Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

3-Aryl- or 3-(*trans*-4-alkylcyclohexyl)- 6-arylcyclohex-2-enones: synthesis, transformations and mesomorphic properties

V. S. Bezborodov; G. M. Sasnouski; V. I. Lapanik; Roman Dabrowski; Jerzy Dziaduszek; V. I. Tyvorskii

To cite this Article Bezborodov, V. S. , Sasnouski, G. M. , Lapanik, V. I. , Dabrowski, Roman , Dziaduszek, Jerzy and Tyvorskii, V. I.(2001) '3-Aryl- or 3-(*trans*-4-alkylcyclohexyl)- 6-arylcyclohex-2-enones: synthesis, transformations and mesomorphic properties', Liquid Crystals, 28: 12, 1755 — 1760

To link to this Article: DOI: 10.1080/02678290110099646

URL: http://dx.doi.org/10.1080/02678290110099646

LIQUID CRYSTALS, 2001, VOL. 28, NO. 12, 1755–1760

3-Aryl- or 3-(*trans*-4-alkylcyclohexyl)- 6-arylcyclohex-2-enones: synthesis, transformations and mesomorphic properties

V. S. BEZBORODOV*, G. M. SASNOUSKI, V. I. LAPANIK
Institute of Applied Physics Problems, 220064 Minsk, Belarus

ROMAN DABROWSKI, JERZY DZIADUSZEK
Military University of Technology, Warsaw 00-908, Poland

and V. I. TYVORSKII
Belarussian State University, 220050 Minsk, Belarus

(*Received 22 January 2000; in final form 28 April 2000; accepted 22 May 2000*)

The synthesis and chemical transformations of 3-aryl- or 3-(*trans*-4-alkylcyclohexyl)- 6-arylcyclohex-2-enones into liquid crystalline compounds are discussed. These 3,6-disubstituted cyclohex-2-enones were prepared by the condensation of appropriate Mannich salts or *trans*-4-alkylcyclohexyl 2-bromoethyl ketones with 4-substituted benzyl methyl ketones.

1. Introduction

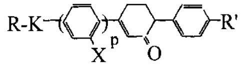
The liquid crystalline derivatives of quaterphenyl and terphenyl, cyclohexylbenzene and *trans*,*trans*-dicyclohexylbenzene are very useful in LC mixtures because they have low melting points and wide temperature ranges of their smectic or nematic phases, low viscosity and an optical anisotropy which increases from the derivatives of cyclohexylbenzene ($\Delta n \sim 0.1$) to the derivatives of quaterphenyl ($\Delta n \sim 0.25$), allowing one to prepare LC compositions for different kinds of LC Displays [1–3]. It has been shown that the introduction of lateral fluoro or chloro substituents, or the replacement of benzene and cyclohexane rings by cyclohexene rings in the molecules of LC compounds, leads to lower melting points to the nematic or smectic phases, increases the perpendicular component of the dielectric anisotropy ($\varepsilon_\perp$) and changes the elastic constant ratio (K_{33}/K_{11}), all of which are parameters of great importance for TN and STN displays [4–6]. Unfortunately, the synthetic routes to such compounds are usually multistage and need low temperatures or an inert atmosphere, palladium-catalysed coupling of arylboronic acids [7, 8] or Grignard coupling of 4-alkylcyclohexanones and 4-(*trans*-4-alkylcyclohexyl)-cyclohexanones [9, 10].

Recently we have described a new approach to preparing liquid crystalline derivatives of cyclohexane, cyclohexene, phenylcyclohexane or biphenyl using 3,6-disubstituted cyclohex-2-enones [11–14]. In this paper we describe continued investigations of 3,6-disubstituted cyclohex-2-enones and show how these compounds can be used for the synthesis of both well known and new liquid crystalline derivatives of *trans*,*trans*-dicyclohexylbenzene, *trans*-cyclohexylcyclohexenylbenzene, terphenyl and quaterphenyl containing fluoro or chloro substituents in lateral positions.

2. Results and discussion

2.1. *Synthesis*

LC derivatives of terphenyl and quaterphenyl have been prepared by the modification of 3,6-diarylcyclohex-2-enones (**1a**, **d**, **g**, **i**, **j**, **l**, **m**, K = benzene, $p = 0$ or 1, X = H or F see table 1 and the structure below), which are formed in high yield (60–75%) by Michael condensation of appropriate Mannich salts with 4-substituted benzyl methyl ketones in the presence of base [15].



