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

A convenient method of synthesis of mesomorphic 2,5-disubstituted cyclohexan-1-ones by a catalytic reduction of 3,6-disubstituted cyclohex-2-en-1-ones

V. Bezborodov[a][b]; G. Sosnovskij[a]; R. Dabrowski[c]; J. Dziaduszek[c]; J. Schirmer[d]; P. Kohns[d]
[a] Institute of Applied Physics Problems, Minsk, Belarus [b] R&D Center, Samsung Display Devices Co. Ltd., Paldal-Do, Korea [c] Military University of Technology, Warsaw, Poland [d] Optikzentrum NRW, Bochum, Germany

To cite this Article Bezborodov, V. , Sosnovskij, G. , Dabrowski, R. , Dziaduszek, J. , Schirmer, J. and Kohns, P.(1996) 'A convenient method of synthesis of mesomorphic 2,5-disubstituted cyclohexan-1-ones by a catalytic reduction of 3,6-disubstituted cyclohex-2-en-1-ones', Liquid Crystals, 21: 2, 237 — 241

To link to this Article: DOI: 10.1080/02678299608032829

URL: http://dx.doi.org/10.1080/02678299608032829

LIQUID CRYSTALS, 1996, VOL. 21, NO. 2, 237–241

A convenient method of synthesis of mesomorphic 2,5-disubstituted cyclohexan-1-ones by a catalytic reduction of 3,6-disubstituted cyclohex-2-en-1-ones

V. BEZBORODOV†, G. SOSNOVSKIJ
Institute of Applied Physics Problems, 220064 Minsk, Belarus

R. DĄBROWSKI*, J. DZIADUSZEK
Military University of Technology, 01-489 Warsaw, Poland

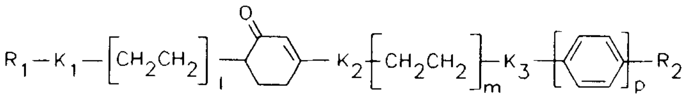
J. SCHIRMER and P. KOHNS
Optikzentrum NRW, D-44799 Bochum, Germany

(*Received 1 December 1995; in final form 2 February 1996; accepted 26 February 1996*)

The preparation of *trans*-2,5-disubstituted cyclohexan-1-ones from 3,6-disubstituted cyclohex-2-en-1-ones by reduction with hydrogen in the presence of palladium on carbon in a basic medium is described. The nature of the mesomorphic phases together with some physical properties of single compounds and of nematic mixtures comprising them are reported. Mesogens containing the *trans*-2,5-disubstituted cyclohexan-1-one ring show a small negative dielectric anisotropy and a low birefringence.

1. Introduction

3,6-Disubstituted cyclohex-2-en-1-ones can be prepared easily by condensation methods [1–5] and they are therefore promising intermediates for the synthesis of different kinds of mesogen containing laterally substituted as well as unsubstituted benzene, cyclohexane or cyclohexene rings [6]. Continuing our interest in manufacturing liquid crystals from the cyclohexenones we have investigated the reduction of compounds **I**:



wherein the terminal substitutents R_1 and R_2 are hydrogen or halogen or alkyl, alkoxy, COOH, $COCH_3$ and CN groups and K_1, K_2 and K_3 are single bonds, CH=CH groups, benzene or cyclohexane rings. The main purpose of this investigation was to find a convenient and a more general method for the preparation of different *trans*-2,5-disubstituted cyclohexanones. Mesogenic cyclohexanones are needed for the synthesis of difluorocyclohexane and fluorocyclohexene derivatives [7, 8] or as components for modifying the electro-optical properties of liquid crystalline mixtures [9].

