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# Liquid Crystals

Publication details, including instructions for authors and subscription information:
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**To cite this Article** Henk, A. , Doren, Van , Van Der Geest, Ralph , Keuning, Cor A. , Kellogg, Richard M. and Wynberg, Hans(1989) 'Synthesis and mesogenic properties of several homologous series of aldose dialkyl dithioacetals. A model for their behaviour', Liquid Crystals, 5: 1, 265 — 283

**To link to this Article: DOI:** 10.1080/02678298908026369

**URL:** http://dx.doi.org/10.1080/02678298908026369

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LIQUID CRYSTALS, 1989, VOL. 5, NO. 1, 265–283

# Synthesis and mesogenic properties of several homologous series of aldose dialkyl dithioacetals

## A model for their behaviour

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Ten homologous series (*n*-butyl through *n*-decyl) of aldose *S*,*S*-acetals (D-glucose, D-galactose, D-mannose, L-rhamnose, 2-deoxy-D-glucose, D-xylose, D-lyxose, D- or L-arabinose, D-ribose and 2-deoxy-D-ribose) have been prepared. Most of these compounds form thermotropic liquid crystals, the exceptions being the entire L-rhamnose series and some of the derivatives with the shortest alkyl chains. All of the compounds have been investigated with differential scanning calorimetry and polarization microscopy. Some temperature dependent powder X-ray data are also presented. A model is proposed which correlates the carbohydrate configuration with the melting behaviour. On the basis of now available behaviourial characteristics, visual inspection, mixing experiments and precedent, the mesophase is identified as smectic $A_d$, the partially overlapping carbohydrate moieties being in the centre and the aliphatic chains pointing outward at an angle of about 62°. Despite the intrinsic chirality of all the carbohydrate mesogens, no evidence for chiral mesophases was found, not even after introduction of a homochiral branched alkyl chain.

## 1. Introduction

Recently the synthesis and thermotropic behaviour of some aldose dialkyl dithioacetals were reported by three different groups [1–3]. These compounds are the first known carbohydrate mesogens with two alkyl chains. It was shown that the occurrence of a mesophase and the temperature range over which a mesophase is observed, depend strongly upon the starting monosaccharide. We are interested in this relationship between the configuration of the carbohydrate moiety and liquid-crystalline properties. In addition there has been no agreement so far on the nature of the mesophase formed (smectic B [1], smectic $A_d$ [2] or perhaps even a discotic mesophase [3]). We decided therefore to subject the aldose *S*,*S*-acetals to a more thorough examination. We report our findings in this paper.

## 2. Experimental

The reaction between aldoses and alkanethiols was first reported in 1894 [4]. Since then much research on the aldose *S*,*S*-acetals has been carried out [5] but the reaction procedure has remained essentially the same: the aldose is dissolved in a small volume of concentrated hydrochloric acid, two equivalents of alkanethiol are added and the

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mixture is stirred until a paste is formed. Water is added to precipitate the product which is then washed several times with water and bicarbonate solution to remove the hydrochloric acid. Small amounts of alkyl 1-thioglycoside are usually formed as a side-product, which can be removed by recrystallization. With some aldoses and longer alkyl chains (≥octyl), addition of anhydrous zinc chloride and calcium chloride will speed up the reaction and increase the yields.

The products were characterized with the aid of N.M.R. spectroscopy and elemental analysis. Liquid-crystalline behaviour was determined visually with a Mettler FP82 hot stage mounted on a Nikon polarization microscope and with a Perkin–Elmer Delta Series DSC7 apparatus. Dr. F. van der Horst (Department of Solid State Physics, University of Groningen) kindly performed temperature dependent powder X-ray measurements (Guinier camera) on a number of compounds to determine the *d* spacings of the mesophases.

## 3. Results

### 3.1. *Synthesis*

Homologous series ranging from *n*-butyl through *n*-decyl of the following ten aldoses were synthesized: D-glucose, D-galactose, D-mannose, L-rhamnose (= 2-deoxy-L-mannose), 2-deoxy-D-glucose, D- or L-arabinose, D-lyxose, D-xylose, D-ribose and 2-deoxy-D-ribose. The pure compounds were obtained after recrystallization from ethanol, methanol, ethyl acetate, ether or hexane. In some cases where the melting points are near room temperature recrystallization was carried out at −20°C and the pure product was obtained by centrifugation at low temperature. A few other derivatives were synthesized starting from L-fucose (= 6-deoxy-L-galactose), D-erythrose, D,L-glyceraldehyde and glycolaldehyde. Finally we prepared two derivatives with a branched alkyl chain (racemic and homochiral 3,7-dimethyloctyl).

### 3.2. *Thermal behaviour*

The transition temperatures and enthalpy data for the ten homologous series of aldose *S*,*S*-acetals are given in tables 1–10. Plotting the transition temperatures as a function of the alkyl chain length leads to figures 1–10. The data for the other derivatives are given in table 11.

Table 1. Transition temperatures† and enthalpy data† for a series of D-glucose *S*,*S*-acetals.

| D-Glucose *S*,*S*-acetal | m.p./°C | $\Delta H$/kJ mol$^{-1}$ | c.p.‡/°C | $\Delta H$/kJ mol$^{-1}$ |
|---|---|---|---|---|
| Dibutyl | 124·8–126·8 | 50·2 | — | — |
| Dipentyl | 115·1–116·4 | 49·1 | — | — |
| Dihexyl§ | 103·1–104·4 | 44·6 | — | — |
| Diheptyl | 102·2–103·6 | 51·2 | 104·7(103·8) | 1·1 |
| Dioctyl | 98·9–100·3 | 47·0 | 116·6(116·1) | 1·3 |
| Dinonyl | 99·0–101·2 | 49·0 | 125·8(125·3) | 1·4 |
| Didecyl | 96·5– 98·7 | 53·1 | 130·8(130·1) | 1·6 |

† Measured at 5 K min$^{-1}$ with a Perkin–Elmer DSC7.
‡ Values in parentheses observed upon cooling.
§ Crystal–crystal transition 99·7–101·0°C, $\Delta H$ = 5·9 kJ mol$^{-1}$.

Table 2. Transition temperatures† and enthalpy data† for a series of D-galactose *S*,*S*-acetals.

| D-Galactose *S*,*S*-acetal | m.p./°C | $\Delta H$/kJ mol$^{-1}$ | c.p.‡/°C | $\Delta H$/kJ mol$^{-1}$ |
|---|---|---|---|---|
| Dibutyl | 125·7–126·2 | 46.4 | — | — |
| Dipentyl§ | 118·4–119·4 | 41·1 | — (109·3) | 1·8 |
| Dihexyl | 115·0–117·1 | 43·7 | 125·7(124·6) | 1·9 |
| Diheptyl‖ | 114·1–116·0 | 44·2 | 136·1(135·5) | 1·9 |
| Dioctyl¶ | 111·8–113·5 | 46·1 | 141·8(141·1) | 1·9 |
| Dinonyl* | 109·1–111·0 | 41·9 | 145·3(145·1) | 1·8 |
| Didecyl | 108·1–110·2 | 46·0 | 147·0(146·1) | 2·0 |

† Measured at 5 K min$^{-1}$ with a Perkin–Elmer DSC 7.
‡ Values in parentheses observed upon cooling.
§ Crystal–crystal transition 110·3–112·4°C, $\Delta H$ = 2·7 kJ mol$^{-1}$.
‖ Crystal–crystal transition 85·6– 86·1°C, $\Delta H$ = 1·4 kJ mol$^{-1}$.
¶ Crystal–crystal transition 73·6– 78·5°C, $\Delta H$ = 16·4 kJ mol$^{-1}$.
* Crystal–crystal transition 74·8– 78·1°C, $\Delta H$ = 22·8 kJ mol$^{-1}$.

