

This article was downloaded by:

On: 26 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

Substituted 1,4-dicyclohexyl-butan-1-ols A new class of liquid-crystalline compounds

K. Müller^a; U. Anker^a; H. -J. Deutscher^a; H. Kresse^b

^a Pädagogische Hochschule, Halle/Saale, Germany ^b Martin-Luther-Universität Halle/Wittenberg, Institut für Physikalische Chemie, Halle/Saale, Germany

To cite this Article Müller, K. , Anker, U. , Deutscher, H. -J. and Kresse, H.(1992) 'Substituted 1,4-dicyclohexyl-butan-1-ols A new class of liquid-crystalline compounds', *Liquid Crystals*, 12: 6, 1013 – 1018

To link to this Article: DOI: 10.1080/02678299208032816

URL: <http://dx.doi.org/10.1080/02678299208032816>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

PRELIMINARY COMMUNICATIONS

Substituted 1,4-dicyclohexyl-butan-1-ols A new class of liquid-crystalline compounds

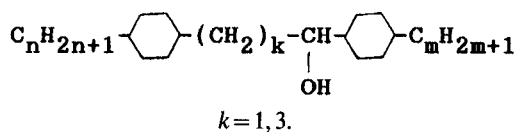
by K. MÜLLER, U. ANKER and H.-J. DEUTSCHER*†
Pädagogische Hochschule, Fachbereich Chemie Hoher Weg 7,
O-4020 Halle/Saale, Germany

and H. KRESSE
Martin-Luther-Universität Halle/Wittenberg,
Institut für Physikalische Chemie, Mühlpforte 1,
O-4050 Halle/Saale, Germany

(Received 2 August 1991; accepted 21 July 1992)

1,4-dicyclohexyl-butan-1-ols with a lateral hydroxyl group in the middle part of the molecule exhibit higher clearing temperatures than those of the respective compounds without this lateral group. A smectic B-like texture and a low temperature additional phase X were found by microscopic and calorimetric investigations. A further unexpected result was the strong increase of the dielectric constant at the S_B/X transition. These preliminary results are explained in terms of hydrogen bridges.

Lateral substitution of calamitic liquid crystals results mainly in a decrease of the clearing temperatures [1]. A partial exception to this rule seems to be the hydroxyl group, due to the strong tendency for association. For example this behaviour is found for aromatic salicylidene derivatives [1(a)] as well as terminal diol and dithiol structures [2, 3]. In order to study the influence of a lateral hydroxyl group in the middle part of a flexible rod-like molecule, compounds with the general formula



were synthesized. They are compared with the respective derivatives in which OH is substituted by H [4].

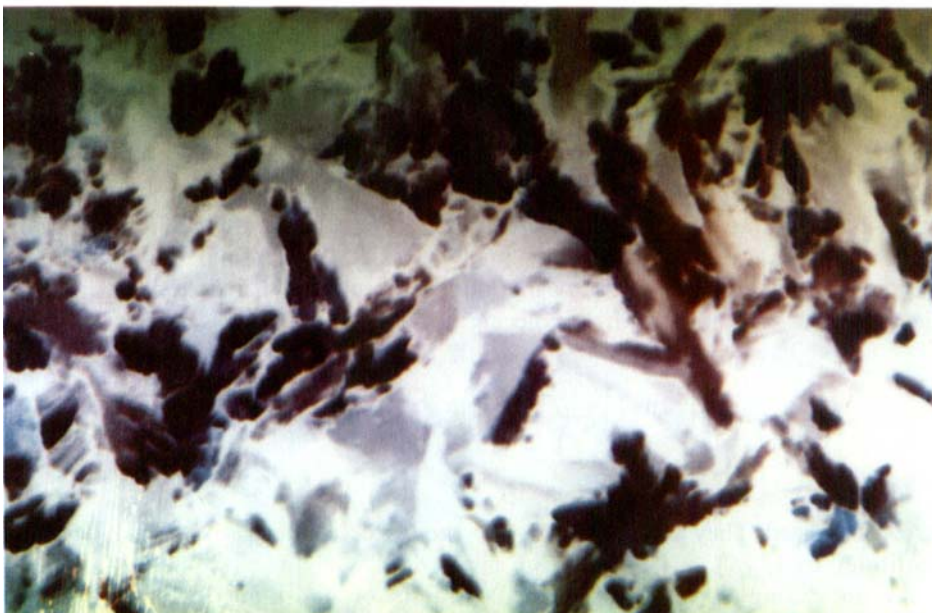
As an example, we describe the synthesis of 4-(4-*n*-butylcyclohexyl)-1-(4-*n*-hexylcyclohexyl) butan-1-ol (A) (see the reaction scheme). Starting from ethyl 4-*n*-butylphenylpropionate we obtained the ethyl 4-*n*-butylcyclohexylpropionate by catalytic high pressure hydrogenation. After reduction of the ester with LiAlH_4 and

