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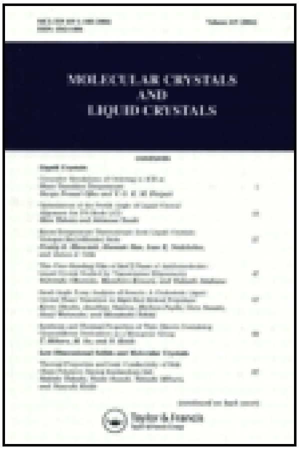

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About the Influence of Geometrical Factors on Liquid Crystalline Properties—The Methylene Group as a Central Spacer Unit

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About the Influence of Geometrical Factors on Liquid Crystalline Properties—The Methylene Group as a Central Spacer Unit

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(*Received April 4, 1987; in final form July 8, 1987*)

The preparation and liquid crystalline properties of four classes of substance with a central methylene spacer unit are described. As a result of our investigations, it is shown that a "one-atomic" central spacer, such as a methylene group, combined with a 1,4-cyclohexylene ring, contributes to the stabilization of the liquid crystalline state in the same way as a —$(CH_2)_5$— moiety.

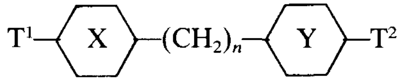
Compounds with this new "crooked" central spacer of course exhibit lower clearing temperatures than compounds with ethylene (CH_2CH_2) spacers etc., but they demonstrate a new quality in relation to the influence of geometrical factors on liquid crystalline properties.

Keywords: geometry of LC-molecules, mesogenic central methylene spacer, mesogenic cyclohexane derivatives

INTRODUCTION

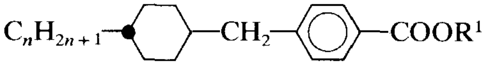
Thermotropic liquid crystalline properties are to be expected, when organic molecules realize certain fundamental requirements of chemical structure i.e. linearity, rigidity or flexibility.[1] This required rodlike geometry of calamitic liquid crystals is excellently provided for instance in substances of the type **A**, if the number of methylene groups is zero or two.[2] Especially in series of alicyclic compounds, high mesophase stabilities were obtained.[2–5]

A:

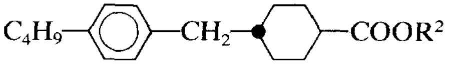


X, Y = aromatic and/or alicyclic rings
T^1, T^2 = terminal groups

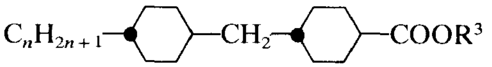
On the other hand, it has been known since the investigations made by Vorländer,[6] that in type **A** substances (with X = Y = phenylene; $n = 1$), the single methylene group causes the total loss of mesomorphic properties, because the angle involved in the central linking moiety of the molecule hinders or disturbs a satisfactory molecular linearity. A comparison of angle correlation parameters J^7 of diphenylmethan ($J = -0.17$) and of good mesogenic structures ($J = +0.39$ to $+0.78$) obviously shows that use of a methylene group as a central spacer unit should be borderline in liquid crystal chemistry. But we have found that it is only necessary to hydrogenate the aromatic ring X in **A** (T^1 = alkyl, Y = phenylene; $n = 1$) to realize a new quality. With suitable choice of T^2, it is possible to obtain stable liquid crystals. The complete hydrogenation of **A** (X = Y = cyclohexylene, $n = 1$) results in compounds with remarkable mesophase stabilities. In this paper we report results on the following classes of "methylene-bridged" type **A** substances:



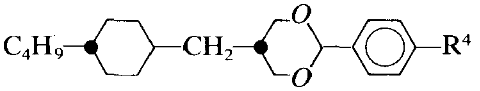
4



6



5



9

RESULTS AND DISCUSSION

4-(4-*n*-Alkylcyclohexyl)methylbenzoic acids 1 were obtained from 4-*n*-alkylcyclohexane carboxylic acids (scheme 1). High pressure hydrogenation of 1 gives the 4-(4-*n*-alkylcyclohexyl)methylcyclohexane carboxylic acids 2.[8,9]