1 a-m

$R = C_3H_7$-C_5H_{11}, F, CH_3O; K = bond or benzene or cyclohexane ring; $p = 0$ or 1;
X = H or F; R' = F, OCH_3, Cl, C_3H_7, C_5H_{11}.

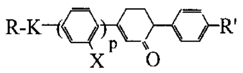
For the preparation of three-ring LC compounds possessing *trans*,*trans*-dicyclohexylphenyl and *trans*-cyclohexylcyclohexenylphenyl cores, we have used a new synthetic pathway (see the scheme below) because the

---

*Author for correspondence; e-mail: bezb@pfp.bsu.unibel.by

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2001 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290110099646

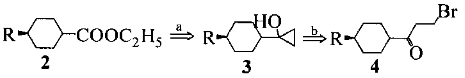
Table 1. Yields and transition temperatures for 3,6-disubstituted cyclohex-2-enones (**1a–m**).



							Transition temperatures/°C						
1	*R*	*K*[a]	*p*	*X*	*R′*	Yield/%	Cr		SmA		N		I
a	CH_3O	—	1	F	F	47	●		—		—	96	●
b	C_3H_7	C	0	—	F	56	●		—		—	105	●
c	C_3H_7	C	0	—	OCH_3	65	●		—	(80)	●	95	●
d	C_4H_9	—	1	H	OCH_3	65	●		—		—	76	●
e	C_5H_{11}	C	0	—	F	55	●		—		—	107	●
f	C_5H_{11}	C	0	—	Cl	48	●		—		—	103	●
g	C_5H_{11}	—	1	H	F	45	●		—		—	85	●
h	C_5H_{11}	C	0	—	OCH_3	52	●		—		—	106	●
i	C_5H_{11}	—	1	H	OCH_3	68	●	63	—		●	75	●
j	CH_3O	—	1	H	C_5H_{11}	72	●	67	—		●	99	●
k	C_5H_{11}	C	0	—	C_3H_7	54	●		—		—	104	●
l	C_5H_{11}	B	1	H	F	64	●	158	●	192	●	213	●
m	C_5H_{11}	B	1	H	OCH_3	71	●	141	●	243	●	250	●

[a] Column *K*: — = bond; C = cyclohexane ring; B = benzene ring.

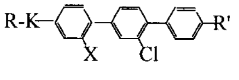
analogous salts cannot be prepared from *trans*-1-acetyl-4-(4-subsituted phenyl)cyclohexanes in yields higher than 50% and some of these products are very difficult to isolate by crystallization from the reaction mixture. The reaction of Grignard reagents with ethyl *trans*-4-alkylcyclohexane-1-carboxylates (**2**) in the presence of tetraisopropoxytitanium, leads in high yields (more than 90%) to 1-(*trans*-4-alkylcyclohexyl)cyclopropanols (**3**). This was the key stage in the new procedure [16]. These compounds with bromine in methanol are easily transformed into 2-bromoethyl ketones (**4**) (yields are more than 90%), which are the precursors of *trans*-4-alkylcyclohexylvinyl ketones used instead of Mannich salts in the condensation with 4-substituted benzyl methyl ketones. Using the 2-bromoethyl ketones (**4**) and 4-substituted benzyl methyl ketones we synthesized the 3-(*trans*-4-alkylcyclohexyl)-6-arylcyclohex-2-enones (**1b**, **c**, **e**, **f**, **h k**, *K* = cyclohexane, *p* = 0) listed in table 1 in yields of 50–65%.



$R = C_3H_7$–C_5H_{11}; $R' = F, OCH_3, Cl, C_3H_7$.
a: 2.5 eq. C_2H_5MgBr; 15 mol % Ti(Oi-$C_3H_7)_4$; ether. b: Br_2; CH_3OH/H_2O.

The aromatization of appropriate 3,6-disubstituted cyclohex-2-enones (chosen from **1a–m**) in boiling benzene under the influence of phosphorus pentachloride gives the chloroterphenyls and quaterphenyls (**5a–f**) (see table 2) in yields of 40–65%; catalytic hydrogenation of these products in the presence of 10% palladium on carbon yields the corresponding *trans*-2,5-disubstituted cyclohexanones (**6a–f**) (see table 3). It should be noted

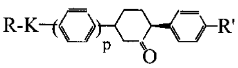
Table 2. Yields and transition temperatures for chloroterphenyls and quaterphenyls (**5a–f**).



