Interactions of Benzocycloalkenols with Tris(dipivalomethanato)europium[1]

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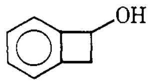
Abstract: $Eu(dpm)_3$ affects chemical shifts in the aromatic proton nuclear magnetic resonance spectra of benzocycloalkenols **1–5** and their acyclic analogs **6** and **7** so that the aromatic coupling constants may be obtained by computer analysis. The coupling constants obtained are of qualitative use only and are not valuable for correlating aliphatic ring size effects on aromatic electronic structure. Possible ways in which the shift reagent affects the coupling constants are discussed. Formation constants for the alcohol–shift reagent complex were correlated with the conformation of the aliphatic substituents. A model (A) for locating Eu(III) in the complex and predicting theoretical induced chemical shifts which agreed well with the actual induced chemical shifts was found. Increased induced shifts for carbinol deuterated alcohols were found to have a D–C–O angle dependence similar to the Ingold–Thorpe effect.

Aromatic spin–spin coupling constants obtained from nuclear magnetic resonance spectra of benzocycloalkenes have proven valuable in studying aliphatic ring size effects on aromatic electronic structure.[3] Lanthanide shift reagents are well known for their ability to simplify Lewis base substrate nmr spectra.[4] We have investigated the effect of tris(dipivalomethanato)europium, $Eu(dpm)_3$, on the aromatic pmr spectra of benzocycloalkenols **1–5** and their acyclic counterparts **6** and **7** for the following reasons: (1) $Eu(dpm)_3$ induced separation of the aromatic proton resonances which are singlets at 60 MHz would permit analysis of the aromatic coupling constants at 60 MHz; (2) correlations between aliphatic ring size and aromatic coupling constants would further promote understanding of steric effects on aromatic electronic structure;[3a,5] and (3) the systematic study would provide useful information about the scope and limitations of shift reagents in organic structure study. Our findings are reported in this paper.



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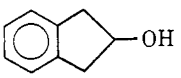

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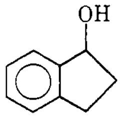

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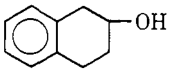

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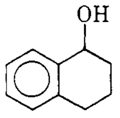

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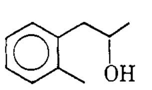

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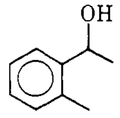

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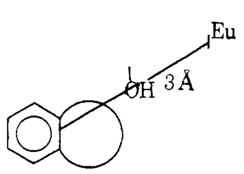
Results

The singlet resonance signal for the aromatic protons began to separate at a $Eu(dpm)_3$/substrate ratio of 0.1 with a substrate concentration of 0.6–0.8 M. At $Eu(dpm)_3$/substrate ratios of 0.3–0.7, the aromatic protons appeared as distinct patterns which were amenable to computer analysis. Proton resonance shifts showed linear dependence with the amount of $Eu(dpm)_3$ added. Lanthanide induced chemical shifts (ICS)[6] were determined for each aromatic proton using a computerized method.[7] Accurate determination of the ICS requires a correct value of the complex formation constant (K_f) as part of the input data. The criterion used for the best input value of K_f was obtaining a value greater than 0.998 for the correlation coefficient of the linear least-squares ICS calculations for each proton in the aromatic nucleus. Values obtained for K_f and ICS are given in Table I. Theoretical ICS values for each proton were calculated from the pseudocontact shift equation:[8] ICS (ppm) $= k(3\cos^2\theta - 1)/R^3$. The model shown below (A) was used to find the Eu(III) location which is necessary to determine θ and R (B).[9] Using Dreiding molecular models (1 in. = 1 Å) with the conformation of the aliphatic ring such that the hydroxyl group was in the most equatorial position possible without putting stress on the models,



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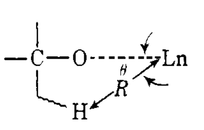

B

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[1] Presented at the 8th Midwest Regional Meeting of the American Chemical Society, Columbia, Mo., Nov 1972.

[2] Taken in part from the M.S. Thesis of P. H. P., 1972.

[3] (a) M. A. Cooper and S. L. Manatt, *J. Amer. Chem. Soc.*, **92**, 1605 (1970); (b) *ibid.*, **91**, 6325 (1969).

