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# Liquid-crystalline glucamine derivatives

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# PRELIMINARY COMMUNICATION

## Liquid-crystalline glucamine derivatives

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The aminoalditol glucamine was transformed into *N*-alkylated derivatives and also into ammonium salts of various organic acids. Studies of the liquid-crystalline properties revealed a series of novel smectic and discotic mesophases. Rules generally applicable to the occurrence of the various phases are presented.

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Glucamine, 1-amino-1-deoxy-glucitol, is easily accessible by reductive amination of glucose [1] and gives rise to a series of components of technical and commercial interest [2]. In particular, the facile regioselective functionalisation at the amino group allows the formation of well-defined products even on a large scale. Along this line the synthesis of liquid-crystalline components derived from glucamine is of theoretical as well as practical relevance. As the simplest approach to liquid crystals of glucamine the formation of salts must be considered. The alkanoates **1**, **2** and **3** show more than 100°C broad enantiotropic $S_A$ phases with clearing points above 200°C.

Generally in monophilic (non-amphiphilic) liquid crystals the additional incorporation of a benzene ring gives rise to an increase in the clearing point of approximately 50–100°C [3]. The increased acidity of benzoic acid compared to alkanoic acids may result in a further increase in the clearing point. Thus, the benzoate **4** was prepared as a contact preparation (see figure 1). This salt gives rise to the formation of an $S_A$ phase with such a high clearing point that it cannot be observed on a Mettler heating stage. Surprisingly, for both the mixtures acid/salt and salt/acid discotic phases with similarly high clearing points result. Previously, discotic phases for carbohydrate derivatives were documented only for lyotropic hexagonal phases [4], and for sugar dithioacetals [5].

Amazingly, in this case the mixture of monophilic (acid) and amphiphilic (salt) liquid crystals leads to the formation of a discotic phase. It must be stressed that this is not a lyotropic hexagonal phase—a trivial case for amphiphiles—but rather a thermotropic phase. Evidently, it is not induced by the solvent, does not form from aggregates but rather from single molecules (molecularly disperse). Both the discotic phases cannot be assigned a particular molecular structure. Only the rather uneven volume ratio of hydrophobic and hydrophilic fragments favours the columnar phase over a layer structure. Those molecular parts with the smaller volume seem to form columns which are surrounded by a sea of dominating fragments. This would lead to

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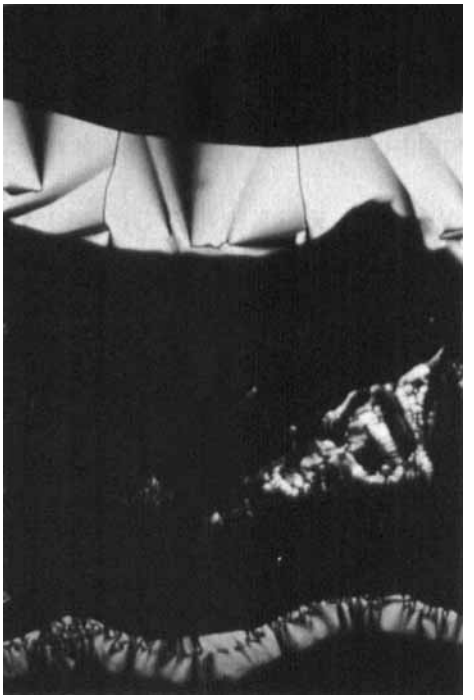

Figure 1. Contact preparation between glucamine and 4-*n*-octadecyloxybenzoic acid. Area is approximately $0{\cdot}6 \times 1{\cdot}0\,mm^2$, $T = 140{\cdot}0°C$, crossed nicols, with cover slide, $\lambda/2$-plate. Bottom, isotropic phase, acid **321**; between, columnar discotic phase, salt + acid; middle, $S_A$ phase, salt **122**; between, columnar discotic phase, salt + amine; top, isotropic phase, amine.

