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Note

Virtual long-range coupling of the anomeric proton of carbohydrates: an n.m.r. spin-simulation study

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N.m.r. signals for anomeric protons of pyranoid sugars normally have a first-order appearance, being sharp doublets with a spacing (coupling constant) of ~3 and ~8 Hz for 1,2-*cis* and 1,2-*trans* geometry, respectively. The numerical value of this spacing is an important diagnostic aid for the assignment of anomeric configuration. In some cases, however, the interpretation of the anomeric proton signal is complicated by virtual long-range coupling[1]. We now report (as an aid, but also as a *caveat*) a spin-simulation[2] study where the chemical shifts and coupling constants used are typical for carbohydrate derivatives. Included are two examples from our synthetic work[3,4] [2-bromoethyl 2,3-di-*O*-benzoyl-6-*O*-benzyl-β-D-glucopyranoside (**1**) and 2-bromoethyl 4,6-*O*-benzylidene-2-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-β-D-galactopyranoside (**2**)].

Fig. 1 shows a series of calculated "anomeric proton" signals (proton A in ABC-, ABCD-, and ABCDE-systems). When the chemical shifts of the B and C protons come closer than 0.05 p.p.m. (entries 18, 20, 22, 24, and 26), the distortion is increased so that even the apparent symmetry of the A signal is lost. Table I shows the parameters used for the calculation of the signals in Fig. 1.

Table II shows the experimental and calculated signals for the anomeric protons of the glycosides **1**[3] and **2**[4]. Determination of the chemical shifts and coupling constants were made by double resonance and 2D-n.m.r. techniques. The spectra were recorded at 19° for 0.08M solutions of **1** and **2** in chloroform-*d* with tetramethylsilane (1%) as internal standard.

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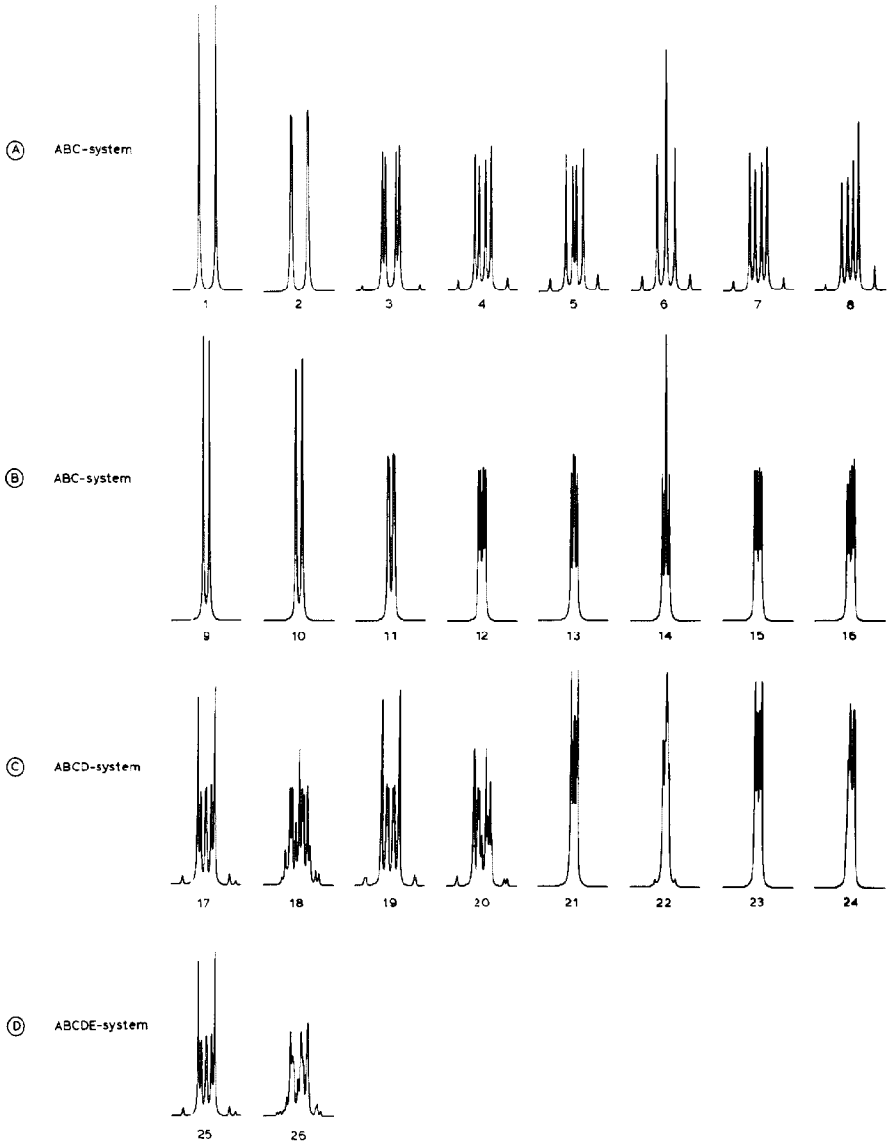


Fig. 1. ^{1}H-N.m.r. spin-simulation (line-width 0.5 Hz) showing the appearance of the "anomeric proton" signal for different sets of parameters (see Table I).

