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THE 2,3-EPOXIDE, A DONOR IN LANTHANIDE SHIFT-REAGENT STUDIES OF CARBOHYDRATE SYSTEMS; THE X-RAY STRUCTURE OF METHYL 2,3-ANHYDRO-4,6-*O*-BENZYLIDENE-β-D-MANNOPYRANOSIDE

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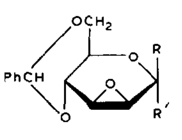
ABSTRACT

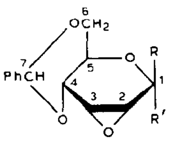
Lanthanide-induced shifts in the ^{1}H-n.m.r. spectra of the methyl 2,3-anhydro-4,6-*O*-benzylidene-D-hexopyranosides [*manno* (**1** and **5**), *allo* (**2** and **6**), *gulo* (**3** and **7**), α and β, respectively, and α-*talo* (**4**)] have been measured. The observed shift data for the α-*manno*, β-*allo*, and β-*gulo* epoxides were in good agreement with those calculated for the $^{\circ}H_5$ conformation of the pyranoid ring using a single-site model. Shifts calculated for the $^{\circ}H_5$ conformation of the β-*manno* epoxide using a two-site model were in excellent agreement with the observed shift data. The ^{13}C-n.m.r. spectra were assigned by decoupling techniques, and n.m.r. line-shifts (^{1}H and ^{13}C) induced by the shift reagents were used in some cases for complete assignment of signals. The solid-state structure of methyl 2,3-anhydro-4,6-*O*-benzylidene-β-D-mannopyranoside (**5**) has been determined by X-ray crystallographic analysis.

INTRODUCTION

It was decided to extend quantitative shift-reagent studies of carbohydrate systems to oxiranes for two reasons. Firstly, the oxirane-ring oxygen should be a suitable, though as yet little used, donor; secondly, a quantitative shift-reagent study could provide conformational data for oxirane carbohydrate systems.



1 R = H,R' = OMe
5 R = OMe,R' = H



2 R = H,R' = OMe
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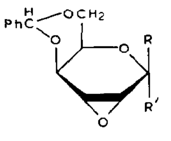

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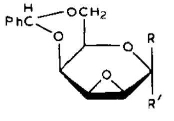

4 R = H,R' = OMe

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RESULTS AND DISCUSSION

The conformations adopted in solution by some 2,3-anhydro-4,6-*O*-benzylidene-D-aldohexopyranosides, as well as related compounds, have been examined [1–4]. On the basis of ^{1}H-n.m.r. coupling data, in particular the $J_{1,2}$ and $J_{4,5}$ values, these authors proposed an $^{\circ}H_5$ conformation for the 2,3-anhydropyranoside ring. Further support for the half-chair conformations has been provided by Catelani *et al.*[5] who reported ^{1}H-n.m.r. data for some model substituted 3,4-epoxytetrahydropyrans. The ^{13}C-chemical shifts and $^{1}J_{C,H}$ values of the *manno* and *allo* epoxides have been determined[6], and ^{1}H- and ^{13}C-n.m.r. spectra of the *manno*, *allo*, and *talo* compounds have been recently recorded[7]. There have been few reports of lanthanide studies which involve the epoxide group as a donor[8,9]. However, recently reported[10] binding-constant results show that simple epoxide rings are approximately equal in binding strength to non-conjugated carbonyl groups.