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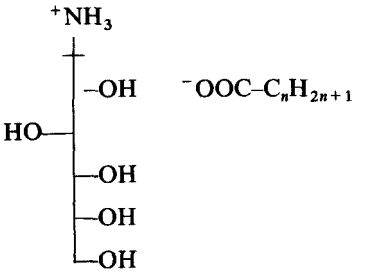
reciprocal structures of both the discotic phases. For the amine rich species the hydrophilic and for the acid rich species the hydrophobic parts form the column. The mesophase in the hydrophilic case exhibits enhanced molecular interactions, and thus the clearing point is higher (240°C in contrast to 199·5°C). Below 130°C this contact preparation allows the observation of four different liquid-crystalline phases: in addition to $S_C$ and $S_A$ phases the two reciprocal discotic phases occur.

In the hydrophilic part of the liquid crystals **1** to **4** the ionic character dominates over the influence of hydroxy groups and must be considered the main reason for the liquid-crystalline properties. For comparison ethanolamine instead of glucamine was used for salt formation, and indeed **5** with considerable less hydroxy groups forms a high melting liquid crystal as well.

In addition to salt formation *N*-alkylation of glucamine is a well-documented reaction which led to *N*-alkylglucamines **6** to **18**. As early as 1944 Hixon and Mitts [6] reported their melting anomalies, and the liquid-crystalline properties were recently elucidated by van Doren *et al.* [7]. These findings can be confirmed and somewhat supplemented. The clearing point first increases on going from $n = 7$ to 12, then remains constant, and slightly decreases above $n = 15$. Obviously a high clearing point for an $S_A$ phase requires both large hydrophobic and hydrophilic areas and their balanced ratio. According to this assumption in compound **18** ($n = 18$) the alkyl chain is supposed to be too long compared to only five unblocked hydroxy groups. Evidence could be obtained

Table 1. Liquid-crystalline salts.




| No. | *n* | Phase transitions | | | | | |
|---|---|---|---|---|---|---|---|
| **1** | 13 | | f | ≈110°C | $S_A$ | 210°C | I |
| **2** | 15 | | C | 107°C | $S_A$ | >220°C | Z |
| **3** | 17 | (105°C) | C | 123°C | $S_A$ | 216°C | I |

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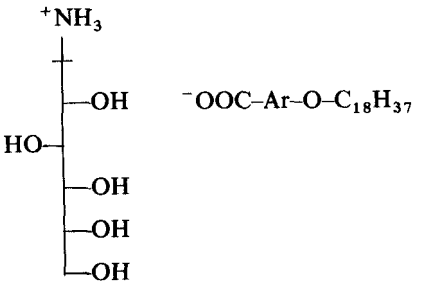
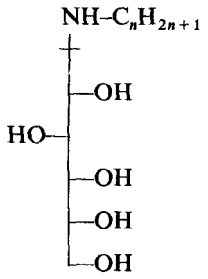



| No. | Phase transitions |
|---|---|
| **4** | C ? $S_A$ >280°C I<br>Acid→$S_C$ D $S_A$ D I ←Amine<br>up to 199·5°C<br>up to >280°C<br>up to 240°C<br>up to 131·7°C |

$HO–CH_2–CH_2–NH_3^+ {}^-OOC–C_{17}H_{35}$.

| No. | Phase transitions |
|---|---|
| **5** | C≈76°C $S_A$ ≈150°C I |

Table 2. Alkylglucamine.