Table 3. Transition temperatures† and enthalpy data† for a series of D-mannose *S*,*S*-acetals.

| D-Mannose *S*,*S*-acetal | m.p./°C | $\Delta H$/kJ mol$^{-1}$ | c.p.‡/°C | $\Delta H$/kJ mol$^{-1}$ |
|---|---|---|---|---|
| Dibutyl | 115·6–117·5 | 42·3 | — | — |
| Dipentyl | 116·3–118·6 | 45·5 | (102)‖ | |
| Dihexyl§ | 116·3–118·3 | 46·3 | 120·6(119·7) | 1·7 |
| Diheptyl | 115·0–117·0 | 47·1 | 134·5(133·6) | 1·9 |
| Dioctyl | 113·0–115·3 | 49·0 | 142·9(142·1) | 1·9 |
| Dinonyl | 111·6–113·5 | 51·2 | 147·7(147·3) | 2·0 |
| Didecyl | 110·2–111·8 | 50·7 | 150·6(150·0) | 1·8 |

† Measured at 5 K min$^{-1}$ with a Perkin–Elmer DSC 7.
‡ Values in parentheses observed upon cooling.
§ Crystal–crystal transition 71·7–74·6°C, $\Delta H$ = 31·6 kJ mol$^{-1}$.
‖ Observed in a crude sample with a Mettler FP82 hot stage.

Table 4. Transition temperatures† and enthalpy data† for a series of 2-deoxy-D-glucose *S*,*S*-acetals.

| 2-Deoxy-D-glucose *S*,*S*-acetal | m.p./°C | $\Delta H$/kJ mol$^{-1}$ | c.p.‡/°C | $\Delta H$/kJ mol$^{-1}$ |
|---|---|---|---|---|
| Dibutyl | 135·4–137·1 | 60·3 | — — | — |
| Dipentyl | 119·4–120·9 | 63·1 | — — | — |
| Dihexyl§ | 112·6–113·8 | 45·0 | — — | — |
| Diheptyl | 113·5–115·2 | 72·4 | — (110·3) | 1·6 |
| Dioctyl | 111·0–112·6 | 65·2 | 117·3(116·6) | 1·7 |
| Dinonyl | 111·3–113·4 | 66·6 | 120·3(119·5) | 1·6 |
| Didecyl | 112·0–113·7 | 66·4 | 122·3(122·1) | 1·6 |

† Measured at 5 K min$^{-1}$ with a Perkin–Elmer DSC 7.
‡ Values in parentheses observed upon cooling (5 K min$^{-1}$).
§ Crystal–crystal transition at 102·2–104·2°C, $\Delta H$ = 16·4 kJ mol$^{-1}$.

Table 5. Transition temperatures† and enthalpy data† for a series of L-rhamnose *S*,*S*-acetals.

| L-Rhamnose *S*,*S*-acetal | m.p./°C | Δ*H*/kJ mol$^{-1}$ | c.p./°C | Δ*H*/kJ mol$^{-1}$ |
|---|---|---|---|---|
| Dibutyl | 114·5–118·8‡ | 37·9 | – | – |
| Dipentyl | 114·0–116·1 | 46·5§ | – | – |
| Dihexyl | 113·9–116·1 | 48·5 | – | – |
| Diheptyl‖ | 114·8–116·2 | 52·4 | – | – |
| Dioctyl | 114·1–115·3 | 54·7 | – | – |
| Dinonyl¶ | 113·3–115·0 | 54·4 | – | – |
| Didecyl* | 111·1–113·0 | 53·5 | – | – |

† Measured at 5 K min$^{-1}$ with a Perkin–Elmer DSC 7.
‡ Melting point is preceded by several other transitions.
§ Includes small crystal–crystal transition from 113·3–113·8°C.
‖ C–C transition 56·2–56·8°C, Δ*H* = 7·3 kJ mol$^{-1}$.
¶ C–C transition 67·6–70·1°C, Δ*H* = 24·7 kJ mol$^{-1}$.
* C–C transition 58·6–59·7°C, Δ*H* = 26·1 kJ mol$^{-1}$.

Table 6. Transition temperatures† and enthalpy data† for a series of D- or L-arabinose *S*,*S*-acetals.

| D- or L-Arabinose *S*,*S*-acetal | m.p./°C | Δ*H*/kJ mol$^{-1}$ | c.p.‡/°C | Δ*H*/kJ mol$^{-1}$ |
|---|---|---|---|---|
| (L-)-Dibutyl | 105·5–108·8 | 41·5 | – | – |
| (L-)-Dipentyl | 93·3– 96·3 | 37·3 | – | – |
| (L-)-Dihexyl§ | 93·0– 95·1 | 39·2 | – (85·0) | 1·4 |
| (D-)-Diheptyl | 90·4– 92·6 | 41·1 | 96·0 (95·8) | 1·5 |
| (D-)-Dioctyl | 87·5– 89·2 | 23·2‖ | 102·0(101·6) | 1·6 |
| (D-)-Dinonyl¶ | 86·4– 89·7 | 40·0 | 103·5(103·0) | 1·6 |
| (D-)-Didecyl* | 85·7– 88·2 | 42·6 | 105·1(104·4) | 1·6 |

† Measured at 5 K min$^{-1}$ with a Perkin–Elmer DSC 7.
‡ Values in parentheses observed upon cooling.
§ Crystal–crystal transition: 71·3–72·6°C, Δ*H* = 6·7 kJ mol$^{-1}$.
‖ During melting at 5 K min$^{-1}$ exothermal recrystallization occurs.
¶ C–C: 79·9–80·6°C, Δ*H* = 2·0 kJ mol$^{-1}$.
* C–C: 80·6–81·5°C, Δ*H* = 0·7 kJ mol$^{-1}$.

Table 7. Transition temperatures† and enthalpy data† for a series of D-lyxose *S*,*S*-acetals.

| D-Lyxose *S*,*S*-acetal | m.p./°C | Δ*H*/kJ mol$^{-1}$ | c.p.‡/°C | Δ*H*/kJ mol$^{-1}$ |
|---|---|---|---|---|
| Dibutyl | 74·4–76·3 | 32·8 | – | – |
| Dipentyl | 69·5–70·6 | 32·4 | (67·8) | 1·2 |
| Dihexyl | 63·7–66·4 | 21·5 | 85·5 (84·4) | 1·4 |
| Diheptyl§ | 65·4–67·9 | 22·5 | 97·7 (96·7) | 1·6 |
| Dioctyl‖ | 63·2–65·4 | 21·5 | 103·8(103·9) | 1·7 |
| Dinonyl | 65·9–68·2 | 43·1 | 107·1(106·6) | 1·5 |
| Didecyl | 65·5–67·3 | 44·8 | 107·6(107·0) | 1·8 |

† Measured at 5 K min$^{-1}$ with a Perkin–Elmer DSC 7.
‡ Values in parentheses observed upon cooling.
§ C–C: 55·9–59·4°C, Δ*H* = 14·8 kJ mol$^{-1}$.
‖ C–C: 53·5–55·6°C, Δ*H* = 14·5 kJ mol$^{-1}$.

Table 8. Transition temperatures† and enthalpy data† for a series of D-ribose *S,S*-acetals.

| D-Ribose *S,S*-acetal | m.p./°C | $\Delta H$/kJ mol$^{-1}$ | c.p.‡/°C | $\Delta H$/kJ mol$^{-1}$ |
|---|---|---|---|---|
| Dibutyl§ | 45·0–51·2 | 23·0 | – | – |
| Dipentyl‖ | 1·9– 4·4 | 2·1 | 46·3 (44·3) | 0·6 |
| Dihexyl‖ | 5·1– 7·1 | 5·2 | 82·5 (81·8) | 1·2 |
| Diheptyl¶ | 41·2–44·2 | 25·0 | 89·1 (88·4) | 1·5 |
| Dioctyl* | 36·3–41·0 | 35·6 | 98·5 (97·0) | 1·6 |
| Dinonyl | 37·1–44·3 | 27·8 | 98·3 (98·1) | 1·4 |
| Didecyl | 47·9–49·5 | 52·4 | 105·2(104·6) | 1·6 |

† Measured at 5 K min$^{-1}$ with a Perkin–Elmer DSC 7.

‡ Values in parentheses observed upon cooling.

§ Melting point preceded by crystal–crystal transition. Also crystal–crystal transition at: 24·1–25·1°C, $\Delta H$ = 1·06 kJ mol$^{-1}$.

‖ Compounds liquefy at room temperature after isolation.

¶ C–C: 33·4°C, $\Delta H$ = 3·92 kJ mol$^{-1}$. C–C: 35·6–36·1°C, $\Delta H$ = 1·76 kJ mol$^{-1}$.

* C–C: 6·2–9·7°C, $\Delta H$ = 1·56 kJ mol$^{-1}$.

