NOTIZEN

Amphiphilic Carbohydrate-Based Mesogens, 2 [1]

Aldose Di-*n*-alkyl Dithioacetals: Novel Double-Tailed Thermotropic Liquid Crystals

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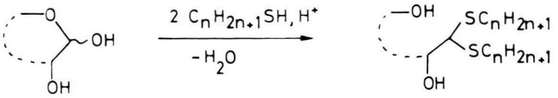
Liquid Crystals, Aldose Di-*n*-alkyl Dithioacetals, Double-Tailed Amphiphiles

Mercaptolyses of the pentoses [D-lyxose (**1**), D-xylose (**2**), L-arabinose (**3**)] and hexoses [D-mannose (**4**), D-glucose (**5**), D-galactose (**6**)] with *n*-alkyl thiols having chain lengths $\geq C_6$ gives mesogenic aldose di-*n*-alkyl dithioacetals **7–12.**

All of the mesogenic carbohydrate derivatives described hitherto are amphiphiles consisting of a carbohydrate headgroup linked to one *n*-alkyl chain [2]. The interest in such compounds has escalated recently and new stable non-glycosidic mesogens which have been reported include 1-O- and S-*n*-alkyl alditols [3, 4], 1-O-*n*-alkyl-2,5-anhydro-hexitols [5], 1-C-*n*-alkyl-2,5-anhydro-L-iditols [6] and the naturally occurring 1-C-*n*-alkyl tetraols [7].

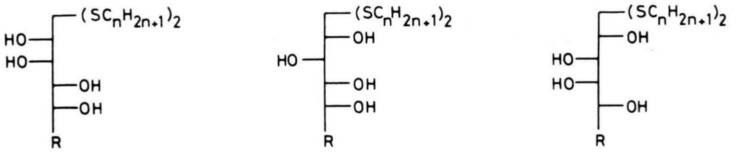
In the course of our work concerned with structure – property correlations of amphiphilic carbohydrates, it has now been found that simple double-tailed aldoses, such as aldose di-*n*-alkyl dithioacetals having sufficiently long *n*-alkyl chains are thermotropic mesogens.

Aldose di-*n*-alkyl dithioacetals are readily prepared by condensation of aldoses with *n*-alkyl thiols in the presence of acid catalyst [8, 9].



Although D-glucose di-*n*-octyl dithioacetal has been reported [10], it was not recognised as being a thermotropic liquid crystal.

Mercaptolyses of the pentoses D-lyxose (**1**), D-xylose (**2**), L-arabinose (**3**) and the hexoses D-mannose (**4**), D-glucose (**5**) and D-galactose (**6**) were easily carried out under standard conditions [11] or in the presence of $ZnCl_2/CaCl_2$ [10] at room temperature.



R	*n*		R	*n*		R	*n*	
H	8	**7a**	H	7	**9a**	H	8	**11a**
H	10	**7b**	H	8	**9b**	H	10	**11b**
CH_2OH	6–10	**8a–8e**	CH_2OH	8	**10a**	CH_2OH	7	**12a**
			CH_2OH	10	**10b**	CH_2OH	8	**12b**

The reaction times varied between 1–8 h, depending on the aldose (**1–6**) and the chain length of the *n*-alkylthiol, and the simple work-up consisted of addition of cold water, filtration and subsequent filtration and subsequent crystallisation from diethyl ether for **7, 8, 10–12.** The D-xylose di-*n*-heptyl and *n*-octyl dithioacetals **9a** and **9b** which are liquid crystals at room temperature were purified by column chromatography. Thus the pure mesogenic **7–12** were obtained in 20–60% yields from the respective educts **1–6** (s. Table). The purities of **7–12** were confirmed to be >98% by GC-analyses [14] after acetylating with acetic anhydride in pyridine.

The liquid crystal ranges of these novel mesogens were determined by polarizing microscopy [12] and by D. S. C. which gave accurate values for both the melting and clearing points. All of the double-tailed **7–12** appear to have smectic B textures (paramorphic truncated focal-conic fan texture as depicted in plate 10 [12]). It should however be noted that the assignment of the correct mesophases to amphiphilic

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Table. Preparations of **7–12**, their phase transition temperatures and enthalpies[a].

Aldose[b] Dithioacetal	Reaction[c] time [h]	Yield[d] [%]	$[\alpha]_D^{20}$ (c, CH_3OH)	MS[e]	m.p. [°C]	ΔH [$kJ\,mol^{-1}$]	c.p. [°C]	ΔH [$kJ\,mol^{-1}$]
7a	1	97 (33)	4.3° (0.5)	424	56.4	15	104.2	1.4
7b	5	45 (24)	11.0° (0.3)	480	63.9	47.1	109.8	1.5
8a	3	79 (61)	10.6° (0.6)	398	113.1	40.8	117.6	1.5
8b	3	80 (40)	10.1° (0.9)	426	109.5	41.3	134.7	1.6
8c	6	55 (50)	10.3° (0.7)	454	110.2	41.8	144.0	1.4
8d	6	(36)	8.0° (0.4)	482	107.0	43.0	138.5	1.4
8e	6	73 (44)	8.3° (0.4)	510	111.4	51	152.0	1.7
9a	2.5	42[f]	− 3.8° (2)	396	<0	–	78.1	1.0
9b	4	53 (25)[f]	− 1° (0.9)	424	<0	–	77.4	0.9
10a	5	73 (60)	− 3.6° (0.6)	454	100.1	48	118.9	1.0
10b	8	50 (35)	− 2° (0.4)	510	96.7	50.8	131.8	1.4
11a	4	75 (55)	17.3° (0.4)	424	83.0	46	101.6	1.3
11b	7	52 (25)	24° (0.4)	480	86.7	45	104.3	1.4
12a	5	62 (50)	8.8° (0.7)	426	115.1	47.9	137.3	2.0
12b	6	40 (22)	15.3° (0.6)	454	110.7	45	142.9	1.9

[a] Determined by D.S.C. using a DuPont 1090 Thermal Analyzer; [b] all products has satisfactory C, H, S analyses; [c] shaking reaction mixture at room temperature; [d] crude product and ( ) after recrystallisation from diethyl ether; [e] molecular weights were confirmed by DCI-MS using ammonia as the reactant gas [13]; [f] purified by column chromatography on silica gel, eluent: ethyl acetate/pentane 4:1 (R_f **9a** 0.31, **9b** 0.35).

carbohydrates is very difficult because *e.g.* miscibility experiments cannot be carried out as the known standard reference compounds are non-hydrogen bonding [15].