2. Results and discussion

2.1. *Synthesis*

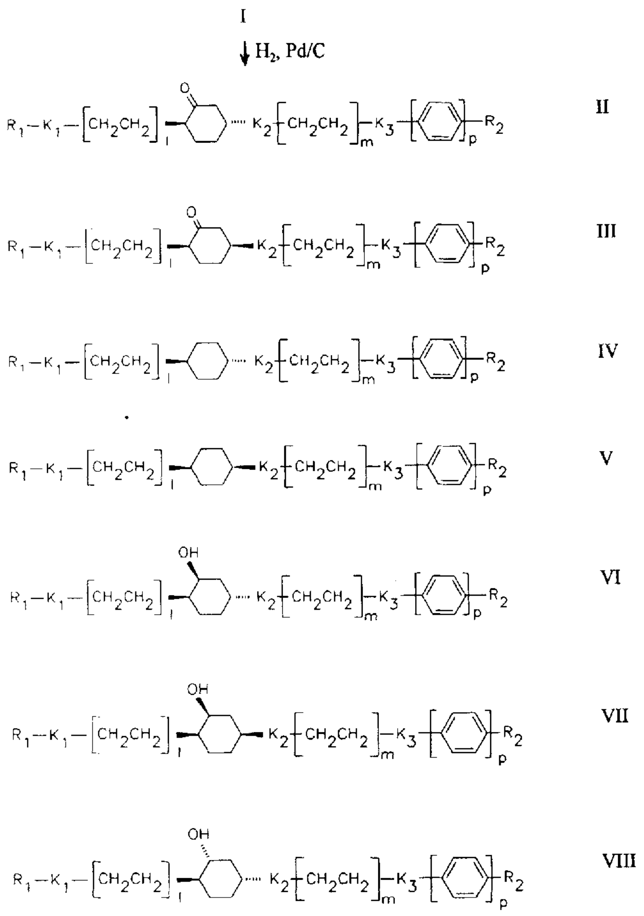
We have investigated a catalytic hydrogenation of unsaturated ketones **I** in the presence of palladium on carbon (10 wt %, product of Merck) in an acidic, neutral or basic medium. It was found that the compounds listed in the scheme are formed and their ratio in the reaction mixture depends strongly on the conditions of the reduction. When R_1 and R_2 are alkyl and $m=0$, $l=0$ and K_1, K_2 and K_3 are single bonds, *cis*- and *trans*-1-alkyl-4-arylcyclohexanes **IV** and **V** are formed in the majority (40–60%) in formic or acetic acid. These hydrocarbons, together with cyclohexanones **II** and **III** and cyclohexanols **VI**, **VII**, and **VIII** are also formed from **I** in isopropyl alcohol containing hydrochloric acid. The hydrogenation of ketones **I** in neutral isopropyl alcohol leads to a mixture containing mainly ketones **II** and **III** and alcohols **VI**, **VII** and **VIII** in yields of about 40–50% and 20–30%, respectively. The highest yield of the required saturated *trans*-ketone **II** was obtained using

---

*Author for correspondence.

†Present address Samsung Display Devices Co. Ltd., R&D Center, 575 Shin-Dong, Paldal-Do, Korea, 445–970.

0267–8292/96 $12·00 © 1996 Taylor & Francis Ltd.



Scheme 1. The reduction products formed from the 3,6-disubstituted cyclohex-2-en-1-ones.

alcohols (ethanol, isopropanol) containing potassium hydroxide. In these media, only ketones **II** and **III** are formed in yields from 90 to 95% and with a ratio of *cis*- to *trans*-isomers of 1 : 7. The 90% yield in the reduction of 3-(4-ethoxyphenyl)-6-pentylcyclohex-2-en-1-one to 2-pentyl-5-(4-ethoxyphenyl)cyclohexanone in an ethanol solution of NaOH has been previously mentioned [9]. We have also found that the reduction of compounds **I** in alkaline solution in the presence of palladium on carbon gives better results than the reduction of **I** by sodium in liquid ammonia (Birch method), ethylene diamine or alkylamines. In the latter case, the mixture of *trans*- and *cis*-ketones **II** and **III** was formed in yields between 70 and 90%. Additionally we have found that the hydrogenation of ketones **I** containing the cyclohexenone ring between two benzene rings (l is 0, K_1 and K_2 are benzene rings in formula **I**) always gives a mixture of all the products listed in the scheme independently of the acidity of the medium in which the hydrogenation was carried out. Unlike the compounds mentioned above, styrylcyclohex-2-en-1-ones **I** (K_2 is the CH=CH group, K_3 is a single bond and $m=0$, $p=1$) or acetylcyclohex-2-en-1-ones **I**, (l is 0, K is a single bond and R_1 is the CH_3CO group) are hydrogenated into *trans*- and *cis*-ketones **II** and **III** in alkaline and acidic media and in the former case both the double bonds (in the bridge and the cyclohexene ring) are reduced simultaneously. In both cases the *trans*-ketones **II** are formed more efficiently.