[4] For general surveys and reviews of nmr shift reagents, see J. R. Campbell, *Aldrichimica Acta*, **4**, 55 (1971); W. DeW. Horrocks, Jr., and J. P. Sipe, III, *J. Amer. Chem. Soc.*, **93**, 6800 (1971); J. K. M. Sanders, S. W. Hanson, and D. H. Williams, *ibid.*, **94**, 5325 (1972); M. R. Peterson, Jr., and G. H. Wahl, Jr., *J. Chem. Educ.*, **49**, 790 (1972); P. L. Corio, S. L. Smith, and J. R. Wasson, *Anal. Chem.*, **44**, 407R (1972); and R. von Ammon and R. D. Fischer, *Angew. Chem., Int. Ed. Engl.*, **11**, 675 (1972).

[5] (a) W. H. Mills and I. G. Nixon, *J. Chem. Soc.*, 2510 (1930); (b) L. D'Albis, *Chem. Mod.*, **5**, 209 (1960); (c) R. D. Rieke, *J. Org. Chem.*, **36**, 227 (1971).

[6] The induced chemical shift (ICS) equals the difference between the complex chemical shift and the substrate chemical shift in ppm.

[7] (a) I. Armitage, G. Dunsmore, L. D. Hall, and A. G. Marshall, *Can. J. Chem.*, **50**, 2119 (1972); (b) T. A. Wittstruck, *J. Amer. Chem. Soc.*, **94**, 5130 (1972).

[8] G. N. LaMar, W. DeW. Horrocks, and L. C. Allen, *J. Chem. Phys.*, **41**, 2126 (1964).

[9] See S. I. Weissman, *J. Amer. Chem. Soc.*, **93**, 4928 (1971), for comments about Eu(III) in contact and pseudocontact interactions.

Table I. Formation Constants (K_f) and Induced Chemical Shifts (ICS)

Compd	K_f[c]	Calcd ICS[a] (ppm) H-1	H-2	H-3	H-4	Obsd ICS[b] (ppm) H-1[c]	H-2[c]	H-3[c]	H-4[c]
1	490 ± 10	7.45	3.44	3.44	4.30	7.35 ± 0.17	3.44 ± 0.17	3.44 ± 0.17	3.60 ± 0.47
2	240 ± 9	4.10	2.58	2.58	4.10	4.24 ± 0.16	2.20 ± 0.09	2.20 ± 0.09	4.24 ± 0.16
3	390 ± 18	12.10	4.43	4.32	5.78	11.80 ± 0.29	4.28 ± 0.30	4.28 ± 0.30	5.67 ± 0.33
4	280 ± 15	3.73	2.00	2.00	3.73	3.91 ± 0.28	2.12 ± 0.10	2.12 ± 0.10	3.91 ± 0.28
5	110 ± 17	15.70	3.44	3.44	4.62	16.00 ± 0.29	3.48 ± 0.21	3.48 ± 0.21	4.95 ± 0.16
6	350 ± 2	10.70	2.57	2.57	3.14	10.40 ± 0.43	2.34 ± 0.10	2.34 ± 0.10	3.48 ± 0.16
7	100 ± 16	18.90	4.90	3.74	3.74	19.40 ± 0.25	4.94 ± 0.06	4.05 ± 0.05	4.05 ± 0.05

[a] Obtained from pseudocontact shift equation $\Delta\nu/\nu = 2.86 \times 10^3(3\cos^2\theta - 1)/R^3$ using model A for locating Eu(III), determining θ, and R. [b] Obtained from computerized plot of $\delta(\text{obsd}) = \alpha(\delta(\text{complex}) - \delta(\text{substrate})) + \delta(\text{substrate})$ as described in the Experimental Section. [c] Errors are reported at the 99% confidence limits (see the Experimental Section).