						Transition temperatures/°C						
5	*R*	*K*[a]	*X*	*R′*	Yield/%	Cr		SmA		N		I
a	CH_3O	—	F	F	41	●		—		—	82	●
b	C_4H_9COO	—	F	F	37	●	60	—		●	83	●
c	C_4H_9	—	H	OCH_3	65	●	74	—		●	95	●
d	C_5H_{11}	—	H	F	61	●	39	—		●	55	●
e	C_5H_{11}	B	H	F	52	●	112	●	189	●	235	●
f	C_5H_{11}	B	H	OCH_3	62	●	115	●	141	●	298	●

[a] Column *K*: — = bond; B = benzene ring.

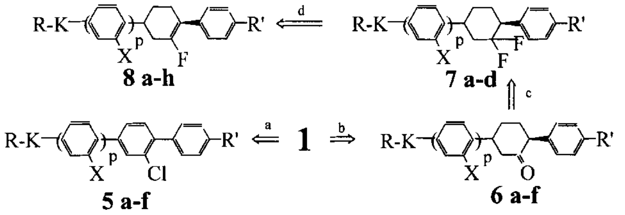
Table 3. Yields and transition temperatures for *trans*-2,5-disubstituted cyclohexanones (**6a–f**).



						Transition temperatures/°C						
6	*R*	*K*[a]	*p*	*R′*	Yield/%	Cr		SmA		N		I
a	C_3H_7	C	0	F	82	●	107	—		●	122	●
b	C_3H_7	C	0	OCH_3	72	●	105	—		●	178	●
c	C_5H_{11}	—	1	OCH_3	45	●		—		—	127	●
d	OCH_3	—	1	C_5H_{11}	40	●	101	—		●	112	●
e	C_5H_{11}	—	1	F	59	●		—		—	84	●
f	C_5H_{11}	B	1	F	44	●	107	●	136	●	181	●

[a] Column *K*: — = bond; B = benzene ring; C = cyclohexane ring.

that in contrast to the hydrogenation of 3-(*trans*-4-alkylcyclohexyl)-6-arylcyclohex-2-enones (**1b**, **c**, **e**, **f**, **h k**, *K* = cyclohexane, *p* = 0) the hydrogenation of 3,6-diarylcyclohex-2-enones (**1a**, **d**, **g**, **i**, **j**, **l**, **m**, *K* = benzene, *p* = 0 or 1) is accompanied by the formation of by-products (2,5-disubstituted cyclohexanols and 1,4-disubstituted cyclohexanes) and this leads to lower yields of the *trans*-2,5-diaryl cyclohexanones (**6**). The *trans*-2,5-disubstituted cyclohexanones (**6a–f**) are prospective intermediates for the synthesis of well known liquid crystalline *trans*-1,4-disubstituted cyclohexanes, which are formed by Wolf–Kishner reduction of the ketones.

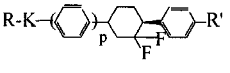


$R = C_3H_7–C_5H_{11}$, F, CH_3O; *K* = benzene or cyclohexane ring; *p* = 0 or 1; *X* = H or F; $R' =$ F, OCH_3, Cl, C_3H_7, C_5H_{11}.
a: PCl_5, benzene. b: H_2; Pd/C; KOH; ethanol. c: DAST.
d: KOH, ethylene glycol.

However, the most interesting direction for further chemical transformations of *trans*-2,5-disubstituted cyclohexanones (**6a–f**) is their interaction with diethylaminosulphur trifluoride (DAST), leading to the corresponding liquid crystalline *gem*-difluoroderivatives (**7a–d**) (table 4) and then, after their dehydrofluorination, to the 2,5-disubstituted 1-fluorocyclohex-1-enes (**8a–h**) (table 5). These compounds are characterized by low melting points, and wide temperature range nematic phases, and they are promising components for LC mixtures for different types of displays.