*Author for correspondence.

†Present address: Veszpremer Strasse 15, 4070 Halle/Saale, Germany.



(a)



(b)

Figure 1. Optical textures of sample A at (a) $T=391$ K (S_B) and (b) $T=377$ K (phase X), magnification about 120.

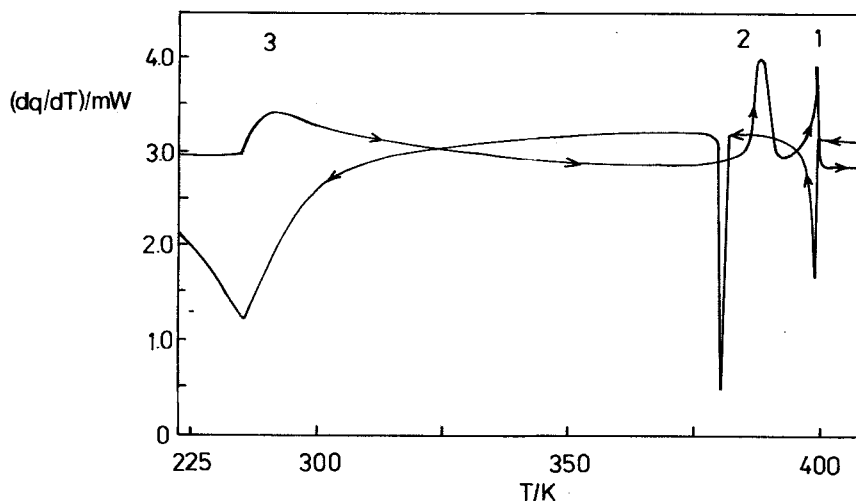
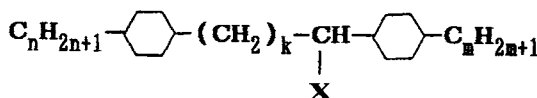


Figure 2. Thermogram of sample A; heating/cooling rate: 0.5 K min^{-1} . The main feature is the hysteresis of the phase transition at 385 K ($\Delta T=8 \text{ K}$) whereas the clearing temperature (399 K) does not show hysteresis. A third phase transition occurs at about 291 K.

Phase transition temperatures (in K) of dicyclohexylalkanols A and B and their analogous alkanes.