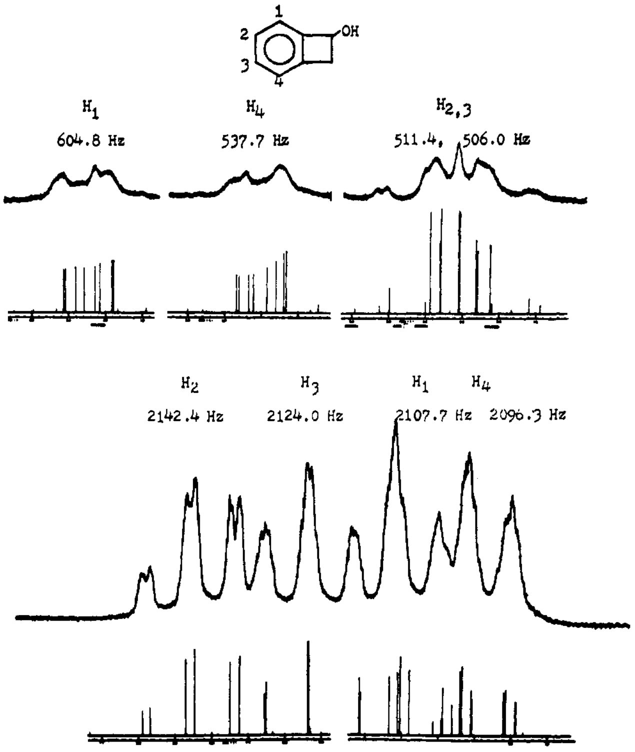

Figure 1. Observed and calculated aromatic ^{1}H magnetic resonance spectra of benzocyclobuten-1-ol (**1**) at: 60 MHz (top) and Eu(dpm)$_3$ substrate ratio of 0.41; and 300 MHz (bottom) at 15% (w/v) concentration. Sweep widths are 50 Hz.

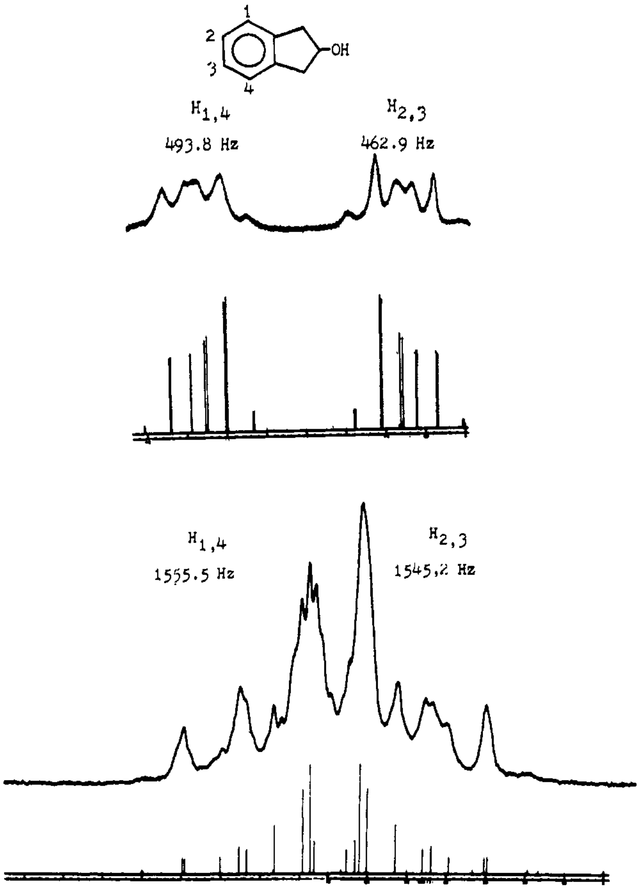

Figure 2. Observed and calculated aromatic ^{1}H magnetic resonance spectra of 2-indanol (**2**) at: 60 MHz and Eu(dpm)$_3$/substrate ratio of 0.41; and 220 MHz (bottom) at 15% (w/v) concentration. Sweep widths are 50 Hz.

a line beginning midway between the atoms common to both rings was drawn through the hydroxyl group and extended for 3 Å[10] where the Eu(III) was placed. With Eu(III) in this position, the geometric factor $(3\cos^2\theta - 1)/R^3$ was evaluated. Multiplication of this quantity by 2.86 × 10^3 [11] (empirically determined) gave the theoretical ICS values reported in Table I. Agreement between the observed and theoretical ICS values is generally good with most differences being less than 0.3 ppm.