The proton NMR spectra (*δ*, ppm) of the 3,6-diarylcyclohex-2-enones (**1a**, **d**, **g**, **i**, **j**, **l**, **m**) showed that a multiplet at 6.52–6.58 belongs to the protons located at the double bond of the cyclohexenone fragment. In the spectra of the 3-(*trans*-4-alkylcyclohexyl)-6-arylcyclohex-2-enones (**1b**, **c**, **e**, **f**, **h**, **k**) the signals of the analogous protons are observed at 6.40–6.43. Two triplets at 2.35–2.39 in the proton NMR spectra of saturated ketones (**6a–f**) correspond to the signals of protons in the cyclohexanone fragment. The signals from protons of the cyclohexane fragment of difluoroderivatives (**7a–d**) are observed in the spectra in the form of triplets at 2.43

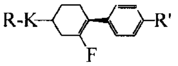
Table 4. Yields and transition temperatures for *trans*-2,5-disubstituted 1,1-difluorocyclohexanes (**7a–d**).



						Transition temperatures/°C						
7	*R*	*K*[a]	*p*	*R′*	Yield/%	Cr		SmA		N		I
a	C_3H_7	C	0	F	51	●	98	—		●	109	●
b	C_5H_{11}	—	1	OCH_3	52	●	58	—		●	82	●
c	C_5H_{11}	—	1	F	44	●		—		—	73	●
d	C_5H_{11}	B	1	F	41	●	84	●	114	●	189	●

[a] Column *K*: — = bond; B = benzene ring; C = cyclohexane ring.

Table 5. Yields and transition temperatures for 1-fluoro-2,5-disubstituted cyclohex-1-enes (**8a–h**).



					Transition temperatures/°C						
8	*R*	*K*[a]	*R′*	Yield/%	Cr		SmB		N		I
a	C_3H_7	C	F	25	●	33	—		●	122	●
b	C_3H_7	C	OCH_3	25	●	56	—		●	188	●
c	C_5H_{11}	C	F	28	●	34	—		●	129	●
d	C_5H_{11}	B	F	21	●	31	—		●	38	●
e	C_5H_{11}	C	OCH_3	28	●	53	—		●	188	●
f	C_5H_{11}	B	OCH_3	30	●	54	—		●	101	●
g	OCH_3	B	C_5H_{11}	28	●	57	—		●	95	●
h	C_5H_{11}	C	C_3H_7	24	●	38	●	120	●	144	●

[a] Column *K*: C = cyclohexane ring; B = benzene ring.

and 2.82. The signals at 1.30–2.82 in the NMR spectra of fluorocyclohexene derivatives (**8a–h**) belong to protons of the cyclohexane and cyclohexene fragments.

2.2. *Mesomorphic properties*

The phase transition temperatures of the 3,6-disubstituted cyclohex-2-enones (**1a–m**) are listed in table 1. As can be seen, the three-ring compounds (**1a–k**), as a rule, are not mesomorphic. The introduction of the additional benzene ring results in the appearance of nematic and smectic A phases in the temperature range 140–250°C for compounds (**1l**, **m**). Saturated ketones (**6a–f**) (table 3) form nematic phases. In particular, 2-aryl-5-(*trans*-4-alkylcyclohexyl)cyclohexanone (**6b**) forms the nematic phase over a wide temperature range compared with 2,5-diarylcyclohexanone (**6a**) and compound (**6e**) containing the end fluorine (table 3). The exchange of the carbonyl group for two fluorines leads to a lowering of the temperature at which smectic and nematic phases are formed and a widening of the temperature range of the nematic phase. Compare the difluorocompounds (**7a–d**) in table 4 with the ketones (**6a–f**). The replacement of the *trans*-1,1-difluoro-2,5-cyclohexylene fragment by the 1-fluoro-2,5-cyclohex-1-enylene fragment results in a sharp decrease in melting point and a broadening of the temperature range of the nematic phase (see table 5). 2,5-Disubstituted 1-fluorocyclohex-1-enes (**8a–h**), especially 1-fluoro-2-aryl-5-(*trans*-4-alkylcyclohexyl)-cyclohex-1-enes (**8a**, **c**), form the nematic phase at 30–35°C and over a temperature range of more than 100°C (table 5). The exchange of the carbonyl group for chlorine, coupled with aromatization of the cyclohexenone fragment, is also accompanied by decreases of more than 30°C in the temperature of formation of the smectic A phase and a broadening of the temperature range of the nematic phase. The chloroterphenyls (**5b–d**), like the difluoroderivatives (**7a**, **b**), have a narrow temperature range of the nematic phase, and the quaterphenyls (**5e**, **f**) form smectic A and nematic phases in the temperature range 112–298°C (table 2).