Table 9. Transition temperatures† and enthalpy data† for a series of D-xylose *S,S*-acetals.

| D-Xylose *S,S*-acetal | m.p./°C | $\Delta H$/kJ mol$^{-1}$ | c.p.‡/°C | $\Delta H$/kJ mol$^{-1}$ |
|---|---|---|---|---|
| Dibutyl | $<0$ | – | – | – |
| Dipentyl | $<0$ | – | 37·4§ | –§ |
| Dihexyl | $<0$ | – | 68·0(67·0) | 0·9 |
| Diheptyl | 6·7–12·2 | 5·1 | 79·0(79·0) | 1·1 |
| Dioctyl | 20·0–22·5 | 25·1 | 87·6(86·5) | 1·0 |
| Dinonyl | 42·1–46·7 | 26·1 | 95·6(95·4) | 1·3 |
| Didecyl | 39·7–42·1 | 22·6‖ | 85·7 | 0·3 |

† Measured at 5 K min$^{-1}$ with a Perkin–Elmer DSC 7.

‡ Values in parentheses observed upon cooling.

§ Observed visually with Mettler FP 82 hot stage.

‖ Includes preceding C–C transitions.

Table 10. Transition temperatures†‡ for a series of 2-deoxy-D-ribose *S,S*-acetals.

| 2-Deoxy-D-ribose *S,S*-acetal | m.p./°C | c.p.§/°C |
|---|---|---|
| Dibutyl | $<rT$ | 29·4(28·0) |
| Dipentyl | $<rT$ | 53·6(52·0) |
| Dihexyl | $<rT$ | 65·7(64·6) |
| Diheptyl | $<rT$ | 75·4(74·4) |
| Dioctyl | $<rT$ | 82·8(79·4) |
| Dinonyl | $<rT$ | 84·2(81·2) |
| Didecyl | $<rT$ | 75·9(72·7) |

† Measured at 5 K min$^{-1}$ with Mettler FP 82 hot stage.

‡ Liquid crystalline at room temperature (rT), no solidification observed.

§ Values in parentheses observed upon cooling.

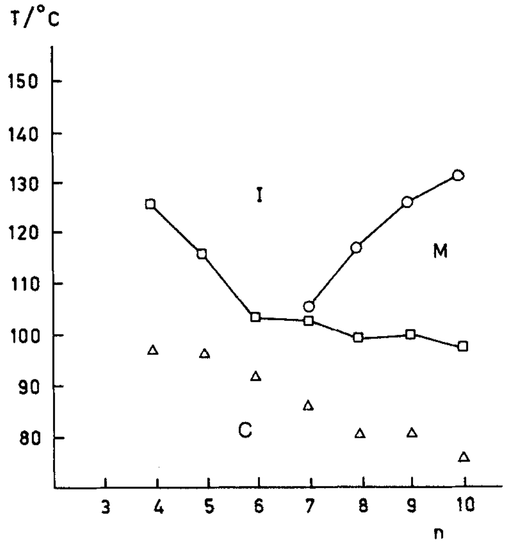


Figure 1. The transition temperatures of a series of D-glucose *S*,*S*-acetals plotted as a function of the number of carbon atoms in the alkyl chains. □, melting point; ○, clearing point; △, recrystallization point.

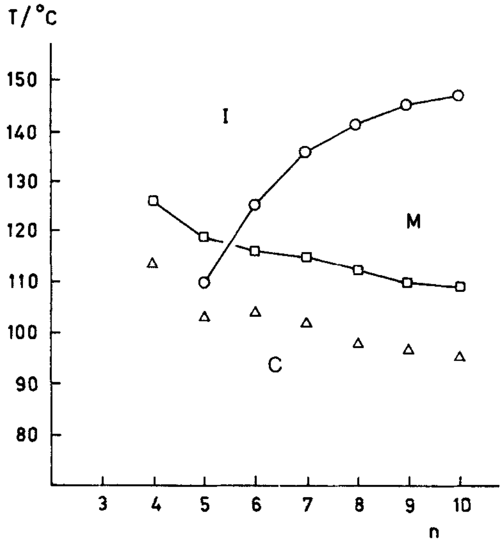


Figure 2. The transition temperatures of a series of D-galactose *S*,*S*-acetals plotted as a function of the number of carbon atoms in the alkyl chains. □, melting point; ○, clearing point; △, recrystallization point.

### 3.3. *Powder X-ray data*

Tables 12 and 13 show the *d* spacings as determined by powder X-ray measurements for a series of D-galactose *S*,*S*-acetals and for the dioctyl dithioacetals of some of the other aldoses.

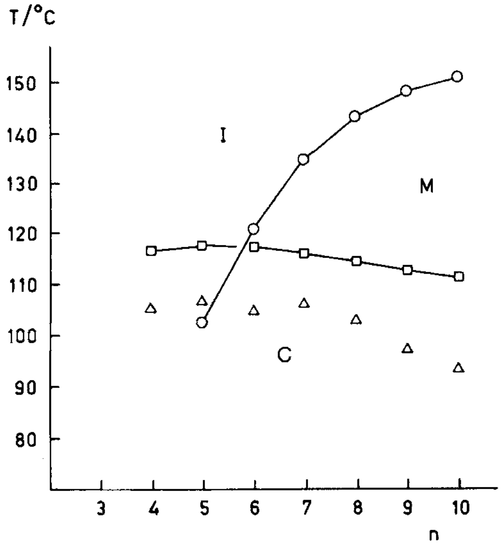


Figure 3. The transition temperatures of a series of D-mannose *S*,*S*-acetals plotted as a function of the number of carbon atoms in the alkyl chains. □, melting point; ○, clearing point, △, recrystallization point.

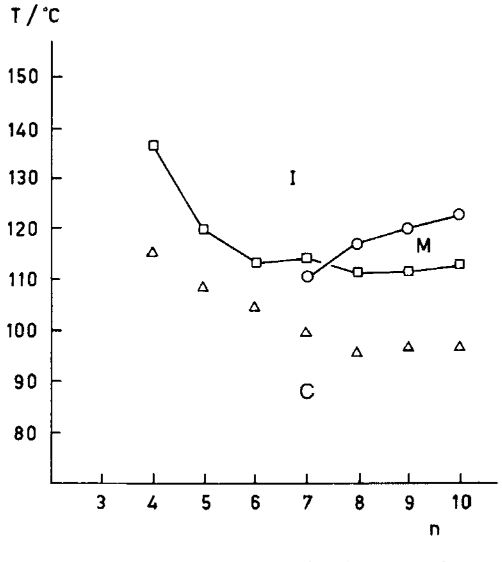


Figure 4. The transition temperatures of a series of 2-deoxy-D-glucose *S*,*S*-acetals plotted as a function of the number of carbon atoms in the alkyl chains. □, melting point; ○, clearing point; △, recrystallization point.

## 4. Discussion

As can be seen from the data in tables 1–11, there is a substantial influence of the starting monosaccharide on the liquid-crystalline behaviour. The absence of a mesophase in the derivatives of 6-deoxysugars has been reported earlier [2, 3]. Thus far it had been assumed that the presence of at least a heptyl chain is required [3, 6, 7] to induce a mesophase, however we have found that in some of the series the pentyl- or

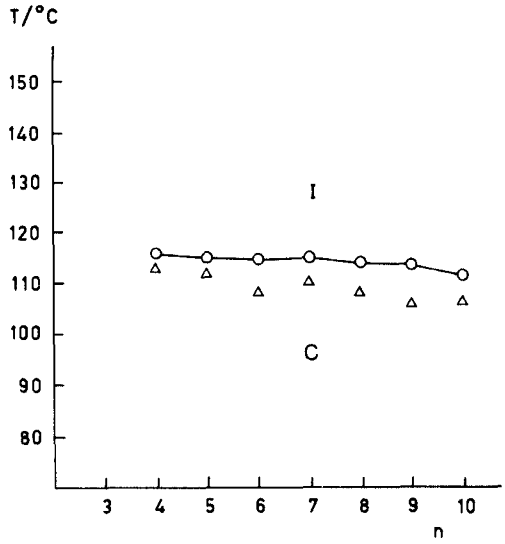


Figure 5. The transition temperatures of a series of L-rhamnose *S*,*S*-acetals plotted as a function of the number of carbon atoms in the alkyl chains. ○, melting point; △, recrystallization point.