Iterative computer analysis using LAOCN3[12] provided the coupling constants given in Table II. Proton shift assignments were made from the calculation which gave the smallest computer determined root-mean-square error. Compounds **1**, **3**, **5**, **6**, and **7** showed AMXY patterns with a shift order of $H_1 > H_4 > H_2 > H_3$ except for **7** which gave a shift order of $H_1 > H_2 > H_3 > H_4$. Compounds **2** and **4** showed AA'XX' and ABXX' patterns, respectively, with the shift orders being $H_1 = H_4 > H_2 = H_3$ and $H_1 > H_4 > H_2 = H_3$, respectively. Good agreement was obtained between these observed shifting orders and those obtained from the theoretical ICS calculations. Aromatic pmr spectra were obtained at 300 MHz for **1**[13] and 220 MHz for **2**[13] and **3**[14] so that a comparison could be

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(10) (a) M. R. Wilcott III, R. E. Lenkinski, and R. E. Davis [*J. Amer. Chem. Soc.*, **94**, 1742 (1972)] suggest a Eu-O distance of 3.0 ± 0.5 Å; (b) S. Farid, A. Ateya, and M. Maggio [*Chem. Commun.*, 1285 (1971)] suggest 2.7 ± 0.4 Å; thus our value of 3 Å is reasonable.

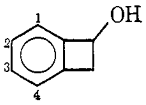
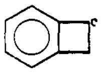
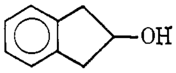
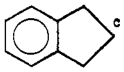
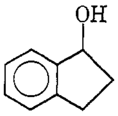
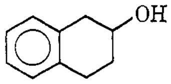
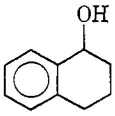
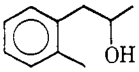
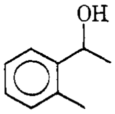
(11) The value of *k* depends on the compound being studied [D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, **1**, 103 (1965)]. The *k* values for **1**–**7** are therefore approximately the same. Farid, *et al.*,[10b] show a *k* value of approximately 10^3 for two secondary alcohols.

(12) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964).

(13) Recorded by the Varian NMR applications laboratory, Palo Alto, Calif.

(14) Recorded by the Morgan Schaffer Corp., Montreal, Quebec, Canada.

Table II. Aromatic Coupling Constants (J) for Compounds 1–7

Compd	J_{12}	J_{13}	J_{14}	J_{23}	J_{24}	J_{34}	RMS[a,b]
 **1** Eu(dpm)$_3$	7.03	1.00	−0.52	8.41	0.59	6.96	0.16
(300MHz)	7.45	0.80	1.87	7.56	0.37	7.59	0.05
 c	7.36	1.00	1.03	7.79	1.00	7.36	0.03
(100MHz)							
 **2** Eu(dpm)$_3$	7.29	1.08	0.04	7.22	1.08	7.29	0.13
(200MHz)	7.88	1.26	0.11	7.68	1.26	7.88	0.11
 c	7.59	1.17	0.48	7.20	1.17	7.59	0.04
(100MHz)							
 **3** Eu(dpm)$_3$	7.20	1.16	−0.52	7.56	1.06	7.77	0.16
 **4** Eu(dpm)$_3$	7.47	1.67	−0.09	7.64	1.67	7.47	0.20
 **5** Eu(dpm)$_3$	7.01	1.88	−0.39	7.11	1.57	7.40	0.29
 **6** Eu(dpm)$_3$	7.01	2.25	0.21	8.23	2.27	6.69	0.22
 **7** Eu(dpm)$_3$	7.60	1.14	1.34	7.88	0.84	8.90	0.29

[a] RMS means root-mean-square error. [b] Parameter set errors were 0.02–0.05. [c] Taken from ref 3a.

Table III. Coupling Constants and Equality Comparison for Benzocyclobuten-1-ol (**1**) and 2-Indanol (**2**)

	1		
	Eu(dpm)$_3$	300 MHz	Null hypothesis 99% confidence
J_{12}	7.03	7.45	Equal
J_{13}	1.00	0.80	Equal
J_{14}	−0.52	1.87	Unequal
J_{23}	8.41	7.56	Unequal
J_{24}	0.58	0.37	Equal
J_{34}	6.96	7.59	Unequal
Rms	0.16	0.05	
Std dev	0.57	0.23	

	2		
	Eu(dpm)$_3$	220 MHz	Null hypothesis 99% confidence
J_{12}	7.29	7.88	Unequal
J_{13}	1.08	1.26	Equal
J_{14}	0.04	0.11	Equal
J_{23}	7.22	7.68	Unequal
J_{24}	1.08	1.26	Equal
J_{34}	7.29	7.88	Unequal
Rms	0.13	0.11	
Std dev	0.16	0.10	

made with the coupling constants obtained from the Eu(dpm)$_3$ shifted spectra. The aromatic protons of **3** were not resolved at 220 MHz but the spectra of **1** (ABCD pattern) and **2** (AA′BB′ pattern) were resolved well enough for computer analysis. Spin decoupling of the aliphatic ring protons did not significantly improve the spectra.[15] Spectra for **1** and **2** are shown in Figures 1 and 2, respectively.

