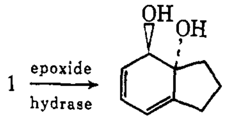
and a spiroketone as well as an isomeric arene oxide(s) from the zwitterion. The products obtained from the intermediates may or may not depend on pH. For example, the diol results only in the formation of 5-hydroxyindan, the intermediate arene oxide(s) essentially only in the formation of 4-hydroxyindan but the spiroketone gives both products in acid and only 4-hydroxyindan in base. Thus, the ultimate products formed from the aromatization of **1** depend on the pH at which the intermediates form as well as the pH at which they react to give products. Three key points emerge which are of considerable significance to the biochemist and biologist studying the metabolic fate of aromatic hydrocarbons: (i) an enzymatically formed arene oxide may rearrange to a new arene oxide prior to undergoing subsequent reactions in the cell, (ii) a phenol can form by a solvolysis pathway without incorporation of molecular oxygen,[8a] and (iii) a number of pathways other than direct nucleophilic opening of an arene oxide are available for the covalent binding of drugs and other xenobiotic substances to cellular constituents—pathways which result from prior chemical reactions of the arene oxide.

The present study may well bear on the mechanism by which the enzyme epoxide hydrase converts **1** into a dihydrodiol (eq 7). The structure of the diol suggested



(7)

homoallylic addition of water[11] to the diene system had occurred. In view of the present results which demonstrate an oxygen walk to form **8** from **1** in aqueous media, an alternate and equally attractive mechanism for the above enzyme-catalyzed reaction emerges; isomerization of **1** to **8**, possibly enzyme catalyzed, followed by normal 1,2-trans opening of **8**. Trisubstituted oxiranes such as **8** are known to be better substrates for the enzyme than tetrasubstituted oxiranes such as **1**.[21]

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Lanthanide Induced Nuclear Magnetic Resonance Shifts. A Structural and Computational Study

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Abstract: The preparation and X-ray crystal structure of the 1:1 complex between 3,3-dimethylthietane 1-oxide (**1**) and tris(dipivalomethanato)europium(III), Eu(dpm)$_3$, are described. The Eu(dpm)$_3$ induced shifts for a group of 13 organic compounds were analyzed using the McConnell–Robertson equation (1) and the C$_2$ shift equation (8). In a number of cases it was found to be advantageous to average the calculated shifts over the molecular conformations. Such averaging is shown to give additional conformational information. For sulfoxide **1** it is shown that neglecting to average the calculated shifts results in an incorrectly assigned pmr spectrum. The structure of the complex is a near perfect wedged octahedron with the Lewis base **1** occupying one of the four equivalent positions of lowest symmetry. The Eu–O bond lengths were 2.33(2) Å to the dpm ligands and 2.40(1) Å to the sulfoxide oxygen. Four formula units of the adduct were distributed in a monoclinic cell ($P2_1/c$) of dimensions a = 14.412(6) Å, b = 20.23(1) Å, c = 15.660(8) Å, and β = 98.55(3)°. The structure's disagreement factor for 2890 diffractometer collected reflections is 0.064 based on F.

Simplification of nmr spectra by the addition of lanthanide shift reagents has proven to be a most significant extension to the usefulness of nmr spectroscopy.[2] The lanthanide induced shifts (LIS) are generally accounted for in terms of pseudocontact interactions, and their magnitudes have been correlated with substrate stereochemistries. Initially the LIS were used in a qualitative sense; however, increasing effort is being directed toward a more quantitative treatment of the data.[3] The spatial dependence of the shifts (S_i^c) for axially symmetric complexes is given by the McConnell–Robertson equation[4a] (eq 1), where ΔH_i

$$S_i^c = \frac{\Delta H_i}{H} = \left\langle \Sigma\left(\chi_{\parallel}, \chi_{\perp}, K, \frac{1}{T}\right) \frac{(3\cos^2\theta_i - 1)}{r_i^3} \right\rangle_{\text{av}} \quad (1)$$

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is the change in field strength at nucleus i, r_i is the distance between the paramagnetic metal and nucleus i, and θ_i is the angle between the principal magnetic axis of the complex and the vector r_i.

Many earlier applications of eq 1 to structural problems have been based on the assumption that the angular term remained fairly constant, thus taking the observed LIS to be proportional to r^{-n}. The exponent n, generally set equal to 3,[4b] was in several instances adjusted to improve the fit between calculated and observed shifts. Often plots of observed shifts *vs.* log r_i were quite linear with slopes near −2.[5] However, the observation that the LIS for a given metal are not always in the same direction[6] showed that this approach was not fully satisfactory with the result that an increasing number of investigators are beginning to interpret LIS data using the full equation (eq 1). Indeed, one finds improved agreement between calculated and observed shifts when the full expression is used, rather than the radial portion only.[7]

We recently pointed out, however, that several difficulties remain in the use of eq 1.[8] One obvious difficulty stems from the fact that the observed shifts are the result of an averaging of molecular orientations, with the consequence that the calculated shifts should be based on a model which mimics the averaging process. In order to partially circumvent this difficulty, most workers have chosen to study fairly rigid molecules and to assume that any remaining conformational mobility could be adequately described by a single average shift reagent–substrate structure (static model).[3] Another difficulty is that the McConnell–Robertson equation, strictly speaking, is only applicable to axially symmetric complexes,[9] while none of the known structures of shift reagent–substrate adducts satisfy this requirement. Yet a third difficulty is that the location of the principal magnetic axis, which is needed to define θ_i, is generally unknown, although it has usually been assumed to be along the lanthanide substrate axis. On the basis of known lanthanide structures,[10] one would conclude that the lanthanide substrate axis is not a principal magnetic axis; nevertheless, these calculations appear to be quite successful. It is the purpose of this paper to examine the apparent success of LIS calculations in the light of X-ray and nmr data, *and to point out that the use of static models can lead to errors in the assignment of nmr spectra.*

Experimental Section

Preparation of Compounds. Reagent grade solvents were dried over Linde 4A Molecular Sieves. Microanalyses were carried out by C. F. Geiger, Ontario, Calif.

3,3-Dimethylthietane.[11] The dibenzoate ester of 2,2-dimethylpropane-1,3-diol (141 g, 0.37 mol) was intimately mixed with sodium sulfide nonahydrate (120 g, 0.50 mol) and introduced in portions over a 0.75-hr period to vigorously stirred dimethyl sulfoxide (300 ml) at 80–90°. After addition was complete, more sodium sulfide nonahydrate (24 g, 0.10 mol) was added, and the temperature of the reaction mixture was raised to 130–140°. The liquids which distilled from the reaction were collected until the distillate was nearly clear, *ca.* 65 ml. Sodium chloride was added to the distillate, the two layers were separated, and the upper organic layer was dried ($CaCl_2$). Distillation gave 32 g (82%) of 3,3-dimethylthietane: bp 116–117° (730) mm) [lit.[12] bp 119–121°]; nmr (neat) δ 1.26 (s, 3, CH_3), 2.92 (s. 2, SCH_2).

3,3-Dimethylthietane 1-Oxide. To an ice-cooled solution of 3,3-dimethylthietane (15 g, 0.147 mol) dissolved in 40 ml of acetic acid, a solution of 31% hydrogen peroxide (16.1 g, 0.147 mol) in 10 ml of acetic acid was added dropwise over 20 min. Excess solvent was removed by distillation at 25 mm, and the residue was distilled, 49–52° (0.5 mm). Since this fraction contained the desired sulfoxide as well as acetic acid which codistilled, it was taken up in ether, treated with solid NaOH, and redistilled to give the desired sulfoxide: bp 52–53° (0.3 mm); mp 35–36°; ir (CCl_4) 2985 m, 1460 m, 1400 m, 1365 m, 1245 m, 1150 m, 1087 s, 1017 s cm^{-1}; nmr ($CDCl_3$) δ 1.26 (s, 3, trans CH_3), 1.30 (s, 3, cis CH_3), 3.00 (d of t, 2, $J + J' = 5.9$, cis OSCH), 3.52 (d of t, 2, $J + J' = 5.9$, trans OSCH).

Preparation of Complex 2. 3,3-Dimethylthietane 1-oxide (600 mg, 4.08 mmol) dissolved in dry (molecular sieves) acetonitrile (0.60 ml) was heated with $Eu(dpm)_3$ (230 mg, 0.329 mmol) until all the material dissolved. Upon cooling the solution, a white precipitate formed which was recrystallized from acetonitrile to give 105 mg (41%) of **2** as white needles: mp 141–142°; ir (KBr) 2900 s, 1575 s, 1525 s, 1505 m, 1450 s, 1400 s, 1350 s, 1240 w, 1225 m, 1170 m, 1145 m, 1060 m, 1015 m, 865 m, 790 m, 815 m cm^{-1}.

Anal. Calcd for $C_{38}H_{67}EuO_7S$: C, 55.67; H, 8.23. Found: C, 55.20; H, 8.26.

Dimethyl Sulfoxide–Tris(dipivalomethanato)europium(III). Recrystallization of $Eu(dpm)_3$ from dimethyl sulfoxide yields this substance as white needles: ir (KBr) 2950 m, 1565 s, 1430 s, 1405 m, 1220 m, 1175 m, 1135 m, 1035 m, 1015 m, 800 m, 795 m cm^{-1}.

Anal. Calcd for $C_{35}H_{63}EuO_7S$: C, 53.91; H, 8.14. Found: C, 54.29; H, 8.35.

