Tetrahedron. Vol. 31, pp. 2581 to 2586. Pergamon Press 1975. Printed in Great Britain

ADDITIVITY OF THE LANTHANIDE INDUCED CHEMICAL SHIFTS IN RIGID COMPOUNDS WITH TWO IDENTICAL FUNCTIONAL GROUPS

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(*Received in UK* 22 *April* 1975; *Accepted for publication* 8 *May* 1975)

Abstract—The NMR spectra of anemonin, tetrahydroanemonin and *cis*-bicyclo[3.3.0]octane-3,7-dione, rigid compounds with two identical functional groups, in the presence of Eu(FOD)$_3$ are studied. The additivity of the lanthanide induced chemical shifts due to "coordination" of europium atoms at both functions is shown, while the *trans* configuration of the lactone rings of anemonin and the *cis* ring fusion in bicyclo[3.3.0]octane-3,7-dione is confirmed.

INTRODUCTION

The development of lanthanide NMR shift reagents has provided a new approach to the determination of configurations in geometrical isomers containing a heteroatom with a lone electron pair. Since lanthanide induced chemical shifts (LICS) of a proton can be related to its distance r_i to the lanthanide atom and the coordination angle φ_i (according to the equation of McConnell and Robertson, $\Delta\delta_i = K(3\cos^2\varphi_i - 1)/r_i^3$), geometrical isomers show characteristic differences in their NMR spectra upon addition of a shift reagent.[1]

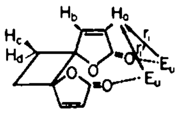
This technique has mainly been applied to monofunctional compounds although some examples have been reported of the use of shift reagents on bifunctional compounds. In such cases doubt appears on the site or sites of coordination. Thus, in some compounds with identical bifunctionality, such as methyl esters of fumaric and maleic acids or mesaconic and citraconic acids,[2] no correlations could be found between the LICS and the geometric factor $(3\cos^2\varphi - 1)/r^3$, apparently because dinuclear complexes were not formed. Nevertheless for bifunctional steroids successful correlations could be made when the additivity of the LICS due to the coordination of the lanthanide atom at the two functional groups was considered.[3] Recently, this additivity has also been observed by Recca and Finocchiaro[4] in some bifunctional amides. These authors point out that although they are considering each carbonyl group complexed with the lanthanide atom in a sort of 1:2 complex, what is really detected is a time-averaged geometry of the complexed molecule in which the lanthanide atoms coordinate with both carbonyl groups. Probably the additivity of the LICS can only be rightly applied when the complexed molecule has a rigid skeleton, since then no conformational problems arise.

In this paper we wish to report our findings on the additivity of LICS in the NMR spectra of rigid molecules with two identical functional groups, in which case there is moreover no need to consider the relative ability of complexation of both groups,[cf3] using europium 1,1,1,2,2,3,3 - heptafluoro - 7,7 - dimethyl - 4,6 - octanedionate, Eu(FOD)$_3$, as NMR shift reagent. These rigid molecules are anemonin, tetrahydroanemonin and *cis*-bicyclo[3.3.0]octane-3,7-dione, compounds that were easily available in our laboratory.

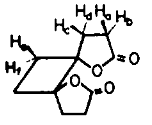
Anemonin (*trans* - 1,7 - dioxadispiro[4.0.4.2]dodeca - 3,9 - dien - 2,8 - dione), **1**, is the dimer of protoanemonin, a compound that is found in ranunculaceae as a glucoside.[5] Its *trans* configuration of the lactone rings was shown by Moriarty *et al.* by X-ray diffraction[6] and by analysis of the cyclobutane ring protons on its 100 MHz NMR spectrum using a LAOCOON II computer program.[7] The *cis* configuration is given in formula **1′**.

Tetrahydroanemonin (*trans* - 1,7 - dioxadispiro [4.0.4.2]dodecane - 2,8 - dione), **2**, is a derivative of anemonin. The *cis* configuration is given in formula **2′**.

cis - Bicyclo[3.3.0]octane - 3,7 - dione, **3**, is the product of hydrolysis and decarboxylation of tetraethyl 3,7 - dioxobicyclo[3.3.0]octane - 2,4,6,8 - tetracarboxylate[8] in which a *cis* configuration for the ring fusion was previously determined.[9] The *trans* configuration is given in formula **3′**.