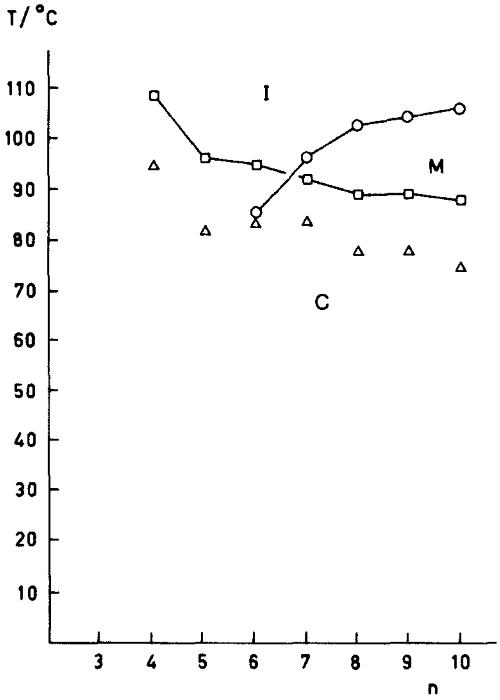


Figure 6. The transition temperatures of a series of D- or L-arabinose *S*,*S*-acetals plotted as a function of the number of carbon atoms in the alkyl chains. □, melting point; ○, clearing point; △, recrystallization point.

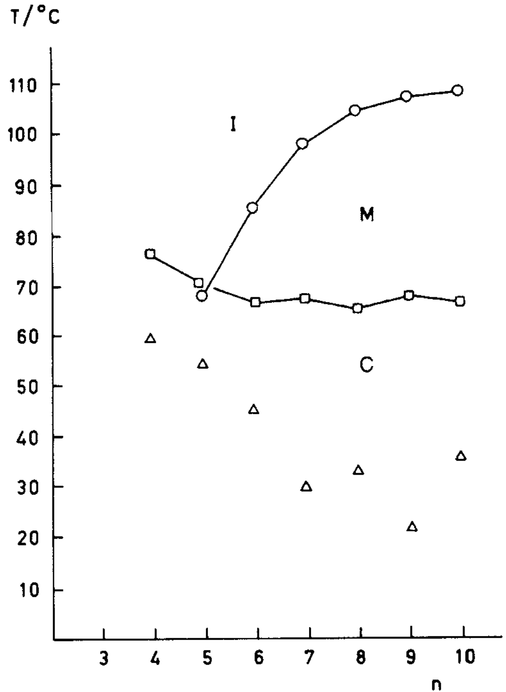


Figure 7. The transition temperatures of a series of D-lyxose *S*,*S*-acetals plotted as a function of the number of carbon atoms in the alkyl chains. □, melting point; ○, clearing point; △, recrystallization point.

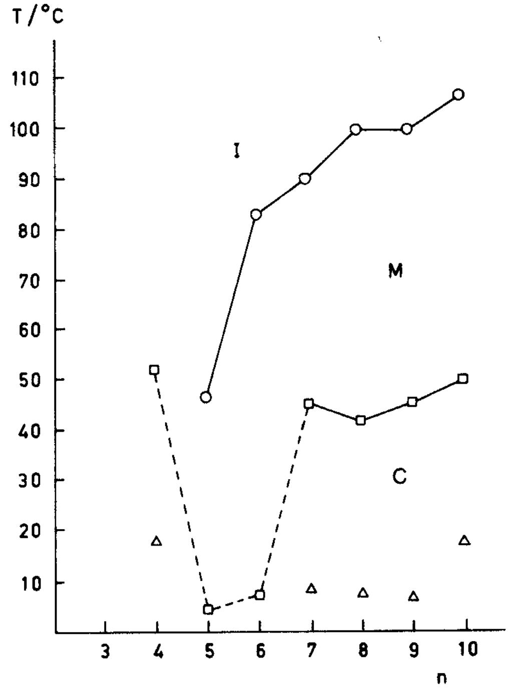


Figure 8. The transition temperatures of a series of D-ribose *S*,*S*-acetals plotted as a function of the number of carbon in the alkyl chains. □, melting point; ○, clearing point; △, recrystallization point.

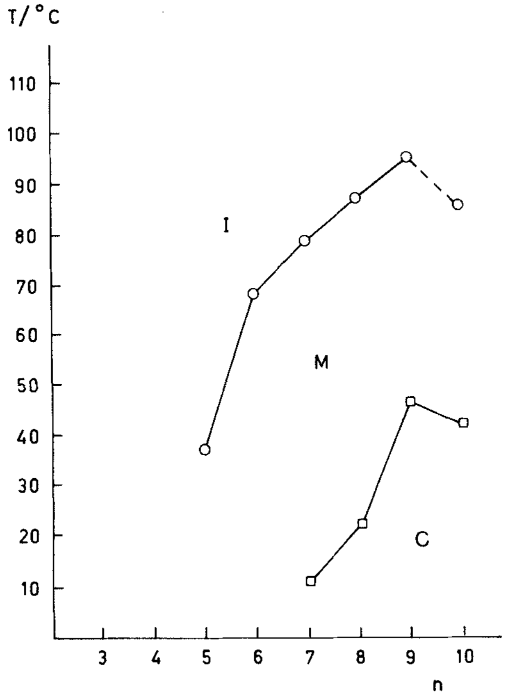


Figure 9. The transition temperatures of a series of D-xylose *S*,*S*-acetals plotted as a function of the number of carbon atoms in the alkyl chains. □, melting point; ○, clearing point.

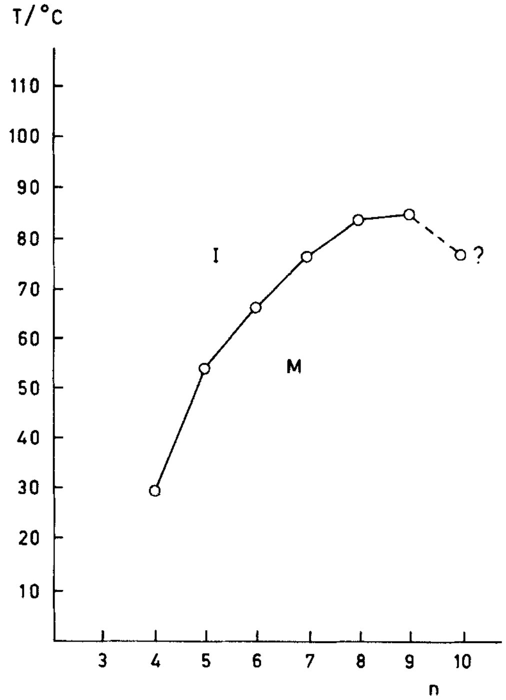


Figure 10. The transition temperatures of a series of 2-deoxy-D-ribose *S*,*S*-acetals plotted as a function of the number of carbon atoms in the alkyl chains. ○, clearing point.

Table 11. Transition temperatures† and enthalpy data† for a number of *S*,*S*-acetals.

| Compound | m.p./°C | $\Delta H$/kJ mol$^{-1}$ | c.p./°C | $\Delta H$/kJ mol$^{-1}$ |
|---|---|---|---|---|
| Glycolaldehyde dioctyl *S*,*S*-acetal | < −20 | – | – | – |
| D,L-Glyceraldehyde dioctyl *S*,*S*-acetal | 1·1–5·0 | 8·8 | – | – |
| D-Erythrose didecyl *S*,*S*-acetal | 28·9–35·0 | 21·8 | 62·4(58·3) | |
| L-Fucose dioctyl *S*,*S*-acetal‡ | 128·0–129·5 | 52·1 | – | – |
| D-Xylose di((*S*)-3,7-dimethyl) octyl *S*,*S*-acetal | < rT | – | 75·4 | 1·5 |
| D-Glucose di((*S*)-3,7-dimethyl octyl *S*,*S*-acetal | 107·7–109·8 | 49·8 | 108·2§ | 1·4 |

† Measured at 5 K min$^{-1}$ with a Perkin–Elmer DSC 7.
‡ Crystal–crystal transition: 74·4–75·6°C, $\Delta H$ = 7·8 kJ mol$^{-1}$.
§ Value obtained upon cooling (5 K min$^{-1}$).