Crystallography. A small 0.1 × 0.1 × 0.35 mm white needle of **2** was selected for study and mounted on its c axis (needle direction) in a borosilicate capillary (0.5 mm diameter × 0.01 mm wall). Precession and Weissenberg photographs indicated that the crystal was monoclinic, and from the systematic extinctions ($0k0$), $k = 2n + 1$ and ($h0l$) $h + l = 2n + 1$, we were able to unambiguously pick the space group as $P2_1/n$ (a nonstandard setting of $P2_1/c$, No. 14). The cell constants, a = 14.412 (6) Å, b = 20.23 (1) Å, c = 15.660 (8) Å, and β = 98.55 (3)° were determined from a least-squares fit of 12 carefully centered reflections using Mo Kα_1 radiation (λ 0.70926 Å). Å The crystal density was 1.19 g/ml, 1.21 g/ml being required for 4 formula units per cell.

Intensity data were collected under computer control using a Picker four-circle diffractometer with a 32.0-cm crystal to scintillation detector distance and a pulse height analyzer adjusted to accept 90% of a reflection's intensity. Zirconium attenuators were automatically inserted into the diffracted X-ray beam to keep the maximum count rate below 10,000 cps. Unique reflections (4300) were collected in the limiting sphere having a maximum sin θ/λ of 0.48 Å^{-1} using Mo Kα radiation made monochromatic by Bragg reflection from a graphite crystal. Background counts of 10 sec were taken at the extremes of 2θ scans which were made at a scan rate of 1°/min over an angular range of 1.5 + 0.692° tan θ. Three standard reflections, remeasured every 50 reflections, showed considerable but uniform decreases in intensity (21% during the course of data collection) which was clearly due to decomposition of the crystal. The data were corrected for the crystal decomposition, and 2890 reflections having intensities greater than 2.0σ were retained. These were corrected for Lorentz and polarization ef-

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Table I

Atom	$X^{a,b}$	Y	Z	$B_{11}{}^{c,d}$	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Eu	0.5151 (1)	0.0900 (0)	0.2985 (1)	5.1 (0)^e	4.3 (0)^e	5.2 (0)^c	0.4 (0)^e	0.6 (0)^e	0.4 (0)^e
S	0.5929 (3)	0.0725 (3)	0.5324 (3)	7.9 (3)	11.5 (4)	6.0 (3)	−1.3 (2)	1.4 (2)	−0.6 (2)
C_2	0.6715 (12)	−0.0005 (9)	0.5479 (13)	4.8 (10)	9.5 (12)	17.7 (18)	1.5 (9)	−2.8 (10)	5.8 (12)
C_3	0.7567 (13)	0.0471 (10)	0.5713 (13)	6.3 (12)	9.2 (13)	9.0 (15)	−3.4 (10)	−0.8 (10)	2.9 (11)
C_4	0.7083 (10)	0.1052 (8)	0.5170 (11)	5.0 (8)	6.8 (11)	10.1 (12)	−2.1 (8)	−0.5 (7)	3.2 (8)
C_5	0.7816 (14)	0.0638 (11)	0.6672 (12)	14.0 (16)	18.9 (21)	4.9 (11)	−2.8 (13)	−2.2 (10)	3.3 (12)
C_6	0.8434 (14)	0.0199 (11)	0.5342 (15)	6.8 (13)	13.3 (16)	18.0 (21)	0.5 (12)	0.4 (13)	1.3 (15)
O	0.5278 (7)	0.0663 (5)	0.4502 (6)	7.3 (5)	7.7 (6)	5.4 (5)	−0.7 (4)	−0.6 (5)	1.8 (5)
2C	0.2175 (12)	0.1852 (10)	0.2871 (14)	3.9 (8)	9.3 (11)	10.5 (14)	3.8 (8)	2.7 (8)	−2.6 (11)
3C	0.2879 (14)	0.1314 (9)	0.2683 (12)	11.6 (16)	7.8 (11)	4.3 (12)	−4.4 (11)	2.7 (11)	−0.7 (10)
4C	0.2638 (11)	0.0924 (11)	0.1893 (14)	6.5 (10)	7.5 (11)	11.6 (15)	2.0 (11)	2.7 (10)	3.5 (13)
5C	0.3269 (14)	0.0428 (9)	0.1603 (11)	7.5 (13)	7.3 (11)	6.9 (12)	−1.8 (10)	−3.1 (10)	1.7 (11)
6C	0.3006 (16)	−0.0033 (11)	0.0787 (13)	10.5 (14)	9.4 (14)	7.5 (14)	−0.4 (12)	−4.9 (11)	−4.1 (11)
7C	0.3221 (16)	−0.0731 (10)	0.1034 (13)	19.7 (19)	5.9 (13)	12.1 (16)	5.1 (12)	−2.9 (13)	−4.1 (11)
8C	0.1205 (14)	0.1676 (11)	0.2475 (17)	5.8 (11)	14.3 (18)	25.3 (26)	2.1 (11)	−0.1 (14)	−6.1 (17)
9C	0.2478 (17)	0.2479 (10)	0.2544 (19)	16.9 (19)	4.1 (9)	30.4 (29)	0.6 (11)	12.6 (18)	0.3 (15)
10C	0.1947 (17)	0.0001 (12)	0.0535 (15)	13.5 (17)	15.2 (19)	14.6 (20)	1.5 (14)	−3.4 (15)	−6.3 (15)
11C	0.3418 (23)	0.0245 (14)	0.0080 (14)	38.1 (39)	19.6 (24)	6.4 (14)	−16.4 (24)	10.6 (19)	−5.4 (15)
1C	0.2183 (17)	0.1853 (13)	0.3784 (15)	21.7 (25)	24.0 (26)	6.4 (13)	13.4 (20)	5.4 (15)	0.3 (16)
3C	0.3654 (7)	0.1265 (5)	0.3144 (7)	4.8 (6)	8.2 (6)	5.3 (6)	0.1 (5)	−0.7 (5)	−0.6 (5)
5C	0.4096 (8)	0.0321 (5)	0.1992 (7)	6.5 (6)	5.5 (6)	6.8 (6)	0.1 (5)	−0.5 (5)	−0.9 (5)
2B	0.8307 (11)	0.0874 (12)	0.2552 (13)	5.0 (8)	11.8 (13)	13.0 (15)	−4.6 (11)	5.0 (9)	−2.1 (13)
3B	0.7411 (13)	0.0546 (9)	0.2753 (11)	10.7 (14)	4.9 (9)	6.9 (12)	−0.1 (10)	0.3 (10)	−1.6 (8)
4B	0.7315 (11)	−0.0145 (10)	0.2739 (11)	5.7 (10)	7.3 (11)	8.3 (12)	−1.8 (9)	0.9 (8)	−0.7 (10)
5B	0.6467 (14)	−0.0481 (7)	0.2896 (10)	8.2 (13)	4.4 (9)	7.8 (11)	0.5 (9)	2.1 (10)	−0.3 (7)
6B	0.6390 (13)	−0.1261 (8)	0.2891 (13)	7.1 (4)					
7B	0.6606 (24)	−0.1484 (10)	0.3771 (17)	39.7 (39)	6.6 (13)	11.2 (19)	1.6 (11)	0.3 (22)	2.6 (12)
8B	0.9043 (14)	0.0380 (11)	0.2459 (20)	8.2 (13)	10.3 (16)	39.1 (38)	−2.1 (11)	14.2 (19)	−5.5 (18)
9B	0.8032 (16)	0.1303 (11)	0.1713 (14)	17.8 (19)	16.7 (19)	6.6 (13)	−9.0 (16)	2.0 (12)	0.9 (13)
10B	0.7100 (20)	−0.1555 (9)	0.2478 (23)	28.8 (30)	4.8 (11)	43.4 (42)	−1.0 (14)	30.1 (31)	−4.5 (17)
11B	0.5451 (14)	−0.1473 (9)	0.2530 (22)	8.7 (13)	5.9 (13)	40.2 (44)	−1.5 (11)	−5.5 (18)	−3.4 (18)
1B	0.8610 (11)	0.1384 (8)	0.3286 (10)	9.7 (11)	10.7 (11)	7.9 (11)	−7.4 (10)	2.5 (8)	−4.9 (10)
3B	0.6744 (7)	0.0936 (5)	0.2889 (7)	5.7 (5)	4.4 (6)	9.9 (7)	−0.5 (5)	1.4 (5)	−1.0 (6)
5B	0.5722 (7)	−0.0193 (5)	0.3065 (7)	5.1 (5)	5.0 (6)	8.3 (7)	0.7 (4)	1.7 (5)	0.6 (5)
2A	0.5517 (15)	0.3073 (8)	0.4087 (12)	12.0 (14)	3.7 (9)	8.6 (12)	−1.9 (10)	0.7 (11)	−5.2 (8)
3A	0.5400 (11)	0.2553 (9)	0.3372 (13)	6.4 (10)	6.3 (11)	9.5 (14)	1.0 (9)	3.0 (9)	2.7 (11)
4A	0.5251 (11)	0.2726 (9)	0.2442 (14)	5.0 (9)	6.8 (11)	9.5 (14)	−0.7 (8)	1.6 (9)	−0.4 (11)
5A	0.5143 (11)	0.2261 (10)	0.1719 (15)	3.9 (9)	6.9 (11)	14.0 (20)	−0.2 (9)	0.7 (9)	1.2 (12)
6A	0.4964 (13)	0.2489 (9)	0.0730 (11)	8.1 (4)					
7A	0.3973 (12)	0.2351 (11)	0.0456 (11)	5.7 (10)	22.5 (21)	9.2 (13)	−5.1 (11)	−2.4 (8)	8.2 (13)
8A	0.5374 (15)	0.3766 (9)	0.3691 (13)	18.0 (18)	4.5 (9)	12.8 (16)	2.2 (10)	−2.5 (13)	−2.8 (10)
9A	0.6524 (13)	0.2988 (9)	0.4528 (12)	7.8 (12)	11.4 (14)	10.0 (14)	0.2 (10)	−3.8 (10)	−3.1 (11)
10A	0.5236 (14)	0.3222 (9)	0.0692 (11)	17.0 (17)	8.7 (13)	7.6 (12)	−3.3 (11)	1.7 (11)	1.8 (10)
11C	0.5615 (15)	0.2073 (10)	0.0291 (12)	18.2 (18)	13.6 (16)	9.0 (13)	7.6 (14)	8.0 (13)	3.1 (12)
1A	0.4909 (17)	0.2948 (12)	0.4670 (14)	16.4 (19)	16.5 (21)	13.0 (18)	−3.2 (14)	10.7 (16)	−4.0 (15)
3A	0.5469 (7)	0.1942 (5)	0.3619 (6)	8.7 (7)	4.5 (6)	4.9 (6)	−0.8 (5)	−0.3 (5)	0.4 (5)
5A	0.5094 (7)	0.1628 (5)	0.1835 (6)	9.7 (7)	4.7 (4)	3.6 (5)	1.2 (5)	0.8 (4)	0.7 (5)