1



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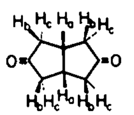

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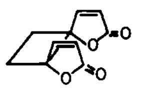
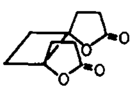
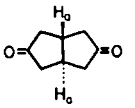


1′



2′



3′

EXPERIMENTAL

M.ps were obtained with a Kofler hot-stage and are uncorrected. NMR spectra were obtained on a Perkin-Elmer R-12A spectrometer. Chemical shifts are given in ppm relative to TMS (δ scale).

Protoanemonin was obtained following the method described by Shaw[10] in which β-acetylacrylic acid is dehydrated with acetic anhydride. Spontaneous dimerization of protoanemonin in acetone yields anemonin, m.p. 150–2° (acetone).

Catalytic hydrogenation of anemonin gave tetrahydroanemonin, m.p. 155° (water).

cis - Bicyclo[3.3.0]octane - 3,7 - dione was obtained following published procedures[8] by hydrolysis and decarboxylation of tetraethyl 3,7 - dioxobicyclo[3.3.0]octane - 2,4,6,8 - tetracarboxylate, m.p. 82–4° (hexane).

4,4-Dimethylbutyrolactone was obtained from levulinic acid and two equivalents of methylmagnesium iodide, b.p. 105–15°/15 torr.

1-Oxaspiro[4.4]nonan-2-one was a by-product in the reaction of

3-(2-hydroxycyclopentyl)propionic acid with polyphosphoric acid, in which the major product was bicyclo[3.3.0]oct-1(5)-en-2-one,[11] and both products were separated by GLC on a Perkin-Elmer F-21 preparative gas chromatograph, using a 1 m × 8 mm 30% EGS on Chromosorb 60/80 column at 170°.

Framework Molecular Models (Prentice-Hall Inc.) were used for measuring distances between europium and protons.

Europium 1,1,1,2,2,3,3 - heptafluoro - 7,7 - dimethyl - 4,6 - octanedionate, Eu(FOD)$_3$, was purchased from Ventron Alfa Products, Beverly, Mass., U.S.A.

RESULTS AND DISCUSSION

The LICS on a particular proton in bifunctional compounds must be due to the coordination of both functional groups with europium atoms and therefore their magnitude be proportional to a geometric factor including the distances to both europium atoms. If both functional groups are identical there should be no problems on group competition and it can be assumed that they are in average equally complexed. On these grounds, the LICS ($\Delta\delta$) on each proton should correlate with $1/r_i^3 + 1/r_i'^3$, (**R**), if the angular dependence is not considered or to $(3\cos^2\varphi_i - 1)/r_i^3 + (3\cos^2\varphi_i' - 1)/r_i'^3$, (**A**), if it is considered. In this paper r_i is the distance in pm between a particular proton and the nearest lanthanide atom while r_i' is the distance to the farthest (see e.g. formula 1). We assumed that the coordination distance of the Eu atom to the oxygen of the carbonyl group is 300 pm[12] and that it remains in the axis of the C=O bond. The measured distance Eu–H$_i$, Eu′–H$_i$ and the calculated values of **R** for 1, 1′, 2, 2′, 3 and 3′ are given in Tables 1, 2, 3, 4, 5 and 6 respectively. Tables 1 and 2 also include the values of φ, φ' and **A** for 1 and 1′.

Table 1. Europium-proton distances (pm), coordination angles (degrees) and geometric factor values **R**(× 10^9) and **A**(× 10^9) for the *trans* configuration of anemonin (1).

	r	r′	R	φ	φ′	A
Eu-H$_a$	580		6.5	24		9.2
Eu′-H$_a$		900			34	
Eu-H$_b$	800		4.1	10		5.7
Eu′-H$_b$		770			30	
Eu-H$_c$	880		2.5	16		4.3
Eu′-H$_c$		1000			17	
Eu-H$_d$	810		3.0	24		5.1
Eu′-H$_d$		950			8	

Table 2. Europium-proton distances (pm), coordination angles (degrees) and geometric factor values **R**(× 10^9) and **A**(× 10^9) for the *cis* configuration of anemonin (1′)

	r	r′	R	φ	φ′	A
Eu-H$_a$	580		6.3	24		8.6
Eu′-H$_a$		940			40	
Eu-H$_b$	800		3.1	10		2.4
Eu′-H$_b$		1000			30	
Eu-H$_c$	880		2.5	16		4.3
Eu′-H$_c$		1000			20	
Eu-H$_d$	810		3.0	24		5.1
Eu′-H$_d$		950			6	

