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Note

N.m.r. (^{1}H and ^{13}C) studies of some *cis*- and *trans*-fused 4,6-*O*-benzylidene-hexopyranoside derivatives

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^{13}C-N.m.r. spectroscopy is now used widely in structural studies of carbohydrates[1–3]. We now report on the assignment of the ^{13}C-n.m.r. spectra of a series of *cis*- and *trans*-fused methyl 4,6-*O*-benzylidene-D-hexopyranosides: *cis*-fused, methyl 4,6-*O*-benzylidene-3-*O*-methyl-β-D-idopyranoside[4] (**12**); *trans*-fused, the 2-*O*-methyl (**1**), 3-*O*-methyl (**2**), 2-*O*-methyl-3-*O*-*p*-tolylsulfonyl (**3**), and 3-*O*-methyl-2-*O*-*p*-tolylsulfonyl[5] (**4**) derivatives of methyl 4,6-*O*-benzylidene-α-D-galactopyranoside[5], the 2-*O*- (**10**) and 3-*O*-methyl[6] (**11**) derivatives of methyl 4,6-*O*-benzylidene-α-D-altropyranoside[6] (**9**), and the 2-*O*-*p*-tolylsulfonyl[7] (**7**), 3-*O*-methyl (**6**), and 3-*O*-methyl-2-*O*-*p*-tolylsulfonyl (**8**) derivatives of methyl 4,6-*O*-benzylidene-α-D-allopyranoside[7] (**5**). N.m.r. line-shifts (^{1}H) induced by Eu(fod)$_3$ were used for some assignments.

^{13}C-N.m.r. data for these glycosides are given in Table I; those for **5** and **9** are taken from previous work[1]. Selective ^{1}H-spin decoupling and off-resonance experiments were used for some compounds. For example, the ^{13}C-n.m.r. spectrum of **5** contained four signals at lowest field due to the six aromatic carbons [137.5 (quaternary carbon), 129.4 (*p*-C), 128.5 and 126.5 p.p.m. (*o*- and *m*-C)]. Selective irradiation of H-7 confirmed that the signal at 102.0 p.p.m. was due to C-7. The signal at 100.7 p.p.m. was assigned to C-1 following selective irradiation of H-1. Likewise, the signals at 68.2, 69.3, 78.4, and 57.5 p.p.m. were assigned to C-2,3,4,5, respectively. The off-resonance spectrum showed that the signal at 56.5 p.p.m. was due to the MeO carbon, and the signal at 69.6 p.p.m. was assigned to C-6.

Comparison of the ^{13}C-n.m.r. data for the α-*allo* compounds **5** and **6** showed that 3-*O*-methylation caused a downfield shift (9.3 p.p.m.) of the resonance for the α-carbon (C-3), a slight upfield shift (0.2 p.p.m.) of the signal for the β-carbon (C-2) having an equatorial hydroxyl group, as expected, and a downfield displacement (1.3 p.p.m.) of the resonance for C-4.

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TABLE I

^{13}C-N.M.R. CHEMICAL SHIFT DATA[a] FOR METHYL 4,6-*O*-BENZYLIDENE-D-HEXOPYRANOSIDES

Compound	*Substituents*		*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*PhCH*	*CH_3O-1*	*Methyl ether*
	2	*3*									
α-galacto series											
1	MeO	HO	98.2	78.4	68.6	76.0	62.4	69.3	101.3	55.6	59.2
2	HO	MeO	100.2	68.0	78.2	72.7	62.9	69.6	101.2	55.7	57.6
3	MeO	TsO	98.6	75.2	78.2	75.1	62.1	69.0	100.7	55.6	59.5
4	TsO	MeO	98.5	76.9	75.0	74.0	62.5	69.1	101.0	55.8	58.5
α-allo series											
5	HO	HO	100.7	68.2	69.3	78.4	57.3	69.6	102.0	56.5	—
6	HO	MeO	100.1	68.0	78.6	79.7	57.5	69.4	102.1	56.5	57.5
7	TsO	HO	98.8	74.4	68.3	78.2	57.6	68.8	101.9	56.3	—
8	TsO	MeO	98.0	74.8	77.1	79.1	57.7	69.0	102.0	56.3	61.4
α-altro series											
9	HO	HO	101.6	69.6	68.8	76.0	57.8	68.8	101.8	55.0	—
10	MeO	HO	99.7	79.1	66.4	76.5	58.2	69.1	102.2	55.6	58.4
11	HO	MeO	101.9	69.8	78.1	77.3	58.6	69.3	102.4	55.8	58.5
β-ido series											
12	HO	MeO	100.2	66.6	78.5	73.2	66.6	69.6	101.5	55.6	58.3

[a]P.p.m. downfield from Me_4Si.