Addition of shift reagent to the sugar epoxides **1**–**7** induced the ^{1}H-n.m.r. shifts given in Table I. In all cases, good linear plots of induced shift *vs.* molar ratio of [LN/subs] were obtained. The observed shift data for the α-*manno* (**1**), β-*allo* (**6**), and β-*gulo* (**7**) epoxides were fitted to an $^{\circ}H_5$ conformation, using the simple single-site axial-symmetry model previously described[11] as model A (Tables II and IIIA). For the *manno* epoxide[12] (**1**), the calculated lanthanide positions for the Pr and Yb reagents are reasonable, as are the Pr and Yb oxygen distances (2.79 and 2.48 Å, respectively) and the agreement factors. The metal co-ordination position is almost equidistant from C-2 and C-3 and indicative of exclusive binding by the epoxide oxygen. The Eu data predict a longer Eu–O distance; however, this difference is probably due to a small contact effect on H-2 and H-3 which reduces the observed shifts. It is well established[13] that contact effects are greater for Eu than for the other reagents. Further confirmation of the co-ordination position predicted for Pr and Yb was obtained from Gd(fod)$_3$ relaxation data[14]. These results are given in Table IIIB. Methyl 2,3-anhydro-4,6-*O*-benzylidene-β-D-allopyranoside[15] (**6**) and the corresponding *gulo* epoxide[16] (**7**) also gave very reasonable results with model A. The metal co-ordination position is almost equidistant from C-2 and C-3, and indicative of exclusive binding by the epoxide oxygen atom (Fig. 1).

Shift reagent data for the α-*allo*[12] (**2**), α-*gulo*[17] (**3**), and α-*talo*[17] (**4**) epoxides are given in Table I. It was not possible to fit shift data for these compounds to the

Fig. 1. *A*, The $^{\circ}H_5$ conformation of the pyranoid ring for the β-D-*allo* (**6**) and β-D-*gulo* (**7**) epoxides; *B*, the $^{\circ}H_5$ conformation of the pyranoid ring for the α-D- (**1**) and β-D-*manno* (**5**) epoxides.

simple single-site model. It is also clear that, for these three compounds, data for the shift reagents are not in close agreement. In fact, the divergence is rather remarkable. The largest differences are observed for H-1 and OMe in **2** and **3**, and for H-1 in **4**. While it is not possible to reach any quantitative conclusions, the following qualitative points can be made. (*a*) The *allo* (**2**) and *gulo* (**3**) data are almost superposable, indicating that both pyranoid rings adopt the same conformation and co-ordinate lanthanide in a similar manner. (*b*) The somewhat larger shifts observed for the OMe group in **2** and **3** relative to **1** suggest some degree of OMe co-ordination. It is only in **2** and **3** that chelation is possible *via* epoxide oxygen and methoxyl. (*c*) The shifts observed for the *talo* epoxide (**4**) have lower OMe values, as expected. However, on going from Eu to Yb, the H-1 shifts show larger differences than those observed for **2** and **3**. Since chelation is unlikely for **4**, this difference is probably due to the existence of more than one conformation in solution.

TABLE I

OBSERVED, RELATIVE SHIFT-GRADIENTS[a,b] (^{1}H) FOR EPOXIDES **1**–**7**

	1			**2**			**3**		
Proton	*Eu*	*Pr*[c]	*Yb*	*Eu*	*Pr*[c]	*Yb*	*Eu*	*Pr*[c]	*Yb*
H-1	6.6	5.6	5.9	5.6	7.6	5.7	6.4	8.6	7.2
H-2	9.7	9.5	10.0	8.0	10.0	9.7	9.7	10.0	9.8
H-3	10.0	10.0	9.8	6.9	9.9	7.5	6.7	9.4	6.9
H-4	8.0	6.4	7.2	2.9	4.6	4.8	3.9	4.0	4.4
H-5	4.0	3.2	4.0	10.0	6.6	10.0	10.0	5.9	10.0
H-6*a*	2.6	2.3	2.5	2.8	2.5	3.3	2.3	1.8	3.4
H-6*e*	2.1	1.9	2.1	0.2	1.5	3.4	1.2	0.0	2.4
PhC*H*	1.7	1.3	1.8	2.0	2.0	2.8	1.3	1.3	1.9
MeO	1.4	1.4	1.5	2.9	5.6	3.1	2.8	6.3	2.7