Table 3. Europoum-proton distances (pm) and geometric factor values **R**(× 10^9) for the *trans* configuration of tetrahydroanemonin (2)

	r	r′	R		r	r′	R
Eu-H$_a$	580		6.9	Eu-H$_d$	780		3.5
Eu′-H$_a$		820		Eu′-H$_d$		900	
Eu-H$_b$	580		6.3	Eu-H$_e$	880		2.6
Eu′-H$_b$		940		Eu′-H$_e$		970	
Eu-H$_c$	780		4.7	Eu-H$_f$	800		2.9
Eu′-H$_c$		730		Eu′-H$_f$		1020	

Table 4. Europium-proton distances (pm) and geometric factor values **R**(× 10^9) for the *cis* configuration of tetrahydroanemonin (2′)

	r	r′	R		r	r′	R
Eu-H$_a$	580		6.4	Eu-H$_d$	780		3.1
Eu′-H$_a$		920		Eu′-H$_d$		1010	
Eu-H$_b$	580		6.0	Eu-H$_e$	900		2.3
Eu′-H$_b$		1060		Eu′-H$_e$		1020	
Eu-H$_c$	780		3.6	Eu-H$_f$	800		3.0
Eu′-H$_c$		880		Eu′-H$_f$		970	

Table 5. Europium-proton distances (pm) and geometric factor values **R**(× 10^9) for the *cis* ring fusion of bicyclo[3.3.0] octane-3,7-dione (3)

	r	r′	R
Eu-H$_a$	800		3.9
Eu′-H$_a$		800	
Eu-H$_b$	580		6.5
Eu′-H$_b$		900	
Eu-H$_c$	580		7.2
Eu′-H$_c$		800	

Table 6. Europium-proton distances (pm) and geometric factor values **R**(× 10^9) for the *trans* ring fusion of bicyclo[3.3.0]octane-3,7-dione (3′)

	r	r′	R
Eu-H$_a$	710		5.6
Eu′-H$_a$		710	
Eu-H$_b$	580		6.5
Eu′-H$_b$		890	
Eu-H$_c$	580		6.5
Eu′-H$_c$		890	

Conventional NMR spectra of anemonin (**1**), *tetrahydroanemonin* (**2**) *and* cis-*bicyclo*[3.3.0]*octane*-3,7-*dione* (**3**). The 60 MHz NMR spectrum of **1** in deteriochloroform shows a band, with a slight insinuation of multiplet, centered at δ 2·48, corresponding to the AA′BB′ system of the four cyclobutane ring protons. The spectrum also contains an AB system (practically two doublets) from the olefinic protons, part A at δ 6·10 and part B at δ 7·72, $J_{AB} = 6$ Hz. From this spectrum nothing can be inferred about the configuration of **1**. (Fig. 1).

In contrast, the 100 MHz NMR spectrum of **1** published by Moriarty shows an excellent pattern of the AA′BB′ system with 23 lines. A LAOCCON II computer program analysis suggested the presence of a two-fold symmetry