Investigations of the electro-optic and dynamic parameters of LC mixtures containing 2,5-disubstituted 1-fluorocyclohex-1-enes (**8**) and chloroterphenyls and quaterphenyls (**5**) have shown that these compounds can be successfully used as components of liquid crystalline mixtures characterized by low threshold and saturation voltages of the twist-effect, step voltage-contrast characteristics and low values of the switch-on and switch-off times.

3. Experimental

Confirmation of the structures of the intermediates and products was obtained using a GC/MS mass spectrometer (HP 5972) and H^1 NMR spectroscopy. The purity of the compounds was checked using a HP 5890 capillary gas chromatograph fitted with an H1 column. Phase transition temperatures were measured using a Linkam heating stage in conjunction with a polarizing PZO microscope and also using a Setaram DSC 92.

3,6-Diarylcyclohex-2-enones (**1a**, **d**, **g**, **i**, **j**, **l**, **m**) and the products of their aromatization–chloroterphenyls and quaterphenyls (**5a–f**) were prepared according to published methods [14].

3.1. *1-(trans-4-Pentylcyclohexyl)-1-cyclopropanol (3)*

The Grignard reagent prepared in the usual way from 6.0 g (0.25 mol) of magnesium and 0.25 mol of ethyl bromide was slowly added during 2 h at room temperature to a vigorously stirred solution of 22.6 g (0.1 mol) of ethyl *trans*-4-pentylcyclohexane-1-carboxylate and 0.02 mol (20 mol %) of tetraisopropoxytitanium in 100 ml of dry ether. The brown reaction mixture was then stirred at room temperature for a further 1 h and decomposed with the cold 10% aqueous sulphuric acid. After washing with water and drying over magnesium sulphate, the solvent was removed. The product, 1-(*trans*-4-pentylcyclohexyl)-1-cyclopropanol (purity about 95%), was used in the next transformation without additional purification; yield 19.5 g (95%).

3.2. *trans-4-Pentylcyclohexyl 2-bromoethyl ketone (4)*

19.5 g (0.095 mol) of 1-(*trans*-4-pentylcyclohexyl)-1-cyclopropanol were dissolved in 100 ml of methanol. 5 ml of water and then 16 g (0.1 mol) of bromine were added during 15 min at room temperature. The bromine colour disappeared continuously, and the final slightly coloured solution was diluted with water and the product twice extracted into methylene chloride. The solvent was removed under vacuum and the 2-bromoketone was used without additional purification; yield 24.7 g (90%).

3.3. *3-(trans-4-Propylcyclohexyl)-6-(4-fluorophenyl)cyclohex-2-enone (1)*

13.0 g (0.05 mol) of 2-bromoketone (**4**) were mixed with 7.6 g (0.05 mol) of 4-fluorobenzyl methyl ketone and 8.7 g (0.15 mol) of potassium hydroxide in 150 ml of dioxan and the resulting mixture was heated and stirred under reflux for 5 h. After cooling and treatment with 10% aqueous sulphuric acid, the product was extracted into benzene. After drying over sodium sulphate and removing the solvent, the ketone was crystallized from ethanol; yield 8.8 g (56%), m.p. 105°C.

3.4. *trans-2-(4-fluorophenyl)-5-(trans-4-Propylcyclohexyl)cyclohexanone (6a)*

6.3 g (0.02 mol) of 3-(*trans*-4-propylcyclohexyl)-6-(4-fluorophenyl) cyclohex-2-enone (**1**) in 200 ml of THF containing 0.5 g of potassium hydroxide were hydrogenated in the presence of 0.5 g of 10% palladium on carbon at 30–40°C with energetic stirring until hydrogen absorption ceased. The catalyst was separated, the alcohol distilled off and the residue dissolved in benzene. The solution was washed with water and dried over anhydrous magnesium sulphate. After evaporation of the solvent the residue was crystallized from isopropanol; yield 5.2 g (82%), m.p. 107°C.