	4			5		6		7	
	Eu	*Pr*[c]	*Yb*	*Eu*	*Pr*[c]	*Eu*	*Pr*[c]	*Eu*	*Pr*[c]
H-1	6.0	3.7	9.8	7.78	7.94	9.19	6.98	6.64	6.92
H-2	6.1	10.0	6.0	10.0	10.0	10.0	9.81	10.0	10.0
H-3	10.0	9.1	10.0	6.07		8.03	8.99	9.94	9.99
H-4	7.3	5.2	9.3	5.68	4.53	5.98	5.28	5.32	5.10
H-5	6.4	4.6	8.1		5.14		10.0	5.93	5.99
H-6*a*	4.6	2.9	7.2	2.14	1.60	3.81	3.22	1.82	2.00
H-6*e*	4.5	3.0	6.2	1.96	1.96	3.24		2.08	2.16
PhC*H*	5.3	3.5	7.2	0.69	0.93	3.34	3.40	1.76	1.92
MeO	1.7	1.2	2.3	4.47	5.38	2.25	2.56	2.37	2.64

[a] P.p.m. per mol of Ln(fod)$_3$ per mol of substrate. [b] All shifts for a given study are normalised to the hydrogen atom which exhibits the greatest induced shift. [c] All Pr(fod)$_3$ gradients are negative.

TABLE II

OBSERVED, SHIFT-GRADIENTS[a] (^{1}H) FOR COMPOUNDS **1**, AND **5-7**

Proton	**1**			**5**		**6**		**7**	
	Eu(fod)$_3$	*Pr(fod)$_3$*	*Yb(fod)$_3$*	*Eu(fod)$_3$*	*Pr(fod)$_3$*	*Eu(fod)$_3$*	*Pr(fod)$_3$*	*Eu(fod)$_3$*	*Pr(fod)$_3$*
H-1	7.4	−13.1	18.7	7.4	−15.5	9.2	−14.3	8.3	−17.1
H-2	10.8	−22.4	31.5	9.5	−19.6	10.4	−20.1	12.6	−24.7
H-3	11.2	−23.6	31.0	5.8	—[b]	8.1	−18.5	12.5	−24.7
H-4	9.0	−15.1	22.8	5.4	− 8.9	6.0	−10.8	6.7	−12.6
H-5	4.5	− 7.6	12.8	—[b]	−10.1	—[b]	−20.5	7.4	−14.8
H-6*a*	2.9	− 5.4	7.9	2.0	− 3.1	3.8	− 6.6	2.3	− 4.5
H-6*e*	2.3	− 4.5	6.7	1.9	− 3.8	3.2	—[b]	2.6	− 5.3
H-7	1.9	− 3.1	5.8	0.7	− 0.8	3.5	− 7.0	2.2	− 4.7
MeO	1.6	− 3.2	4.9	4.3	−10.5	2.3	− 5.3	3.0	− 6.5

[a] P.p.m. per mol of Ln(fod)$_3$ per mol of substrate. [b] Obscured.