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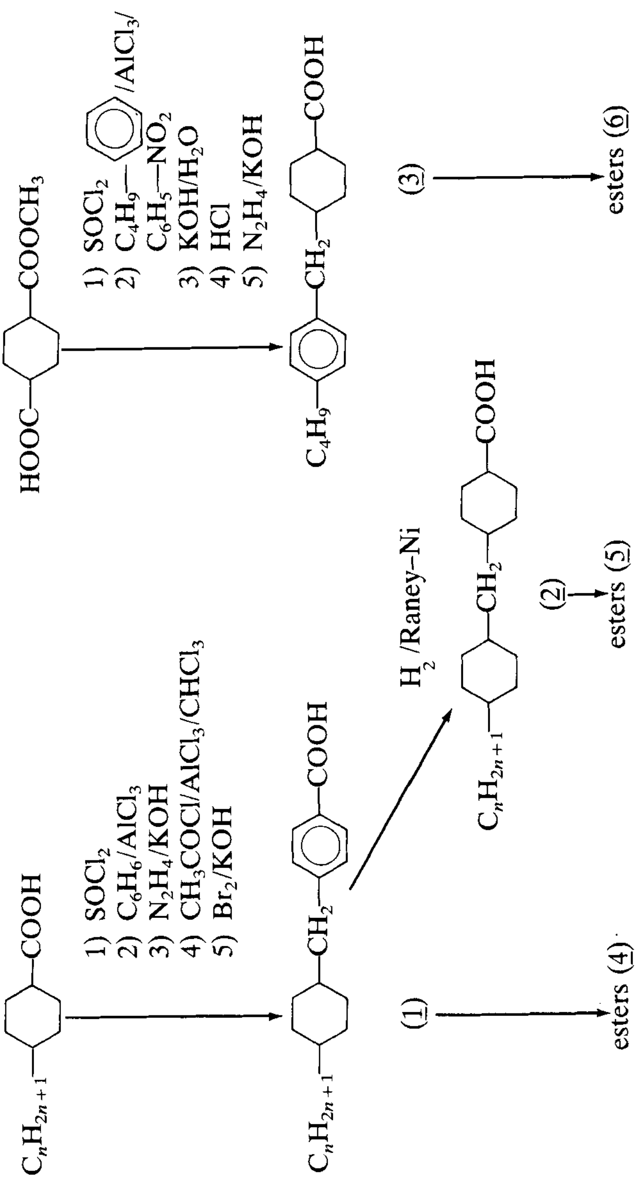
scheme 1

scheme 2



The synthesis of 4-(4-*n*-butylbenzyl)cyclohexane carboxylic acid (3) was realized starting from the 4-methoxycarbonyl-cyclohexane carboxylic acid (scheme 2). The esters 4–6 were prepared by interaction of the acid chlorides, obtained from the acids 1–3 and thionyl chloride, with the appropriate phenols and cyclohexanols in dry pyridine, followed by fractional recrystallization to separate the trans-isomers (Tables I–III). The esters 4 exhibit nematic phases when the hydroxy components contain two or more rings. Contrary to this, the esters 6 are not mesomorphic. Liquid crystalline esters 5 were obtained from the acid 2 and simple phenols and cyclohexanols. These significant distinctions in the behaviour of the esters 4–6 demonstrate excellently the dominant influence of geometrical factors on the liquid crystalline state. Since the only distinction is the change of the rings, it is possible that the more flexible cyclohexane ring (in 4.6 and 5.15) allows a better lathlike molecular structure to be adopted in combination with the methylene group, compared with the rigid phenylene ring (in 6.3).

However, it should also be pointed out that the esters (6) exhibit two regions of high polarisability and polarity separated by the cyclohexyl-CH_2 unit. As pointed out by Eidenschink and others[18] such separations of coherent regions of high polarity/polarisability do lead to suppression of liquid crystal behaviour.

