures for the stepwise synthesis of complex substances such as polypeptides and polynucleotides. This method has proved a great success in the field of peptide synthesis.[1] More recently, the application of this procedure to oligonucleotide synthesis has been investigated in a number of laboratories.[2-7] However, desired sequences obtained through the present method of solid-phase synthesis are accompanied with several truncated sequences.[8]

Since it is evident that the formation of truncated sequences cannot be avoided in solid-phase synthesis, we hope to prepare desired sequences exclusively by taking advantage of separation on a solid phase, thereby overcoming the limitation of the solid-phase synthesis.

This report describes a new method of preparing oligothymidylate derivatives which may be applied to the preparation of other pure oligothymidylate sequences. The coupling reactions of nucleotides in this method were carried out in solution in the absence of polymer. In the next stage, the desired oligonucleotide was separated from the other by-products using an ion exchange resin employing salt formation or molecular adsorption between the protecting group and the ion exchange resin. A basic *N*,*N*-dimethyl-*p*-phenylenediamino group was chosen as a protecting group on the nucleoside 5′-phosphate end. This group was intro-

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