TABLE IIIA

CALCULATED, SHIFT-GRADIENTS (^{1}H) FOR MODEL A FOR COMPOUNDS **1**, **6** AND **7**, AND FOR MODEL D FOR COMPOUND **5**

Proton	**1**			**6**		**7**		**5**	
	Eu(fod)$_3$	*Pr(fod)$_3$*	*Yb(fod)$_3$*	*Eu(fod)$_3$*	*Pr(fod)$_3$*	*Eu(fod)$_3$*	*Pr(fod)$_3$*	*Eu(fod)$_3$*	*Pr(fod)$_3$*
H-1	7.4	−13.0	18.7	9.5	−14.3	8.1	−16.9	7.4	−15.4
H-2	10.8	−22.5	31.5	10.3	−19.7	12.6	−24.9	9.7	−19.9
H-3	11.2	−23.5	31.0	8.1	−18.7	12.4	−24.5	5.5	
H-4	9.0	−15.2	23.1	6.0	−11.1	6.7	−13.2	5.4	− 8.8
H-5	4.6	− 7.8	12.5		−20.9	7.7	−15.4		− 9.8
H-6*a*	2.7	− 5.2	7.8	3.4	− 5.9	2.7	− 5.3	2.1	− 3.2
H-6*e*	2.3	− 4.1	6.2	3.5		2.6	− 5.1	1.8	− 3.3
H-7	2.1	− 3.3	5.6	3.2	− 6.2	2.2	− 4.2	0.7	− 0.8
r Eu···O-2,3 (Å)		3.48		2.5		3.24		*r* Eu···OMe (Å)	3.48
R		1.23%		3.4		2.6		*r* Eu···O-2,3 (Å)	3.19
r Pr···O-2,3 (Å)		2.79		2.5		3.25		R	2.3%
R		1.55%		3.2		2.7		*r* Pr···OMe (Å)	3.25
r Yb···O-2,3 (Å)		2.48						*r* Pr···O-2,3 (Å)	2.80
R		1.22%						R	2.4%

TABLE IIIB

Gd(FOD)$_3$ LINE-BROADENING DATA FOR **1**

Proton	*Relative values of* r^{-6}	*Broadening ratios*
H-1	5.2	0
H-2	8.0	9
H-3	10.0	10
H-6*e*	0.41	~0
H-7	1.22	1.2

Attempts to fit the shift data for the β-D-*manno* epoxide[15] (**5**) to model A were not successful. The relatively large shift gradient for the methoxyl group is indicative of binding of the lanthanide to the methoxyl oxygen. Indeed, the methoxyl oxygen and the epoxide oxygen are in an orientation ideal for chelation to lanthanide. When the shift data for **5** were fitted to the $^{O}H_5$ conformation, using the chelation model D[14], the reasonable fit described in Table IIIA resulted. The data rule out the presence of other non-chair conformations and show that **5** is indeed restricted to its only possible half-chair form. Calculated lanthanide positions for the Pr and Eu reagents are reasonble. The Pr and Eu oxygen distances (2.80 and 3.19 Å, respectively) and the agreement factors are reasonable. No satisfactory fits of observed to calculated shift data could be made when Model D was applied to either a set ot $^{O}H_5$ or $^{1,4}B$ co-ordinates for the α-D-*allo* (**2**) and α-D-*gulo* (**3**) epoxides. Attempts were made to derive calculated shifts, using a model involving both half-chair and boat co-ordination to lanthanide in rapid equilibrium. However, this "Isomer" model contained too many variable parameters and the calculated R-factor minima were not well-defined.

^{13}C-N.m.r. chemical shift data for the 2,3-anhydro-4,6-*O*-benzylidene-α- and -β-D-gulopyranosides (**3** and **7**) are presented in Table IV, together with the values for the oxiranes **1**, **2** and **4–6**, which are in close agreement with values reported for these compounds. The data for **3** and **7** provide further support for observations[6,7] on the effect of the oxirane ring on the chemical shift values of adjacent carbon atoms. For example, there is a downfield shift (~2 p.p.m.) in the C-4 signals for the *gulo* epoxides (**3** and **7**), in which the oxirane ring is *cis* to the equatorial H-4, relative to the C-4 signals for the α-D-*talo* (**4**) and β-D-*talo*[7] isomers, in which the oxirane ring is *trans* to the equatorial H-4. Comparison of the ^{13}C-n.m.r. data for the *manno* epoxides (**1** and **5**), in which the oxirane ring is *cis* to the axial H-4, with the oppositely configured *allo* isomers (**2** and **6**) shows the expected upfield shift (2.8 p.p.m.) in the resonances for the C-4 atoms of **1** and **5**. Furthermore, in the spectra of the α-D-*gulo* and -*talo* epoxides (**3** and **4**), there is an upfield shift (2.4→8.4 p.p.m.) in the C-5 signals, together with similar shifts (2.6→2.9 p.p.m.) for the C-1 signals, with respect to the corresponding signals in the spectra of the β-D-*gulo* and β-D-*talo*[7] anomers, as expected.