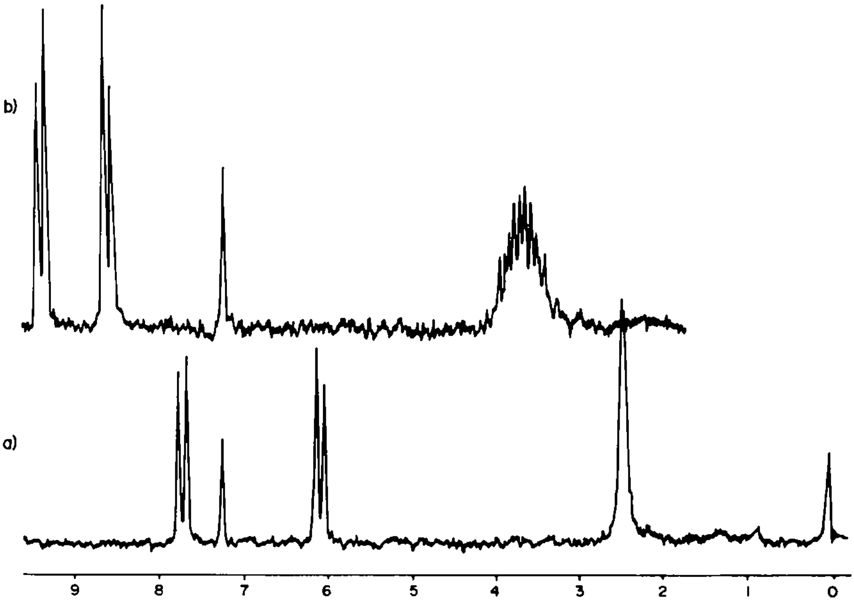


Fig. 1. (a) 60 MHz NMR spectrum of anemonin (CDCl$_3$); (b) 60 MHz NMR spectrum of anemonin with Eu(FOD)$_3$, MR = 0·6 (CDCl$_3$).

axis and consequently a *trans* configuration for **1** could be assigned.

The 60 MHz NMR spectrum of **2** is more complex. Adjacent to the absorption of the AA'BB' system of the cyclobutane ring protons appears the ABCD system of the non-equivalent protons of the lactone rings. The spectrum cannot be interpreted in first degree of approximation (Fig. 2).

The 60 MHz NMR spectrum of **3** is not directly interpretable while the 100 MHz NMR spedtrum shows a complex absorption at δ 3·04 corresponding to the methine protons and singlet absorptions at δ 2·700, 2·620, 2·500, 2·420, 2·220, 2·168, 2·032 and 1·980 with intensity ratios reminding the AB part of an ABX system (δ_A 2·120, δ_B 2·540, J_{AB} = 19 Hz, J_{AX} = 5·2 Hz and J_{BX} = 8·0 Hz) due to the methylene protons. (Fig 3).

To our knowledge no NMR spectra of **2** and **3** have yet been reported.

Spectra of anemonin with added Eu(FOD)$_3$. The addition of Eu(FOD)$_3$ to a solution of **1** in deuteriochloroform changes dramatically its NMR spectrum. A 0·11 mM solution of **1** *vs* a 0·067 mM concentration of Eu(FOD)$_3$, which represents a 0·6 molar ratio (MR) of shift reagent *vs* substrate, gives the spectrum reported in Fig. 1, showing a multiplet for the cyclobutane ring protons centered at δ 3·75 (14 lines) and an AB system for the olefinic protons (part A at δ 8·75, part B at δ 9·50, J_{AB} = 6·0 Hz).

Successive additions of Eu(FOD)$_3$, even at MR above 1·0 shift progressively the bands showing that both carbonyl groups of the lactone rings are "coordinated" by the lanthanide shift reagent. Table 7 reports the observed LICS on each particular proton for different MR. (The δ values of these protons can be estimated with good approximation directly from the spectra with Eu(FOD)$_3$).

It can easily be seen that the LICS are dependent on the

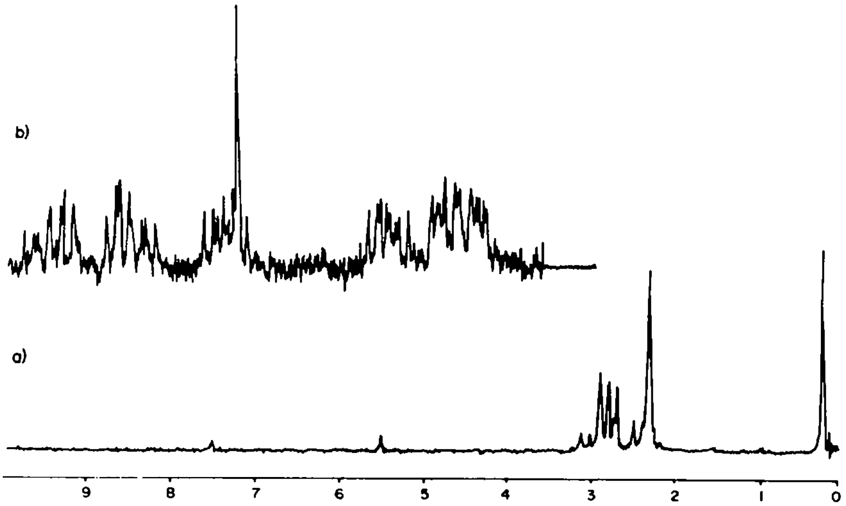


Fig. 2. (a) 60 MHz NMR spectrum of tetrahydroanemonin (CDCl$_3$); (b) 60 MHz NMR spectrum of tetrahydroanemonin with Eu(FOD)$_3$, MR = 1·6 (CDCl$_3$).