The coupling constants for **1** and **2** obtained by the two different shifting methods were tested for equality using the Null hypothesis.[16] Standard deviations for the coupling constants were taken as the square root of the sum of the squares of the standard errors provided by LAOCN3. The coupling constant comparison is shown in Table III.[17] Lack of fine structure in most spectra prevented exact computer fits, but all root-mean-square errors were less than 0.3 which was acceptable to us in view of the types of resonances obtained.

Discussion

The singlet appearance of the aromatic protons of compounds **1–7** is due to a small $\Delta\nu/J$ ratio where $\Delta\nu$ is the chemical shift difference (Hz) between the aromatic protons.[18a] An increase in the magnetic field strength from 14.1 kG (60 MHz) to 23.5 kG (100 MHz), or 70.5 kG (300 MHz), causes $\Delta\nu$ to be 1.67, 3.67, or 5.0 times greater[19] while J remains unaffected.[20] Thus $\Delta\nu/J$ can be increased and simplified spin–spin splitting patterns obtained.

Sometimes high field strengths are not sufficient for effecting $\Delta\nu/J$ ratios large enough to produce simplified spectra. Figures 1 and 2 show that the spectra of **1** at 300 MHz and **2** at 220 MHz are spread enough to allow analysis but cannot be considered simple spectra. A spectrum of **3** at 220 MHz produced only a broad absorbance which could not be analyzed. Spectral simplification by using Eu(dpm)$_3$ to effect large $\Delta\nu/J$ ratios must be viewed with some ambivalence. Isotropically induced shifts given in Table I show the shift reagent's selectively for various protons. This is due to both the angle (θ) and distance (R^{-3}) parameters which describe the isotropic shift dependence. Thus **1–7** all possess two protons (H$_1$, H$_4$ for **1–6**; H$_1$, H$_2$ for **7**) with induced shifts and $\Delta\nu/J$ ratios large enough to provide simplified spectra. Paramagnetic broadening due to the lanthanide ion prevents fine structure determination and difficulty in assigning line frequencies which in turn increases the error in the computer spectral analysis. Evidence is presented later for an effect on J by the shift reagent. Thus, simplified spectra expected on the basis of the increases in $\Delta\nu/J$ are not entirely realized due to unfavorable effects of the Eu(dpm)$_3$.

Structure–reactivity implications for the interactions of **1–7** with Eu(dpm)$_3$ can be made from the results given in Table I. The complex formation constant (K_f)[21] decreases for the α-hydroxy compounds (**1**, **3**, **5**, **7**) with increasing ring size. The α-hydroxyl group is also becoming coplanar with the aromatic ring as the ring size increases. Steric interactions between the aromatic ring and the Eu(dpm)$_3$ would account for the change observed in K_f. Thus, K_f is largest for **1** whose hydroxyl group is almost perpendicular[22] to the aromatic ring and least for **7** whose hydroxyl group is nearly coplanar with the aromatic ring.[23] Supporting evidence comes from the good agreement between observed *vs.* theoretical ICS values. Molecular models with the hydroxyl group in the most equatorial (coplanar) position possible furnished the parameters for the theoretical ICS calculations. Larger, flexible aliphatic rings allow more coplanarity between the α-hydroxy group and the aromatic ring. The conformation used to calculate the theoretical ICS for **7** is shown below.

The β-hydroxy compounds **2** and **4** show nearly equal K_f values while K_f for **6** is slightly larger; also a large difference exists between the H$_1$ induced shift for **6** as compared with either **2** or **4**. This suggests a conformation for acyclic **6** which contrasts the alicyclic conformations. The staggered conformation shown below for **6** proved satisfactory for the theoretical ICS calculation which agrees well with the observed ICS. Other conformations for **6** or **7** were unsatisfactory.

The narrow range of K_f values (100–490) and possible differences in oxygen basicity due to variable

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(15) The lower field triplet for H$_2$ of compound **1** (2142.4 Hz, Figure 1, bottom) sharpens markedly on irradiation of the carbinol carbon hydrogen. Thus long-range coupling occurs between a benzylic carbon and an aromatic meta proton. R. Freeman, N. S. Bhacca, and C. A. Reilly [*J. Chem. Phys.*, **38**, 293 (1963)] have reported a similar effect in methyl salicylate. Assumptions that benzylic protons couple more strongly with aromatic protons ortho to the benzylic proton may be incorrect; see ref 3a.