TABLE II

OBSERVED, RELATIVE SHIFT-GRADIENTS[a,b] (^{1}H) FOR COMPOUNDS **1**, **2**, **6**, AND **10–12**

Compound	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*a	*H-6*e	*H-7*	*OH*	*MeO-1*	*Methyl ether*
1	6.4	8.8	10	3.5	3.1	1.4	1.5	1.4	14.7	1.9	3.8
2[c]	6.7	9.1	10	3.7	3.7	1.7	1.6	1.7		1.7	2.9
6	9.6	10	8.3	6.8	9.3	3.4	2.4	2.6	14.0	−2.5	−2.3
10	5.7	9.1	10	5.5	9.2	3.2	2.5	3.2	24.3	1.1	3.0
11	3.6	10	3.0	3.0		1.3	0.9	0.9	9.1	0.7	0.8
12	5.9	10	3.5	2.2	3.3	1.4	1.5	1.0	11.7	3.8	1.1

[a]P.p.m. per mol of Eu(fod)$_3$ per mol of substrate. [b]All shifts for a given compound are normalised to the hydrogen(s) which exhibit the greatest induced shift. [c]Accurate shift data could not be obtained for the hydroxyl proton since its signal broadened almost to the baseline with increasing Eu(fod)$_3$/substrate ratio. Good straight-line plots of induced shift *vs.* molar ratio of shift reagent to substrate were obtained for all protons, excluding H-5 (Compound **11**).

TABLE III

OBSERVED AND CALCULATED, RELATIVE SHFIT-GRADIENTS (^1H) FOR MODEL A FOR COMPOUND **11**, AND FOR MODEL D FOR COMPOUND **12**

Proton	**11**			**12**	
	Obs.	*Calc.*		*Obs.*	*Calc.*
H-1	13.3	13.3	H-1	15.6	16.0
H-2	37.4	37.4	H-2	26.6	26.5
H-3	11.0	11.0	H-3	9.3	9.5
H-4	11.0	10.7	H-4	6.0	6.1
H-6*a*	4.9	4.8	H-6*a*	3.7	3.7
H-6*e*	3.4	3.3	H-6*e*	4.0	4.2
H-7	3.5	3.9	H-7	2.6	2.6
Eu···O-2 (Å)		3.38	Eu···O-1 (Å)		3.48
R		1.25%	Eu···O-2 (Å)		2.51
			R		1.88%

Comparison of the ^{13}C-n.m.r. data for the *α-altro* compounds **9–11** showed that 2-*O*-methylation caused upfield shifts in the resonances for the *β*-carbons (1.9 and 2.4 p.p.m. for C-1 and C-3, respectively) and strong deshielding (9.5 p.p.m.) of the *α*-carbon (C-2), as expected. Likewise, 3-*O*-methylation caused the expected downfield shift (9.3 p.p.m.) for the C-3 signal and deshielding of the *β*-carbons (0.2 and 1.3 p.p.m. for C-2 and C-4, respectively).

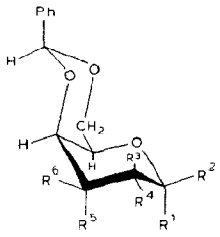
Comparison of the data for **5** and **7** showed that 2-*O*-sulfonylation caused upfield shifts in the resonances for the *β*-carbons (1.9 and 1.0 p.p.m. for C-1 and C-3, respectively) and strong deshielding of the *α*-carbon (6.2 p.p.m. for C-2).

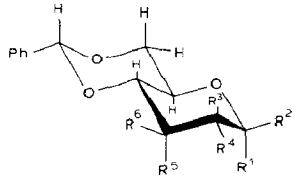
The above data should be of use in aiding the assignment of ^{13}C-n.m.r. spectra of related carbohydrate structures.