Table 12. The *d* spacings of a series of D-galactose *S*,*S*-acetals at their melting and clearing points.

| Compound | *d* spacing/Å† | |
|---|---|---|
| | m.p. | c.p. |
| D-Galactose dihexyl dithioacetal | 24·5 | 24·3 |
| D-Galactose diheptyl dithioacetal | 25·8 | 25·1 |
| D-Galactose dioctyl dithioacetal | 26·8 | 26·0 |
| D-Galactose dinonyl dithioacetal | 28·2 | 26·9 |
| D-Galactose didecyl dithioacetal | 29·1 | 27·6 |

† Estimated standard deviations in the least significant digit, ±0·1 Å.

Table 13. The *d* spacings of the dioctyl dithioacetals of several aldoses at their melting and clearing points.

| Compound | *d* spacing/Å† | |
|---|---|---|
| | m.p. | c.p. |
| D-Glucose dioctyl dithioacetal‡ | 25·7 | 25·7 |
| 2-Deoxy-D-glucose dioctyl dithioacetal | 25·6 | 25·6 |
| D-Galactose dioctyl dithioacetal | 26·8 | 26·0 |
| D-Mannose dioctyl dithioacetal | 26·6 | 25·9 |
| L-Rhamnose dioctyl dithioacetal | –§ | –§ |
| D-Xylose dioctyl dithioacetal | 26·0‖ | 24·7 |

† Estimated standard deviations in the least significant digit, ±0·1 Å.
‡ Two separate lines are observed upon cooling (25·7 and 25·5 Å) at the clearing point.
§ No mesophase observed.
‖ Value measured at room temperature (25°).

even the butyl derivative will form a mesophase. The smallest carbohydrate moiety that will still yield a thermotropic *S*,*S*-acetal is D-erythrose, a $C_4$-monosaccharide. No liquid-crystalline behaviour could be observed in the *S*,*S*-acetals of glyceraldehyde and glycolaldehyde.

### 4.1. *Relationship between carbohydrate configuration and transition temperatures*

The crystal structures of several carbohydrate liquid crystals are known [8–14]. With the exception of acyclic compounds containing an ester or amide function [12–14] they are all very similar. The carbohydrate moieties are positioned head-to-head in layers that are held together by a network of hydrogen bonds. The aliphatic chains point outward (at an angle). There is nearly complete interdigitization with the hydrocarbon chains of the next layer. Jeffrey [6] proposes the following model for the thermotropic liquid crystal formation of carbohydrate derivatives: thermotropic liquid crystal formation can be seen as a two-stage melting process. At the melting point the hydrocarbon chains that are held together by weak van der Waals interactions disengage from the three dimensional crystal lattice while the hydrogen bonded carbohydrate layers remain intact, thus forming the backbone of the smectic layer. At the clearing point the carbohydrate layers melt and an isotropic liquid is formed.

The model is only qualitative but it allows us to make the following general predictions with regard to the transition temperatures of the aldose *S*,*S*-acetals:

- within one homologous series the clearing points would remain more or less constant, whereas the melting points would rise as we go to longer alkyl chains,
- when derivatives of the same molecular weight and the same alkyl chain length are compared, roughly the same melting points would be expected,
- the clearing points could show considerable variation as they are determined by the strength of the hydrogen bonded network, which in turn is determined by the carbohydrate configuration (see figure 11).

These consequences are obviously at odds with the experimental results.

We believe that the following qualitative model is in better agreement with the experimental results:

- the melting point is determined by the breakdown of the network of hydrogen bonds,
- upon melting the conformation of the carbohydrate moieties changes to form hydrogen bonded dimers that are the smectic species (similar to the 4-alkyl benzoic acid derivatives [15]). Layer formation is induced in a similar way as in classical liquid crystals (i.e. by stacking forces), possibly aided by some hydrogen bonding of the hydroxyl groups which are not involved in the formation of the dimer,
- at the clearing point these forces are no longer able to keep the layers intact and an isotropic liquid is formed.

The experimental data can now be more readily explained.

- Even though we have no crystallographic data for thermotropic *S*,*S*-acetals, we assume that the carbohydrate moiety is in the all-trans extended chain conformation in the solid state (cf. D-ribose *S*,*S*-diethyl acetal [16] and the *N*-alkyl-gluconamides [14]). This implies that there should be a considerable influence of the configuration of the hydroxyl groups on the strength of the network of hydrogen bonding. The carbohydrate portion of the D-xylose *S*,*S*-acetals has all

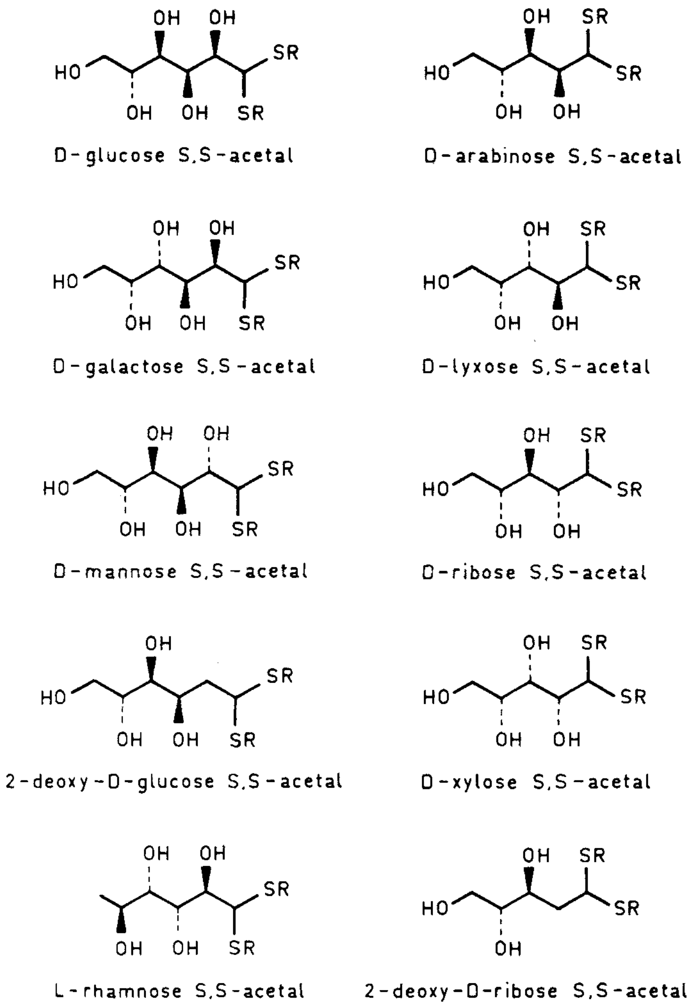
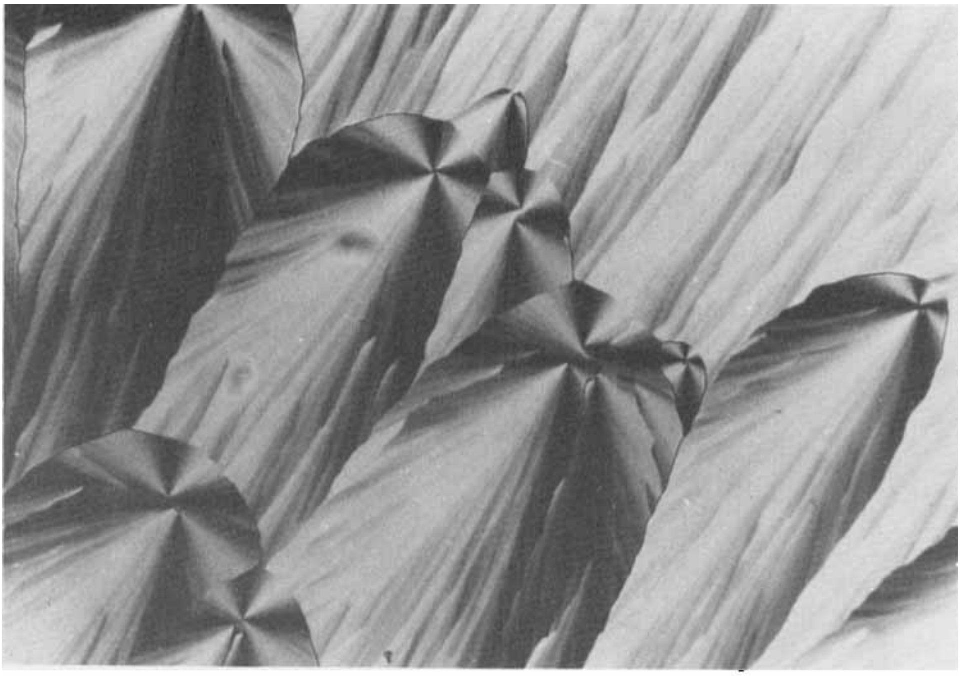