(16) W. J. Youden, "Statistical Methods for Chemists," Wiley, New York, N. Y., 1951, p 24.

(17) For a preliminary report, see T. B. Patrick and P. H. Patrick, *J. Amer. Chem. Soc.*, **94**, 6230 (1972).

(18) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969: (a) p 91; (b) p 368.

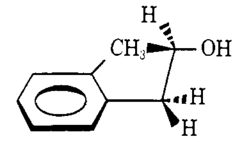
(19) L. F. Johnson, *Anal. Chem.*, **43**, 28A (1971).

(20) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Permagon Press, Elmsford, N. Y., 1965, Chapter 3.

(21) Lanthanide–substrate stoichiometry was determined to be 1:1 by the method described by J. W. ApSimon, H. Beierbeck, and A. Fruchier, *J. Amer. Chem. Soc.*, **95**, 939 (1973).

(22) (a) G. L. Handgrove, Jr., *U. S. At. Energy Comm.*, **70**, 8803 (1959); (b) G. Fraenkel, Y. Aschi, M. S. Mitchell, and M. P. Cava, *Tetrahedron*, **20**, 7179 (1964).

(23) F. H. Hon, H. Matsumura, H. Tanida, and T. T. Tidwell, *J. Org. Chem.*, **37**, 1778 (1972).



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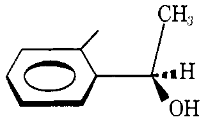

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electron distribution in the alicyclic and acyclic compounds necessitate suggestive rather than authoritative conformation conclusions.

Two sets of facts pertained in the study of the coupling constants' utility. Firstly, usual values of aromatic coupling constants are: ortho, 5–9.4 Hz; meta, 0.8–3.0; and para, 0.4–1.0.[18b] Secondly, the para coupling constant in benzocycloalkenes increases on going from large to small fused aliphatic rings.[3a] Inspection of Table II reveals that the ortho, meta, and para coupling constants obtained from the Eu(dpm)$_3$ shifted spectra fall within the expected range. The para coupling constant, however, does not increase with decreasing ring size as expected. The expected increase in the para coupling constant on going to small ring sizes is observed from the analyzed spectra of **1** and **2** recorded at 300 and 220 MHz, respectively. A statistical comparison for equity of the coupling constants obtained for **1** and **2** at 300 and 220 MHz, respectively, *vs.* coupling constants obtained from the Eu(dpm)$_3$ shifted spectra using the Null hypothesis (Table III)[17] shows that both **1** and **2** possess ortho coupling constants which are unequal and **1** obtains unequal para coupling constants. Thus a systematic error is introduced into the coupling constant value when Eu(dpm)$_3$ is present. This may be expected if J(substrate) does not equal J(complex) since an average signal is observed.

Weak interactions between the Eu(dpm)$_3$ and the aromatic nucleus may account for the coupling constant change. This is consistent with the theory of heavy atom effects on coupling constants through electron orbital motions.[24] Eu(dpm)$_3$ fixing of the aliphatic ring conformation would also account for the change. Lanthanide fixing of conformations has been reported.[25] It is, however difficult to visualize much fixing of the conformation of **1** which is a fairly rigid system.[22] Mechanisms such as chemical exchange spin decoupling,[26] lanthanide substituent effects,[27] or changes in hydrogen bonding of the alcohol to the π electrons of the aromatic system (suggested by a referee) are also possible. All of these effects should show a concentration dependence on the amount of Eu(dpm)$_3$ present. However, we were unable to detect any significant change in the coupling constants from the Eu(dpm)$_3$ shifted spectra in the Eu(dpm)$_3$/substrate ratio range of 0.3–0.7. Thus, if concentration dependence is present, it either reaches a maximum before the 0.3 ratio or changes only very slightly in the 0.3–0.7 ratio range.

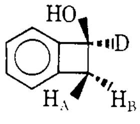
Hydrogen bonding of the alcohol to the aromatic π electrons did not affect the aromatic coupling constants of **1** at 300 MHz as evidenced from the following facts. The 300-MHz spectra of the aromatic protons of **1** were identical at both 0.83 and 1.3 M concentrations of **1** in carbon tetrachloride solution. Also, replacement of the hydroxyl proton with deuterium did not change the absorption frequencies of **1** (0.83 M in carbon tetrachloride solution). These control experiments were carried out by Mr. Lewis Cary[18] on a Varian HR-300 instrument at 35.0 ± 0.5° probe temperature.