Eu(fod)$_3$-induced shifts. — Table II shows the relative shift gradients for the 2-*O*- (**1**) and 3-*O*-methyl (**2**) *α*-D-*galacto* derivatives, the 3-*O*-methyl *α*-D-*allo* derivative (**6**), the 2-*O*- (**10**) and 3-*O*-methyl (**11**) *α*-D-*altro* derivatives, and the 3-*O*-methyl *β*-D-*ido* derivative (**12**), derived from the experimental plots of induced shift *vs.* molar ratio of shift reagent to substrate. The chemical shift for the hydroxyl signal for **12** is accompanied by a larger than normal chemical shift for the resonance of MeO-1. Furthermore, the MeO-1 oxygen and the hydroxyl oxygen are oriented ideally for chelation to lanthanide. When the shift data for **12** were fitted to the $^4C_1$ conformation, using the chelation model D[8], which involves alternate co-ordination and magnetic-axis generation by each of the ligating atoms, axial symmetry about each lanthanide–oxygen bond, and only four unknown parameters, the reasonable fit described in Table III resulted. Compound **12** adopts the $^4C_1$ form in chloroform solution[9]. The chemical shift for the hydroxyl signal for the 3-*O*-methyl *α-altro* derivative (**11**), together with the relatively small values for the resonances of the methoxyl protons, indicates exclusive binding with the shift

reagent by the hydroxyl oxygen. The shift data for **11** were fitted to the $^4C_1$ conformation using the simple single-site model A[10], in which the magnetic axis is coincident with the europium–oxygen bond and with axial symmetry in the $Eu(fod)_3$-substrate adduct, and gave a reasonable Eu distance of 3.38 Å from the co-ordinating oxygen (Table III).

Attempts to fit the shift data for **1**, **2**, **6**, and **10** to either models A or D were not successful. However, the following qualitative points can be made. (*a*) The data for the *galacto* 2-*O*- (**1**) and *galacto* 3-*O*-methyl (**2**) derivatives are almost identical, indicating that the europium is co-ordinated in a similar manner. (*b*) The negative (*i.e.*, upfield) induced shifts observed for MeO-1 and MeO-3 in the 3-*O*-methyl *allo* derivative **6** show that the magnetic axis makes an angle greater than the magic angle (54.7°) with the Eu–H vectors of these groups. Therefore, it is possible that the angular contribution to the observed shift could be dominant and could make calculation of induced shift less reliable. (*c*) The relatively marked induced shifts observed for H-1/5 for **1**, **2**, **6**, and **10** contrast with the more rapid fall in induced shift, in the order H-2, H-1, H-3, observed for **11** and **12**. These data, together with the chemical shifts for the OMe signals of the former, suggest that Eu co-ordinates to more than the single, dominant, hydroxyl donor site in these systems.





Compound		R^1	R^2	R^3	R^4	R^5	R^6
1	*α-galacto*	MeO	H	H	MeO	H	OH
2		MeO	H	H	OH	H	MeO
3		MeO	H	H	MeO	H	OTs
4		MeO	H	H	OTs	H	MeO
12	*β-ido*	H	MeO	OH	H	MeO	H

Compoud		R^1	R^2	R^3	R^4	R^5	R^6
5	*α-allo*	MeO	H	H	OH	OH	H
6		MeO	H	H	OH	MeO	H
7		MeO	H	H	OTs	OH	H
8		MeO	H	H	OTs	MeO	H
9	*α altro*	MeO	H	OH	H	OH	H
10		MeO	H	MeO	H	OH	H
11		MeO	H	OH	H	MeO	H

EXPERIMENTAL

The benzylidenehexopyranoside derivatives **1–4**, **5**, **7**, and **9–12** were prepared as described[4–7]. Methyl 4,6-*O*-benzylidene-3-*O*-methyl-2-*O*-*p*-tolylsulfonyl-α-D-allopyranoside (**8**), prepared by Purdie methylation of **7**[7], had m.p. 173–175° [from chloroform–light petroleum (b.p. 40–60°)], $[\alpha]_D$ +52° (*c* 1, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 7.84 and 7.45–7.34 (d, 2 H; and m, 7 H; Ph and MeC_6H_4), 5.46 (s, 1 H, PhC*H*), 4.61 (d, 1 H, $J_{1,2}$ 4.2 Hz, H-1), 4.53 (t, 1 H, $J_{2,3}$ 3.6