D-glucose S,S-acetal
D-arabinose S,S-acetal
D-galactose S,S-acetal
D-lyxose S,S-acetal
D-mannose S,S-acetal
D-ribose S,S-acetal
2-deoxy-D-glucose S,S-acetal
D-xylose S,S-acetal
L-rhamnose S,S-acetal
2-deoxy-D-ribose S,S-acetal

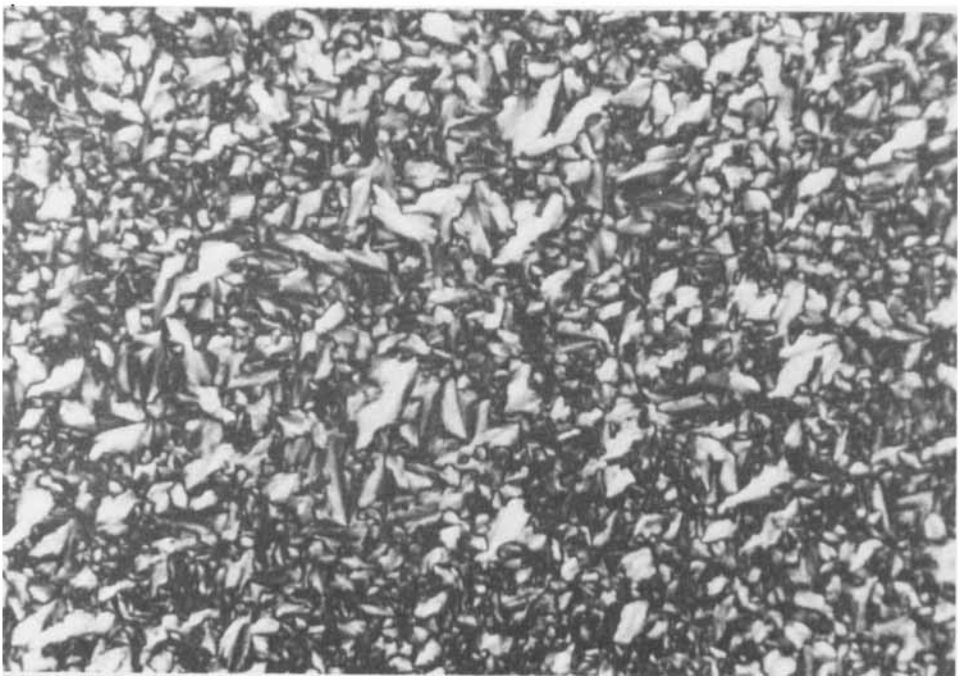
Figure 11. The configuration of the aldose *S*,*S*-acetals in the extended chain conformation.

its hydroxyl groups on one side of the molecule in the extended chain conformation. This is detrimental to the formation of a network of hydrogen bonds. The melting points of the xylose *S*,*S*-acetals should, consequently, be lower than those of the corresponding D-lyxose, D-ribose, D-arabinose derivatives, which is exactly what we find. Idose is the hexose with the same configurational features, but we have so far been unable to synthesize a long chain *S*,*S*-acetal based on idose. However, the reported low melting point of D-idose dibenzyl dithioacetal [17] does suggest similar behaviour.

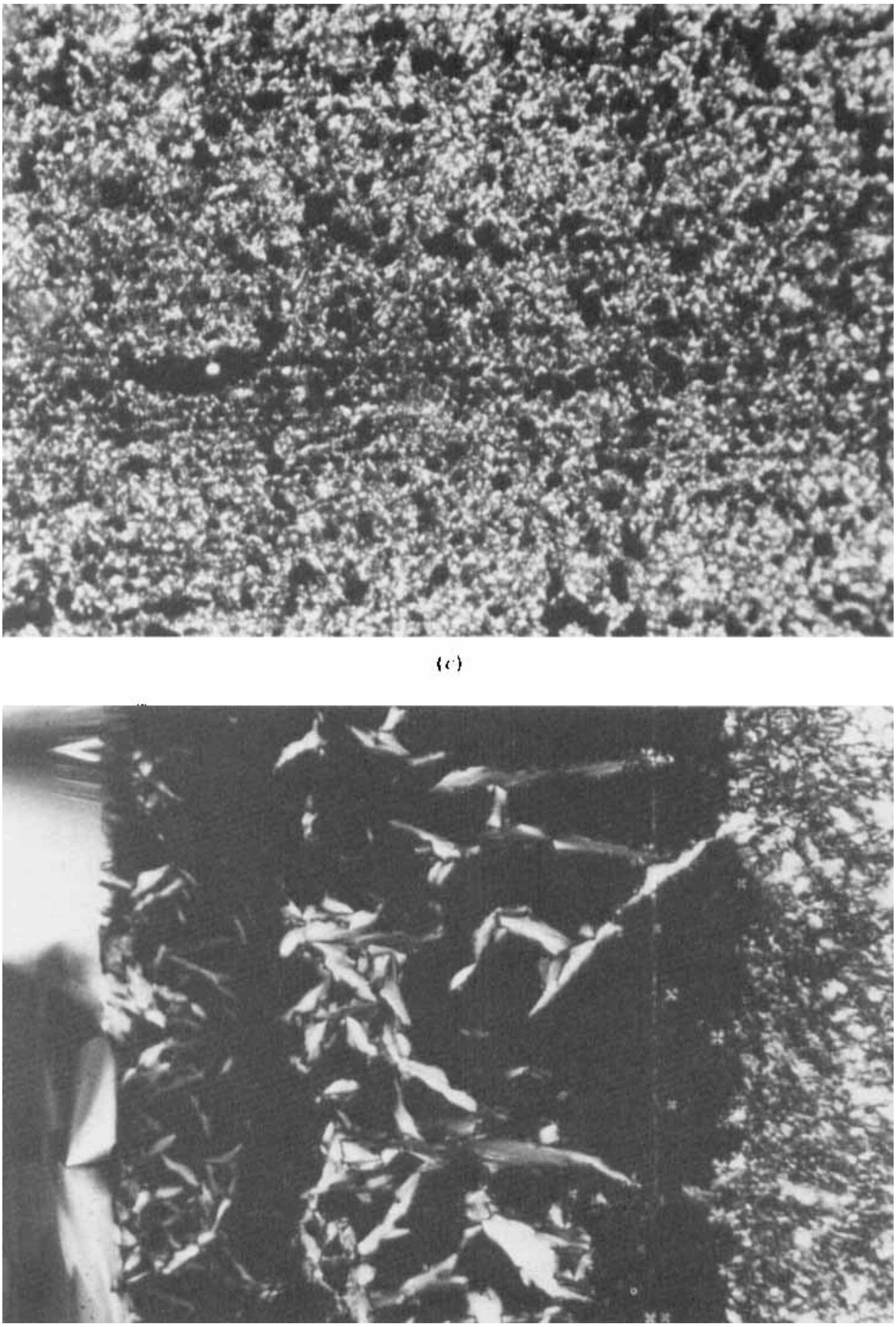
- The melting points within a series should remain more or less constant.
- The longer the alkyl chain, the more stable the layers. This only holds true for moderate chain lengths. The clearing points reach their maximum for $R$ = *n*-dodecyl or *n*-tridecyl [2]. Longer chains have a tendency to coil, which leads to destabilization of the layer.
- A branched alkyl chain should and does lead to lower clearing points, whereas the melting point is not greatly influenced.



(a)



(b)



(*c*)

(*d*)

Figure 12. The texture of the mesophases of (*a*) D-glucose dinonyl dithioacetal; (*b*) 1-(nonyl) amino-1-deoxy-D-glucitol; (*c*) a 1 : 1 mixture of D-glucose dinonyl dithioacetal and 1-(nonyl)amino-1-deoxy-D-glucitol; (*d*) a contact preparation of D-glucose dinonyl dithioacetal and 1-(nonyl)amino-1-deoxy-D-glucitol.