2.2. *Mesomorphic properties*

The 2,5-disubstituted cyclohexanones are listed in table 1. The phase transition temperatures for the pure *trans*-isomers (compounds **II**) isolated from the reduction products by crystallization are given. Cyclohexanones **II** are strongly smectogenic compounds and smectic A and smectic B phases are mainly exhibited. The nematic phase was however observed with some structures with hydrogen or fluorine atom as a terminal substituent and also with the structures with the $-CH_2-CH_2-$ spacer between the rings. For other structures, the nematic phase exists in a narrow temperature range, but only for compounds with short alkyl or alkoxy terminal groups. It is interesting that molecules containing cyclohexyl-cyclohexanone fragments give the nematic phase more effectively than molecules containing a phenyl-cyclohexanone fragment—see for example, compounds **II**9 and **II**23. This is the opposite relation to that for known mesogens containing a bicyclohexyl and a cyclohexylphenyl fragment [10].

2.3. *Dielectric and optical anisotropy*

Dielectric constants and refractive indices were measured for the nematic phase and the isotropic phase of the single nematic compound **II**25, (figures 1 (*a*) and 1 (*b*)) and for a multicomponent mixture A at a temperature of 20°C.

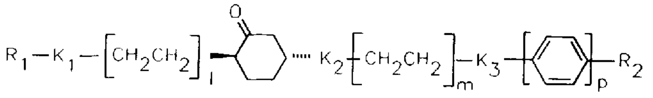
The broad range nematic mixture A was prepared from the compounds **II**8, 21, 25, 26, 27 (some of them are smectics) by dissolving them in non-polar 4-(*trans*-4-propylcyclohexyl)pentylbenzene. The mixture A had the composition in wt %:

4-(*trans*-4-propylcyclohexyl)pentylbenzene	35·4
Compound **II**8	7·3
Compound **II**21	2·9
Compound **II**25	29·3
Compound **II**26	17·8
Compound **II**27	7·3

Mixture A had the following properties: $T_{N,I}$ 63–72°C; N–S_A 3°C; $\Delta\varepsilon$ at 20°C −0·5; $\varepsilon_\parallel$ 3·8; $\varepsilon_\perp$ 4·3; Δn at 589·7 nm 0·0746; n_e at 589·7 nm 1·4965; n_o at 589·7 nm 1·5713

The wavelength-dependent refractive indices n_o and n_e of mixture A at 20°C are shown in figure 2 (*a*). The wavelength-dependent birefringence is compared in

Table 1. Yields and transition temperatures of 2,5-disubstituted cyclohexan-1-ones II 1–25.



										Transition temperatures/°C								
N	R_1	K_1	*l*	K_2	*m*	K_3	*p*	R_2	Yield/%	Cr		S_B		S_A		N		I
1	CH_3	—	0	—	0	—	1	OC_2H_5	44	●	43	—		—		—		●
2	C_4H_9	—	0	—	0	—	1	OC_4H_9	47	●	45	—		●	(36)	—		●
3	C_5H_{11}	—	0	—	0	—	1	OC_4H_9	58	●	47	—		●	53	—		●
4	C_5H_{11}	—	0	—	0	—	1	OC_5H_{11}	52	●	56	—		●	(47)	—		●
5	C_5H_{11}	—	0	—	0	—	1	OC_2H_5	48	●	44	—		—		—		●
6	C_4H_9	—	0	—	1^a	—	1	OC_2H_5	51	●	59	—		—		●	(20)	●
7	C_5H_{11}	—	0	—	1^a	—	1	OCH_3	47	●	72·5	—		—		—		●
8	C_5H_{11}	—	0	—	1^a	—	1	OC_2H_5	46	●	68	—		—		●	(36)	●
9	C_3H_7	—	0	B	0	—	1	H	56	●	97	—		●	(81)	—		●
10	C_4H_9	—	0	B	0	—	1	H	60	●	59	—		●	95	—		●
11	C_4H_9	—	0	B	0	—	1	CH_3	55	●	105	—		●	124	●	160	●
12	C_5H_{11}	—	0	B	0	—	1	H	64	●	75	—		●	96	—		●
13	C_5H_{11}	—	0	B	0	—	1	CH_3	61	●	84	—		●	148	●	152	●
14	C_5H_{11}	—	0	B	0	—	1	F	59	●	74	—		—		●	126	●
15	C_5H_{11}	—	0	B	0	—	1	OCH_3	70	●	112	—		—		●	178	●
16	C_6H_{13}	—	0	B	0	—	1	C_2H_5	56	●	68	—		●	171	—		●
17	COOH	—	1	—	0	—	1	CH_3	48	●	118	—				—		●
18	COOH	—	1	—	0	—	—	OC_2H_5	52	●	150	—				—		●
19	$COCH_3$	—	0	—	0	—	1	OC_2H_5	62	●	47	—				—		●
20	CN	—	1	B	0	C	0	C_5H_{11}	44	●	139	—				—		●
21	C_3H_7	—	0	B	0	C	0	C_3H_7	68	●	139	—				●	(137)	●
22	C_5H_1	—	0	B	0	C	0	C_3H_7	75	●	99	●	142·5	—		●	152	●
23	C_3H_7	—	0	C	0	—	1	H	82	●	85	—				●	104	●
24	C_3H_7	—	0	C	0	—	1	C_3H_7	86	●	140	●	(107)	—		●	(137)	●
25	C_5H_{11}	—	0	C	0	—	1	H	86	●	70	—		—		●	103	●
26	C_5H_{11}	—	0	C	0	—	1	C_3H_7	87	●	44	●	148	—		●	164	●
27	C_4H_9	C	1	C	0	—	1	H	82	●	61	●	225	—		—		●
28	H	B	1	—	1^a	—	1	OC_2H_5	59	●	66	—				—		●