3.5. *trans-1,1-Difluoro-2-(4-fluorophenyl)-5-(trans-4-propylcyclohexyl)cyclohexane (7a)*

A mixture of 3.16 g (0.01 mol) of *trans*-5-(*trans*-4-propylcyclohexyl)-2-(4-fluorophenyl)cyclohexanone and 2.4 g (0.015 mol) of DAST in 100 ml of benzene was at reflux during 10 h and after cooling was poured into aqueous KOH. The organic layer was washed with water and dried over sodium sulphate. After removing the benzene, the residue was dissolved in hexane and filtered through aluminium oxide to remove coloured impurities. After evaporation of the solvent, the *gem*-difluoro derivative was isolated by of chromatography on silica gel using hexane as eluent; yield 1.7 g (51%), m.p. 98°C.

3.6. *1-Fluoro-2-(4-fluorophenyl)-5-(trans-4-propylcyclohexyl)cyclohex-1-ene (8a)*

1.5 g (4.4 mmol) of the *gem*-difluoro derivative (**7**) was mixed with 50 ml of ethylene glycol and 2 g of KOH. The reaction mixture was boiled with slow stirring (during 8–10 h) while distilling out volatile material. After removing part of the solvent, the residue was cooled, diluted with hexane and washed with dilute hydrochloric acid and then with water. The hexane solution was filtered through a column of aluminium oxide or silica gel and, after evaporating the solvent, the residue was crystallized from isopropanol; the yield 0.35 g (25%), m.p. 33°C.

4. Conclusion

The results presented demonstrate that liquid crystalline 2-aryl-5-(*trans*-4-alkylcyclohexyl)-1-fluorocyclohex-1-enes, chloroterphenyls and quaterphenyls can be used for the development of liquid crystalline materials for nematic display applications with decreased power consumption and fast response times.

References

[1] Chan, L. K. M., Gray, G. W., and Lacey D., 1985, *Mol. Cryst. liq. Cryst.*, **123,** 185.

[2] Coates, D., 1990, *Liquid Crystals; Application and Uses*, Vol. 1, edited by B. Bahadur (Singapore: World Scientific Publications), p. 91.

[3] Nishi, T., Matsubara, A., Okada, H., Onnagawa, H., Sugimori, S., and Miyashita, K., 1995, *Jpn. J. appl. Phys.*, **34,** 236.

[4] Osman, M. A., and Nuynh-Ba, M., 1983, *Z. Naturforsch.*, **38b,** 1221.

[5] Plach, H., Bartmann, E., Poetsch, E., Naemura, S., and Rieger, B., 1992, *SID Dig.*, p. 13.

[6] Guy, S. C., 1993, *Displays*, **13,** 32.

[7] Emsley, J. W., Celebre, G., de Luca, G., Longeri, M., and Lucchesini, F., 1994, *Liq. Cryst.*, **16,** 1037.

[8] Hird, M., Gray, G. W., and Toyne, K. J., 1991, *Mol. Cryst. liq. Cryst.*, **206,** 187.

[9] Eidenschink, R., Erdmann, D., Krause, J., and Pohl, L., 1977, *Angew. Chem.*, **89,** 103.

[10] Sugimori, S., Kojima, T., and Tsuji, M., 1982, German patent application DE 3 739 130.

[11] Bezborodov, V. S., and *Dabrowski*, *R*., 1997, *Mol. Cryst. liq. Cryst*., **299,** 1.

[12] Bezborodov, V. S., Dabrowski, R., Dziaduszek, J., and Petrov, V. F., 1997, *Liq. Cryst*., **23,** 69.

[13] Sasnovski, G., Bezborodov, V., Dabrowski, R., and Dziaduszek, J., 1997, *Mol. Cryst. liq. Cryst*., **303,** 313.

[14] Bezborodov, V. S., Dabrowski, R., Dziaduszek, J., Czuprinski, K., and Raszewski, Z., 1996, *Liq. Cryst*., **20,** 1.

[15] Bezborodov, V. S., Dabrowski, R., Dziaduszek, J., Sasnovski, G., and Petrov, V. F., 1998, *Liq. Cryst*., **24,** 647.

[16] Kulinkovich, O. G., Sviridov, S. V., and Vasilevski, D. A., 1991, *Synthesis*, 234.