[a] Fractional monoclinic coordinates. [b] The numbers in parentheses (all tables) refer to the standard deviation of the last significant digits of the preceding number. [c] B isotropic, (Å),^{2} is given here if the atom was refined isotropically. [d] The form of the anistropic temperature factors is $\exp(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{12} + 2hlb_{13} + 2klb_{23})$. The expression $B_{ij} = a_i{}^*a_j{}^*$, where $a_j{}^*$ is the jth reciprocal lattice vector, was used to convert the anisotropic parameters into the same units as the isotropic parameters. [e] The errors for these temperature factors are all less than 0.05.

fects,[13] but not for absorption. The mass absorption coefficient is 14.8 and the range of transmission factors was 0.88–0.81.

The structure was readily solved by Patterson and Fourier techniques and refined anisotropically by full-matrix least-squares methods to final unweighted and weighted residuals of 0.064 and 0.053.[14,15] The standard deviation of an observation of unit weight is 0.83. Positional and thermal parameters are given in Table I and derived parameters are given in Tables II–V.

LIS Calculations. The objectives of this calculation, as we see it, should be to permit correct judgment of assignments, to choose from among conformers, and to settle minor questions of geometrical isomerization. In addition, provision for rapid accurate assembly of data input to the calculation is an important consideration.

We have found, *vide supra*, that the first consideration can be satisfied only by fitting each data set with a variety of static and rotamer averaged models, the final choice being guided by proper statistical tests of the fits. The latter requirement is best satisfied by the choice of the chemist's standard Dreiding model as a natural coordinate system[16] with simple coordinate transformations being applied by the computer to place the molecule properly in the dipolar field of the lanthanide shift reagent.

Two programs have been written to perform these LIS calculations. In one case (PSEUDO) the shift reagent is placed at the center

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(13) The programs used were local versions of Eiss' REDAT for data reduction; Zalkin's FORDAP for Patterson and electron density maps; Busing, Levy, and Martin's ORFLS for least-squares refinement; Johnson's ORTEP for drawings; and Rao's GEOM for distance, angles, and planes.

(14) $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma W(|F_o| - |F_c|)^2/\Sigma WF_o{}^2)^{1/2}$, where $W = 4F^2/L^2\sigma^2(I)$, L is the reciprocal Lorentz-polarization correction, and $\sigma(I) = [P + (t/20)^2B + (0.045\ I)^2]^{1/2}$. P is the peak count, t is time spent scanning the peaks in seconds, B is the background count, and I is the integrated intensity. See P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967).

(15) Atomic scattering powers for valence C, neutral S, and O were taken from J. A. Ibers in "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 202, Table 3.3.1.A. The europium values are from Table 3.3.1.B.

The real and imaginary part of the anomalous dispersion for europium was taken from D. H. Templeton, *ibid.*, p 215, Table 3.3.2.C.

(16) Clearly, an interactive computer based model building system such as that described by K. B. Wiberg, [*J. Chem. Educ.*, 47, 113 (1970)] is a useful garnishment to this approach.

Table II. Geometry of Coordination Sphere

O–O bond or O–Eu–O angle[a]		Length, Å $\sigma = 0.01$ Å	Angle, degree $\sigma = 0.5°$
O(3A)	O(5A)	2.84	74.9
O(3B)	O(5B)	2.75	72.0
O(3C)	O(5C)	2.76	72.9
		⟨2.78⟩	⟨73.3⟩
O	O(3C)	3.16	83.9
O(3C)	O(5A)	3.21	87.4
O(5A)	O(3B)	3.03	81.4
O(3B)	O	3.57	98.0
		⟨3.49⟩	⟨90.2⟩
O(5B)	O	2.98	77.6
O(5C)	O(5A)	3.04	81.7
O(5C)	O(5B)	2.87	75.6
		⟨2.96⟩	⟨78.3⟩
O(3A)	O	2.97	77.3
O(3A)	O(3B)	3.07	82.3
O(3A)	O(3C)	2.95	78.3
		⟨3.00⟩	⟨79.3⟩

[a] The atom designations are the same as those used in Figures 4–6. The oxygen atoms are designated according to the chelate ring to which they are attached, either A, B, or C, and the carbon atom to which they are bound, either 3 or 5. The sulfoxide oxygen is designated simply as O.

Table III. Geometry of 3,3-Dimethylthietane 1-Oxide

Distances, Å		Angles, deg	
Eu,O	2.40 (1)	Eu,O,S	141.9 (7)
O,S	1.48 (1)	OSC_2	110.0 (7)
S,C_2	1.85 (2)	OSC_4	112.7 (7)
S,C_4	1.84 (2)		
C_2,C_3	1.56 (2)	C_2SC_4	75.8 (8)
C_3,C_4	1.55 (2)	$C_2C_3C_4$	93.6 (13)
C_3,C_5 (trans)	1.55 (3)	$C_2C_3C_5$	115.3 (15)
C_3,C_6 (cis)	1.54 (3)	$C_4C_3C_5$	113.0 (14)
		$C_2C_3C_6$	110.0 (14)
		$C_4C_3C_6$	112.6 (14)
		$C_5C_3C_6$	112.1 (14)
		SC_2C_3	89.1 (12)
		SC_4C_3	89.9 (11)
		Ring puckering angle 35.4°	

Table IV. Least-Square Planes[e] and Deviation (Å)

	Plane I[a,d]	Plane II[b]	Plane III[c]
l	−0.1694	0.6708	0.0064
m	−0.8865	0.2167	0.0021
n	−0.4307	−0.7093	−1.0000
d	−5.2202	1.6071	−4.5079
	−0.08 (O)	0.020 (Eu)	−0.32 (O_{3C})
	0.09 (O_{3C})	−0.006 (O_{5C})	1.46 (O_{5C})
	0.09 (O_{3B})	−0.006 (O_{5B})	0.10 (O_{3C})
	−0.09 (O_{5A})	−0.009 (O_{3A})	−0.19 (O_{5B})
			−1.04 (O_{3A})

[a] The equatorial plane of the wedged octahedron. [b] The axial plane of the wedged octahedron. [c] The pseudo pentagonal bipyramid plane seen down the O–Eu axis. [d] Equations of the planes are of the form $lx + my + nz - d = 0$. [e] The angles between the best planes: I and II, 90.0°; I and III, 64.7°; and II and III, 44.4°.

of the coordinate system and the molecule in question is allowed to move with respect to it, while in the other (AVSHIFT) the situation is reversed. In either case the relative position(s) of the substrate and the shift reagent are adjusted to properly place the molecule in the dipolar field of the lanthanide shift reagent. Placement is considered to be "correct" when the sum of the square errors between calculated and observed shifts is minimized. That is to say, that the quantity $\Sigma(S_i^{\circ} - S_i^{c})^2$, where S_i^{c} is the calculated LIS for nucleus *i* and S_i° is the observed LIS (eq 2 and 3), is minimized.

$$S_i^{c} = K(3\cos^2\theta_i - 1)r_i^{-3} \tag{2}$$

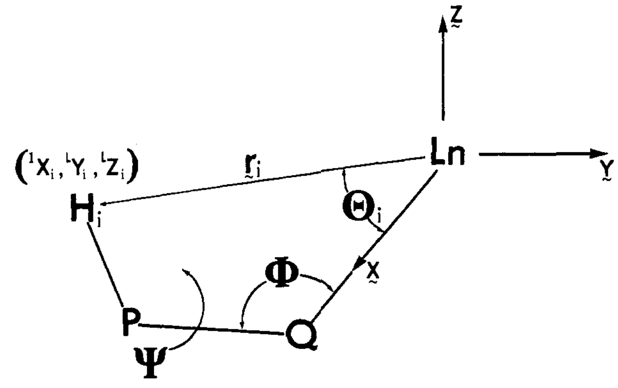

Figure 1. The coordinate frame (*x*, *y z*; with *x* assumed to be coincident with the principal magnetic axis) showing the meaning of the coordinate transformations required to bring the substrate into proper position in the lanthanide's dipolar field.