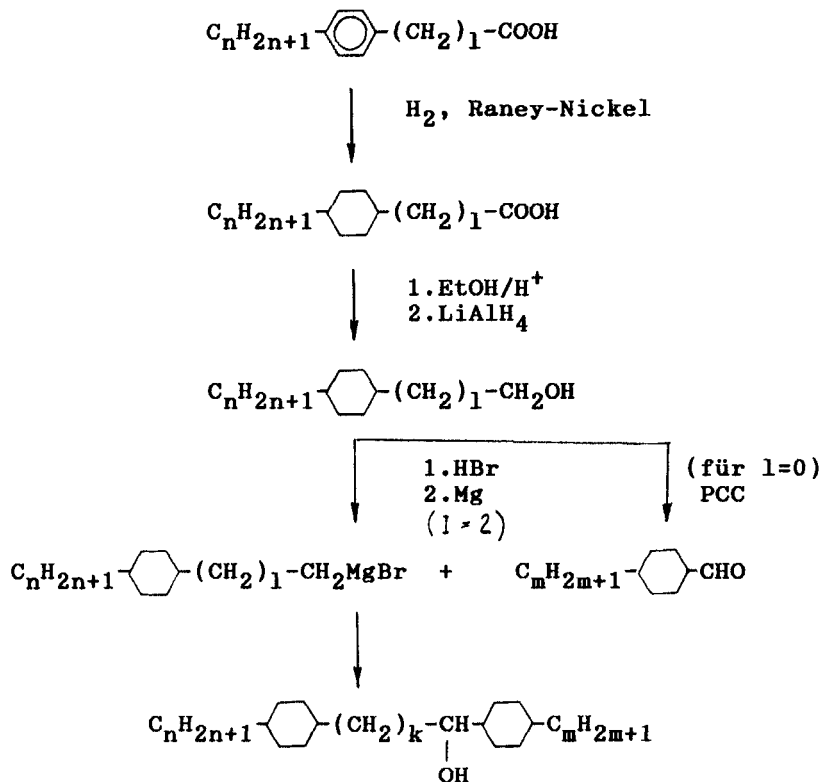


	<i>n</i>	<i>m</i>	<i>k</i>	<i>X</i>	<i>C</i>	Phase X	<i>S_B</i>	<i>I</i>	Ref.
A	4	6	3	OH	● 290	●	389 ● 399	●	
B	5	5	1	OH	● 321	—	● 410	●	
C	6	6	3	H	● 339	—	● 374	●	[4]
D	5	5	1	H	● 320	—	● 381	●	[8]

esterification with HBr to 3-(4-*n*-butylcyclohexyl)propylbromide (bp 121–124°C/0.26 kPa) we carried out the Grignard reaction of 4-*n*-butylcyclohexylpropylmagnesiumbromide with 4-*n*-alkyl-cyclohexylcarbaldehyde (pentyl-bp 142–146°C/3.3 kPa, hexyl-bp 118–121°C/0.4 kPa) in THF. In a similar way 1,2-bis-(4-*n*-pentylcyclohexyl)ethanol (B) was synthesized from 4-*n*-pentylcyclohexylmethylbromide (bp 138–140°C/1 kPa). The pure products were obtained as a racemic mixture by recrystallization from methanol.

A. 4-(4-*n*-butylcyclohexyl)-1-(4-*n*-hexylcyclohexyl)butan-1-ol. Elemental analysis, calculate: C 82.45 per cent, H 13.61 per cent; found: C 82.36 per cent, H 13.31 per cent; MS, *m/e*: 360 (M-18), $^1\text{H NMR}$ (CDCl_3): $\delta = 0.75\text{--}1.88$ (C-H, C-H₂, C-H₃), 3.13(m, 1H, OCH); $^{13}\text{C NMR}$: $\delta = 14.13$ (CH₃), 23.04–43.79 (CH₂, CH), 76.2 (OCH); IR(CCl_4): 3640, 1060 cm^{-1} (OH), 2950, 2860, 1450 cm^{-1} (CH₃), 2925, 2850, 1465, 1210 cm^{-1} (CH₂), 750 cm^{-1} (butylene).

B. 1,2-bis-(4-n-pentylcyclohexyl)ethanol. Elemental analysis calculated: C 82.22 per cent, H 13.22 per cent; found: C 82.39 per cent, H 13.15 per cent; $^1\text{H NMR}$ (CDCl_3): $\delta = 0.75\text{--}1.8$ (C-H, C-H₂, C-H₃), 3.46(m, 1H, OCH); IR(CCl_4): 3640, 1060 cm^{-1} (OH), 2970, 2930, 2880, 1460 cm^{-1} (alkyl).



Schema of synthesis, $k = 1, 3$.

The existence of mesophases was proved by microscopic and calorimetric investigations. For the samples A and B smectic mesophases were detected. Photographs of the optical textures in figure 1 show, that the high temperature phase can be identified as a smectic B [5]. The mixture of compounds A and C (contact method) indicates complete miscibility of these B phases.

Calorimetric measurements carried out with a Perkin-Elmer DSC-7 are presented in figure 2. With a heating rate of 0.5 K min^{-1} phase transitions at about 290 K (C/X); 389 K (X/S_B) and 399 K (S_B/I) were detected. On cooling phase transitions at 399 K ($\Delta H = 15.6 \text{ kJ mol}^{-1}$), 381 K ($\Delta H = 15.3 \text{ kJ mol}^{-1}$) and 285 K were found. The strong supercooling of the S_B/X transition of 8 K indicates a phase transition which is connected with a major molecular reorganization (see, for example, [6]). For sample with the less flexible ethyl group in the middle part (for example, compound B) only a liquid-crystalline B phase could be detected.