The X-ray investigation of the nematic 4-cyanophenyl trans-4-(trans-4-*n*-butylcyclohexyl)methylcyclohexanoate (CBMC) confirms the all-trans-configuration of the acid 2 in its liquid crystalline esters, as well as the extensive geometrical likeness of CBMC to 4-cyanophenyl trans-4-*n*-pentylcyclohexanoate (CPPCH).[8] In Table VI it is shown, that the esters 5 and analogous trans-4-*n*-nonylcyclohexanecarboxylates (where 1,4-cyclohexylene in 5 is replaced by —$(CH_2)_4$—) of similar molecular length exhibit clearing temperatures of the same order. The (trans-4-*n*-butylcyclohexyl)methyl group causes as a rule higher melting points and higher clearing temperatures than the *n*-nonyl group.

This means that a methylene group as a central spacer unit contributes to the stabilization of the liquid crystalline state if this spacer is incorporated into an alicyclic ring† in the zigzag conformation of a terminal alkyl group. Simultaneously we are able to confirm that cisoid structures of 1,4-disubstituted cyclohexanes in combination with

---

†For a comparison of the transition temperatures of a range of cyanophenyl esters derived from different alicyclic carboxylic acids, see Table V.

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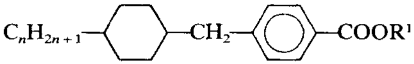
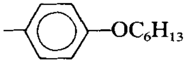
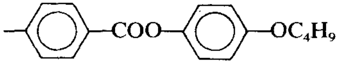
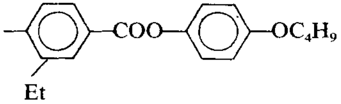
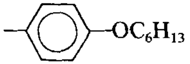
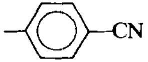
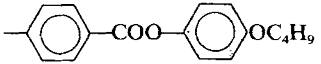
TABLE I

Transition temperatures (°C) of some 4-(trans-4-*n*-alkylcyclohexyl)methylbenzoates (*4*)

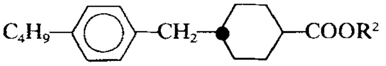


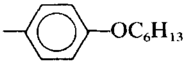
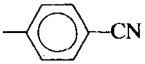
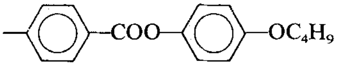
No	*n*	R¹	K		N		I
4.1	2		·	49	—	—	·
4.2	2		·	115	·	174.5	·
4.3	2		·	85–87	(·	84)	·
4.4	4		·	49	—	—	·
4.5	4		·	73	—	—	·
4.6	4		·	124	·	161	·

In Tables I–VI, the following conventions have been used: K = crystal, S = smectic, N = nematic, I = isotropic liquid; monotropic transitions are indicated by (   ).

TABLE II

Melting points (°C) of some trans-4-(4-*n*-butylbenzyl)-cyclohexanoates (*6*)

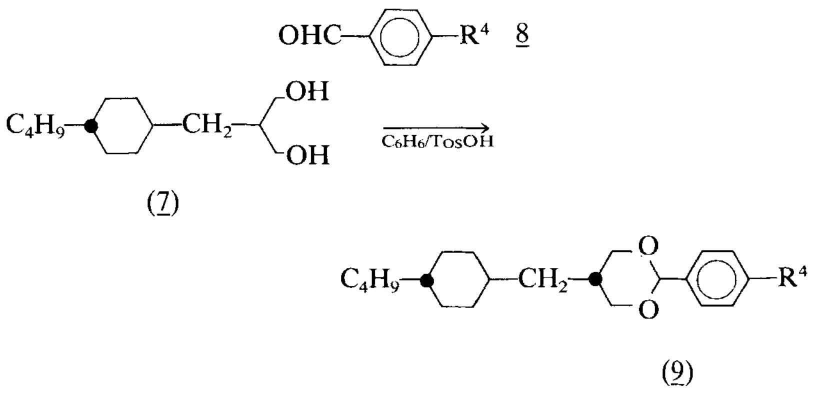


No	R^2	K	I
6.1		· 74	·
6.2		· 56,5	·
6.3		·118	·

a "crooked" spacer do not promote the formation of mesophases, because their structures cannot realize a conformation with satisfactory linearity.

