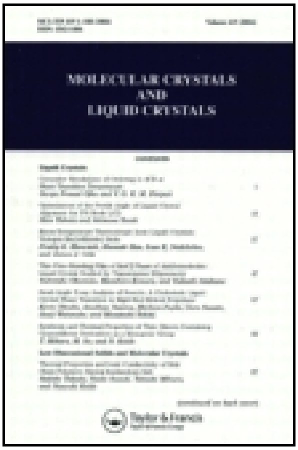

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

New Naphthalene Derivatives with Liquid Crystalline Glassy States

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To cite this article: W. Schäfer , G. Uhlig , H. Zaschke , D. Demus , S. Diele , H. Kresse , S. Ernst & W. Wedler (1990): New Naphthalene Derivatives with Liquid Crystalline Glassy States, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 191:1, 269-276

To link to this article: http://dx.doi.org/10.1080/00268949008038604

Mol. Cryst. Liq. Cryst. 1990, Vol. 191, pp. 269–276
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Printed in the United States of America

NEW NAPHTHALENE DERIVATIVES WITH LIQUID CRYSTALLINE GLASSY STATES

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(Submitted for publication September 1, 1989)

Abstract New derivatives of α- and β- naphthol have been synthesized all of which have glass transitions near to room temperature. The former are isotropic liquids, the latter are monotropic nematic with probable biaxiality in the glassy state. The compounds have been investigated by calorimetry, viscosimetry, dielectric and X-ray measurements.

Keywords liquid crystal, nematic, glassy phase, biaxiality, naphthol derivatives, dielectric anisotropy

INTRODUCTION

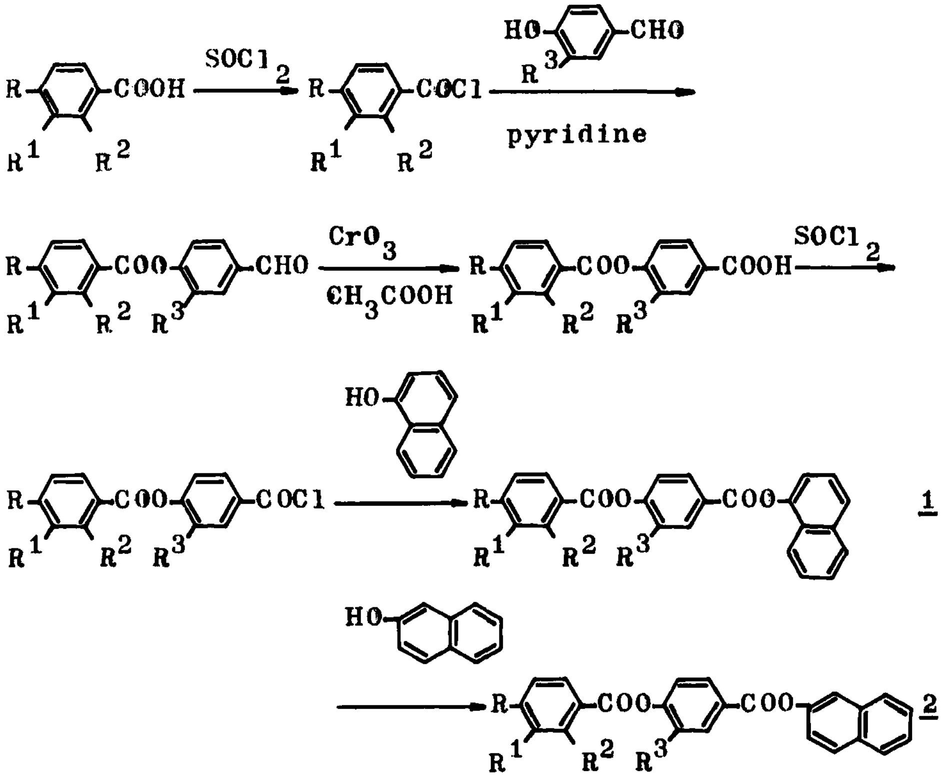
The glass-forming tendency is closely connected with a great ascent of viscosity by cooling a liquid phase and with an effective prevention of crystallization. This tendency can be influenced by the chemical structure of the molecules.

In low molecular substances bulky substituents and sidegroups may cause a glass-transition behaviour. Additionally to the bulky structure mesogenous molecules must possess a great length-to-breadth-ratio. VORLÄNDER et al. /1/ for the first time described such "bulky" molecular species. In continuation of this tradition we investigated α- and β- naphthylesters. The "bulky" part of these compounds is the condensed naphthalene cycle system.

The aim of our work was to find stable, easy to produce substances and mixtures for electro-optical storage modules /2/, /3/.