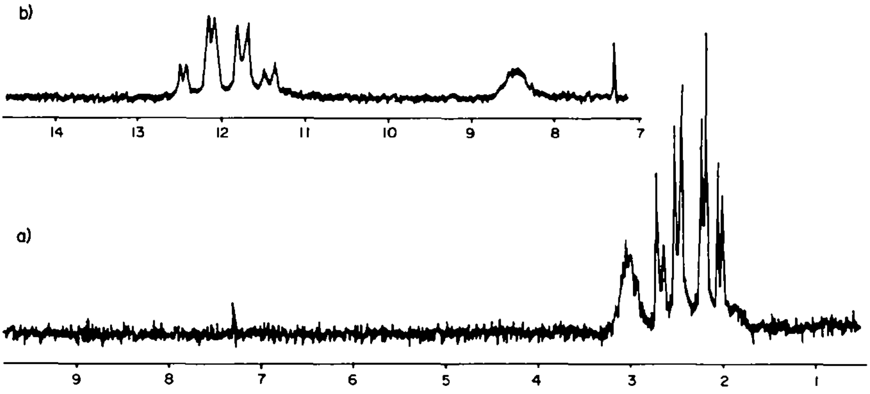


Fig. 3. (a) 100 MHz MHz NMR spectrum of bicyclo 3.3.0 octane-3,7-dione ($CDCl_3$); (b) 60 MHz NMR spectrum of bicyclo[3.3.0]octane-3,7-dione with $Eu(FOD)_3$, MR = 185 ($CDCl_3$).

Table 7. NMR chemical shifts and LICS of the protons of anemonin at different MR of $Eu(FOD)_3$

MR	δ_{H_a}	$\Delta\delta_{H_a}$	δ_{H_b}	$\Delta\delta_{H_b}$	δ_{H_c}	$\Delta\delta_{H_c}$	δ_{H_d}	$\Delta\delta_{H_d}$
0	6.10	-	7.72	-	2.46	-	2.50	-
0.6	8.70	2.60	9.50	1.78	3.55	1.09	3.90	1.40
1.2	9.75	3.65	10.20	2.48	4.05	1.59	4.44	1.94
1.8	10.20	4.10	10.50	2.78	4.27	1.81	4.65	2.15

distance between the protons and the europium atom but no straight line emerges when $\Delta\delta$ is plotted *vs* $1/r_i^3$. Nevertheless when the values of LICS are plotted *vs* **R**, straight lines passing through the coordinates origin can be drawn for structure **1** regardless the MR considered. On the other hand, no straight lines can be drawn for structure **1'**: in fact, one point—the one corresponding to H_b—falls out of the best regression line. (Fig. 4 gives one set of these plots for MR = 1·2).

Even more satisfactory results emerge when the angular factor (i.e. **A**) is taken into account (Fig. 5). Again the point corresponding to H_b falls very far away of the best straight line drawn for **1'**.

These results clearly show: (i) that the observed LICS arise from the effects of the average coordination of the two carbonyl groups present in the molecule by the lanthanide atoms; (ii) anemonin has a *trans* configuration in their lactone rings.

Spectra of tetrahydroanemonin with added $Eu(FOD)_3$. The addition of $Eu(FOD)_3$ in a MR of 1·0 to a solution of tetrahydroanemonin in deuteriochloroform changes also tremendously the spectrum of this compound. In a MR of 1·6 the change is still more appreciable (Fig. 2). Table 8 reports the LICS observed on each particular proton. Six groups of bands are easily identifiable and on grounds of symmetry and their chemical shifts they can be assigned as follows:

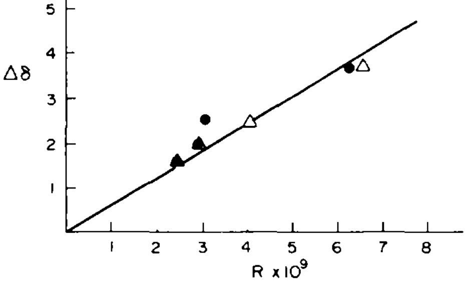


Fig. 4. The geometric factor values $\mathbf{R}(1/r_i^3 + 1/r_i'^3)$ corresponding to the *cis* (●) and *trans* (△) configuration of anemonin as a function of the LICS at MR 1·2.