Hz, H-2), 3.87 (bs, 1 H, H-3), 3.66 (t, 1 H, $J_{5,6a}$ 9.5, $J_{6a,6e}$ 10.1 Hz, H-6*a*), 3.56 (dd, 1 H, $J_{3,4}$ 3.3, $J_{4,5}$ 9 Hz, H-4), 3.47 (s, 3 H, MeO-3), 3.33 (s, 3 H, MeO-1), and 2.44 (s, 3 H, Ts-Me). The overlapping 2-proton envelope (δ 4.4–4.2) was due to H-5,6*e*. During the shift study, these resonances were resolved to give a q ($J_{5,6e}$ 5.1 Hz, H-6*e*) and a m (H-5). Complete assignment was possible by spin-decoupling of the normal and shifted spectra.

Anal. Calc. for $C_{22}H_{26}O_8S$: C, 58.65; H, 5.82. Found: C, 58.48; H, 5.85.

Methyl 4,6-*O*-benzylidene-3-*O*-methyl-α-D-allopyranoside (**6**), obtained by conventional detosylation of **8** (125 mg, 0.3 mmol) with methanolic 2M sodium methoxide (5 mL), had m.p. 130–133°, $[\alpha]_D$ +116° (*c* 1.1, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 7.49–7.35 (m, 5 H, Ph), 5.49 (s, 1 H, PhC*H*), 4.66 (d, 1 H, $J_{1,2}$ 4.4 Hz, H-1), 4.33 (q, 1 H, $J_{5,6e}$ 5.1, $J_{6a,6e}$ 10.3 Hz, H-6*e*), 4.13 (m, 1 H, H-5), 3.86 (d, 1 H, $J_{3,4} = J_{2,3}$ = 2.8 Hz, H-3), 3.63 (s, 3 H, MeO-3), 3.46 (s, 3 H, MeO-1), and 2.98 (d, 1 H, $J_{2,OH}$ 12 Hz, HO-2). The overlapping 3-proton envelope (δ 3.8–3.6) was due to H-2,4,6*a*. During the shift study, these resonances were resolved to give a t ($J_{5,6a}$ 10 Hz, H-6*a*), a dd ($J_{3,4}$ 2.6, $J_{4,5}$ 9.6 Hz, H-4), and a m (H-2).

Anal. Calc. for $C_{15}H_{20}O_6$: C, 60.80; H, 6.80. Found: C, 60.41; H, 6.81.

^{1}H-N.m.r. data . — *(a) Methyl 4,6-O-benzylidene-2-O-methyl-*α*-D-galacto-pyranoside* (**1**): δ 7.54–7.36 (m, 5 H, Ph), 5.56 (s, 1 H, PhC*H*), 5.0 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 3.68 (s, 1 H, H-5), 3.61 (dd, 1 H, $J_{2,3}$ 10 Hz, H-2), 3.53 (s, 3 H, MeO-2), 3.45 (s, 3 H, MeO-1), and 2.50 (d, 1 H, $J_{3,OH}$ 8.1 Hz, HO-3). The overlapping 4-proton envelope (δ 4.3–4.0) was due to H-3,4,6*a*,6*e*). During the shift study, these resonances separated to give two well resolved dd (H-6*a*,6*e*), a s (H-4), and a bs (H-3). The coupling constants ($J_{6a,6e}$ 12.4, $J_{5,6a} = J_{5,6e}$ = 1.8 Hz) confirm that H-5 is symmetrically disposed with respect to H-6*a*,6*e*.

(b) Methyl 4,6-O-benzylidene-3-O-methyl-α*-D-galactopyranoside* (**2**): δ 7.43–7.25 (m, 5 H, Ph), 5.48 (s, 1 H, PhC*H*), 4.87 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 4.30 (d, 1 H, $J_{3,4}$ 3.3 Hz, H-4), 4.22 (d, 1 H, $J_{6a,e}$ 12.5 Hz, H-6*e*), 3.59 (s, 1 H, H-5), 3.50 (dd, 1 H, $J_{2,3}$ 10.1, $J_{3,4}$ 3.5 Hz, H-3), 3.43 (s, 3 H, MeO-3), 3.39 (s, 3 H, MeO-1), and 2.24 (d, 1 H, $J_{2,OH}$ 6.8 Hz, HO-2). The 2-proton envelope at δ 4.15–4.05 was assigned to H-2,6*a*. During the shift study, these resonances separated to give a bs (H-2) and a d (H-6*a*).