The new mesogens **7–12** offer manifold possibilities as intermediates in the syntheses of other types of amphiphilic carbohydrates by conventional dithioacetal transformations [9].

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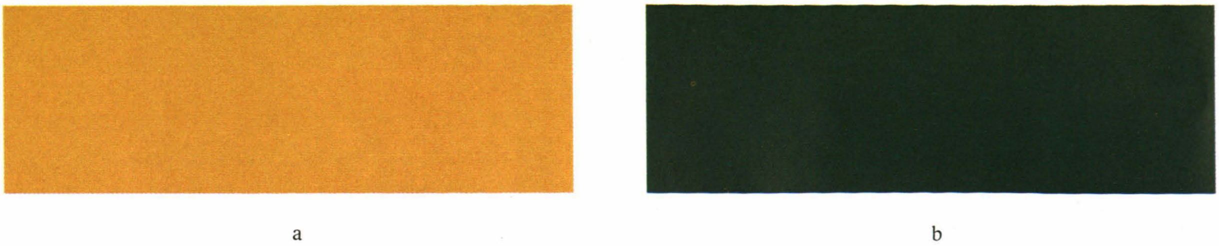

Abb. 1: Farbabzüge von gelbem (a) und grünem Sodalith (b)
Die Proben wurden durch einstündiges Erhitzen von farblosem Thiocyanat-Sodalith auf 1000 °C unter Stickstoff (a) bzw. in Luft oder Sauerstoff erhalten.

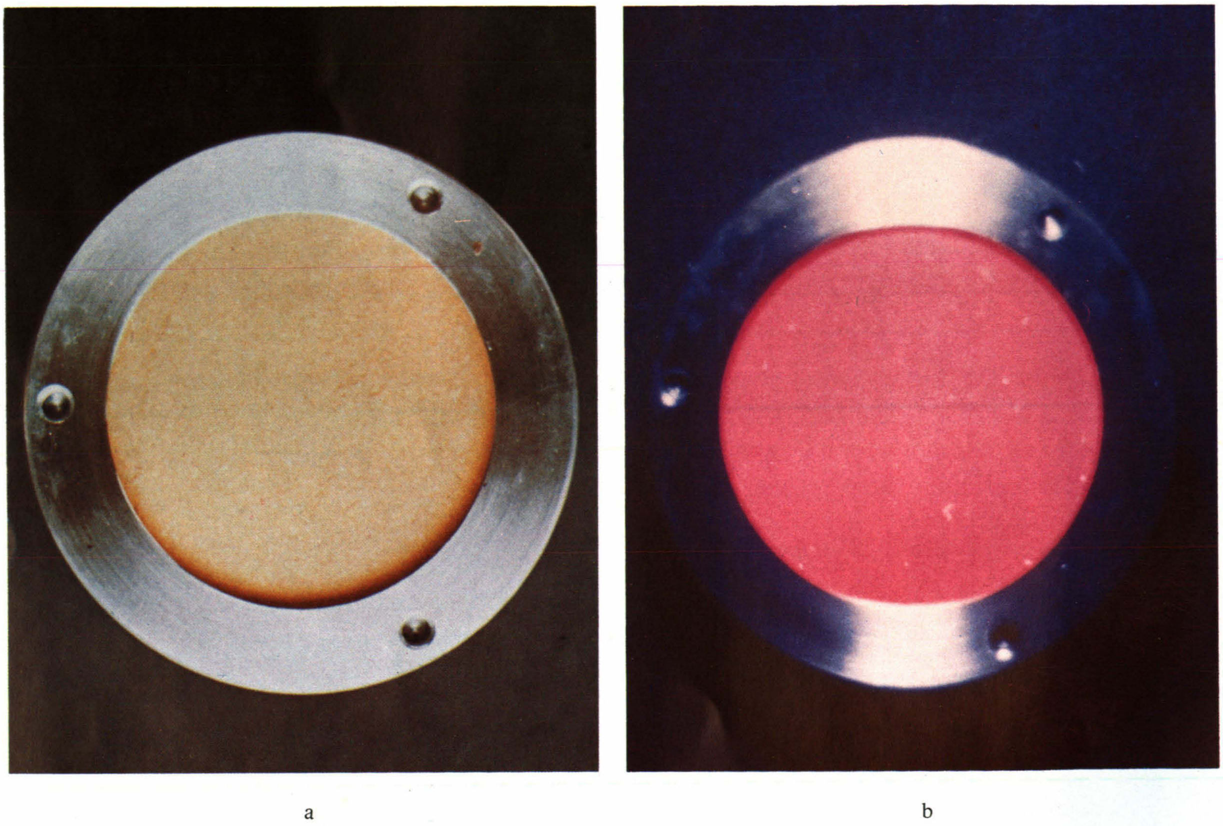

Abb. 2: Ultramarin-Gelb II im Tageslicht (a) und im UV-Licht mit einer Wellenlänge von 370 nm.