Table V. Intermolecular Approaches Less Than 4.0 Å

Contact[a]	Distance, Å
C_{7C}–C_{11A}	3.94 (3)
S–S	3.99 (1)
S–O	3.33 (1)
S–O_{5B}	3.87 (1)
C_2–C_{3C}	3.89 (2)
C_2–O_{3C}	3.43 (2)
C_5–C_{4C}	3.98 (3)
C_5–C_{5C}	3.96 (3)
O–O	3.26 (1)
C_{7A}–C_{9A}	3.68 (2)
C_{8B}–C_{8A}	3.88 (3)

[a] The atoms of the thietane ring are labeled as shown in Figure 5. The chelate ring atoms are labeled according to their type, location, and chelate ring designation. Thus C_{4B} refers to carbon atom number four on chelate ring B.

where the terms have their usual significance[3,4a]

$$S_i^{\circ} = S_i^{f} - S_i^{b} \tag{3}$$

where S_i^{f} = chemical shift of unperturbed resonance and S_i^{b} = chemical shift of the fully bound substrate.[17] Scaling of the calculated shifts to the observed shifts is accomplished by forcing *K* (eq 2) to be of such a value that ΣS_i^{c} equals ΣS_i°.

The program PSEUDO has several additional features and, therefore, it will be discussed in more detail. As presently coded it requires the substrate donor atom to be placed at the origin of a right-handed cartesian coordinate system. Also, it is usually an advantage to have some donor atom–substrate bond (*e.g.*, O–C of an alcohol) parallel to the *X* axis. The program then removes the substrate molecule from the origin using the coordinate transformation (Figure 1) given below.

$$\begin{vmatrix} ^{L}X_i \\ ^{L}Y_i \\ ^{L}Z_i \end{vmatrix} = \begin{vmatrix} XG \\ 0 \\ 0 \end{vmatrix} + \phi \cdot \psi \cdot \begin{vmatrix} ^{D}X_i \\ ^{D}Y_i \\ ^{D}Z_i \end{vmatrix}$$

where Φ and ψ are transformation matrices, ($^{D}X_i$, $^{D}Y_i$, $^{D}Z_i$) represents input Dreiding model coordinates for a given atom (*i*), and ($^{L}X_i$, $^{L}Y_i$, $^{L}Z_i$) represent that atom's position in the lanthanide's coordinate system (Figure 1) after consideration of the La–Q bond length (XG), the La–Q–P bond angle (ϕ) and the P–Q torsion angle (ψ). In this transformed coordinate system the geometrical portion

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(17) S^{b} can be determined from a fit of equilibrium constants and chemical shifts to the raw data: (a) K. Roth, M. Grosse, and D. Rewicki, *Tetrahedron Lett.*, 435 (1972); (b) J. Bouquart and J. Chuche, *ibid.*, 2337 (1972); (c) T. A. Wittstuck, *J. Amer. Chem. Soc.*, **94**, 5130 (1972); (d) I. Armitage, G. Dunsmore, L. D. Hall, and A. G. Marshall, *Can. J. Chem.*, **50**, 2119 (1972); (e) B. L. Shapiro and M. D. Johnston, Jr., *J. Amer. Chem. Soc.*, **94**, 8185 (1972). Generally, however, the slope of the LIS concentration plots have been used.

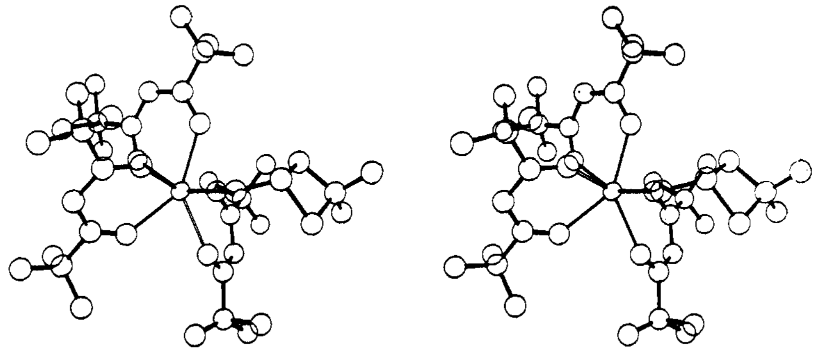

Figure 2. The structure of the Eu(dpm)–sulfoxide adduct, **2**.

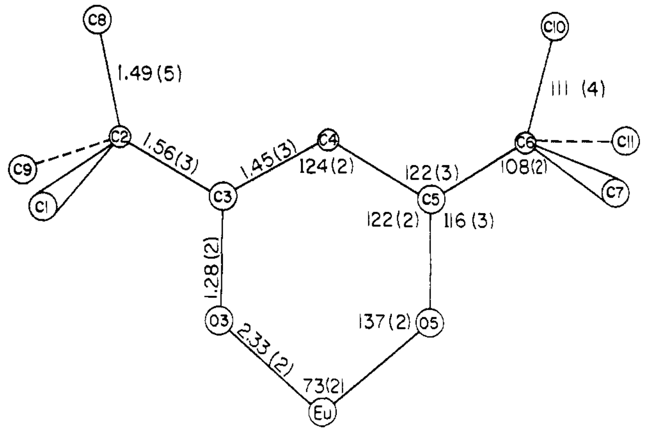

Figure 3. Average structural parameters for the dpm ligands.

of the dipole field, eq 2, simplifies to eq 4. Optimization of the

$$S_i^{c} = K(3\,{}^{\mathrm{L}}X_i^{2} - r_i^{2})r_i^{-5} \qquad (4)$$

parameters[18] to minimize the sum of the square errors, $\Sigma(S_i^{o} - S_i^{c})^2$, is a nonlinear problem. Thus, we have chosen an interactive procedure based on producing an improved calculated shift (${}^{\mathrm{N}}S_i^{c}$) from the old estimate (${}^{o}S_i^{c}$) and those parameter changes which are expected to produce improvement. A Taylor series expansion in ${}^{o}S_i^{c}$ (truncated at the first term) is sufficient to accomplish this.

$${}^{\mathrm{N}}S_i^{c} = {}^{o}S_i^{c} + \Delta\mathrm{XG}\frac{\delta\,{}^{o}S_i^{c}}{\delta\mathrm{XG}} + \Delta\phi\frac{\delta\,{}^{o}S_i^{c}}{\delta\phi} + \cdots \qquad (5)$$

Equation 5 and the requirement that

$$\frac{\delta\sum(S_i^{o} - S_i^{c})^2}{\delta\mathrm{XG}} = 0;\ \frac{\delta\sum(S_i^{o} - S_i^{c})^2}{\delta\phi} = 0;\ \cdots \qquad (6)$$

lead to the least-squares normal equations[19] in which we have dropped subscripts for convenience, and the sums are as usual over all observations. At the end of each refinement cycle the parameter changes are tested for convergence. If further parameter refinement seems necessary, after appropriate dampening, the changes are added to the previous parameter estimates thus providing an input parameter set for the next cycle of refinement. Derivatives required in (7) are evaluated numerically, and standard deviations for the refined parameters are estimated from the inverse normal equation matrix in the usual way.[19–21] Since the optimization process is strongly nonlinear, we, like Willcott and Davis,[3f] have chosen the crystallographic disagreement factor, R_2, as a measure of goodness of fit and have used Hamilton's R factor tables for hypothesis testing.[19,22]

$$\begin{vmatrix} \Sigma\left(\frac{\delta S}{\delta\mathrm{XG}}\right)^2 & \Sigma\left(\frac{\delta S}{\delta\mathrm{XG}}\cdot\frac{\delta S}{\delta\phi}\right) & \cdots \\ \Sigma\left(\frac{\delta S}{\delta\mathrm{XG}}\cdot\frac{\delta S}{\delta\phi}\right) & \Sigma\left(\frac{\delta}{\delta\phi}\right)^2 & \cdots \\ \cdots & \cdots & \cdots \end{vmatrix} \cdot \begin{vmatrix} \Delta\mathrm{XG} \\ \Delta\phi \\ \cdots \end{vmatrix} = \begin{vmatrix} \Sigma\left(\frac{\delta S}{\delta\mathrm{XG}}(S_1^{o} - S_i^{c})\right) \\ \Sigma\left(\frac{\delta}{\delta\phi}(S_i^{o} - S_i^{c})\right) \\ \cdots \end{vmatrix} \qquad (7)$$

Orienting the substrate molecule with respect to the lanthanide rather than optimizing the lanthanide coordinates with respect to fixed substrate in the usual manner[3,23] leads to several computational conveniences.

Most importantly, rotamer averaging is readily treated, since one can easily include several torsion angles, with and without symmetry constraints, and their contributing mole fractions as adjustable parameters.

Contributions to the LIS from nonaxial asymmetry[9] (eq 8) can be

$$S_i^{c} = Kr_i^{-3}[(3\cos^2\theta_i - 1) + K_o/K_{\mathrm{A}}\sin^2\theta_i\cos 2\Omega_i] \qquad (8)$$
$$\text{where } \cos\Omega_1 = r_iY$$

approximated since the only unknown (K_o/K_{A}) can be optimized to give the relative contribution from the orthorhombic term. Finally, the principal magnetic axis can be aligned in any direction and this direction optimized, *vide supra*.