SYNTHESIS

We synthesized the ester 1 and 2 according to the following scheme, using standard procedures:



R = alkyloxy, -CN

R^1 = -H, -Cl, -Br, $-CH_3$, $-NO_2$, $-OC_2H_5$

R^2 = -H, $-CH_3$; R^3 = $-OCH_3$, -H, -Br

The pure esters were obtained by repeated crystallization with ethanol/toluene until their transition temperatures were constant.

RESULTS AND DISCUSSION

We investigated the thermal behaviour of the compounds by calorimetric measurements using a Perkin-Elmer DSC-2 calorimeter which was constantly cooled by an ethanol-CO_2-mixture. We used substance amounts of 4 - 6 mg, placed in capsules of aluminium. All measurements were made in the following way:

1. Heating the crystalline material into the isotropic phase (20 K min^{-1}).
2. Cooling down the liquid phase (20 or 40 K min^{-1}) into the glassy state.
3. Second heating of the glassy phase into the isotropic phase (20 K min^{-1}).

In cases of an intensive tendency of crystallization we had to cool down the liquid phase outside the calorimeter realizing a greater cooling rate.

Table 1 gives some examples of calorimetric data, observed at pure compounds. Generally one can point out the following facts:

a) α - naphthalene esters, apart from some exceptions, form only isotropic liquid phases. Unlike that β - naphthalene esters form nematic mesophases.

b) α - naphthalene esters have higher glass transition temperatures T_g^{ON} than analogously constructed β - naphthalene esters.

c) The longer are the alkyl, acyl and alkyloxy chains, the lower is the glass transition temperature T_g^{ON}.

d) Additional side groups and polar substituents rise the glass transition temperature T_g^{ON}.

One can conclude, that glass-forming tendency and mesogenity are faced contrary to each other.

In order to realize our aim we were interested in not crystallizing substances. Pure compounds are not able to satisfy this demand. The crystallization, however, is strongly hindered in mixtures. Therefore we created some mixtures of glass-forming components. Figure 1 shows the DSC-plot (steps 2 and 3) of a four component mixture. Only the clearing point of the nematic phase and the glass transition-interval are visible. Planning the glass transition behaviour in the mixture is very easy. Are $T^{ON}_{g\,i}$ the characteristic temperatures of the glass transitions of the components and x_i their molar fractions, one can estimate the T^{ON}_{g} of the mixture using the formula

$$T^{ON}_{g} = \sum x_i \, T^{ON}_{g\,i} \, . \qquad (1)$$

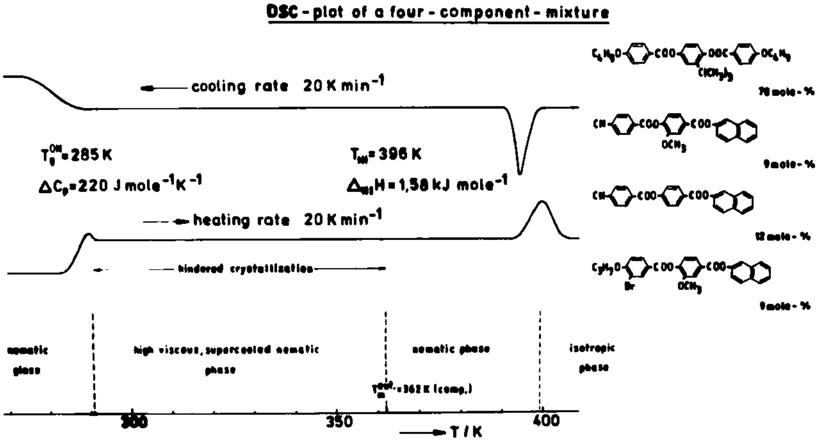


FIGURE 1 DSC-plot of a four component mixture

An advantage of our compounds is the non-symmetrical molecular construction which makes possible a synthesis of highly polar molecules. We made measurements of the dielectric anisotropy of the mentioned mixture, which was oriented by a magnetic field. As a result we found two relaxation mechanisms parallel and perpendicular to the direction of the magnetic field (see figure 2), corresponding to a rotation of the molecules around the long ($f_{R\perp}$) and the short ($f_{R\parallel}$) axis. Both mechanisms show a typical VOGEL-FULCHER-TAMMANN-behaviour with characteristic VFT-temperatures $T_{\infty 1}$ = 255 K (mechanism 1) and $T_{\infty 2}$ = 231 K (mechanism 2).