The observed influence of a methylene spacer on the mesomorphic properties of the alicyclic esters 4–6 is also probable in the class of trans-5-(trans-4-*n*-butylcyclohexyl)methyl-1,3-dioxans 9 (Tables IV and VI). Compounds 9 were prepared by interaction of 2-(trans-4-*n*-butylcyclohexyl)methylpropan-1,3-diol (7) with 4-substituted benzaldehydes 8.

scheme 3



EXPERIMENTAL

Melting points and transition temperatures were determined using a Boetius polarizing microscope. All new compounds have satisfactory

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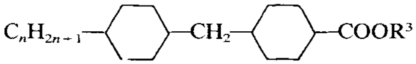
TABLE III

Transition temperatures (°C) of some trans-4-(trans-4-*n*-alkylcyclohexyl)methylcyclohexanoates (5)



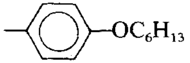
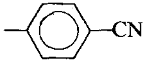
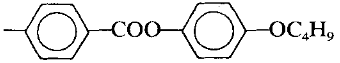
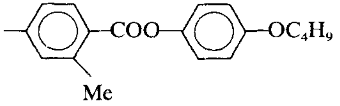
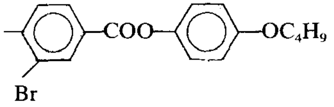
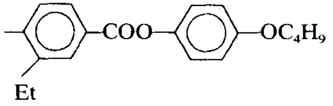
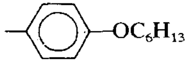
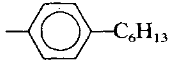
No	*n*	R^3	K		S_1	S_2		S_3	N		I
5.1	2		·	73	—	(·	57,5	· 60)	·	83,5	·
5.2	2		·	95	—	(·	94)	—	·	95	·
5.3	2		·	95	—	·	155	—	·	216,5	·
5.4	2		·	64	—	—		—	·	161	·
5.5	2		·	82	—	—		—	·	178	·
5.6	2		·	52,5	—	—		—	·	131	·
5.7	4		·	61	—	·	80,5	—	·	95	·
5.8	4		·	54	—	·	69,5	—	—	—	·

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TABLE III (*Continued*)

Transition temperatures (°C) of some trans-4-(trans-4-*n*-alkylcyclohexyl)methylcyclohexanoates (5)

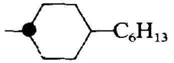
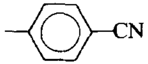
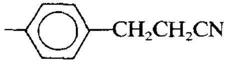
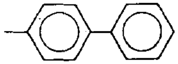
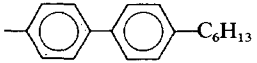
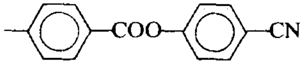
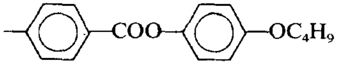
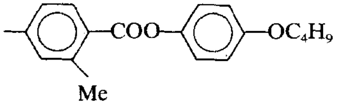
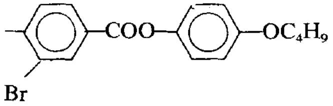
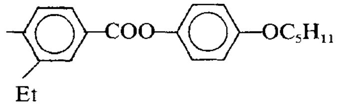
No	n	R^3	K		S_1	S_2		S_3	N		I
5.9	4		·	32	—	·	116	—	—	—	·
5.10	4		·	110	—	—		—	(·	108)	·
5.11	4		·	114,5	—	(·	90)	—	—	—	·
5.12	4		·	125	—	(·	105)	—	·	145	·
5.13	4		·	90,5	—	·	160	· 174	·	186,5	·
5.14	4		·	88,9	· 110	·	188	—	·	242	·
5.15	4		·	85,5	—	(·	74)	· 126	·	191,5	·
5.16	4		·	68	—	—		—	·	164,5	·
5.17	4		·	78	—	—		—	·	170	·
5.18	4		·	59	—	—		—	·	126	·

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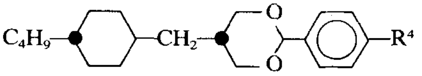
TABLE IV

Transition temperatures (°C) of some trans-5-(trans-4-*n*-butylcyclohexyl)methyl-1,3-dioxans (*9*)