The transition temperatures are compared in the table with those of the respective dicyclohexylalkanes. Generally the clearing temperatures of the hydroxyl substituted compounds are higher (sample A/sample C: 25 K; B/D: 29 K). In order to obtain

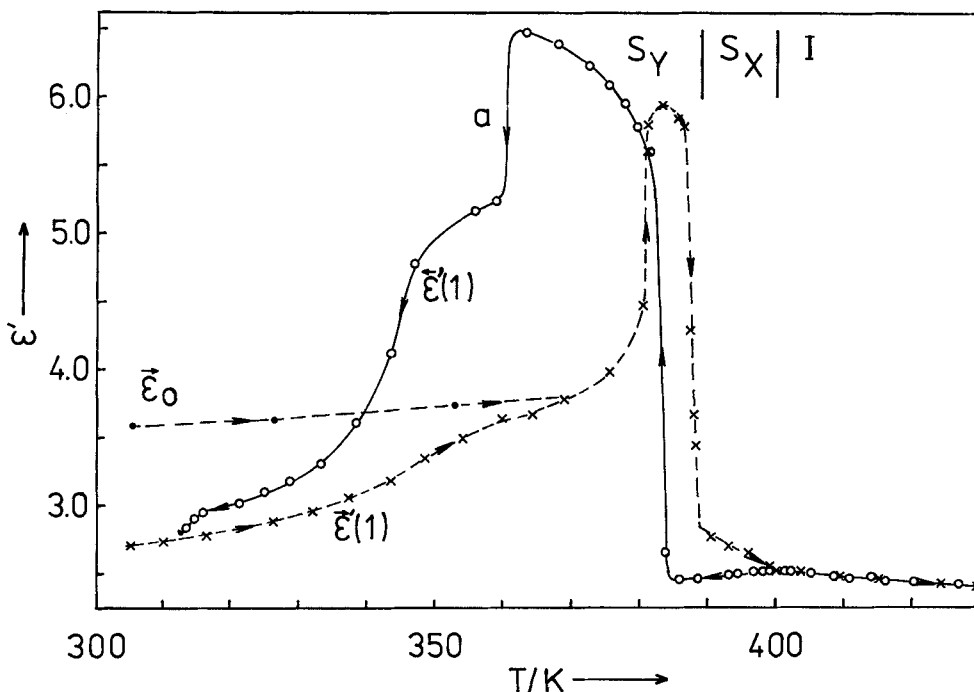


Figure 3. Dielectric constants of A at a frequency, f , of 1 kHz measured during cooling ($-O-$) and heating ($-X-$). ϵ_0 static dielectric constant during heating estimated from the absorption measurements (Cole-Cole plot). a: decrease of $\epsilon'(1)$ with time; waiting time: 1 h 45 min.