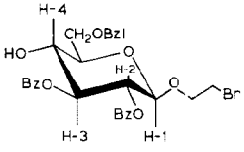
TABLE I

PARAMETERS USED FOR THE CALCULATION OF THE "ANOMERIC PROTON" PATTERNS IN FIG. 1

A Entry:		*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*
P.p.m.	A	4.50	4.50	4.50	4.50	4.50	4.50	4.50	4.50
	B	3.00	3.20	3.23	3.24	3.245	3.25	2.99	4.29
	C	3.50	3.30	3.27	3.26	3.255	3.25	3.01	4.31
J (Hz)	A,B	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8
	A,C	0	0	0	0	0	0	0	0
	B,C	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
B Entry:		*9*	*10*	*11*	*12*	*13*	*14*	*15*	*16*
P.p.m.	A	4.50	4.50	4.50	4.50	4.50	4.50	4.50	4.50
	B	3.00	3.20	3.23	3.24	3.245	3.25	2.99	4.29
	C	3.50	3.30	3.27	3.26	3.255	3.25	3.01	4.31
J (Hz)	A,B	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
	A,C	0	0	0	0	0	0	0	0
	B,C	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
C Entry:		*17*	*18*	*19*	*20*	*21*	*22*	*23*	*24*
P.p.m.	A	4.50	4.50	4.50	4.50	4.50	4.50	4.50	4.50
	B	3.29	3.29	3.29	3.29	3.29	3.29	3.29	3.29
	C	3.31	3.31	3.31	3.31	3.31	3.31	3.31	3.31
	D	4.30	3.30	4.30	3.30	4.30	3.30	4.30	3.30
J (Hz)	A,B	7.8	7.8	7.8	7.8	3.0	3.0	3.0	3.0
	A,C	0	0	0	0	0	0	0	0
	A,D	0	0	0	0	0	0	0	0
	B,C	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
	B,D	0	0	0	0	0	0	0	0
	C,D	9.5	9.5	2.0	2.0	9.5	9.5	2.0	2.0
D Entry:		*25*			*26*				
P.p.m.	A	4.50			4.50				
	B	3.29			3.29				
	C	3.31			3.31				
	D	4.30			3.30				
	E	3.10			3.10				
J (Hz)	A,B	7.8	B,D	0	7.8				
	A,C	0	B,E	0	0	0			
	A,D	0	C,D	9.5	0	9.5			
	A,E	0	C,E	0	0	0			
	B,C	10.0	D,E	9.5	10.0	9.5			

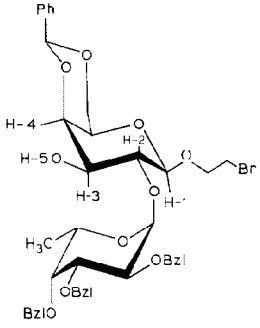
TABLE II

^{1}H-N.M.R SPECTRA DEPICTING THE ANOMERIC PROTON (H-1) SIGNAL OF THE 2-BROMOETHYL GLYCOSIDES **1** AND **2**



1

	P.p.m.	*J (Hz)*	
Experimental data[a]			
H-1	4.78	$J_{1,2}$ 7.8	$J_{2,4}$ 0
H-2	5.46	$J_{1,3}$ 0	$J_{3,4}$ 10.0
H-3		$J_{1,4}$ 0	
H-4	3.97	$J_{2,3}$?	
Calculated data[b]			
H_A	4.78	$J_{A,B}$ 7.8	$J_{B,D}$ 0
H_B	5.4545	$J_{A,C}$ 0	$J_{C,D}$ 10.0
H_C	5.4600	$J_{A,D}$ 0	
H_D	3.98	$J_{B,C}$ 10.0	



2

Experimental data[a]			
H-1	4.45	$J_{1,2}$ 7.6	$J_{2,4}$ 0
H-2	3.87	$J_{1,3}$ 0	$J_{2,5}$ 0
H-3		$J_{1,4}$ 0	$J_{3,4}$ 1.7
H-4	4.21	$J_{1,5}$ 0	$J_{3,5}$ 6
H-5	3.57	$J_{2,3}$?	$J_{4,5}$ 0
Calculated data[b]			
H_A	4.45	$J_{A,B}$ 7.62	$J_{B,D}$ 0
H_B	3.875	$J_{A,C}$ 0	$J_{B,E}$ 0
H_C	3.865	$J_{A,D}$ 0	$J_{C,D}$ 1.65
H_D	4.20	$J_{A,E}$ 0	$J_{C,E}$ 6.0
H_E	3.57	$J_{B,C}$ 9.7	$J_{D,E}$ 0

[a]Varian XL-200 spectrometer. [b]The line-width used in the calculations was 1.3 Hz.

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