Moreover, we investigated an oriented sample by X-rays. The mixture, consisting of compounds 4

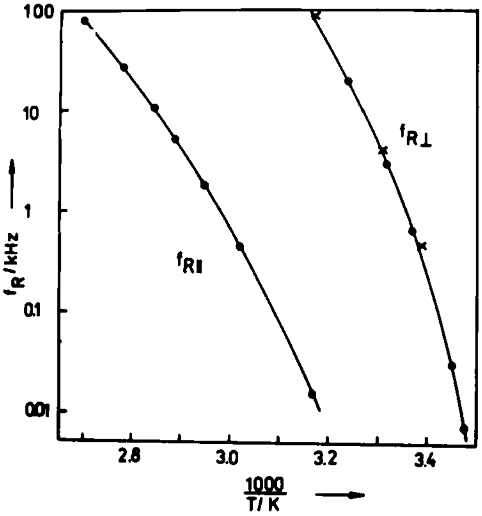


FIGURE 2 VFT-behaviour of the two relaxation mechanisms in the glass-forming liquid-crystalline mixture from fig. 1 (f_R - relaxation frequencies)

(50 mole-%), 5 (30 mole-%) and 6 (20 mole-%) (see table 1) has a characteristic onset-glass-transition point T_g^{ON} of 310 K and a clearing point of 399.7 K.

Reflexes of several orders, caused by cybotactic groups, are visible (see figure 3). The wide-angle reflexes of the lateral distances give a hint to a possible biaxiality of this nematic glass.

TABLE 1 Calorimetric data of selected compounds.

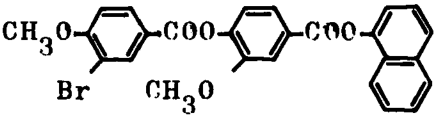
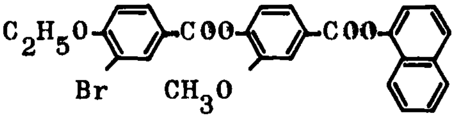
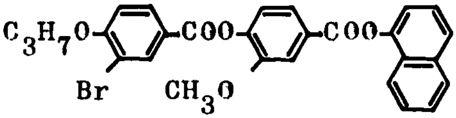
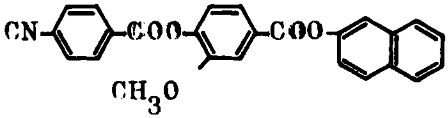
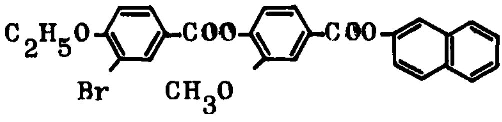
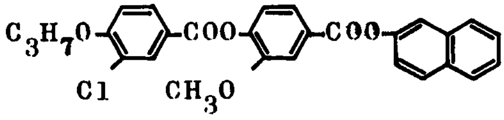
Formula of compound	T_g^{ON}/K	T_{cryst}^{max}/K
α - Naphthylesters		
1. 	326	425
2. 	321	401
3. 	313	?
β- Naphthylesters		
4. 	313	397
5. 	312	398
6. 	299	366

TABLE 1 (continued)

	Cr		N		Is	ΔC_p/J mole^{-1}K^{-1}
1.	+	432.2	/		+	151
2.	+	447.7	/		+	164
3.	+	422.2	/		+	125
4.	+	463.0	(+	449.2)	+	150
5.	+	422.0	(+	382.2)	+	165
6.	+	428.4	(+	362.4)	+	179

	$\Delta_m H$/kJ mole^{-1}	$\Delta_{NI}H$/kJ mole^{-1}
1.	41.6	–
2.	45.2	–
3.	38.2	–
4.	33.8	1.24
5.	46.5	1.04
6.	43.6	0.79

All temperatures in K. T^{max}_{cryst} – temperature of the maximum of the crystallization peak in the DSC-output.

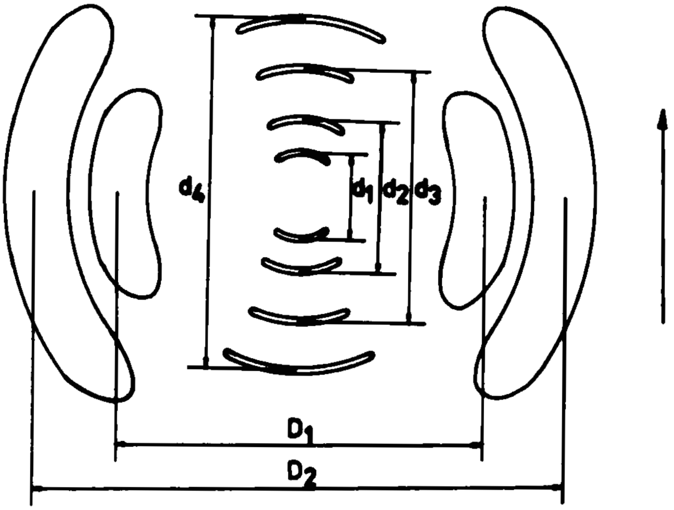


FIGURE 3 Sketch of X-ray-reflexes in a glassy nematic mixture (see text); sample oriented in the direction of the arrow

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