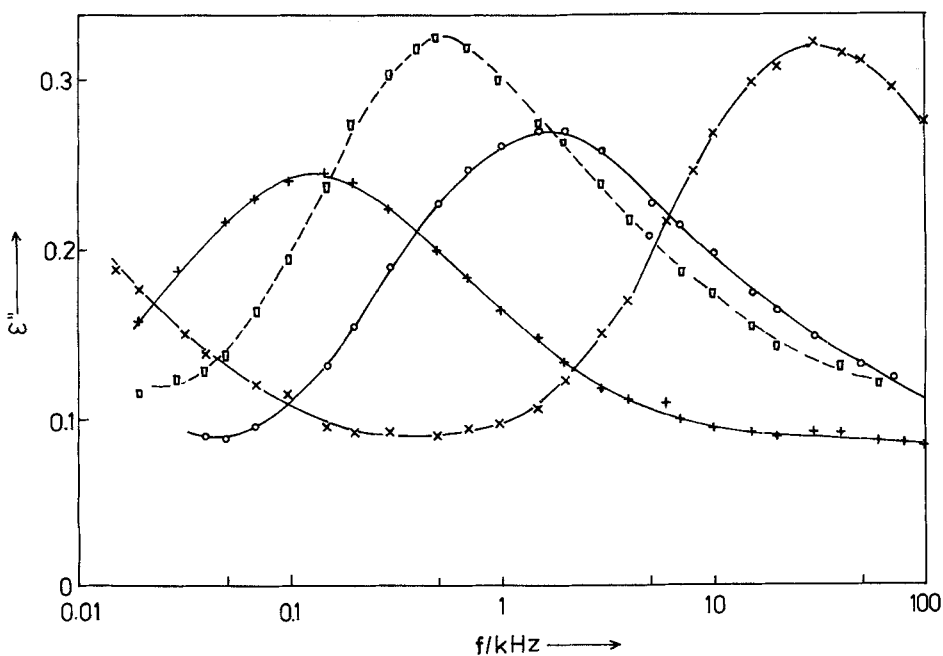


Figure 4. Dielectric absorption curves of A measured during heating: $T_1 = 354.1$ K ($-+-$); $T_2 = 326.6$ K ($-O-$); $T_3 = 305.1$ K ($-X-$) and cooling: $T_4 = 316.0$ K ($-□-$).

preliminary information about the structural changes dielectric measurements were carried out. All attempts to orient samples of compounds A and B at the I/S_B transition in a magnetic field of 0.6 T were unsuccessful. Nevertheless the dielectric data of an unoriented sample of A are of interest. In the isotropic state ϵ' measured at a frequency f , of 1 kHz is about 2.55 at 410 K. At the phase transition I/S_B only a change in the slope of ϵ' as a function of temperature takes place. In contrast a stepwise increase of ϵ' at the S_B/X transition to ϵ' of about 6 was detected. Using the relation $\epsilon'_1 = (1/3)(\epsilon'_{\parallel} + 2\epsilon'_{\perp})$ for a uniaxial crystal and $\epsilon'_{\parallel} = 6.0$ we obtain $\epsilon'_{\perp} = 0.8$. Such a value of ϵ'_{\perp} is quite impossible. Therefore, the increase of ϵ' can only be explained by the interaction of the hydroxyl groups. A broad two phase range at the S_B/X transition can be excluded from the calorimetric data. On the other hand the dielectric constant decreases with time indicating a reorganization of the dipoles. Measurements during heating, performed 15 h later, gave evidence for a dielectric absorption as shown in figure 3. The activation energy E_A , of 105 kJ mol⁻¹ agrees well with data attributed to rotation of the molecules around the short molecular axis [7] (see figure 4).

From these preliminary results we conclude that the interaction of the hydroxyl group is responsible for the increased mesophase stability and also for the increase of the dielectric constant in the additional X phase. This low temperature phase is very probably a low temperature smectic state but we have yet to exclude a solid phase with a high mobility of the hydroxyl groups.

Further investigations as to the nature of these effects are in progress.

References

- [1] (a) DEMUS, D., DEMUS, H., and ZASCHKE, H., 1976 and 1982, *Flüssige Kristalle in Tabellen I and II* (Deutscher Verlag für Grundstoffindustrie, Leipzig), see [305, 553 (a)]. (b) KELKER, H., and HATZ, R., 1980, *Handbook of Liquid Crystals* (Verlag Chemie, Weinheim).
- [2] TSCHERSKE, C., BREZESINSKI, G., KUSCHEL, F., and ZASCHKE, H., 1989, *Molec. Crystals liq. Crystals Lett.*, **6**, 139.
- [3] PIETSCHMANN, N., BREZESINSKI, G., KUSCHEL, F., TSCHERSKE, C., and ZASCHKE, H., 1990, *Molec. Crystals liq. Crystals Lett.*, **7**, 39.
- [4] DEUTSCHER, H.-J., MÜLLER, K., WEBER, M., SCHMIDT, M., and FRACH, R., *J. prakt. Chem.* (in the press).
- [5] DEMUS, D., and RICHTER, L., 1978, *Textures of Liquid Crystals* (Deutscher Verlag für Grundstoffindustrie, Leipzig).
- [6] DEMUS, D., MARZATKO, D., SHARMA, N. K., and WIEGELEBEN, A., 1980, *Cryst. Res. Technol.*, **15**, 331.
- [7] KRESSE, H., 1983, *Adv. liq. Crystals*, **6**, 109.
- [8] PRAEFCKE, K., SCHMIDT, D., and HEPPKE, G., 1980, *Chemikerzeitung*, **104**, 269.