— Dimer formation is much less favourable when the hydroxyl group at C–6 is missing, thus explaining the absence of a mesophase in the rhamnose *S*,*S*-acetals.

### 4.2. *The mesophase*

The plots in figures 1–10 reveal a fairly typical behaviour for homologous series with a smectic mesophase [18] (with the exception, of course, of the L-rhamnose series in figure 5). The observed textures show a strong resemblance with the focal conic texture of the smectic A phase of *n*-decyl 4-(4′-phenylbenzylideneamino)cinnamate featured on the cover of Gray and Goodby [19]. Praefcke *et al.* [3] noted, however, that other typical smectic A characteristics such as bâtonnets, oily streaks as well as homeotropic areas coexisting with sharply defined focal conic, fan-like domains cannot be observed. Attempts to confirm the nature of the mesophase of carbohydrate liquid crystals by classical miscibility studies have been unsuccessful [20], making it very difficult to compare directly carbohydrate liquid crystals to the better known systems with an aromatic or alicyclic core. It is assumed that all carbohydrate liquid crystals reported so far with one aliphatic chain should be classified as smectic $A_d$ [7]. Temperature dependent powder X-ray data for several of the *S*,*S*-acetals are very similar to those for *S*-heptyl 1-thio-α-D-glucopyranoside [11, 22] and 1-(octyl)amino-1-deoxy-D-glucitol [21].

Praefcke *et al.* [3] have concluded that the mesophase for the *S*,*S*-acetals must be different from those reported earlier, because 1-*O*-octyl-β-D-glucopyranoside and D-lyxose dioctyl dithioacetal had immiscible mesophases.

We prepared an equimolar mixture of D-glucose *S*,*S*-dinonylacetal and 1-(nonyl)amino-1-deoxy-D-glucitol [21] (m.p. 124·5–127°C, c.p. 154·6°C) that was subjected to several heating and cooling cycles. A homogeneous sample is obtained which forms a single mesophase with a mosaic-like texture (see figure 12). The DSC cooling curve of the 1 : 1 mixture is compared with the curves of the pure components in figure 13. A contact preparation was cooled from isotropic to 125°C. After several hours a narrow band was visible where mixing had occurred. We repeated the entire experiment with D-glucose dinonyl dithioacetal and *S*-nonyl 1-thio-α-D-glucopyranoside [22] and obtained very similar results. We conclude therefore that the mesophase of the thermotropic *S*,*S*-acetals may be characterized as smectic $A_d$. (At the XIIth ILCC conference strong evidence for a hexagonal mesophase in the *S*,*S*-acetals was presented by K. Praefcke, B. Kohne, A. Eckert and M. Levelut. This would render our calculations incorrect for these compounds (as they are based on a $S_{A_d}$ phase) but nevertheless useful to present as a method of gathering information on the conformation of molecules in a bimolecular smectic layer.)

Performing a few simple calculations on the powder X-ray data for the series of D-galactose *S*,*S*-acetals (*n*-hexyl through *n*-decyl, see table 12) leads to very interesting results. Extrapolation of the *d* spacings at the melting point of the compounds (see table 12) would lead to a *d* spacing of about 18·6 Å for the imaginary mesophase of D-galactose dimethyl dithioacetal. One molecule of D-galactose dimethyl dithioacetal is approximately 12·0 Å long in the extended chain conformation. This implies that the maximum overlap (i.e. with the sugar moieties perpendicular to the plane of the layer) is of the order of 5·4 Å. If the alkyl chains were also perpendicular to the plane of the layer, addition of one methylene group (on both sides) would lead to a layer that is approximately 2·5 Å wider. For D-galactose dihexyl dithioacetal the *d* spacing would then be 18·6 + 5 × (2·5) = 31·1 Å. We find an actual *d* spacing of 24·5 Å, only

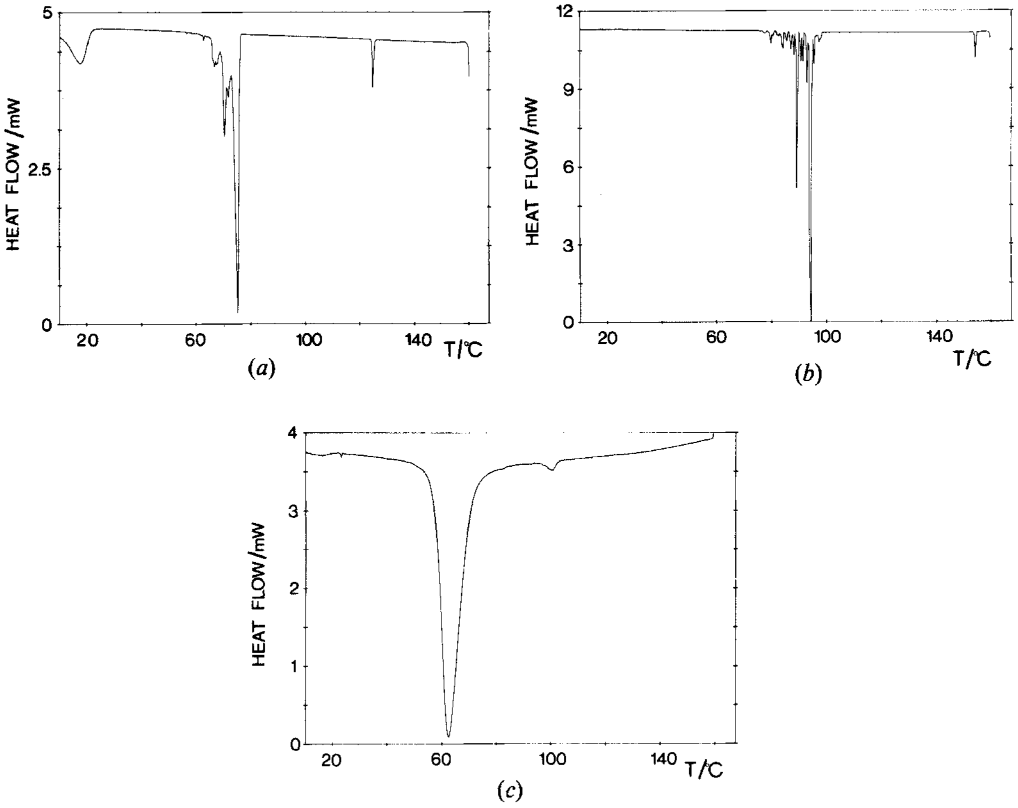


Figure 13. The D.S.C. cooling curves of (*a*) D-glucose dinonyl dithioacetyl (*b*) 1-(nonyl)amino-1-deoxy-D-glucitol and (*c*) their equimolar mixture. The cooling rate used was 5°C/min.

Table 14. The calculated tilt angle, $\alpha$, for the alkyl chains in the smectic layer.

| D-Galactose *S*,*S*-acetal | $\delta_{\mathrm{dcalc}}$/Å | At m.p. $\delta_{\mathrm{dexp}}$/Å | At m.p. $\alpha$/°† | At c.p. $\delta_{\mathrm{dexp}}$/Å | At c.p. $\alpha$/°† |
|---|---|---|---|---|---|
| di-Hexyl | 12·5 | 5·9 | 61·8 | 5·7 | 62·8 |
| di-Heptyl | 15 | 7·2 | 61·3 | 6·5 | 64·3 |
| di-Octyl | 17·5 | 8·2 | 62·1 | 7·4 | 65·0 |
| di-Nonyl | 20 | 9·6 | 61·3 | 8·3 | 65·5 |
| di-Decyl | 22·5 | 10·5 | 62·2 | 9·0 | 66·4 |

† Calculations based on: $\cos\alpha = [\delta_{\mathrm{d(exp)}}][\delta_{\mathrm{d(calc)}}]^{-1}$.

