present data are consistent with product formation occurring only by processes 1 and/or 4. The theoretical and stereochemical aspects of these reactions will be discussed in detail in a later publication. Further studies are being directed toward the determination of the stereochemistry of attack at $C_2$, and the effect of the nature of R and R′ and the dienophile on the direction of the cycloaddition reaction.

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## Nuclear Magnetic Resonance Spectra of Tris[2,2,6,6-tetramethyl-3,5-heptanedionato] Complexes of the Lanthanides. Temperature Dependence of Shift Reagents

*Sir:*

Study of the tris[2,2,6,6-tetramethyl-3,5-heptanedionato] (tris(dpm)) chelates of the rare earth elements by nmr has been biased heavily toward the tris(dpm) derivative of europium,[1,2] which has enjoyed spectacular success as a deshielding shift reagent; the analogous derivative of praeseodymium, capable of displacing the signals of a sample to higher field with only a slight increase of line width, has also been studied,[3,4] and recent comparative studies have shown that the former complex displays superior magnetic[5] and solubility[6] properties. As tris(dpm) derivatives have been prepared[7] from the entire rare earth group (except cerium and promethium), we undertook to measure the nmr parameters of *tert*-butyl protons of these chelates, both alone and in the presence of potential ligands. Cyclohexanone or 1-hexanol as ligand produced approximately equal changes in chemical shift of the *tert*-butyl resonances of any given complex, although the magnitude and direction of such changes varied broadly from one central atom to the next (Table I). Table II details the concomitant alterations produced in the 100-MHz nmr spectrum of cyclohexanone. The direction of displacement is also a function of the central atom, and the magnitude of this effect, which varies from slight (Sm) to enormous (Dy, Ho), is nearly linear with the proportion[1,4,6] of complex present; the extent of broadening of signals is essentially a function only of the central atom. Direct measurements of relaxation times of the complexes are in progress. (Also under current investigation are the dipyridyl and 1,10-phenanthroline 1:1 adducts of the tris(dpm) compounds of the entire rare earth series[5] for the purpose of relaxation studies.)

**Table I.** Chemical Shifts and Line Widths (at Half-Height) of the *tert*-Butyl Proton Signals of $M(dpm)_3$ in $CCl_4$, in the Presence of Oxygen-Containing Species

| | Ligand | | | | | |
|---|---|---|---|---|---|---|
| | None | | Cyclohexanone | | 1-Hexanol | |
| M | Ppm[a] | Width[b] | Ppm[a] | Width[b] | Ppm[a] | Width[b] |
| Pr | 0.6 | 40 | 2.8 | 2 | | |
| Nd | 0.8 | 16 | 2.1 | 10 | | |
| Sm | 1.08 | 7 | 1.2 | 6 | | |
| Eu | 0.48 | 10 | −0.5 | 5 | −0.6 | 20 |
| Gd | 0.9 | 1500 | 1.8 | 800 | | |
| Tb | 17.4 | 250 | 16.0 | 170 | 17.7 | 60 |
| Dy | 17.7 | 180 | 21.9 | 130 | 20.3 | 120 |
| Ho | 5.3 | 180 | 7.3 | 180 | 8.8 | 180 |
| Er | −3.6 | 250 | −6.2 | 70 | −5.5 | 45 |
| Tm | 12.8 | 400 | 15.2 | 240 | 17.9 | 170 |
| Yb | −0.3 | 60 | −1.9 | 20 | | |
| Lu | 1.14 | | | | | |

[a] Downfield from TMS. [b] In hertz, approximately.

**Table II.** Chemical Shifts and Line Widths (at Half-Height) of Signals of the α-, β-, and γ-Methylene Protons of Cyclohexanone (0.1 *M*) in a Saturated Solution[a] of $M(dpm)_3$ in $CCl_4$

| | α | | β | | γ | |
|---|---|---|---|---|---|---|
| M | δ[b] | Width[c] | δ[b] | Width[c] | δ[b] | Width[c] |
| Pr | −8.8 | (>20)[d] | −2.8 | (~20)[d] | −2.0 | (~20)[e] |
| Nd | −3.1 | (>20)[e] | −0.4 | (>20) | −0.1 | (>20) |
| Sm[g] | ~1.1 | (>20)[e] | ~1.1 | (>20) | ~1.1 | (>20) |
| Eu | 5.4 | (~15)[d] | 3.8 | (~15)[d] | 3.5 | (~15)[e] |
| Gd[f] | | | | | | |
| Tb | −23.8 | (75) | −12.4 | (32) | −9.2 | (24) |
| Dy | −51.6 | (85) | −21.2 | (25) | −16.2 | (21) |
| Ho | −49.0 | (92) | −21.6 | (29) | −16.4 | (22) |
| Er | 28.0 | (61) | 13.0 | (>20) | 10.5 | (>20) |
| Tm[h] | −42.2 | (90) | −17.3 | (38) | −13.1 | (34) |
| Yb | 14.6 | (23) | 7.4 | (>20) | 6.1 | (>20) |
| None | 2.45( | ~15)[d] | | ~2.00 | 1.70 | |