| No. | n | Phase transitions | | | | | | References | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **6** | 4 | | | — | | | | C | 128°C | | | I | [6] |
| **7** | 5 | | | — | | | | C | 130°C | | | I | [6] |
| **8** | 7 | | | — | | | | C | 128·1°C | $S_A$ | 113·8°C | I | [7] |
| | | | | | | | | C | 127°C | | | I | [6] |
| **9** | 8 | (82°C) | C | 122·6°C | $S_A$ | 141·8°C | I | C | 122·9°C | $S_A$ | 142·5°C | I | [7] |
| **10** | 9 | | | — | | | | C | 127·0°C | $S_A$ | 154·6°C | I | [7] |
| **11** | 10 | (82°C) | C | 122·8°C | $S_A$ | 168·9°C | I | C | 125·1°C | $S_A$ | 165·6°C | I | [7] |
| **12** | 11 | | | — | | | | C | 126·0°C | $S_A$ | 167·9°C | I | [7] |
| **13** | 12 | (107°C) | C | 124·2°C | $S_A$ | 174·8°C | I | C | 124·0°C | $S_A$ | 173·6°C | I | [7] |
| **14** | 13 | | | — | | | | C | 127·5°C | $S_A$ | 173·0°C | I | [7] |
| **15** | 14 | (87°C) | C | 123·5°C | $S_A$ | 174·9°C | I | C | 125·0°C | $S_A$ | 173·4°C | I | [7] |
| **16** | 15 | | | — | | | | C | 128·1°C | $S_A$ | 172·8°C | I | [7] |
| **17** | 16 | (87°C) | C | 124·8°C | $S_A$ | 171·8°C | I | C | 126·6°C | $S_A$ | 170·9°C | I | [7] |
| | | | | — | | | | C | 124°C | X | ? | I | [6] |
| **18** | 18 | (107°C) | C | 126·0°C | $S_A$ | 165·3°C | I | C | 119°C | X | ? | I | [6] |

Contact preparation with glucamine: **9** $T_{c\,max}=141{\cdot}8°C$;
**18** $T_{c\,max}=230°C$.

by experiments to obtain contact preparations between the free glucamine and either of the *N*-alkylamines **9** ($n=8$) and **18** ($n=18$). Even though the short chain derivative **9** absorbs glucamine the clearing point decreases. For the long chain derivative **18** the clearing point rises to 230°C, more than 60°C above that of the pure liquid crystal. Such a high clearing point cannot be understood by the molecular structure but rather the balanced hydrophobicity–hydrophilicity ratio.

By reaction of *N*-alkylglucamine with chloroacetic acid interesting ionic surfactants for use in cosmetics were recently obtained [2]. For the zwitterionic compound **19** a clearing point of 169·5°C was observed which is rather low for ionic compounds. The carboxymethyl group may be assumed to be responsible for such reduced mesomorphic properties because it covers the centre of the molecule almost like a hump. A completely different figure is observed with the sodium salts **20** to **25**. The long chain homologues **22** to **25** show an $S_A$ phase the clearing point of which increases by more than 100°C for $n=12$ to 14. Evidently this can be interpreted that such an extremely polar hydrophilic end requires a heavy alkyl chain for the formation of a lamellar phase. For the short chain compounds **20** and **21** the hydrophilic part is dominant, and in this case presently unknown mesophases, possibly discotic and cubic, are observed.

Alkyl glucamines can form liquid-crystalline salts as well, for example some 4-*n*-alkoxybenzoates **26** to **31** were obtained in contact preparations (see figures 2 and 3). In

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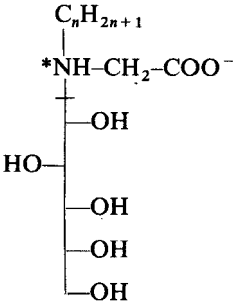
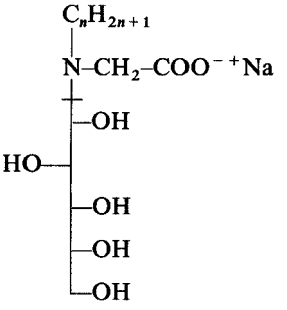
Table 3. Carboxymethylated glucamine.