Results and Discussion

Structure of the Eu(dpm)$_2$–Sulfoxide Adduct. In Figure 2 we show the overall structure of the one-to-one complex, **2**. A covalent Eu–O single bond has been

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[18] Steepest descent methods have also been used in this study (AVSHIFT); however, since we discuss only the least-squares procedure used by PSEUDO we refer the interested reader to the following detailed references: (a) D. A. Pierre, "Optimization Theory with Applications," Wiley, New York, N. Y., 1969, p 296; (b) D. J. Wilde, "Optimization Seeking Methods," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1964.

[19] W. C. Hamilton, "Statistics in Physical Science," Ronald Press, New York, N. Y., 1964.

[20] $\sigma_i^2 = \sigma^2 A_{ii}^{-1}$; where A_{ii}^{-1} is the ith diagonal element of the inverse normal equation matrix, σ^2 is the variance, and σ_i is the estimated standard deviation of the ith fitted parameter.

[21] See paragraph at end of paper regarding supplementary material.

[22] W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

[23] (a) N. S. Angerman, S. S. Danyluk, and T. A. Victor, *J. Amer. Chem. Soc.*, **94**, 7137 (1972); (b) M. Ochiai, E. Mizuta, O. Aki, A. Morimoto, and T. Okada, *Tetrahedron Lett.*, 3245 (1972); (c) J. W. Apsimon and H. Beirbeck, *ibid.*, 581 (1972); (d) H. L. Ammon, P. H. Mazzocchi, W. J. Kopecky, Jr., H. J. Tamburin, and P. L. Watts, Jr., *J. Amer. Chem. Soc.*, **95**, 1968 (1973); (e) G. Montaudo and P. Finocchiaro, *J. Org. Chem.*, 37, 3434 (1972); (f) P. V. Demarco, B. J. Cerimele, R. W. Crane, and A. L. Thakkar, *Tetrahedron Lett.*, 3539 (1972); (g) I. M. Armitage, L. D. Hall, A. G. Marshall, and L. G. Werbelow, *J. Amer. Chem. Soc.*, **95**, 1437 (1973).

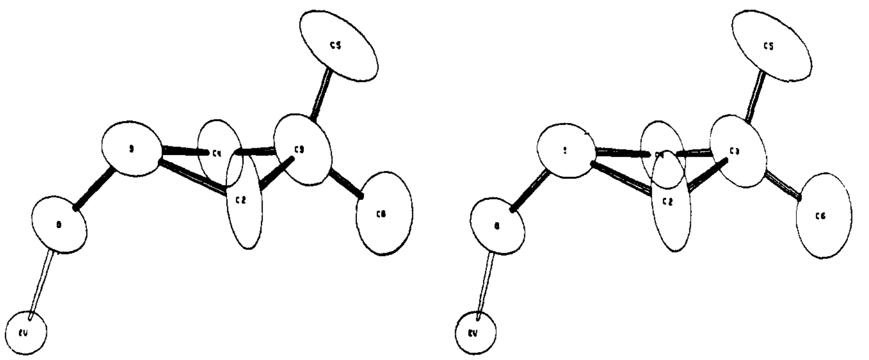

Figure 4. The structure of 3,3-dimethylthietane 1-oxide.

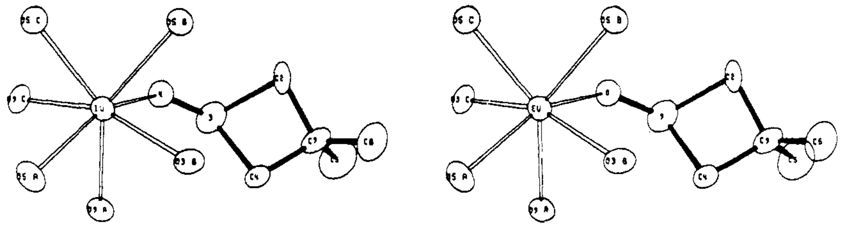

Figure 5. The coordination sphere of europium showing the position of the sulfoxide in the wedged octahedral coordination polygon.

formed between the sulfoxide, **1**, and the $Eu(dpm)_3$ complex with the dpm ligands moving aside from their idealized trigonal positions to provide a cleft in which the sulfoxide substrate rests. Average bond lengths and angles for the three dipivalomethanato ligands are given in Figure 3.

The sulfoxide ring (Figure 4, Table III) is puckered[24] by 35° and has the expected equatorial-oxygen conformation.[25]

The coordination sphere is an ideal wedged octahedron[10b] with the Eu–O(3A) bond serving as the twofold axis (Figure 5, Tables II and IV). Although the local point symmetry is C_{2v}, it is important to note the sulfoxide lies in a position of lowest symmetry. The same coordination symmetry is extant in the two other known seven coordinate lanthanide $(dpm)_3$ structures,[10a,b] and it is interesting to point out that in $Dy(dpm)_3 \cdot H_2O$ the water molecule lies in the position of lowest symmetry.[10a] Praseodynium in the dimer of $Pr(dpm)_3$ is in the center of a wedged octahedral polygon as a result of oxygen bridging by dpm ligands. In this case, however, the bridge oxygens (*i.e.*, coordinated substrate) lie on the unique axis of the wedged octahedron.[10b] The seven coordinate complex, $Ho(C_6H_5COCHCOC_6H_5)_3 \cdot H_2O$, is the only complex of this general type which is known to have axial symmetry. Water and the Ho atom lie on the threefold axis.[10g] While generalizations are difficult at this time, there may be some preference for the unique axial position by bulky substrate molecules. Molecular packing in crystals of **2** appears to be rather loose (Table V) and we feel has no role in the conformation of substrate or adduct.

General Aspects of LIS Calculations. (a) The direction of the principle magnetic axis is certainly the major question raised by this structure. The implication (supported by the structures previously reported[10]) is that pseudocontact shift calculations should not be made using the axially symmetric McConnell–Robertson equation.[4a] For purposes of computation, however, all previous workers have assumed that the lanthanide substrate bond is coincident with the principle magnetic axis of the shift reagent–substract adduct. Indeed, in this and all other reported $Ln(dpm)_3$–substrate structures the substrate does not lie on so much as a twofold axis of symmetry; thus in fact even the orthorhombic χ tensor approximation[9] may be difficult to apply. Furthermore, there is no possibility of independent determination of the diagonalized χ tensor from solution studies.

We have tried to circumvent this problem by adjusting the angle between the principal magnetic axis and lanthanide–donor atom bond axis[26] simultaneously with the usual distance, bond angle, and torsion angle parameters. This has been attempted for all of the substrates reported here, *vide supra*, with no improvement in the fit of the data. Furthermore, this angle has either become optimal at *ca.* 0° or has been indeterminate.

This result (which supports the assumption implicit in current approaches to LIS calculations) may be rationalized in several ways. First, many large substrate molecules (possibly all substrates, since no solution structures have been determined) may lie on the symmetry axis of the adduct, which approximates a fourfold axis, even though in fact it is only a twofold

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[24] S. Kumakuka, T. Shimozawa, Y. Ohnishi, and A. Ohno, *Tetrahedron*, 27, 767 (1971), and references therein.

[25] (a) C. R. Johnson and W. O. Siegel, *J. Amer. Chem. Soc.*, 91, 2796 (1969); (b) W. O. Siegel and C. R. Johnson, *Tetrahedron*, 27, 341 (1971), and references therein.

[26] (a) This approach has been independently suggested by C. L. Honeybourne, *Tetrahedron Lett.*, 1095 (1972). Also since this paper was submitted several analytical (b–d) and (e) computational studies have appeared in the literature, which show that a nonzero angle will simply appear as a pregeometrical constant. (b) H. Huber, *Tetrahedron Lett.*, 3559 (1972); (c) W. DeW. Horrocks, Jr., and J. P. Sipe, III, *Science*, 177, 994 (1972); (d) J. M. Briggs, G. P. Moss, E. W. Randall, and K. D. Sales, *J. Chem. Soc., Chem. Commun.*, 1180 (1972); (e) G. E. Hawkes, D. Liebfritz, D. W. Roberts, and J. D. Roberts, *J. Amer. Chem. Soc.*, 95, 1659 (1973).

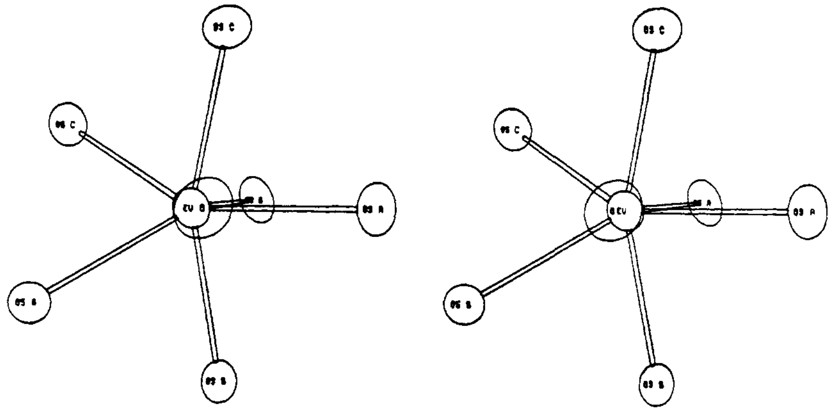

Figure 6. A view of europium's coordination sphere along the europium–oxygen axis.

axis. Second, even if the substrate lies in a low symmetry region, the expected 12–15-fold rotational barrier is most likely quite low and the resulting free rotation will result in a higher symmetry average environment. Third, the symmetry along the lanthanide–donor atom bond (Figure 6, Table IV) can be crudely described as a fivefold axis and coupled with free rotation, and the known fluxional characteristics of lanthanide complexes could represent the axial symmetry required.