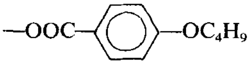
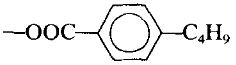
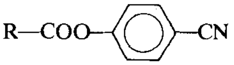
No	R^4	K	S		N		I
9.1	$—OC_6H_{13}$	· 99	—		—	—	·
9.2	—CN	· 88	—		(·	75)	·
9.3	$—OOC—C_4H_9$	· 72	(·	60)	—	—	·
9.4		·107	—		·	190,5	·
9.5		· 97	—		·	162	·
9.6		·122	—		·	181	·

TABLE V

Comparison of transition temperatures (°C) of compounds with different alicyclic ring systems



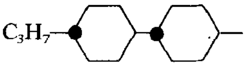
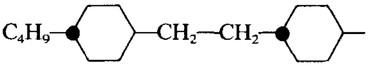
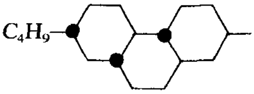
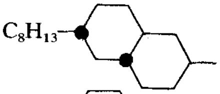
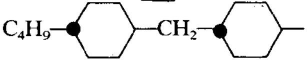
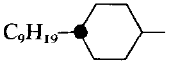
R	K	S		N		I	Lit.
	· 93	—		·	210	·	10
	· 90,5	(·	64,5)	·	197	·	4
	· 79	—		·	185	·	11
	· 64,5	—		·	121,5	·	13
	·110	—		(·	108)	·	5,10
	· 62	·	69	·	82,5	·	12

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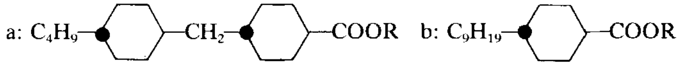
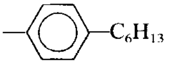
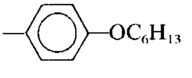
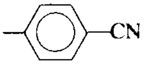
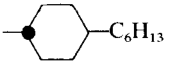
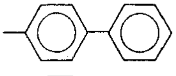
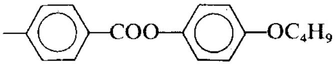
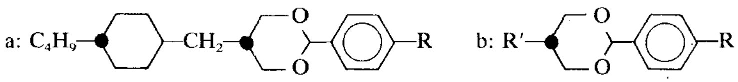
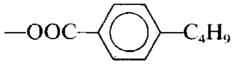
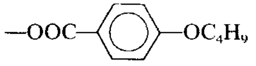
TABLE VI

Comparison of the transition temperatures (°C) of substances of similar molecular length containing the (trans-4-*n*-butylcyclohexyl)methyl group or the 4-*n*-nonyl group



R		K	S_1	S_2	N	I
	a	· 54	· 69,5		— —	·
	b	· 42	· 61		— —	·
	a	· 61	· 80,5		· 95	·
	b	· 47,5	· 70	· 77,5	· 82	·
	a	·110	— —		(· 108)	·
	b	· 62	· 69		· 82,5	·
	a	· 32	· 116		— —	·
	b	· 40	· 86		— —	·
	a	·125	(· 105)		· 145	·
	b	· 64,5	· 96,5		· 126,5	·
	a	· 85,5	(· 74)	· 126	· 191,5	·
	b	· 71	· 178		· 198,5	·



R		K	N	I	Lit.
—CN	a	· 88	(· 75)	·	
	b (R' = C_9H_{19})	· 65	(· 58)	·	16
	a	· 97	· 162	·	
	b (R' = C_7H_{15})	· 66	· 131	·	17
	a	·107	· 190,5	·	
	b (R' = C_7H_{15})	·103	· 174	·	16

infrared spectral properties and elemental analyses. All 4-(4-*n*-alkylcyclohexyl)methylbenzoic acids 1 and 4(-4-*n*-alkylcyclohexyl)methylcyclohexanecarboxylic acids 2 were prepared by the same methods described below for *n*-C_4H_9.[8,9] The 4-substituted benzaldehydes 8 were available commercially or were prepared from 4-hydroxybenzaldehyde by well known methods.[2,14]

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4-(4-*n*-butylbenzyl)cyclohexanecarboxylic adid (3)