| No. | *n* | Phase transition |
|---|---|---|
| **19** | 12 | C 152·7°C $S_A$ 169·5°C I |




| No. | *n* | Phase transitions | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **20** | 8 | | C | ? | M | 164·5°C | | I |
| **21** | 10 | | C | ? | M | >260°C | | I |
| **22** | 12 | (116°C) | C | 124·9°C | | | $S_A$ 174·9°C | I |
| **23** | 14 | | C | ? | | | $S_A$ >280°C | Z |
| **24** | 16 | | C | <130°C | | | $S_A$ >240°C | Z |
| **25** | 18 | | C | <100°C | | | $S_A$ >250°C | Z |

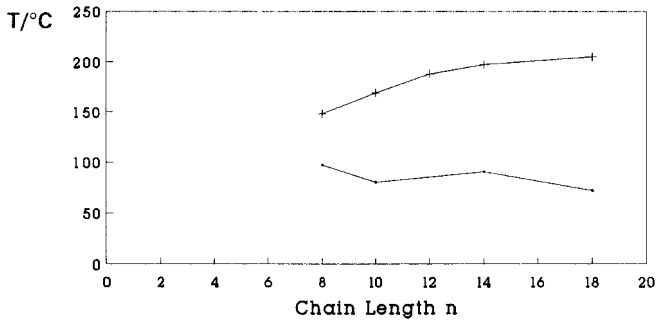



Figure 2. Alkylglucamine 4-*n*-octadecyloxybenzoates. $T_{CD}$ (■) and $T_{DI}$ (+).

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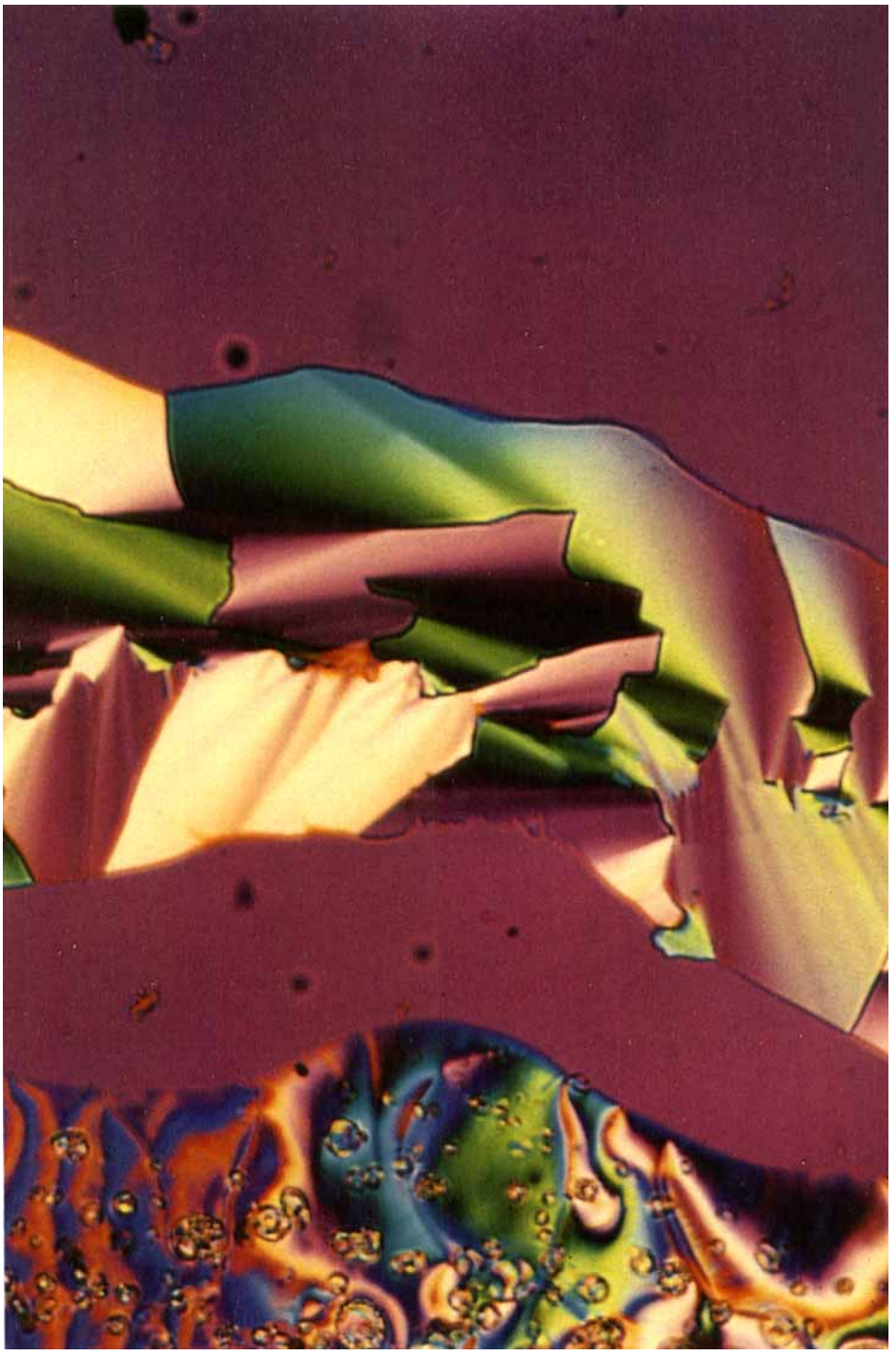