Nonetheless, optimization of the direction of the principal magnetic axis invariably results in placing it along the lanthanide–donor bond, and we conclude that this assumption is proper for solution studies.[26]

(b) An obvious suggestion based on the wedged octahedral structure for **2** is that an orthorhombic form for the dipolar field (8) may result in improved fits to LIS data.[9] This equation has been tested for all the examples discussed in this paper, *vide supra*, and while improvements have resulted they have been of marginal significance. Furthermore, contributions by the orthorhombic term have been small, averaging out at about 5–10% of the axial term.[27]

We conclude that in most cases the orthorhombic contribution to the LIS need not be considered, and our rationalization of this result patterns itself after those arguments made for the orientation of the magnetic axis, *vide infra*.

(c) Rotamer averaging of the computed LIS *vs.* using averaged atom positions frequently leads to quite different results. Generally speaking, equivalent or superior fits are obtained by rotamer averaging and in several instances the correct proton assignments were inconsistent with the one arrived at by using a static model (*i.e.*, averaged atom positions). The only exceptions to this rule have been several small mirror symmetry molecules (*vide supra*) in which the static model generally gave superior fits than the rotamer averaged models. The following section fully illustrates these points.

We conclude that no assignment or structural study should be regarded as complete until all reasonable rotamer averagings have been tested.

(d) Based on our experiences with rotamer averaging, the question of how to properly treat methyl groups naturally arises. We have concluded after comparisons with compounds **1**, **4**, and **7** that the concept of a point methyl group (*i.e.*, averaged positions) is the best approach to this problem; for example, compare entries 2 with 13 and 1 with 14 in Table VIII. Exhaustive testing with randomly placed methyl groups in the dipolar field, however, suggests that difficulties may be expected with the point methyl approximation when it lies in a region of high dipole gradient.[28] In that case treatment of any kind is difficult, and it is probably best to eliminate that observation from the optimization process at least initially.

(e) Finally, we note that the average lanthanide–donor atom bond lengths calculated from the LIS data are 0.3–0.5 Å longer[2e] than those obtained by X-ray diffraction methods. We have tried to attribute this to a failure of the point dipole model with minor success. Also, it is clear that shift reagent–substrate correlation times may be longer than adduct lifetimes, thus averaging in small amounts of substantially longer distances.

Regardless of the cause, we must conclude that bond lengths determined by this method are often *ca.* 0.5 Å longer than the sum of covalent radii. The calculated lanthanide–donor atoms for all the molecules investigated are recorded in Tables VIII–XI.

3,3-Dimethylthietane 1-Oxide (1)

The case history of **1** is especially interesting because the standard LIS calculation (static model) clearly leads to an incorrect assignment of the pmr spectrum. First, however, a brief review of the previous conformational[25] and pmr[29] studies on this molecule is in order so that the LIS dilemma may be placed in proper perspective.

It is clear that the molecule strongly prefers the equatorial-oxygen conformation, as indicated by the large chemical shift difference between the α-methylene protons and the long-range coupling exhibited between H_{cis} and Me_{trans} and between H_{trans} and H'_{trans}. The literature coupling[29] constants, chemical shifts, and proton assignments agree with our own and are recorded in Table VI. The upfield methylene resonance ($\delta_{ppm} \approx 3.0$) is long-range coupled to the upfield methyl group, thereby requiring these two groups to be axially positioned and therefore is assigned to H_{cis} and Me_{trans}. The fact that this places H_{cis} upfield of H_{trans} is in accord

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[27] W. DeW. Horrocks, Jr., and J. P. Sipe, III, 13th Experimental NMR Conference, Asilomar, 1972, paper 5.1.

[28] R. M. Wing, T. A. Early, and J. J. Uebel, *Tetrahedron Lett.*, 4153 (1972).

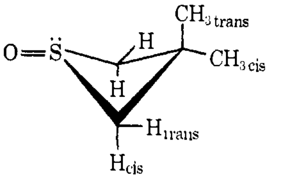
[29] W. Wucherpfennig, *Tetrahedron Lett.*, 765 (1970).

Table VI. Nmr Parameters for 3,3-Dimethylthietane 1-Oxide

Assignment	Shift (δ) Lit.[a]	Shift (δ) This work		Coupling constants Lit.[a]	Coupling constants This work
H_{trans}	3.41	3.52	$J(H_{cis}/H_{trans})$	−11.0	−11.8
H_{cis}	2.96	3.02	$J(H_{cis}/CH_{3,trans})$	0.8	0.8
Me_{trans}	1.22	1.23	$J(H_{trans}/H'_{trans})$	5.7	5.5
Me_{cis}	1.31	1.32	$J(H_{trans}/H'_{cis})$	0.1	

[a] Reference 29.

with the known upfield shifting experienced by protons anticoplanar to lone pair electrons.



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When the nmr spectrum of **1** is taken in the presence of Eu(dpm)$_3$, H_{cis} is shifted more rapidly than H_{trans} and Me_{trans} is shifted more rapidly than Me_{cis}, which causes a reversal in the ordering of each pair when the ratio Eu(dpm)$_3$/(**1**) ≈ 0.16. The Δ_{Eu} values for each proton set are recorded in Table VII.

Table VII. Δ_{Eu} Values for 3,3-Dimethylthietane 1-Oxide

Proton	H_{cis}	H_{trans}	Me_{cis}	Me_{trans}
$\Delta_{Eu}{}^{obsd}$ (Hz)[a]	490.0	284.0	133.0	164.0
$\Delta_{Eu}{}^{calcd}$ (Hz)[b]	490.0	283.8	132.9	164.2

[a] $\Delta_{Eu} = \delta - \delta_{Eu}{}^{1:1}$, see ref 5. All shifts are in hertz at 60 MHz. [b] Using the axially symmetric model with averaging; see text for further details. This corresponds to entry 1 in Table VIII.

Since we know the proton and conformational assignments, we are in a position to test whether it would have been possible to make these assignments using shift data alone. The first four entries in Table VIII record r(Eu–O), $\phi(\angle$EuOS), and R factors for **1** in the equatorial-oxygen conformation using the atom coordinates determined from the X-ray analysis.[30] Entries 1 and 2 give the fits observed for the correct resonance assignments with and without rotamer averaging, respectively, while 3 and 4 give the same data with the methyl resonance assignments reversed. If one attempted to assign the methyl resonances on the basis of shift calculations using the static, axially symmetric model as is frequently done, the methyl groups would have been incorrectly assigned since the R factor for the incorrect assignment is 2.8 times larger than that for the correct assignment. In fact, an R factor ratio of that magnitude permits one to reject the correct assignment at the 92% confidence level! However, when one includes the chemically reasonable expectation that the observed shifts are averaged over three rotational conformations about the O–S bond, one finds a drastic improvement in the R factor for the correct assignment (entries 1 and 2). The R factor ratio of *ca.* 62 allows one to say that the rotamer averaged model is statistically better at the 99% confidence level. By the same token, we find no statistical improvement in the fit for the incorrect assignment using the averaging model (entries 3 and 4), and the correct assignment is now supported at the 92% confidence level.[31] The calculated rotamer populations for entry 1 are also chemically reasonable, with 9% of the anti lone pair conformation and 45.5 ± 0.1% each of the equivalent gauche conformations. It is also gratifying to find that the bond angles and lengths for this best value case are chemically more reasonable than for the other entries (2–4).

Table VIII. R Factors and Eu(dpm)$_3$ Locations for Various Models and Assignments of Sulfoxide **1**

Entry	r	ϕ	10^2R	Assignment	Conformation[g]	Model[e]
1[a]	2.53 (1)	113.0 (3)	0.10	*b*	Bent-O$_e$	Three site averaging
2	0.83 (1.8)	146 (13)	6.21	*b*	Bent-O$_e$	Static
3	3.66 (17)	104 (4)	1.04	*c*	Bent-O$_e$	Three site averaging
4	1.55 (50)	134 (8)	2.23	*c*	Bent-O$_e$	Static
5	4.09	156	3.68	*b*	Planar	Static
6	2.54	113	3.52	*b*	Planar	Three site averaging
7	1.15	144	10.32	*c*	Planar	Static
8	2.53	112	2.01	*c*	Planar	Three site averaging
9	0.00	144	16.5	*d*	Bent-O$_a$	Static
10	2.09	113	11.97	*d*	Bent-O$_a$	Three site averaging
11	3.40	169	9.23	*c*	Bent-O$_a$	Static
12	3.60	137	8.06	*c*	Bent-O$_a$	Three site averaging
13	0.60 (1.86)	150 (7)	5.90	*b*	Bent-O$_e$	Static and methyl averaging[f]
14[a]	2.29 (1)	114.8 (2)	0.04	*b*	Bent-O$_e$	Three site and methyl averaging[f]

[a] The rotamer populations for this case and their standard errors are 0.09 (1) anti to lone pair, and 0.455 (1) gauche to lone pair. [b] The Δ_{Eu} assignments were $H_{cis} > H_{trans} > Me_{trans} > Me_{cis}$. This is the correct assignment of the nmr spectrum; see text and ref 29. [c] The Δ_{Eu} assignments were $H_{cis} > H_{trans} > Me_{cis} > Me_{trans}$. [d] The Δ_{Eu} assignments were $H_{trans} > H_{cis} > Me_{cis} > Me_{trans}$. [e] All calculations employed the axially symmetric equation and methyl protons were treated as a point proton at the geometric mean. [f] The shifts of each proton in a methyl set were calculated and then averaged. [g] The entry "bent-O$_e$" refers to a puckered thietane ring in which the sulfoxide oxygen is pseudoequatorial. The atomic coordinates were those found from the X-ray structure. In like manner "bend-O$_a$" refers to an identically puckered ring in which the oxygen is pseudoaxial.