The structure of methyl 2,3-anhydro-4,6-*O*-benzylidene-β-D-mannopyrano-

TABLE IV

^{13}C CHEMICAL-SHIFT DATA[a] FOR EPOXIDES **1**–**7**

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-OMe*	*C-7*[b]
1	97.2	50.7	53.9	75.1	62.0	69.5	55.6	102.5
2	95.3	53.2	50.7	77.9	60.0	68.9	55.9	102.8
3	95.1	51.3	51.1	70.6	59.7	69.9	55.8	101.1
4	96.7	49.1	49.6	68.7	59.8	69.3	55.9	101.0
5	99.7	50.7	53.8	74.8	68.4	69.2	57.4	102.4
6	98.3	51.8	55.4	77.6	60.7	69.7	56.2	101.2
7	98.0	51.3	55.4	70.5	62.1	69.0	57.0	102.8

[a] In p.p.m. downfield from Me_4Si for solutions in $CDCl_3$. [b] Benzylidene-methine carbon.

side (**5**) in the solid state was investigated by X-ray crystallography. The positional and thermal parameters of the non-hydrogen atoms, with calculated standard deviations, are listed in Table V, and those for hydrogen atoms are in Table VI. A perspective view of the molecule showing the numbering is given in Fig. 2. Bond lengths and bond angles are presented in Tables VII and VIII.

At 1.428 (17) Å, the C-2–C-3 bond (epoxide ring) is 0.109 Å ($\sim 6\sigma$) shorter than the average sp^3 (C–C) bond (1.537Å). The equatorial anomeric C-1–O-1 bond [1.391(15) Å] is significantly shorter than the mean C–O bond-length (1.478 Å).

The presence of the epoxide ring has flattened the pyranose ring relative to the ordinary chair form. C-1, C-2, C-3, and C-4 are coplanar (within ± 0.009Å), plane A, and O-5 and C-5 lie above (0.389Å) and below (0.462Å) this plane, respectively. Thus, the pyranose ring is best described as having a half-chair conformation. The epoxide ring (C-2, O-2, C-3) makes an angle of 76.97° with plane A.

The benzylidene ring adopts a slightly distorted chair conformation: C-6, O-6, C-4, and O-4 are coplanar (within 0.011Å), plane B; C-5 lies 0.739Å below, and

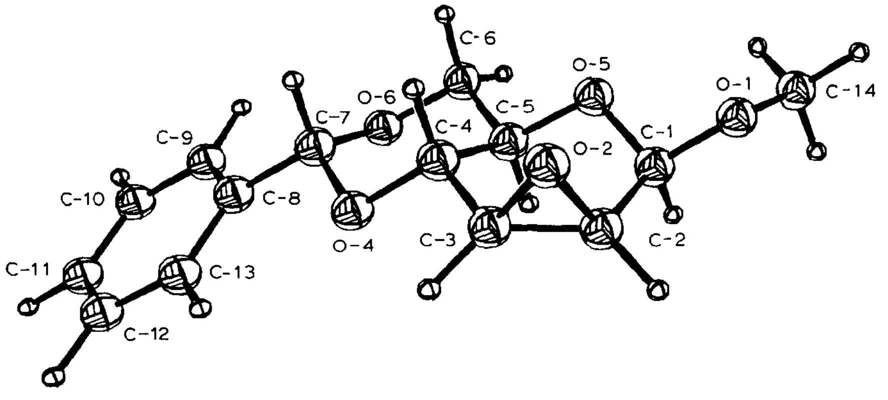

Fig. 2. ORTEP[23] drawing of methyl 2,3-anhydro-4,6-*O*-benzylidene-β-D-mannopyranoside, and the numbering scheme for the atoms.