(c) Methyl 4,6-O-benzylidene-2-O-methyl-3-O-p-tolylsulfonyl-α*-D-galacto-pyranoside* (**3**): δ 7.83 and 7.47–7.34 (d, 2 H; and m, 7 H; Ph and MeC_6H_4), 5.42 (s, 1 H, PhC*H*), 4.41 (d, 1 H, $J_{3,4} = J_{4,5}$ = 3.5 Hz, H-4), 4.25 (dd, 1 H, $J_{5,6e}$ 1.8, $J_{6a,e}$ 12.6 Hz, H-6*e*), 4.03 (dd, 1 H, H-6*a*), 3.81 (dd, 1 H, $J_{1,2}$ 3.4, $J_{2,3}$ 10.2 Hz, H-2), 3.64 (bs, 1 H, H-5), 3.39 (s, 3 H, MeO-1), 3.27 (s, 3 H, MeO-2), and 2.39 (s, 3 H, Ts-Me). The overlapping 2-proton envelope (δ 5.0–4.9) was due to H-1,3. During the shift study, these protons gave a d (H-1) and an unresolved dd (H-3). These assignments were made by spin-decoupling of the normal and shifted spectra.

(d) Methyl 4,6-O-benzylidene-3-O-methyl-2-O-p-tolylsulfonyl-α*-D-galacto-pyranoside* (**4**): δ 7.84 and 7.45–7.31 (d, 2 H; and m, 7 H; Ph and MeC_6H_4), 5.51 (s, 1 H, PhC*H*), 4.96 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.9 (dd, 1 H, $J_{2,3}$ 10 Hz, H-2), 4.30

(d, 1 H, $J_{4,5}$ 3.5 Hz, H-4), 4.25 (bd, 1 H, $J_{6a,e}$ 12.6 Hz, H-6*e*), 4.10 (bd, 1 H, H-6*a*), 3.7 (dd, 1 H, $J_{3,4}$ 3.5 Hz, H-3), 3.64 (bs, 1 H, H-5), 3.41 (s, 1 H, MeO-3), 3.28 (s, 3 H, MeO-1), and 2.42 (s, 3 H, Ts-Me).

*(e) Methyl 4,6-*O*-benzylidene-α-*D*-allopyranoside* (**5**): δ 7.5–7.35 (m, 5 H, Ph), 5.43 (s, 1 H, PhC*H*), 4.76 (d, 1 H, $J_{1,2}$ 4.2 Hz, H-1), 4.36 (q, 1 H, $J_{5,6e}$ 5, $J_{6a,e}$ 10.4 Hz, H-6*e*), 4.28 (t, 1 H, $J_{2,3} = J_{3,4}$ = 3 Hz, H-3), 4.11 (m, 1 H, H-5), 3.64 (dd, 1 H, $J_{4,5}$ 9.6 Hz, H-4), 3.36 (s, 3 H, MeO), 2.93 (d, 1 H, $J_{2,OH}$ 11.7 Hz, HO-2), and 2.62 (d, 1 H, $J_{3,OH}$ 6.6 Hz, HO-3). The 2-proton envelope (δ 3.79–3.73) was due to H-2,6*a*. During the shift study, these resonances were resolved to give a t ($J_{5,6a}$ 10 Hz, H-6*a*) and a bs (H-2).

*(f) Methyl 4,6-*O*-benzylidene-2-*O*-*p*-tolylsulfonyl-α-*D*-allopyranoside* (**7**): δ 7.83 and 7.46–7.34 (d, 2 H; and m, 7 H; Ph and MeC_6H_4), 5.53 (s, 1 H, PhC*H*), 4.82 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.52 (t, 1 H, $J_{1,2}$ 3.5 Hz, H-2), 4.32 (q, 1 H, $J_{5,6e}$ 5, $J_{6a,e}$ 10 Hz, H-6*e*), 3.72 (t, 1 H, $J_{5,6a}$ 9.7 Hz, H-6*a*), 3.45 (dd, 1 H, $J_{3,4}$ 3.3, $J_{4,5}$ 9.7 Hz, H-4), 3.43 (s, 3 H, MeO-1), 3.05 (d, 1 H, $J_{3,OH}$ 7.4 Hz, HO-3), and 2.42 (s, 3 H, Ts-Me). The 2-proton envelope (δ 4.2–4.0) was assigned to H-3,5. During the shift study, these resonances separated to give a m (H-3) and a sextet (H-5). These assignments were made by spin-decoupling of the normal and shifted spectra.