[a] Except Ho, which is much more soluble; $[M(dpm)_3]$ is slightly less than 0.1 *M*. [b] In parts per million. [c] In hertz. [d] Sufficiently resolved to permit identification of multiplicity. [e] Evidence of fine structure, but not resolved enough for identification. [f] Not observed; overlap possible as *tert*-butyl resonance is very broad. [g] These values were determined by adding cyclohexanone and observing emergence of resonances from beneath the *tert*-butyl signal. [h] These values are reversed in sign from analogous data reported by Hart, *et al.*,[3] for $Tm(ClO_4)_3[OP(NMe_2)_3]_4$ in acetonitrile, but similar reversals have been produced (E. R. Birnbaum and T. Moeller, *J. Amer. Chem. Soc.*, **91**, 7274 (1969)) by altering ligands in Pr and Nd complexes.

In general, the solubility of all 12 compounds in carbon tetrachloride is modest at best, and, as noted for the Eu analog, enhanced somewhat by the presence of a coordinating substrate; Ho and, to a lesser extent, Dy are slight exceptions in being rather less insoluble. Solutions of complexes in the present study were prepared by dissolving 15 ± 3 mg of the appropriate solid in 0.3 ml of warmed carbon tetrachloride that had been stored for at least 1 week over NaOH pellets.

It was found that the use of untreated $CCl_4$ as a solvent for such studies promoted decomposition of at least several of the complexes; the *tert*-butyl resonances of solutions of $Pr(dpm)_3$, $Nd(dpm)_3$, and $Sm(dpm)_3$ in untreated carbon tetrachloride were shown to diminish upon standing and/or dilution, with concurrent appearance of a second signal. During investigation of this phenomenon, it was further noted that these signals displayed substantial shifts of field

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(1) C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969); *J. Org. Chem.*, **35**, 2834 (1970); P. V. DeMarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *J. Amer. Chem. Soc.*, **92**, 5734, 5737 (1970); G. M. Whitesides and D. W. Lewis, *ibid.*, **92**, 6979 (1970).

(2) J. K. M. Sanders and D. H. Williams, *Chem. Commun.*, 422 (1970); G. H. Wahl, Jr., and M. R. Peterson, Jr., *ibid.*, 1167 (1970).

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(5) D. R. Crump, J. K. M. Sanders, and D. H. Williams, *Tetrahedron Lett.*, 4419 (1970).

(6) J. K. M. Sanders and D. H. Williams, *J. Amer. Chem. Soc.*, **93**, 641 (1971).

(7) J. Selbin, N. Ahmad, and N. S. Bhacca, *Inorg. Chem.*, in press.

position (on the order of several parts per million, reversible on cooling) as the probe temperature was increased gradually to about 75°. We prepared a sample of 2-heptanone (~0.1 *M*) in carbon tetrachloride, added the maximum amount of Eu(dpm)$_3$, and recorded the nmr spectrum of the sample at temperatures throughout the liquid range of CCl$_4$. Proportional enhancement of all signals in the substrate is observed (Table III) as the sample temperature is lowered, and suggests possible utility of reduced temperature determinations in cases where the limited solubility of the lanthanide complex is inadequate, or of variable temperature studies in lieu of measurements at a number of different relative concentrations.

**Table III.** Temperature-Dependent Chemical Shifts[a] of Protons of 2-Heptanone in CCl$_4$ Containing Eu(dpm)$_3$

| *T*, °C | C-7 | C-6 | C-5 | C-4 | C-1 | C-3 |
|---|---|---|---|---|---|---|
| −30[b] | 1.06 | 1.48 | 2.12 | 2.93 | 3.71 | 3.99 |
| −12 | 1.04 | 1.44 | 2.04 | 2.81 | 3.52 | 3.82 |
| 0 | 1.02 | 1.38 | 1.93 | 2.55 | 3.25 | 3.55 |
| 35 | 1.01 | 1.37 | 1.91 | 2.49 | 3.18 | 3.48 |
| 66 | 0.99 | 1.32 | 1.75 | 2.28 | 2.93 | 3.23 |
| Ref[c] | 0.90 | 1.19 | ~1.39 | ~1.55 | 2.01 | 2.31 |

[a] Parts per million. [b] Freezing occurs after a few minutes. [c] 2-Heptanone in CCl$_4$.