Figure 3. Contact preparation between octadecylglucamine **18** and 4-*n*-octadecyloxybenzoic acid. Area is approximately $0{\cdot}3 \times 0{\cdot}5\,mm^2$, $T = 170{\cdot}0°C$, crossed nicols, with cover slide, $\lambda/2$-plate. Bottom, $S_C$ phase of the acid; middle, columnar discotic phase of the salt **31**.

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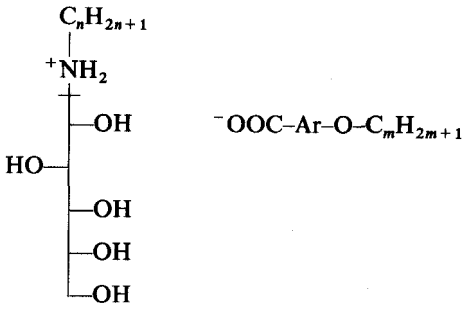
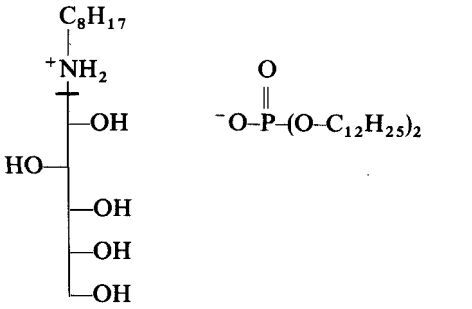
Table 4. Alkylglucamine salts.




| No. | *n* | *m* | Phase transitions | | | | |
|---|---|---|---|---|---|---|---|
| **26** | 8 | 8 | C | ? | D | 126·6°C | I |
| **27** | 8 | 18 | C | 97·1°C | D | 148·0°C | I |
| **28** | 10 | 18 | C | 80°C | D | 168·6°C | I |
| **29** | 12 | 18 | C | ? | D | 188·0°C | I |
| **30** | 14 | 18 | C | 90·5°C | D | 197·0°C | I |
| **31** | 18 | 18 | C | 72°C | D | 204·5°C | I |




| No. | Phase transition | | | | |
|---|---|---|---|---|---|
| **32** | C | ? | D | 151°C | I |