Thus, we are unable to unequivocally determine why J(complex) does not equal J(substrate), but we can point out that a serious problem exists in the use of lanthanide shift reagents for determining aromatic coupling constants.

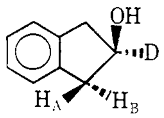
Isotope Studies

Replacement of the carbinol carbon hydrogen with deuterium produced slightly increased shifts in the protons α to the carbinol carbon atom for compounds **8**, **9**, and **10** shown in Table IV. Increased isotropic shifts in deuterated compounds have been attributed mainly to an increase in K_f resulting from either increased oxygen basicity or deuterium bonding.[28,29]

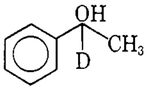
Table IV. Per Cent Shift Increase for Deuterated Alcohols



8



9



10

8		9		10
H$_A$	H$_B$	H$_A$	H$_B$	CH$_3$
0.39	1.5	1.3	2.8	2.6
(1.0)[a]		(2.0)[a]		(2.6)[a]

[a] Average.

The average per cent shift increase becomes larger in the order **10** > **9** > **8**, while the D–C–O angle increases in the order **8** > **9** > **10**. The isotope shift increase dependence on angle changes parallels the Ingold–Thorpe effect[30] in that the geminal groups influence the interaction of both the hydroxyl group and the deuterium atom with Eu(III). Thus K_f may in part be increased by Eu(III)–deuterium attraction. Selectivity of H$_B$ (1.3% increase) over H$_A$ (0.9% increase) on going from **8** to **9** supports Eu(III)–deuterium attraction. This suggestion is still tentative since problematical factors such as electron-distribution effects on oxygen basicity and possible symmetry axis changes remain.

Experimental Section

Instruments and Calculations. Spectra were recorded on Varian T-60, HR-220, and HR-300 spectrometers operating at a probe temperature of 35°. Frequency determination was made using a

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(24) M. Barfield and D. M. Grant, *Advan. Magn. Resonance*, **1**, 149 (1965).

(25) J. F. Caputo and A. R. Martin, *Tetrahedron Lett.*, 4547 (1971).

(26) J. Reuben, and J. S. Leigh, Jr., *J. Amer. Chem. Soc.*, **94**, 2789 (1972).

(27) B. L. Shapiro, M. D. Johnston, Jr., and R. L. R. Towns, *ibid.*, **94**, 4381 (1972).

(28) (a) C. C. Hinckley, W. A. Boyd, and G. V. Smith, *Tetrahedron Lett.*, 879 (1972); (b) *J. Amer. Chem. Soc.*, **93**, 6319 (1971).

(29) (a) A. M. Grotens, J. Smid, and E. deBoer, *J. Magn. Resonance*, **6**, 612 (1972); (b) A. M. Grotens, C. W. Hilbens, E. deBoer, and J. Smid, *Tetrahedron Lett.*, 2067 (1972).

(30) Discussed by G. S. Hammond in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **83**, 1368 (1961).

Monsanto 101B Frequency Counter on the T-60 instrument. Frequencies were obtained directly from the chart paper which had been precalibrated immediately prior to recording the spectra on the HR-220 and HR-300 instruments. Carbon tetrachloride solutions (0.50 ml) which were 0.6–0.8 *M* in the alcohol were used in the Eu(dpm)$_3$ experiments. Eu(dpm)$_3$ was added in 10-mg portions and the peak positions were then measured accurately. Many spectra were used to obtain a set of accurate frequencies. Aliphatic ring coupling constants for **1** and **2** were the same regardless of the instrument used. This served as an indication that instrument differences were not responsible for coupling constant variations in the coupling constant comparison (Table III).