B = benzene ring, C = cyclohexane ring.

[a] This $-CH_2CH_2-$ group is formed by reduction of a $-CH{=}CH-$ group.

● means phase present; — means phase not present.

figure 2(*b*) with the birefringence of a Demus ester mixture.

The dispersion characteristic of mixture A at different constant temperatures is given in figure 3.

The solid lines are experimental data and the dotted lines are fits using the single bond model equation [11]:

$$\Delta n(\lambda,T) = G(T)[\lambda^2\lambda_o^2/(\lambda^2 - \lambda_o^2)] \qquad (1)$$

The values of the coefficients *G* and λ_o are shown in table 2. The G-values (a kind of order parameter) decrease with increasing temperature (disorder of the LC), while the λ_o value does not depend on temperature at temperatures far from the clearing point. This is as expected. The coefficient *G* is correlated with the order parameter *S* by the equation [11]:

$$G(T) = gNZS\ (f_{\parallel}^{*} - f\perp^{*}) \qquad (2)$$

The above data show that the cyclohexanones **II** containing saturated rings joined to a single benzene ring are mesogens with a small negative dielectric anisotropy and a very low birefringence, and with a low spectral dependence in the visible spectral range.

3. Experimental

3.1. *Structures and physical properties*

Confirmation of the structures of products was obtained using GC/MS mass spectrometry (HP 5972 MSD), ^1H NMR spectrometry (Varian-Gemini 200 MHz, in $CDCl_3$) and IR spectrometry (Perkin Elmer). Phase transition temperatures were measured using a Linkam heating stage, in conjunction with a polarizing PZO microscope. In some cases the results were confirmed by differential scanning calorimetry

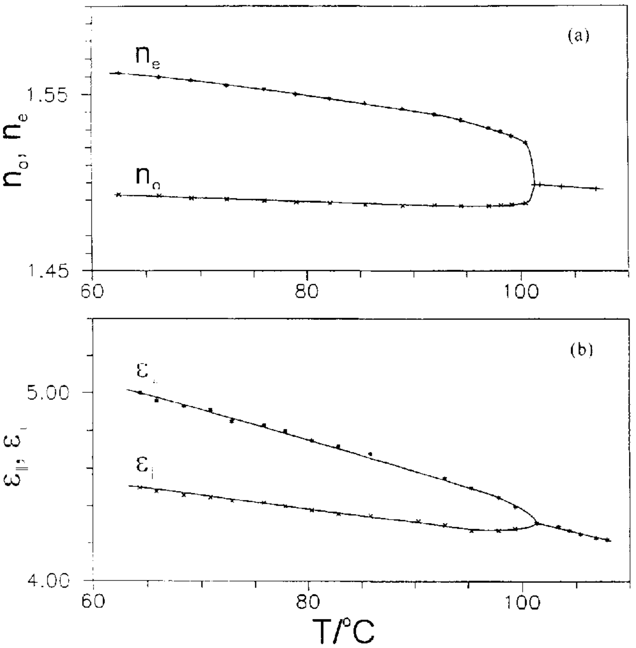


Figure 1. Temperature-dependent refractive indices (*a*) and dielectric constants (*b*) of the liquid crystal **II** 25. The optical indices were measured using an Abbé refractometer. Experimental data at temperature $T–T_{N-I}=-10°$ are as follows: $n_e=1·5399$, $n_o=1·4872$, $\Delta n=0·0527$, $\varepsilon_{\parallel}=4·33$, $\varepsilon_{\perp}=4·60$, $\Delta\varepsilon=-0·27$.