TABLE V

FRACTIONAL ATOMIC CO-ORDINATES FOR **5**

Atom	x	y	z
O-1	0.9155(10)	−0.3275	0.5797(5)
O-2	0.5733(10)	−0.4213(31)	0.5822(4)
O-4	0.4236(9)	0.0711(29)	0.7338(4)
O-5	0.8131(9)	−0.1876(31)	0.6938(5)
O-6	0.5935(9)	0.1784(32)	0.8444(5)
C-1	0.8189(14)	−0.1174(41)	0.6130(7)
C-2	0.6552(15)	−0.1460(41)	0.5683(7)
C-3	0.5203(15)	−0.1427(40)	0.6129(7)
C-4	0.5400(12)	−0.1227(42)	0.7031(6)
C-5	0.6992(13)	0.0035(38)	0.7278(6)
C-6	0.7174(15)	0.0017(41)	0.8185(7)
C-7	0.4451(13)	0.0656(40)	0.8170(6)
C-8	0.3260(15)	0.2648(36)	0.8506(7)
C-9	0.3415(15)	0.3635(42)	0.9291(7)
C-10	0.2290(15)	0.5427(44)	0.9597(8)
C-11	0.0991(15)	0.6291(40)	0.9146(7)
C-12	0.0818(16)	0.5226(45)	0.8378(8)
C-13	0.1925(14)	0.3532(41)	0.8053(8)
C-14	1.0758(15)	−0.2631(48)	0.5985(8)

TABLE VI

FRACTIONAL ATOMIC CO-ORDINATES FOR THE HYDROGEN ATOMS OF **5** WITH ATTACHED C ATOMS IN BRACKETS

Atom		x	y	z
H-1		0.860	0.112	0.607
H-2		0.689	−0.021	0.518
H-3		0.415	−0.009	0.609
H-4		0.527	−0.348	0.726
H-5		0.714	0.233	0.707
H-61		0.827	0.101	0.839
H-62		0.711	−0.227	0.841
H-7	(C-7)	0.434	−0.167	0.836
H-8	(C-9)	0.442	0.298	0.966
H-9	(C-10)	0.244	0.617	1.020
H-10	(C-11)	0.013	0.774	0.938
H-11	(C-12)	−0.022	0.579	0.802
H-12	(C-13)	0.176	0.282	0.744
H-13	(C-14)	1.147	−0.433	0.572
H-14	(C-14)	1.200	−0.265	0.662
H-15	(C-14)	1.104	−0.043	0.576

TABLE VII

BOND LENGTHS (Å) FOR **5**

O-1–C-1	1.392(15)	O-1–C-14	1.428(14)
O-2–C-2	1.435(17)	O-2–C-3	1.424(16)
O-4–C-4	1.443(14)	O-4–C-7	1.411(12)
O-5–C-1	1.410(13)	O-5–C-5	1.444(14)
O-6–C-6	1.417(15)	O-6–C-7	1.424(13)
C-1–C-2	1.564(16)	C-2–C-3	1.429(17)
C-3–C-4	1.531(15)	C-4–C-5	1.516(15)
C-5–C-6	1.535(14)	C-7–C-8	1.494(17)
C-8–C-9	1.399(16)	C-8–C-13	1.398(16)
C-9–C-10	1.380(19)	C-10–C-11	1.370(16)
C-11–C-12	1.385(17)	C-12–C-13	1.359(18)