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## Balanced Zero-Differential-Overlap Approximations in Nonempirical Molecular Orbital Calculations[1]

*Sir:*

We have made a critical study of the effects of various diatomic zero-differential-overlap (ZDO) approximations in nonempirical molecular orbital theory.[2] More particularly, we sought to identify the most effective ways to approach Hartree–Fock wave functions and energies by methods involving zero differential overlap. We found that the errors associated with ZDO approximations depend not only upon the integrals thereby neglected but also upon the way in which the molecular energies are determined. As a result, we searched for methods which minimize the error associated with a given level of ZDO approximation. In this communication we report such methods and some data indicating their effectiveness.

Our actual calculations were carried out for a series of homopolar and heteropolar diatomic molecules: LiH, BH, NH, HF, BF, LiF, CO, C$_2$, N$_2$, and F$_2$. For each molecule we used the minimal Slater-type atomic orbital basis set of Ransil[3] and made ground-state Hartree–Fock calculations for a range of internuclear separations by several methods involving ZDO approximations. The ZDO approximations were applied in the original STO basis to both the one- and two-electron integrals involving the two-center charge distributions under consideration. We also made corresponding calculations without integral approximations. The results were evaluated by comparing the interatomic potential curves and the bond-order matrices produced from the various calculations. In general, we found the comparisons to be insensitive to basis-set choice, to exhibit strong qualitative regularities, and to vary only slightly with the polarity of the molecules. These facts gave us confidence that our conclusions could be extrapolated to more accurate calculations and to larger molecules.

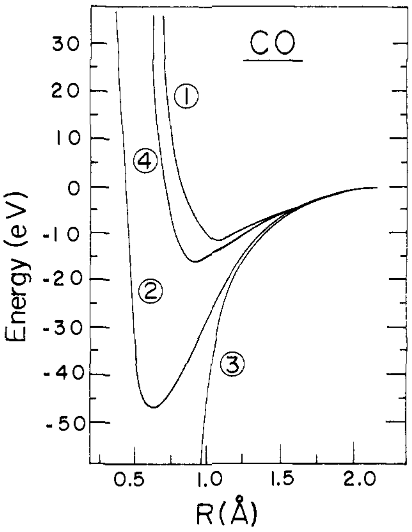

Figure 1. Calculated minimal-basis Hartree–Fock interatomic potential curves for CO: curve 1, without neglect of integrals; curve 2, core–valence ZDO; curve 3, core–valence ZDO for electron-repulsion integrals only; curve 4, core–valence ZDO balanced-error calculation (described in text).

Not unexpectedly, we found that two-center core–core and core–(π valence) differential overlaps could be set to zero with essentially negligible effect. For example, in CO, the assumption of two-center 1s–1s and/or 1s–2pπ ZDO produced errors of the order of 0.05% in the bond-order matrices and raised total energies by 0.0001–0.001 eV. On the scale used for the CO potential curves shown in Figure 1, these ZDO approximations yield curves indistinguishable from those obtained not using integral approximations (curve 1).

We next considered the neglect of the larger differential overlaps of the two-center core–(σ valence) type. This level of approximation has a significant effect, as illustrated by CO calculations assuming 1s–2s and 1s–2pσ ZDO. At the equilibrium internuclear separation, the bond-order matrix elements exhibited errors averaging 7%. However, the potential curve was more substantially affected (curve 2), yielding an equilibrium separation, dissociation energy, and force constant very different from those given by the more accurate calculations. The errors in the potential curves and bond-order matrices became even larger as the ZDO approximations for any or all of the one-electron integrals were removed. This situation is illustrated for CO (curve 3).

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(2) We gratefully acknowledge the assistance of Dr. H. J. Monkhorst, who has conducted similar investigations (H. J. Monkhorst, Ph.D. Thesis, University of Groningen, The Netherlands, 1968).

(3) B. J. Ransil, *Rev. Mod. Phys.*, 32, 239 (1960).