(Setaram DSC92). Ordinary (n_o) and extraordinary (n_e) refractive indices for compound **II**25 were measured by the standard method using an Abbé refractometer and Na_D light (589·7 nm). In order to measure their wavelength-dependent properties, the liquid crystals were filled into commercial cells supplied by EKMO (Minsk, Rep. Belarus) and Displaytech (Boulder, Colorado). The liquid crystals were aligned by the parallel rubbed polyimide layers and the thicknesses of the cells were measured by interferometry before filling [12]. The birefringence of the liquid crystals was obtained by using the method of Wu [13] modified by us in two details. Firstly, we used a fast optical multichannel analyser which allowed us to obtain a spectrum covering the entire visible range in a few milliseconds. Secondly, we found that with the small layer thicknesses used the interferences from the reflections at the two liquid crystal surfaces became very important. Therefore we considered the entire cell as an etalon with different optical thicknesses for polarizations parallel or perpendicular to the fast axis of the liquid crystal and expanded the evaluation of Wu. The refractive indices were obtained from the transmission maxima and the evaluation of suitable polarized white light using again the multichannel analyser. The details of the method are described elsewhere [14]. The dielectric anisotropy was measured by a capacitative method as described in [15].

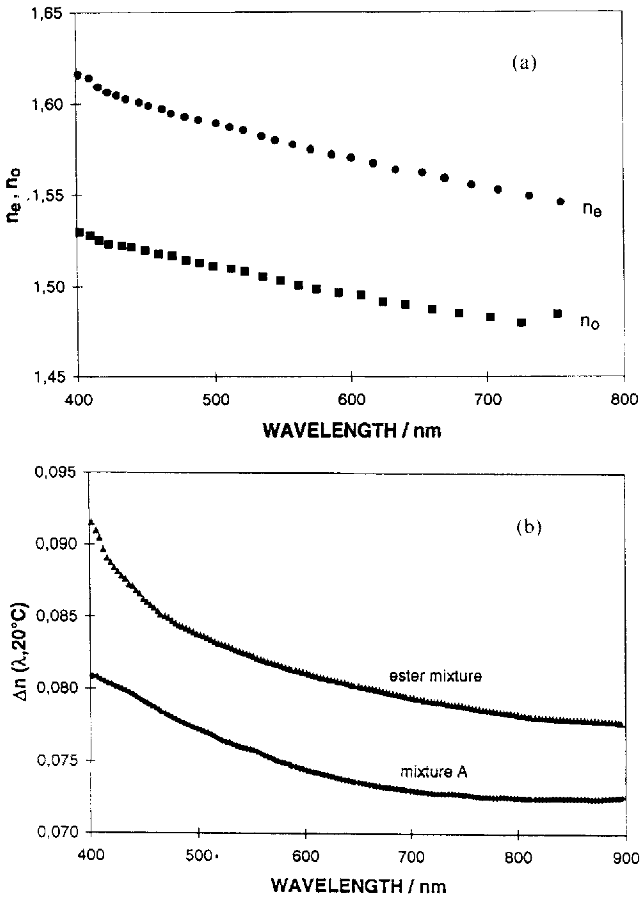


Figure 2. The wavelength-dependent refractive indices of mixture A at 20°C (*a*) and a comparison (*b*) of the wavelength-dependent birefrigence of mixture A and of an ester mixture (4-methoxyphenyl, 4-ethoxyphenyl and 4-pentyloxyphenyl *trans*-4-butylcyclohexanoate in mol ratio 1 : 1 : 1; T_{N-I} 65°C) at 20°C.

3.2. *General method for the preparation of trans-2,5-disubstituted cyclohexan-1-ones*

The 3,6-disubstituted cyclohex-2-en-1-ones **I** (0·2 mol) dissolved either in ethyl or isopropyl alcohol (200 ml) containing potassium hydroxide (0·02 mol) were hydrogenated by gaseous H_2 in the presence of 1 g of 10 wt % palladium on carbon at 40°C with vigorous stirring until hydrogen absorption ceased. The catalyst was separated by filtration, the alcohol was distilled off and the residue was 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 isopropyl alcohol until the phase transition temperatures were constant (2 or 3 times normally).