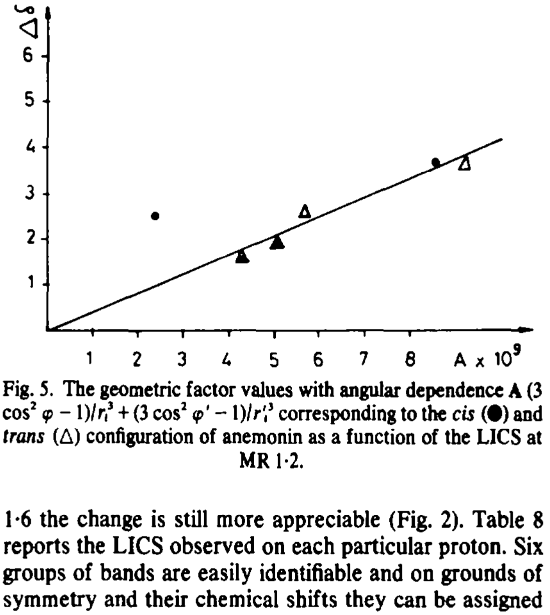


Fig. 5. The geometric factor values with angular dependence **A** $(3\cos^2\varphi - 1)/r_i^3 + (3\cos^2\varphi' - 1)/r_i'^3$ corresponding to the *cis* (●) and *trans* (△) configuration of anemonin as a function of the LICS at MR 1·2.

Bands at δ 9·55 (2 H) and 8·58 (2 H) must correspond to the α-methylene of the lactone rings (protons H_a and H_b respectively). Bands at δ 7·44 (2 H) and 5·52 (2 H) must correspond to the β-methylene of the lactone rings, but interestingly one proton is much more down-field shifted than the other (the bands at δ 7·44 are temptatively assigned to proton H_c since as molecular models show this proton is expected to be much more affected by the europium atoms "coordinated at both carbonyl groups". From these bands the following coupling constants are found: $J_{ab} = 18$ Hz, $J_{ac} = J_{bd} = 9{\cdot}3$ Hz, $J_{ad} = J_{bc} = 6{\cdot}7$ Hz and $J_{cd} = 13{\cdot}3$ Hz. The value of J_{ab} may seem too high but it is known[13] that geminal coupling constants increase with the presence of electronegative groups.

Bands at δ 4·50 (2 H) and 4·85 (2 H) correspond to the complex AA'BB' system of the cyclobutane protons.

Therefore, the addition of the $Eu(FOD)_3$ makes possible an analysis by inspection of the ABCD system of the lactone ring protons, but still does not make possible the elucidation of the configuration of the lactone rings. To this end, the experimental spectral data from tetrahydroanemonin were submitted to a similar treatment to that described for anemonin. In this case it is impossible to evaluate from the spectrum of tetrahydroanemonin the δ values of the protons H_a, H_b, H_c and H_d

Table 8. NMR chemical shifts and LICS of the protons of tetrahydroanemonin at different MR of Eu(FOD)$_3$. Here the Δδ values refer to the differences in chemical shifts observed at MR 1·6 with respect to MR 1·0

MR	δH_a	$\Delta\delta H_a$	δH_b	$\Delta\delta H_b$	δH_c	$\Delta\delta H_c$	δH_d	$\Delta\delta H_d$	δH_e	$\Delta\delta H_e$	δH_f	$\Delta\delta H_f$
0	?	--	?	-	?	-	?	-	2.08	-	2.08	--
1.0	7.36	-	6.68	-	5.95	-	4.45	-	3.70	-	4.00	-
1.6	9.55	2.19	8.58	1.90	7.44	1.49	5.52	1.07	4.50	0.80	4.85	0.85

due to the complexity of the ABCD system and therefore the measurements of LICS from the initial values cannot be done. Nevertheless it is possible to measure the difference in chemical shifts observed at MR 1·6 with respect to MR 1·0, and plot these values *vs* the geometric factor **R**. Again a straight line is found for structure **2** but a dispersion of points arises for structure **2'** (Fig. 6). Consequently the relationship $\Delta\delta = K(1/r_i^3 + 1/r_i'^3)$, in which K is the slope of the straight line for a given MR, can be used to evaluate the initial values of the chemical shifts of the protons H_a, H_b, H_c and H_d since those of H_e and H_f are previously known. From a calculation of this type the following approximate values were obtained: $H_a = 2{\cdot}8$, $H_b = 2{\cdot}6$, $H_c = 2{\cdot}9$ and $H_d = 2{\cdot}2$.