TABLE VIII

BOND ANGLES (°) FOR **5**

C-14–O-1–C-1	112(1)	C-3–O-2–C-2	60.0(8)
C-7–O-4–C-4	107.6(9)	C-5–O-5–C-1	109.1(9)
C-7–O-6–C-6	113(1)	O-5–C-1–O-1	108(1)
C-2–C-1–O-1	107(1)	C-2–C-1–O-5	111(1)
C-1–C-2–O-2	115(1)	C-3–C-2–O-2	59.6(8)
C-3–C-2–C-1	119(1)	C-2–C-3–O-2	60.4(8)
C-4–C-3–O-2	113(1)	C-4–C-3–C-2	119(1)
C-3–C-4–O-4	111(1)	C-5–C-4–O-4	109(1)
C-5–C-4–C-3	110(1)	C-4–C-5–O-5	108(1)
C-6–C-5–O-5	112(1)	C-6–C-5–C-4	108(1)
C-5–C-6–O-6	106(1)	O-6–C-7–O-4	112(1)
C-8–C-7–O-4	109(1)	C-8–C-7–O-6	107(1)
C-9–C-8–C-7	121(1)	C-12–C-8–C-7	121(1)
C-13–C-8–C-9	117(1)	C-10–C-9–C-8	121(1)
C-11–C-10–C-9	121(1)	C-12–C-11–C-10	118(1)
C-13–C-12–C-11	122(1)	C-12–C-13–C-8	120(1)

C-7 lies 0.657Å above, this plane. The plane formed by atoms O-6, C-7, and O-4 makes an angle of 124.41° with plane B, while the C-4, C-5, C-6 plane intersects B at 123.9°. Plane A of the pyranose ring lies at an angle of 37.15° to plane B. The phenyl ring is oriented at an angle of 13.17° to plane B.

Weak contacts exist between O-2 and the C-2 and C-3 atoms of neighbouring molecules (3.276 and 3.281 Å, respectively). The structure is broadly similar to that of the α-D-mannopyranoside previously determined[18].

EXPERIMENTAL

The 2,3-anhydro compounds **1–7** were prepared as described[12,15–17]. N.m.r. spectra were recorded with Jeol MH-100 (^{1}H) and GX-270 (^{1}H,^{13}C) spectrometers

TABLE IX

CRYSTALLOGRAPHIC DATA FOR 5 ($C_{14}H_{16}O_5$)

A crystal with approximate dimensions of 0.35 × 0.40 × 0.38 mm was used for data collection

Monoclinic: space group $P2_1$
a = 8.632 (2), b = 4.421 (2), c = 16.957 (4) Å
β = 93.71 (1)
U = 645.76 Å^3, μ = 0.63 cm^{-1}, $F000$ = 280.00
Diffractometer: Hilger and Watts Y290
Radiation Mo-$K\alpha$ (λ = 0.71069 Å), graphite monochromator
Range $2 < \Theta < 24°$
Final full-matrix least-squares cycle

Reflections with $I > 3\sigma(I)$	533	
No. of variable parameters	76	
Max. shift/ESD	<0.001	
Residuals	$R = 0.073$	$R_w = 0.073$

Final difference E map
Max. peak = 0.143 e/Å^3; min. peak = −0.133 e/Å^3

$R = [\Sigma|F_0 - F_c|]/\Sigma|F_0|$ $\quad R_w = [[\Sigma w(|F_0 - F_c|)^2]/[\Sigma w(|F_0|)^2]]^{1/2}$
$w = 1/[(\sigma F_0)^2 - 0.0004{*}F_0^2]$

for solutions in $CDCl_3$ (internal Me_4Si). Appropriate quantities of shift reagent were added to sample solutions, and spectra were recorded after each addition. Good straight-line plots of induced shift *vs.* molar ratio of shift reagent to substrate were obtained for all the compounds studied. Calculations using Models A and D were made by the grid-search procedure[11,14].

Crystallographic data are given in Table IX. Unit-cell parameters were determined by least-squares refinement of the setting angles ($\Theta \geqq 10°$) of 12 reflections. The space group $P2_1$ was uniquely determined by the optical activity of the compound and the systematic absences. Lorentz and polarisation corrections were applied. The initial phases were found by direct methods[19]. In the subsequent least-squares refinement using SHELX 76[19], all atoms were treated as having isotropic thermal parameters and hydrogen atoms were included as fixed contributors in calculated positions.

The atomic scattering factors for non-hydrogen and hydrogen atoms and the anomalous-dispersion correction factors for non-hydrogen atoms were taken from the literature [20–22].

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