One might ask whether either the planar- or the axial-oxygen conformation gives as good a fit to the data

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(30) The locations of the protons were calculated from the known locations of the carbons by assuming r(CH) = 1.1 Å and $\angle$(HCH) = 109°.

(31) Because the number of degrees of freedom is only one, it is not possible to reject these chemically unreasonable models at higher confidence levels. We have recently obtained cmr LIS data with the help of Dr. William Jankowski (Varian Associates). These data now support the correct assignment above the 95% confidence level.

Table IX. Best Least-Squares Fits of LIS Data Using the Static Model[a]

Entry	Molecule	r (Å)[b]	θ[c]	τ[d]	% R[e]	Ref
1	*cis*-4-(*p*-Chlorophenyl)thiane 1-oxide (**8**)	2.67	101	0	2.96[f]	This work
2	*exo*-2-Thiabicyclo [2.2.1]heptane 2-oxide (**3**)	2.40	124	2	0.95	*i*
3	*endo*-2-Thiabicyclo[2.2.1] heptane 2-oxide (**6**)	1.81	143	3	0.86[f]	*i*
4	*trans*-4-*tert*-Butylcyclohexanol (**12**)	2.78	118	0	1.76[f]	5
5	*cis*-4-*tert*-Butylcyclohexanol (**9**)	3.81	125	0	2.97[f]	5
6	Borneol (**7**)	3.44 (7)[h]	122 (3)[h]	109 (6)[h]	5.02	3a
7	Borneol (**7**)	3.24	109	139	2.26	3b (cmr data)
8	Borneol (**7**)	3.40 (9)[h]	118 (2)[h]	127 (6)[h]	4.14[f]	5
9	Isoborneol (**4**)	3.71 (11)[h]	113 (2)[h]	42 (4)[h]	3.90	5
10	Cyclooctatetraene dimer epoxide (**11**)	3.14	121	9[g]	7.2	6b
11	2-Adamantanol (**10**)	3.50	132	0	2.67[f]	*j*
12	*endo*-5-Norbornen-2-ol (**5**)	2.88	132	44	3.32	3e

[a] Equation 1 is used without rotamer averaging. Unless otherwise noted all LIS are from pmr spectra. [b] The distance between metal and coordination site, Q. [c] The bond angle made by the metal coordination site bond. [d] The dihedral angle looking down the metal–coordination site, as measured from the CH, or S→: vector. [e] The R factor: $R^2 = \Sigma(\text{shift calculated} - \text{shift observed})^2/\Sigma(\text{shift observed})^2$; see ref 3e. [f] This fit is statistically better at the 97% confidence level than that obtained using the dynamic model. [g] Assumed to be in the symmetry plane perpendicular to the epoxide ring plane. [h] The standard deviations for the last significant figures. [i] R. R. Frazer and Y. Y. Wigfield, *Chem. Commun.*, 1471 (1970). [j] G. H. Wahl, Jr., and M. R. Peterson, Jr., *ibid.*, 1167 (1970).

Table X. Best Least-Squares Fits of LIS Data Using the Dynamic Model

Entry	Molecule	r (Å)[a,i]	θ[b,i]	τ[c,i]	% rotamer populations[d,i]	% R[e]	Ref
1	*cis*-4-(*p*-Chlorophenyl)thiane 1-oxide (**8**)	3.41	110	*f*	0, 50, 50 (0)	8.4	This work
2	*exo*-2-Thiabicyclo[2.2.1]heptane 2-oxide (**3**)	3.08 (6)	120 (1)	*f*	2, 54, 44 (2)	0.38	*j*
3	*endo*-2-Thiabicyclo[2.2.1]heptane 2-oxide (**6**)	2.22 (14)	126 (3)	*f*	4, 45, 51 (2)	2.57	*j*
4	*trans*-4-*tert*-Butylcyclohexanol (**12**)	3.37 (40)	133 (11)	*f*	15, 42, 42 (9)	4.78	5
5	*cis*-4-*tert*-Butylcyclohexanol (**9**)	2.51 (20)	155 (18)	*f*	2, 49, 49 (6)	6.92	5
6	Borneol (**7**)	3.56	120	*f*	2, 5, 92	4.16	3a
7	Borneol (**7**)	3.00	118	*f*	0, 8, 92	3.35	3b (cmr data)
8	Borneol (**7**)	3.05	124	*f*	0, 14, 86	6.60	5
9	Isoborneol (**4**)	3.13 (7)	127 (2)	*f*	3, 22, 75	3.55	5
10	Cyclooctatetraene dimer epoxide (**11**)	2.94 (8)	128	14[g]	17,[h] 83 (3)	4.39	6b
11	2-Adamantanol (**10**)	3.15	125	*f*	0, 50, 50	9.97	*k*
12	*endo*-5-Norbornen-2-ol (**5**)	2.80	135	*f*	0, 37, 63	3.39	3e

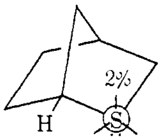
[a] Distance between metal and site of coordination. [b] The metal ···Q···X bond angle. [c] The metal ···Q/X···Y dihedral angle. All rotamer positions are assumed to be 120° apart unless specified otherwise. [d] Unless otherwise specified, the first number refers to the population of the unique site. [e] The R factor: $R^2 = \Sigma(\text{shift calculated} - \text{shift observed})^2/\Sigma(\text{shift observed})^2$; see ref 3e. [f] Not adjusted; assumed to be 180, ±60°. [g] The two rotamers are assumed to 180° apart. The angle between the plane containing the oxygen atom and its lone pairs and the oxygen–metal vector. [h] Exo isomer. [i] The standard deviations for the last significant places are given in parentheses for selected cases. [j] Footnote *i*, Table IX. [k] Footnote *j*, Table IX.

as the equatorial-oxygen conformation does. Entries 5–12 give the pertinent data for these conformations using various proton assignments and methods of calculation. In all cases the planar- and axial-oxygen models can be rejected at least at the 93% confidence level and in all but one (entry 8) at the 95% level.

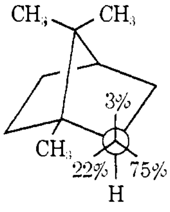
A Potpourii of Computer-Fitted Molecules. The LIS spectra of a number of molecules have been fitted during the course of this work, and it is these results which form the basis for the general conclusions given above. A detailed listing of the parameter sets used and their optimal values are given in Tables IX–XI.

Rotamer averaging was decidedly significant for asymmetric molecules and indeed gave conformers and populations consistent with what one might expect on the basis of normal steric effects.

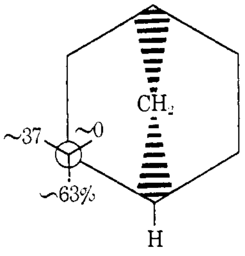
Compare, for example, *exo*-2-thiabicyclo[2.2.1]heptane 2-oxide (**3**) with isoborneol (**4**). Both have very little, if any, of the exo rotamer (2–3%) as expected. In addition, the rotamer which is syn to C_1 is more populated in the case of exo sulfoxide (**3**) (44%) than in isoborneol (22%) where the presence of a methyl group probably is sterically unfavorable. Similarly, *endo*-5-norborne-2-ol (**5**), borneol (**7**), and endo sulfoxide (**6**) all have very little, if any, of the anti rotamer (*ca.* 0%) and the introduction of a C_1–Me group appears to reduce the population of the corresponding gauche rotamer. The approximately isosteric series, *cis*-4-(*p*-chlorophenyl)thiane 1-oxide (**8**), *cis*-4-*tert*-butylcyclohexanol (**9**), and 2-adamantanol (**10**), all have the anti rotamer unpopulated, presumably because of unfavorable interactions with the syn diaxial protons. The accuracy of these populations is difficult to judge; however, it is clear that the analysis of LIS data gives a very sensitive measure of populations because of their very



3
exo sulfoxide



4
isoborneol

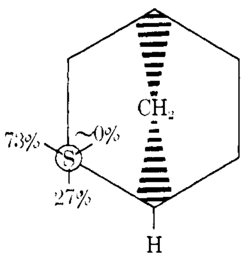


5
endo-5-norbornen-2-ol

Table XI. Best Least-Squares Fits of LIS Data Using Dynamic Model II[a]