A computerized method was used to determine the lanthanide–substrate formation constants (K_f) and the induced chemical shifts (ICS)[7] reported in Table I. The interaction between the lanthanide shift reagent (Ln) and the substrate (S) gave an Ln:S complex with 1:1 stoichiometry under our conditions as determined from the initial slopes of plots of observed shifts (δ(obsd)) *vs.* Ln/S according to a described method.[21] The equilibrium

$$\mathrm{Ln} + \mathrm{S} \overset{K_f}{\rightleftarrows} \mathrm{Ln{:}S}$$

was thus considered operational and K_f values were assigned from 1 to 1000 in increments of one in order to determine the molar concentration of Ln:S. Concentrations of Ln and S were measured accurately to ±0.001 *M*. The concentration of Ln:S was then determined from the equation: $\mathrm{Ln{:}S} = [(\mathrm{Ln} + \mathrm{S} + K_f^{-1}) \pm \mathrm{SQRT}((\mathrm{Ln} + \mathrm{S} + K_f^{-1})^2 - 4(\mathrm{Ln})(\mathrm{S}))]/2$ within the limits $0 < \mathrm{Ln{:}S/S} < \mathrm{S}$ or Ln, whichever is smaller. The nmr fast exchange limit, $\delta(\mathrm{obsd}) = \alpha(\delta(\mathrm{complex}) - \delta(\mathrm{substrate})) + \delta(\mathrm{substrate})$ where δ is the chemical shift in ppm with δ(TMS) = 0, $\alpha = \mathrm{Ln{:}S/S}$, and (δ(complex) − δ(substrate)) equals the induced chemical shift (ICS). ICS was obtained from a linear least-squares plot of δ(obsd) *vs.* α with ICS being the line slope. The best value of K_f was found when the linear least-squares plot gave a correlation coefficient greater than 0.9988. The errors reported in Table I were obtained at the 99% confidence level using the standard deviation of ICS, the number of data points used, and *t*[16] values.

Coupling constants were calculated using the LAOCN3 program.[12] Frequencies used in the iterative calculations for **1** and **2** at 220 and 300 MHz, respectively, were those obtained from the aliphatic ring spin decoupled spectra even though spin decoupling gave only minor improvements in the spectra. Frequencies used for the Eu(dpm)$_3$ shifted spectra were those obtained from the frequency counter with an average of at least four determinations. Spin decoupling did not improve these frequency determinations.

All computer calculations were done on an IBM 360/40 computer.[31]

Materials. Tris(dipivalomethanato)europium, mp 189–191.5°, was obtained from Alfa Inorganics, Inc., Beverly, Mass. Alcohols **1–7** were prepared by known procedures: benzocyclobuten-1-ol (**1**), mp 60–61° (lit.[32] mp 58.5–59.5°); 2-indanol (**2**), mp 66.5–68° (lit.[33] mp 69°); 1-indanol (**3**), mp 53–54 (lit.[33] mp 52.5°); 2-tetralol (**4**), bp 107–109° (0.5 mm) (lit.[34] bp 140° (12 mm)); 1-tetralol (**5**), bp 85–89° (0.2 mm) (lit.[35] bp 132–134° (12 mm)); 1-(2-tolyl)-2-propanol (**6**), n^{23}_{D} 1.5217 (lit.[36] n^{25}_{D} 1.5226); 1-(2-tolyl)-1-ethanol (**7**), bp 69–71° (0.5 mm) (lit.[37] bp 107–108° (20 mm)). Deuterated alcohols **8–10** were prepared by reduction of the corresponding ketone[38] with LiAlD$_4$ (Alfa Inorganics). Ir and nmr data were consistent with the structure assignments. Aldrich Spectrograde carbon tetrachloride was used in all cases. Alcohols **1–10** were distilled or sublimed directly before use. Freshly sublimed Eu(dpm)$_3$ was used in all cases.

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(31) We thank Dr. Thomas D. Bouman of this department for his guidance in computer use and programming.

(32) H. H. Wasserman and H. Solodar, *J. Amer. Chem. Soc.*, **87**, 4002 (1965).

(33) W. F. Whitmore and A. I. Gebhart, *ibid.*, **64**, 912 (1942).

(34) W. Huckel, W. Egeter, and F. Mossner, *Justus Liebigs Ann. Chem.*, **645**, 162 (1961).

(35) G. Baddeley, J. W. Rasburn, and R. Rose, *J. Chem. Soc.*, 3168 (1958).

(36) M. S. Newman, B. Magerlein, and W. Wheatley, *J. Amer. Chem. Soc.*, **68**, 2112 (1946).

(37) F. Eisenloher and L. Schulz, *Ber.*, **57**, 1808 (1924).

(38) We thank Dr. R. J. Spangler for a generous gift of benzocyclobutenone; see R. J. Spangler and J. H. Kim, *Tetrahedron Lett.*, 1249 (1972).