No attempt to include the angular factor dependence is made since good results are obtained using only the distance factor **R**.

To confirm the hypothesis that the H_c proton of **2** is much more down-field shifted than H_d due to the coordination of the shift reagent at both carbonyl groups, the spectrum of 4,4-dimethylbutyrolactone (a molecule that can be visualized as a "moiety" of **2**) was studied. The conventional 60 MHz NMR spectrum in deuteriochloroform shows a singlet at δ 1·45 (6 H) and a relatively simple AA'BB' system of the two methylene groups centered at δ2·35 (Fig. 7). The addition of Eu(FOD)$_3$ simplifies the spectrum giving a perfect A_2X_2 system for the two methylene group, i.e. the protons on each

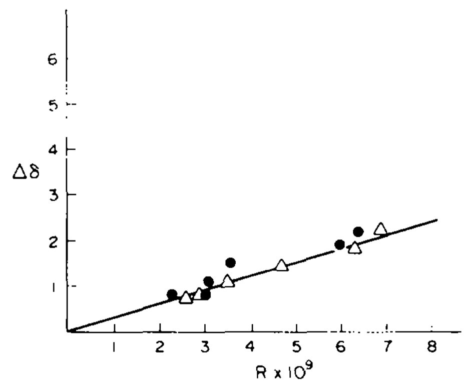


Fig. 6. The geometric factor values **R** $(1/r_i^3 + 1/r_i'^3)$ corresponding to the *cis* (●) and *trans* (△) configuration of tetrahydroanemonin as a function of the relative LICS from MR 1·0 to MR 1·6.

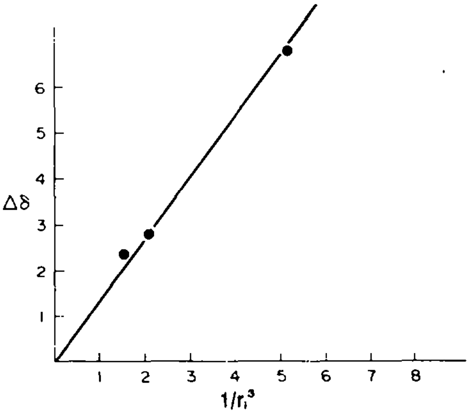


Fig. 8. The geometric factor values $1/r_i^3$ of 4,4-dimethylbutyrolactone as a function of the LICS at MR 0·3.

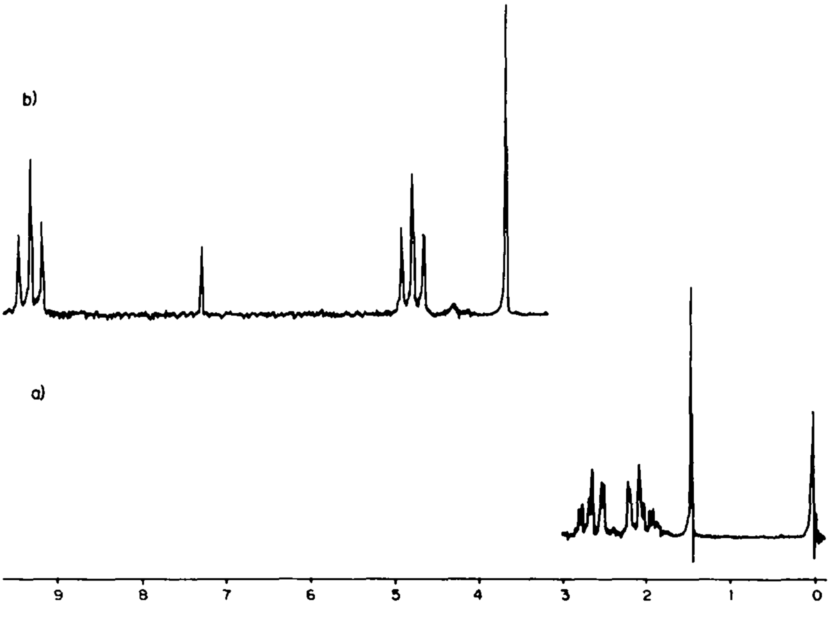


Fig. 7. (a) 60 MHz NMR spectrum of 4,4-dimethylbutyrolactone (CDCl$_3$); (b) 60 MHz NMR spectrum of 4,4-dimethylbutyrolactone with Eu(FOD)$_3$, MR 0·3.