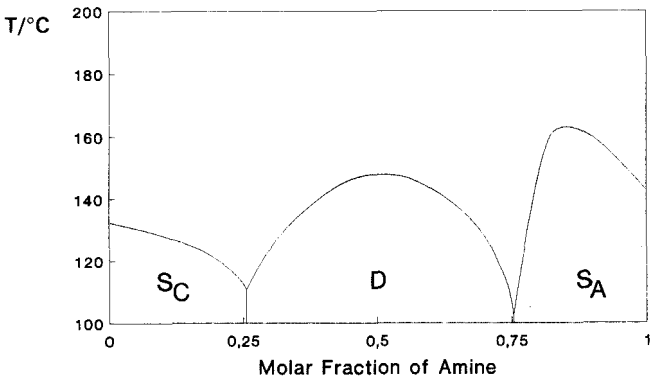



Figure 4. Schematic diagram of the contact preparation of **9** and 4-*n*-octadecyloxybenzoic acid, formation of **27**.

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either case only discotic phases were formed, and their clearing points rise with the chain length of the alkyl amine as well as the alkoxybenzoic acid (see table 4). Obviously these salts cannot adopt tripodal structures as previously assigned to sugar dialkyl mercaptals [5]. In almost all cases by addition of 4-*n* alkoxybenzoic acid to the amine the clearing point of the $S_A$ phase is decreased. Only for the short chain octyl glucamine does a stabilization result (see figure 4). Similarly, the interpretation can be based on the improved ratio of hydrophobic and hydrophilic molecule fragments. In addition to these compounds with two alkyl chains also for the bis-dodecylphosphate **32** with their alkyl chains a discotic phase is observed.

These findings result in the following résumé.

(i) Discotic and cubic phases do not represent extraordinary cases for amphiphilic liquid crystals, however, in addition to smectic phases they represent even weighted alternative and general cases.

(ii) The simplest approach to the preparation of liquid-crystalline amino polyols is represented by salt formation.

(iii) A particular construction of defined supramolecular structures for the interpretation of liquid-crystalline properties does not significantly add to their understanding.

With regard to the present findings and those of previous studies in this series [8, 9] the particular properties of amphiphilic liquid crystals are proposed for further discussion.

(i) The clearing properties of an amphiphilic crystal may be compared to the separation of a paraffin–polyol mixture. Of course, the clearing point is lower for chemically linked components than the mixing temperature of a comparable mixture of solvents.

(ii) Amphiphilic liquid crystals show the occurrence of phases and their properties are similar to those of lyotropic liquid crystals with the exception of the nematic phase.

(iii) Reentrant isotropic phases may occur for amphiphilic liquid crystals.

(iv) Form and relative weight of the molecular fragments determine the nature of the mesophase: for smectic phases a linear, rope-like molecular structure and minor differences of polar and non-polar fragments are required.
Discotic phases are enforced by bent molecular structures, or linear structures with large differences of polar and non-polar fragments, or disc-like [10] or disc segment-like [5] molecules.
The formation of cubic phases is supported by rather heavily bent molecular structures, or linear structures with extreme differences of polar and non-polar fragments, or spherical or spherical-segment [11] molecules.

(v) There is a floating transition between amphiphilic and monophilic liquid crystals [12].

(vi) There is no advantage to construct distinct supramolecular aggregates (multimer) for the explanation of liquid-crystalline conditions.

(vii) Higher ordered smectic phases (for example $S_B$) only occur if the diameter of the polar head group is comparable to the size of the alkyl group [13].

(viii) Tilted phases could not be obtained yet because they cannot represent low temperature phases for closely engaged or compressed $S_{A_d}$ phases. However, for alternative molecular geometries they could be considered.

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Compounds **1–3** and **6–25** were provided by Hüls AG, Marl. The salts **4** and **5** and **26–32** were obtained in contact preparations. The transition temperatures were determined on a polarising microscope Olymbus BH equipped with a Mettler FP 82 heating stage. The phase assignment is based on characteristic textures.

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