*(g) Methyl 4,6-*O*-benzylidene-2-*O*-methyl-α-*D*-altropyranoside* (**10**): δ 7.5–7.34 (m, 5 H, Ph), 5.60 (s, 1 H, PhC*H*), 4.73 (s, 1 H, H-1), 4.31 (q, 1 H, $J_{5,6e}$ 5.1, $J_{6a,e}$ 10 Hz, H-6*e*), 3.91 (dd, 1 H, $J_{4,5}$ 10, $J_{3,4}$ 3 Hz, H-4), 3.83 (t, 1 H, $J_{5,6a}$ 10 Hz, H-6*a*), 3.48 (d, 1 H, $J_{2,3}$ 3.2 Hz, H-2), 3.44–3.43 (2 s, 6 H, MeO-1,2), and 3.0 (d, 1 H, $J_{3,OH}$ 7.1 Hz, HO-3). The 2-proton envelope (δ 4.2–4.1) was due to H-3,5. During the shift study, these resonances separated to give a bm (H-3) and a m (H-5). These assignments were made by spin-decoupling of the normal and shifted spectra.

*(h) Methyl 4,6-*O*-benzylidene-3-*O*-methyl-α-*D*-altropyranoside* (**11**): δ 7.48–7.34 (m, 5 H, Ph), 5.54 (s, 1 H, PhC*H*), 4.55 (s, 1 H, H-1), 3.56 (s, 3 H, MeO-3), 3.40 (s, 3 H, MeO-1), 2.63 (d, 1 H, $J_{2,OH}$ 5.3 Hz, HO-2). The 2-proton envelope (δ 4.4–4.2) was assigned to H-5,6*e*. During the shift study, these resonances separated to give a q ($J_{5,6e}$ 5.1 Hz, $J_{6a,e}$ 10.1 Hz, H-6*e*) and a m (H-5). The 2-proton envelope at δ 4.1–3.98 was due to H-3,4 and was not resolved in the shift study. The 2-proton envelope at δ 3.9–3.7 was assigned to H-2,6*a*. During the shift study, these protons gave a t ($J_{5,6a}$ 10 Hz, H-6*a*) and a m (H-2).

*(i) Methyl 4,6-*O*-benzylidene-3-*O*-methyl-β-*D*-idopyranoside* (**12**): δ 7.48–7.35 (m, 5 H, Ph), 5.53 (s, 1 H, PhC*H*), 4.62 (s, 1 H, $J_{1,2}$ <1 H, H-1), 4.4 (d, 1 H, $J_{6a,e}$ 12.8 Hz, H-6*e*), 4.10 (d, 1 H, H-6*a*), 4.03 (s, 1 H, H-4), 3.61 (s, 3 H, MeO-3), 3.48 (s, 3 H, MeO-1), and 3.2 (d, 1 H, $J_{2,OH}$ 9.1 Hz, HO-2). The 3-proton envelope at δ 3.8–3.6 was assigned to H-2,3,5. During the shift study, partial resolution of these resonances gave a d (H-2), but the resonances for H-3,5 were not resolved. The H-6*a*,6*e* resonances were resolved to give two dd ($J_{5,6a} = J_{5,6e}$ = 1.8 Hz).

N.m.r. spectra were recorded at 24° with a Jeol GX-270 spectrometer for solutions in $CDCl_3$ (internal Me_4Si). Shift reagent was added until the molar ratio of reagent to substrate was 0.35, and spectra were recorded after each addition.

Good straight-line plots of induced shfit *vs.* molar ratio of shift reagent to substrate were obtained for all the compounds studied. Calculations were made by the grid-search procedure[8,10]. For model D, each point in a grid-search procedure has two calculated-shift contributions (one from each magnetic axis). These were added with equal weights, and scaled to experimental shift-gradients. The best fit was that which had the lowest *R*-factor, where $R = [\sum_i (G_{calc_i} - G_{obs_i})^2 / \sum_i (G_{obs_i})^2]^{0.5} \times 100$.

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