methylene are equally shifted; a plot of $\Delta\delta_{H_i}$ *vs* $1/r_i^3$ gives a straight line starting at the coordinates origin (see Table 9 and Figs. 7 and 8).

Analogously the 60 MHz NMR spectrum of 1-oxaspiro[4.4]nonan-2-one in deuteriochloroform shows a relatively simple AA'BB' system centered at δ 2·38 for the methylene protons of the lactone ring and a broad band at δ 1·4–2·0 corresponding to the other methylene protons. The addition of Eu(FOD)$_3$ in a MR = 0·21 transforms the AA'BB' system in an A_2X_2 pattern as in the later case.

Table 9. Europium-proton distances (pm), LICS at MR 0·3 (ppm) and geometric factor values $1/r_i^3(\times 10^9)$ for 4,4-dimethylbutyrolactone

	r	$\Delta\delta$	$1/r_i^3$
Eu-H_a	580	6.83	5.1
Eu-H_b	780	2.83	2.1
Eu-H_c	850	2.29	1.6

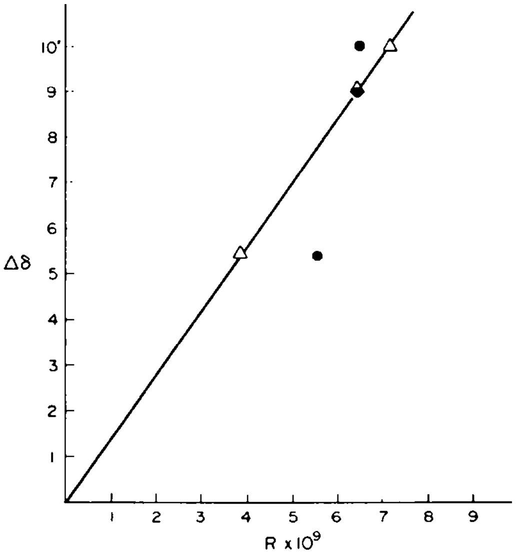


Fig. 9. The geometric factor values **R** ($1/r_i^3 + 1/r_i'^3$) corresponding to the *cis* (Δ) and *trans* (●) configuration of bicyclo[3.3.0]octane-3,7-dione as a function of the LICS at MR 1·85.

Table 10. NMR chemical shifts and LICS of the protons of *cis*-bicyclo[3.3.0]octane-3,7-dione at different MR of Eu(FOD)$_3$

MR	δ_{H_a}	$\Delta\delta_{H_a}$	δ_{H_b}	$\Delta\delta_{H_b}$	δ_{H_c}	$\Delta\delta_{H_c}$
0	3.04	-	2.54	-	2.12	-
0.4	4.44	1.40	4.65	2.11	4.65	2.53
0.8	5.95	2.91	7.45	4.91	7.58	5.46
1.18	7.18	4.14	9.31	6.77	9.97	7.85
1.85	8.50	5.46	11.64	9.10	12.24	10.12

60 MHz NMR spectra of cis-*bicyclo*[3.3.0]*octane*-3,7-*dione with added* Eu(FOD)$_3$. Table 10 reports the observed LICS on each particular proton of *cis*-bicyclo[3.3.0]octane-3,7-dione at different MR. In Fig. 3 the spectrum at MR 1·85 is shown.

Plots of the *R* values *vs* the observed LICS at different MR give once more straight lines for the established *cis* configuration (structure 3) and no correlation for the *trans* ring fusion (structure 3') (Fig. 9).

These results clearly demonstrate the validity of the additivity of the LICS when two identical functional groups are present in a rigid molecule and in the particular cases studied, the *trans* configuration of anemonin and the *cis* ring fusion of bicyclo[3.3.0]octane-3,7-dione have been confirmed.

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