Spectral data for *trans*-2-pentyl-5-[4-(*trans*-4-propyl-

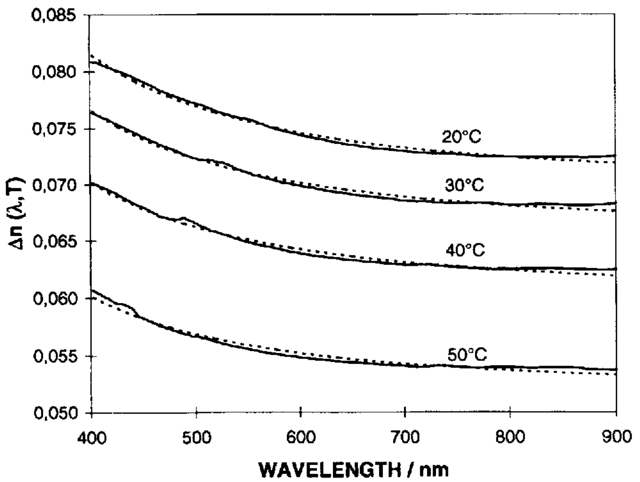


Figure 3. The wavelength-dependent birefrigence of the mixture A at different temperatures. Solid lines: measured values. Dotted lines: fits of the measured values to equation (1); the fit parameters are listed in table 2.

Table 2. Coefficients of equation (1) for mixture A.

Temperature/°C	$G(T)/10^{-6}$ nm^{-2}	λ_0/nm
20	3·02	152·0
30	2·85	151·8
40	2·62	151·5
50	2·32	149·4

cyclohexyl)phenyl]cyclohexan-1-one are given by way of illustration: m/z 368 (M^+, 3·4%) 350 (9·2%), 298 (26·3%), 280 (11·7%), 228 (100%); IR(KBr) 1720 cm^{-1} (C=O).

4. Conclusion

The reduction of 3,6-disubstituted cyclohexen-1-ones by hydrogen in the presence of the catalyst palladium on carbon in alkaline media gives *trans*-2,5-disubstituted cyclohexan-1-ones in high yield, except for structures wherein the benzene rings are directly joined to both sides of the cyclohexenone ring. Mesogens containing a cyclohexanone ring show only smectic phases when they consist of two ring molecules, but it is interesting that those mesogens which contain a cyclohexyl-cyclohexanone moiety form the nematic phase more easily than those containing a phenyl-cyclohexanone moiety. Mesogens in which the cyclohexanone ring is a single polar group have a small negative dielectric anisotropy and their birefringence and the dispersion of the birefringence are the lowest among known molecules of moderate polarity.

This work was supported by the Polish Committee for Scientific Research under grant No 3P405 003 07 and by the European Community under grant CIPACT 940157.

References

[1] Bezborodov, V., Dąbrowski, R., Dziaduszek, J., Czupryński, K., and Raszewski, Z., 1996, *Liq. Cryst.*, **20**, 1.

[2] Bezborodov, V., Dąbrowski, R., Trochimiec, D., Dziaduszek, J., Sosnovskij, G., and Lapanik, W., Polish Patent Application P-304749.

[3] Brettle, R., Dunmur, D. A., Farrand, L. D., Hindley, N. J., and Morson, C. M., 1993, *Chem. Lett.*, 1663.

[4] Hataaki, Y., and Koichi, K., Japanese Patent 62185036; C.A., 108,131286u.

[5] Hataaki, Y., Japanese Patent 62203634; C.A., 110,75026m.

[6] Bezborodov, V., Dąbrowski, R., and Dziaduszek, J., 1994, *SPIE*, **2372**, 242.

[7] Hird, M., Toyne, K. J., Slaney, A. J., Goodby, J. W., and Gray, G. W., 1993, *J. chem. Soc., Perkin Trans.*, **2**, 2337.

[8] Reiffenrath, V., and Plach, H., DE 4427266.

[9] Hataaki, Y., and Koichi, K., Japanese Patent 61268 648; C.A., 106,224634e.

[10] Coates, D., 1990, *Liquid Crystals Applications and Uses*, Vol. 1, edited by B. Bahadur, (Singapore: World Scientific) Chap. 3.

[11] Wu, S. T., 1986, *Phys. Rev. A*, **33**, 1270.

[12] Kinzer, D., 1985, *Mol. Cryst. liq. Cryst. Lett.*, **5**, 147.

[13] Wu, S. T., Efron, U., and Hess, L. D., 1984, *Appl. Opt.*, **23**, 3911.

[14] Kohns, P., Schirmer, J., Schulz, H., Muravski, A. A., and Yakovenko, S. Y., 1995, *Mol. Cryst. liq. Cryst.* (submitted).

[15] Raszewski, Z., 1987, *Electron. Tech.*, **20**, 53.