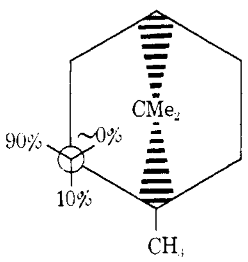
		Parameters varied[b]									
Entry	Molecule	r(Å)	θ	τ_1	τ_2	τ_3	N_1	N_2	N_3	% R	Ref
1	*cis*-4-(*p*-Chlorophenyl)thiane 1-oxide (**8**)	2.94	100	(0)	160[c]	(200)	0	(50)	(50)	2.72	This work
2	*exo*-2-Thiabicyclo[2.2.1]heptane 2-oxide (**3**)	2.93	119	(0)	143[c]	227	(0)	63	(37)	0.36	*g*
		3.07	120	(0)	120	240[d]	2	54	(44)	0.34	
		3.00	120	(0)	(120)	241	3	54	(43)	0.49	
3	*endo*-2-Thiabicyclo[2.2.1]heptane 2-oxide (**6**)	2.53	136	(0)	(120)	209	0	27	(73)	0.45	*g*
		2.36	137	(0)	119	208	(0)	26	(74)	0.25	
		2.52	136	(0)	119	210	(0)	27	(73)	0.42	
4	*trans*-4-*tert*-Butylcyclohexanol (**12**)	3.33	132	(0)	98[c]	(262)	0	(50)	(50)	3.93	5
5	*cis*-4-*tert*-Butylcyclohexanol (**9**)	3.89	124	(0)	158[c]	(202)	0	(50)	(50)	2.61	5
6	Borneol (**7**)	3.42	117	(0)	(120)	235	0	10	(90)	2.03	5
		3.30	119	(0)	120	235	0	10	(90)	2.85	
		3.05	124	(0)	120	(240)	0	14	(86)	6.60	
		3.23	110	(0)	116	223	(0)	3	(97)	2.16	3b (cmr data)
7	Isoborneol (**4**)	3.10	126	(0)	135	(240)	2	(17)	80	2.42	5
		3.24	125	(0)	(120)	237	0	15	(85)	4.93	
		1.82	134	(0)	188	209	6	(20)	74	3.89	
8	*endo*-5-Norbornen-2-ol (**5**)	2.95	113	(0)	(120)	244	2	9	(89)	2.06	3e
9	2-Adamantanol (**10**)	1.64	133	(0)	164[c]	(196)	9	(45)	(45)	2.9	*h*
10	Cyclooctatetraene dimer epoxide (**11**)	2.77	125	7[d,e]	199[d,f]	13[e]	(87)[f]			3.07	6b

[a] In this model any combination of the following variables may be independently adjusted as desired: the metal ligand bond length (r), the metal–ligand bond angle (θ), up to three independent rotamer angles (τ), and up to two of their corresponding populations (N). Only pmr data are listed. [b] Only those parameters which are not shown in parentheses were varied independently. The others were either fixed at the listed value or derived from symmetry or mass balance considerations. [c] Symmetry requires that $\tau_3 = 360 - \tau_2$ and $N_3 = N_2 = [1 - N_1]/2$. [d] The dihedral angle between the plane containing the oxygen atom and its lone pairs and the oxygen–metal vector. [e] Exo isomer. [f] Endo isomer. [g] Footnote *i*, Table IX. [h] Footnote *j*, Table IX.



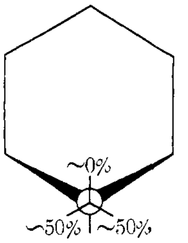
6

endo sulfoxide



7

borneol



8, 9, 10

cis-4-Ar-thiane 1-oxide
cis-4-*tert*-butylcyclohexanol
2-adamantanol

low estimated standard error (< 1 %), and because of the very high significance levels for these models.[32]

It should be pointed out that while a minimal (fixed angle) dynamic model often results in significantly better fits, it results in poorer fits for some molecules (many of which have mirror symmetry), *cf.* entries 1, 3, 4, and 11, Tables IX and X, and in other cases the fits are statistically identical, *cf.* entries 6–9 and 12.

One of the obvious deficiencies of the minimal dynamic model lies in the fixed nature of the torsional angles. It is certainly reasonable to expect torsional angles to vary somewhat from their ideal 60 or 180° values in order to minimize nonbonding interactions, although practically speaking, one may not always be able to include the additional parameters required by such a general model because of the sparcity of observed LIS. We have attempted such an approach in those cases where it was feasible. The results (Table XI) are that one is able to fit the observed shifts at least as well as the static model, with mirror symmetry molecules now the exclusive exception. However, in general, the position of the lanthanide and the rotamer populations remains essentially unchanged. It is important to note that small changes in parameters often can produce significant decreases in the R factor, with the consequence that the general rotamer model should be tested if at all possible.

The assignments which we have used to obtain the data listed in Tables IX–XI are usually those given in the literature; however, three exceptions do exist. The first is for entry 2, exo sulfoxide (**3**). We feel that exo protons H_5 and H_6 should be reversed. Using the original assignment one gets R factors of 2.23 and 2.07 with and without averaging, respectively, while the reverse assignments give R factors of 0.38 and 0.95. The original assignment can be rejected at >97 % confidence level ($R = 2.07/0.38 = 5.4$; $R_{2,1,97.5} = 4.5$).[3e,f,22]

The second involves the cyclooctatetraene dimer epoxide (**11**) reported by Willcott,[6b] in which clearly the resonances assigned to H_{15} and H_{16}, and also H_1 and H_{10}, must be reversed ($R = 1.5$, $R_{13,2,99.5} = 1.37$). Thus, the original assignment can be rejected at the 99.5 % confidence level.[33]

The third involves 2-adamantanol. It occurred to us that the assignments between cis- and trans-H_4 (H_9)

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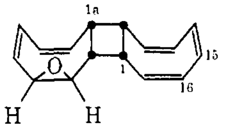
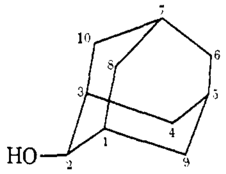
(32) The standard errors and significance levels quoted in this paper may be too liberal. If so this is a result of using a unit weighting scheme for the data. A method for assessing proper weights from the raw data has been developed and is being evaluated. We will report on this aspect of LIS structure analysis as soon as sufficient examples of its utility have been documented.

(33) M. R. Willcott, *et al.*, have communicated to us privately that they also have reversed the H_{15}–H_{16} assignments.



11

and between H$_5$ and H$_7$ may be inverted since they presumably were based on distance only considerations. To test this we obtained the best least-squares[34] fit using the three different assignments, and find that the fit with the cis, trans-H$_4$(H$_9$) assignments reversed is much better (R 2.67) than either the original assignments (R 4.24) or the one with H$_5$ and H$_7$ reversed (R 8.68). The latter two models may be rejected at about the 98 and 99.5% confidence levels.



2-adamantanol

Summary and Conclusions

The analysis of LIS data using the McConnell–Robertson equation (eq 1) appears to be justifiable on the grounds of its apparent success. This success can be rationalized for one to one (seven coordinate) shift reagent–substrate complexes in terms of the approximate axial symmetry about the substrate–lanthanide bond and the averaging which results from rotation about this bond. Neglecting to average the shifts calculated by eq 1 over appropriate molecular orientations can result in incorrectly assigned spectra, as shown for 3,3-dimethylthietane 1-oxide. In this case it was necessary to average the calculated shifts of the three conformations resulting from rotation about the EuO–SR$_2$ bond, in order to properly fit the spectrum. Such averaging gives additional conformational information. Thus, it is our feeling that a variety of computational models should be applied to any structural problems. Models which closely mimic the internal motion(s) of a molecule are in our opinion the most reliable.[35]

The use of the C$_2$ shift equation (eq 8) and the explicit averaging of methyl protons, as opposed to treating them as a centrally located point nuclei, appears to be unnecessary in the molecules studied.

Acknowledgments. We thank Mr. Thomas A. Early for his help in preparing data sets. The purchase of the diffractometer was made possible by a National Science Foundation departmental instrument grant and a National Institutes of Health biomedical grant. Partial support for this research came from National Science Foundation Grant No. GP-19254 (R. M. W).

Supplementary Material Available. Documentation, listings, and sample computer runs will appear following these pages in the microfilm edition of this volume of the journal. A compilation of the observed and calculated structure factor amplitudes will also be included. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $5.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-6046.

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(34) The static model R factors were used since they were lowest.

(35) A similar conclusion has been recently expressed by Armitage, *et al.*, ref 23g.

Organic Ions in the Gas Phase. XXVII. Long-Range Intramolecular Interactions in 4-*n*-Alkyl Trimellitic Esters

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Received December 27, 1972

Abstract: Several decomposition products in the mass spectra of 4-*n*-alkyl esters of trimellitic anhydride stem from processes involving abstraction of an alkyl hydrogen by an oxygen atom in the anhydride group. Such hydrogen migration to the formally distant functional group occurs also in 4-*n*-alkyl trimellitimidates and 1,2-dimethyl 4-*n*-alkyl trimellitates, though not in methyl *n*-alkyl iso- or terephthalates. The mass spectra of triglycerides of long-chain aliphatic acids give evidence for a similar process, and a parallel in a different context has been reported in the photoinduced hydrogen migration from the alkyl chain to the ketonic oxygen in *n*-alkyl *p*-benzoylbenzoates. Deuterium labeling, ionizing voltage dependence, and metastable scanning data indicate that loss of small olefin molecules from 4-*n*-alkyl trimellitate anhydrides is a clean two-step process, consisting simply of hydrogen abstraction followed by β carbon–carbon bond cleavage. Thus, the carbon-number distribution of the olefins lost translates directly into a probability distribution of abstraction from the various alkyl carbons. This probability varies smoothly and symmetrically about a maximum which shifts slowly with increasing chain length to positions on the chain more remote from the ester linkage. The evidently low activation energies of reactions initiated by hydrogen abstraction support molecular coiling—internal solvation—rather than flailing as the mechanism by which the formally distant radical site and alkyl hydrogen in the gaseous molecule are brought into proximity.

In a preliminary study of the mass spectra of 4-*n*-alkyl esters of trimellitic anhydride (TMA), **1**, we found that esters in which the alkyl group contains six or more carbons lose C$_n$H$_{2n-2}$, that is, the alkyl group less three hydrogen atoms, in competition with

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(1) (a) Standard Oil Company; (b) Amoco Chemicals Corporation.