5·9 Å wider than the value calculated for D-galactose dimethyl dithioacetal. To account for these results, the alkyl chains must point away from the plane of the carbohydrate moieties at an angle of ~62° as derived from a simple calculation. ($\alpha$ is the tilt angle of the aliphatic chains calculated from the formula $\cos\alpha = [\delta d(\mathrm{exp})][\delta d(\mathrm{calc})]^{-1}$ where $\delta d(\mathrm{exp})$ is the measured $d$ spacing $-18{\cdot}6$ Å, the latter being the calculated length for the dimeric D-galactose dimethyl dithioacetal and $\delta d(\mathrm{calc})$ is the calculated $d$ spacing were the alkyl chains arranged perpendicularly to the plane of the layer $-18{\cdot}6$ Å. The cosine relationship follows naturally.)

The calculations of the tilt angles, $\alpha$, for the D-galactose *S*,*S*-acetals can be found in table 14. As can be seen from the values at the clearing point, $\alpha$ becomes larger with

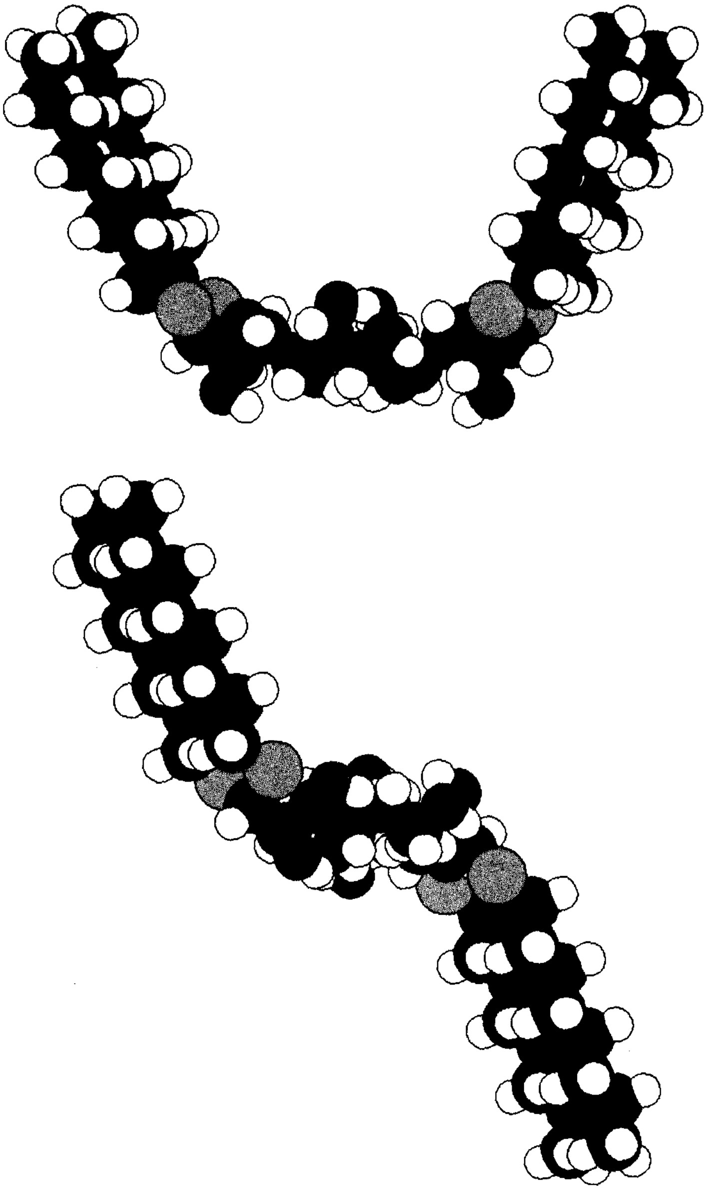


Figure 14. CPK models of two possible conformations of the proposed dimers of D-galactose dioctyl dithioacetal in the liquid-crystalline phase.

higher temperatures. This leaves us with two alternatives for the structure of the layer, namely a *Z*-like shape if the aliphatic chains are located on either side of the carbohydrate core, or a *U*-like fish-bone structure with both hydrocarbon chains on the same side of the carbohydrate core (see figure 14). We are unable to exclude either possibility on the basis of currently available experimental data, molecular modelling experiments are planned which may provide the necessary information.

### 4.3. *Introduction of chirality in the alkyl chain*

Even though the aldose *S,S*-acetals are obviously chiral molecules, no evidence whatsoever has been found for the formation of chiral mesophases. In fact this holds true for all reported non-disc like thermotropic carbohydrate mesogens [6]. We synthesized racemic and (*S*)-3,7-dimethyloctanethiol (straightforward reactions from racemic and (*S*)-citronellol respectively) and used them for the synthesis of D-glucose and D-xylose *S,S*-acetals. The compounds with a homochiral alkyl chain have a texture that appears to be different from that of the mixture of diastereomers formed in the reaction with racemic thiol, but they have exactly the same clearing points. Only one mesophase is observed and this is completely miscible with the mesophase of D-glucose didecyl dithioacetal. Moreover none of the characteristic textures of chiral phases [19] were observed. We must conclude therefore that the mesophase is not chiral.

## References

[1] DAHLHOFF, W. V., 1987, *Z. Naturf.* (*b*), **42**, 661.
[2] VAN DOREN, H., BUMA, T. J., KELLOGG, R. M., and WYNBERG, H., 1988, *J. chem. Soc. chem. Commun.*, p. 461.
[3] ECKERT, A., KOHNE, B., and PRAEFCKE, K., 1988, *Z. Naturf.* (*b*), **43**, 878.
[4] FISCHER, E., 1894, *Ber.*, **27**, 673.
[5] See for instance: STANEK, J., CERNY, M., KOCOUREK, J., and PACAK, J., 1963, *The Monosaccharides* (Academic Press), chap. 24.
[6] JEFFREY, G. A., 1986, *Accts chem. Res.*, **19**, 168.
[7] PFANNEMÜLLER, B., WELTE, W., CHIN, E., and GOODBY, J. W., 1986, *Liq. Crystals*, **1**, 357.
[8] (*a*) MOEWS, P. C., and KNOX, J. R., 1976, *J. Am. chem. Soc.*, **98**, 6628.
[8] (*b*) JEFFREY, G. A., YEON, Y., and ABOLA, J., 1987, *Carbohydr. Res.*, **169**, 1.
[9] CARTER, D. C., RUBLE, J. R., and JEFFREY, G. A., 1982, *Carbohydr. Res.*, **102**, 59.
[10] BHATTACHARJEE, S., and JEFFREY, G. A., 1983, *Molec. Crystals liq. Crystals*, **101**, 247.
[11] VAN DOREN, H. A., VAN DER GEEST, R., VAN BOLHUIS, F., KELLOGG, R. M., and WYNBERG, H., 1988 (submitted for publication).
[12] BHATTACHARJEE, S., and JEFFREY, G. A., 1985, *Molec. Crystals liq. Crystals*, **131**, 245.
[13] (*a*) TINANT, B., DECLERCQ, J. P., and VAN MEERSSCHE, M., 1986, *Acta crystallogr.* C, **42**, 579.
[13] (*b*) MÜLLER-FAHRNOW, A., HILGENFELD, R., HESSE, H., SAENGER, W., and PFANNEMÜLLER, B., 1988, *Carbohydr. Res.*, **176**, 165.
[14] MÜLLER-FAHRNOW, A., ZABEL, V., STEIFA, M., and HILGENFELD, R., 1986, *J. chem. Soc. Chem. Commun.*, 1573.
[15] BRYAN, R. F., HARTLEY, P., MILLER, R. W., and SHEN, M. S., 1980, *Molec. Crystals liq. Crystals*, **62**, 281.
[16] DUCRUIX, A., HORTON, D., PASCARD, C., WANDER, D., and PRANGÉ, T., 1978, *J. chem. Res.*, (S) 470.
[17] SORKIN, E., and REICHSTEIN, T., 1945, *Helv. chim. Acta.*, **28**, 940.
[18] KELKER, H., and HATZ, R., 1980, *Handbook of Liquid Crystals* (Verlag Chemie), p. 47.
[19] GRAY, G. W., and GOODBY, J. W., 1984, *Smectic Liquid Crystals—Textures and Structures* (Leonard Hill), Plate 1.
[20] GOODBY, J. W., 1984, *Molec. Crystals liq. Crystals*, **110**, 205.
[21] VAN DOREN, H. A., 1987 (unpublished results).
[22] VAN DOREN, H. A., VAN DER GEEST, R., KELLOGG, R. M., and WYNBERG, H., 1988 (submitted for publication).