A mixture of 4-methoxycarbonylcyclohexane carboxylic acid chloride (38.4 g, 0.19 mol) and *n*-butylbenzene (33.5 g, 0.25 mol) was added to aluminium chloride (40.1 g, 0.3 mol) in nitrobenzene (100 cm^3) with stirring and cooling to room temperature. After the addition, the mixture was stirred at 35–40°C for 5 h. The cooled reaction mixture was poured into crushed ice/conc. hydrochloric acid. The product was isolated by chloroform extraction. The organic layer was washed with water, dried (Na_2SO_4), and the solvent was removed. The residue was fractionated under reduced pressure to give methyl 4-(4-*n*-butylbenzoyl)-cyclohexanoate (21.0 g, 37%; bp 120–130°C/0.1 kPa). A mixture of this ester and potassium hydroxide (5.6 g, 0.1 mol) in water (100 cm^3) was boiled for 2 h. The cooled, clear solution was neutralized with concentrated hydrochloric acid to produce 15.5 g of the crude 4-(4-*n*-butylbenzoyl)cyclohexane carboxylic acid. Recrystallization (3x) from ethanol gave the pure ketocarboxylic acid (10.8 g, 54%, mp 155–160°C).

A mixture of this acid (10 g, 0.035 mol), potassium hydroxide (9.7 g, 0.17 mol), and hydrazine hydrate (10 g of a 50% aqu. solution, 0.1 mol) in triethylene glycol (100 cm^3) was boiled for 40 h. Under distillation conditions, the temperature was increased to 210–225°C to complete the reaction (about 10 h). The cooled reaction mixture was poured into water (500 cm^3), neutralized with concentrated hydrochloric acid and shaken with ether. After washing the extract with water, drying (Na_2SO_4), and removing the solvent, 7.2 g of a viscous oil was obtained. Recrystallization (4x) from *n*-hexane gave the pure acid 3 (2.6 g, 27%; mp 58–59°C).

Esterification

A solution of the phenolic or alcoholic component in dry pyridine was added to an equimolar amount of the crude acid chloride, formed by reaction of the acids 1, 2, or 3 with thionyl chloride. After allowing to stand at room temperature for about 15 h, the reaction mixture was poured into a mixture of crushed ice and conc. hydrochloric acid. The product was isolated by ether extraction. The ether solution was washed with acid (1 M aqueous HCl), base (1 M aqueous KOH), and water and dried (Na_2SO_4). The solvent was then removed. Recrystallization from ethanol or methanol/acetone until transition temperatures were constant gave the pure esters 4, 5, and 6.

2-(trans-4-*n*-butylcyclohexyl)methylpropan-1,3-diol (7)

A solution of diethyl 2-(4-*n*-butylcyclohexyl)methylmalonate (21 g, 0.07 mol) in dry ether (20 cm^3) was added dropwise to a stirred and cooled mixture of lithium aluminium hydride (2.8 g, 0.07 mol) in dry ether (130 cm^3). After addition, the mixture was stirred for 3–4 h. After allowing to stand overnight, the mixture was hydrolyzed carefully by addition of ice/water. The precipitate was dissolved by addition of the necessary amount of 10% aqueous sulphuric acid. The organic layer was separated and the aqueous layer shaken with ether. The combined ether extracts were washed (H_2O, and 5% aqueous $NaHCO_3$) and dried (Na_2SO_4). After removing the solvent, 14.1 g of a viscous residue were obtained. Recrystallization from *n*-hexane gave trans-7 (6.3 g; 41%; K 71 S 115 I) (see Ref. 15).

trans-5-(trans-4-*n*-butylcyclohexyl)methyl-1,3-dioxans 9

In a flask fitted with a water separator, trans-7 (3.3 mmol), the appropriate benzaldehyde 8 (3 mmol), and toluene-*p*-sulphonic acid (50 mg) in benzene (50 cm^3) were heated under reflux for 4 h. The cooled reaction mixture was washed (H_2O and 5% aqueous $NaHCO_3$) and dried (Na_2SO_4). After removing the solvent, the residue was recrystallized from ethanol or methanol/acetone (1:1) until constant transition temperatures were obtained. This gave the pure all-trans-1,3-dioxans (9).

References

1. (a) G. W. Gray, "Molecular geometry and the properties of non-amphiphilic liquid crystals," in *Advances in Liquid Crystals* (Ed. G. H. Brown), Vol. *2*, pp. 1–72, Academic Press, New York, San Francisco, London, 1976. (b) Proc. Freiburger Arbeitstagung "Flüssigkristalle," 1982.
2. See for example: a) F. Janecke, Dissertation, Halle, 1910; b) D. Coates and G. W. Gray, *J. Chem. Soc., Perkin Trans. II*, 863 (1976); c) R. Eidenschink, D. Erdmann, J. Krause and L. Pohl, *Angew. Chem.*, **89**, 103 (1977); *Phys. Lett.*, **60A**, 421 (1971); d) G. W. Gray and D. G. McDonnell, *Mol. Cryst. Liq. Cryst.*, **53**, 147 (1979); e) H.-M. Vorbrodt, Dissertation, Halle, 1982; f) M. Schadt, M. Petrzilka, P. R. Gerber, A. Villiger and G. Trickner, *Mol. Cryst. Liq. Cryst.*, **94**, 139 (1983).
3. See for example: a) R. Eidenschink, D. Erdmann, J. Krause and L. Pohl., *Angew. Chem.*, **90**, 133 (1978); b) K. Praefcke, D. Schmidt and G. Heppke, *Chem. Zeit.*, **104**, 269 (1980); c) G. W. Gray and B. M. Nicholas, EP 152, 697 (1985).
4. H.-J. Deutscher, R. Frach, K. Pilorz, M. Schellenberger and V. Weiss, *Wiss. Zeitschrift der PH Halle XXIV* (1986) M 2/86, pp. 12–16.
5. H. Takatsu, K. Takeuchi and H. Sato, *Mol. Cryst. Liq. Cryst.*, **108**, 157 (1984).
6. D. Vorländer, *Z. Phys. Chem. A.*, **126**, 449 (1927).

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7. C. Destrade, Ngyen Tinh and H. Gasparoux, *Mol. Cryst. Liq. Cryst.*, **59**, 273 (1980).
8. U. Baumeister, W. Brandt, H. Hartung, W. Wedler, H.-J. Deutscher, R. Frach and M. Jaskolski, *Mol. Cryst. Liq. Cryst.*, **130**, 321 (1985).
9. D. Demus, R. Frach, H.-J. Deutscher and H. Zaschke, Patent appl. DD WP C 07 C 256 067 (1983); DE 3,436,814 (1984).
10. a) R. Eidenschink, J. Krause, L. Pohl and J. Eichler in "Liquid Crystals" (Ed. S. Chandrasekhar), Heyden, London, Philadelphia, Rheine, p. 515 (1980); b) J. Krause, R. Eidenschink and L. Pohl, US Patent 4,229,315 ( ).
11. H.-J. Deutscher, S. Richter and H. Zaschke, *Mol. Cryst. Liq. Cryst.*, **127**, 407 (1985).
12. All *n*-nonylcyclohexane carboxylates were produced by H.-J. Deutscher, B. Laaser, W. Dölling and H. Schubert, *J. Prakt. Chem.*, **320**, 191 (1978).
13. W. Schäfer, H. Altmann, H. Zaschke and H.-J. Deutscher, *Mol. Cryst. Liq. Cryst.*, **95**, 63 (1983); *Wiss. Hefte PH Köthen* 2/82, p. 133 (1982).
14. H.-J. Deutscher, H.-M. Vorbrodt and H. Zaschke, *Z. Chem.*, **21**, 9 (1981).
15. a) S. Diele, E. Geissler, H.-M. Vorbrodt and H. Zaschke, *Mol. Cryst. Liq. Cryst. Lett.*, **102**, 181 (1985); b) A. Kolbe, H.-M. Vorbrodt and C. Tschierske, *Z. Chem.*, **26**, 33 (1986).
16. H.-M. Vorbrodt, S. Deresch, K. Kresse, A. Wiegeleben, D. Demus and H. Zaschke, *J. prakt. Chem.*, **323**, 902 (1981).
17. Y. Y. Hsu, US Patent 4.200.580 (1980).
18. R. Eidenschink, *Kontakte* (*Merck*), **1**, 15 (1979) and *3*, 12 (1980).