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Searching for photochromic liquid crystals
Spironaphthoxazine substituted with a mesogenic group

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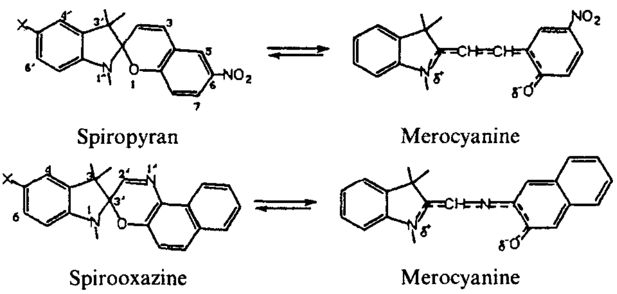
A number of photochromic spiropyrans and spirooxazines containing mesogenic groups were synthesized. Only one of them, spiro-indoline-naphthoxazine with mesogenic substituent, 4-(4-heptylbenzoyloxy)benzoyloxy in 5-position, revealed mesomorphic properties. Its phase behaviour, photochromism and alignment in the electric field was investigated. A structure of the mesophase is discussed.

1. Introduction

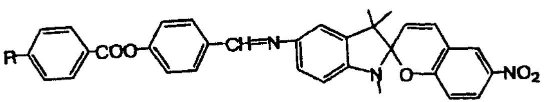
Many spiropyrans and spirooxazines exhibit photo- and thermochromic properties associated with the following reversible reaction [1, 2].



Spiropyran Merocyanine

Spirooxazine Merocyanine

Earlier we reported mesomorphic properties of spiropyran molecules containing mesogenic groups attached to the 5′-position through a Schiff base link [3–6]



R = CN, OCH_3, OC_6H_{13}

QLC

These compounds form a metastable mesophase by heating of amorphous films prepared by fast evaporation of their benzene solutions.

The temperature range of the mesophase lies much below the crystal melting point. For example, the spiropyran with X = CH_3O–Ph–COO–Ph–CH=N– gives a

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mesophase between 50–130°C, while the melting point of the spiropyran crystals is ~ 200°C. The mesophase is not monotropic and is not formed on cooling of the melt. The appearance of the texture characteristic for the mesophase, on heating of an amorphous film coincides with an increase of merocyanine concentration in the film to 3–5 mol %.

The mesomorphic films crystallize with time. However, their alignment in an electrostatic field of more than 0.5 kV/mm makes them stable indefinitely in super-cooled conditions at room temperature. The order parameter of the merocyanine in such aligned films was rather low, about 0·3–0·4. The aligned films exhibit optical nonlinearity and generate second harmonics because of the non-centrosymmetric orientation and high hyperpolarizability of the merocyanine molecules. These materials were named quasi-liquid crystals (QLCs).

More detailed studies indicated that the QLCs represent an intrinsic two-component spiropyran-merocyanine mesophase with properties that are substantially determined by strong interactions between these components which are in thermal equilibrium with each other. The merocyanine content of the QLCs can be varied only by changing the temperature because the material is thermochromic but not photochromic.

The absence of photochromic properties is associated presumably with attachment of mesogenic groups to the spiropyran molecules, since the corresponding unsubstituted spiropyran exhibits strong photochromism.

In the present paper we describe our attempts to synthesize a photochromic compound with mesomorphic properties. We report on synthesis and brief characterization of a number of spiropyrans and spirooxazines containing mesogenic groups. We also give a more detailed examination of a spiro-indoline-naphthoxazine substituted with a mesogenic group in the 5-position. This compound yielded a stable mesomorphic glass with pronounced photochromic properties.

2. Experimental section (results)

2.1. *Chemicals*

The following chemicals were used without further purification: Benzyl *p*-hydroxybenzoate (TCI); 5-nitrosalicylaldehyde (Eastman Kodak); 4-methoxybenzoic acid (BDH); 4-cyanobenzoic acid (Aldrich); methyl iodide (Merck); 4-methoxyphenylhydrazine hydrochloride 98 per cent (Aldrich); boron tribromide (Merck); methyl isopropyl ketone (Merck); 1-nitroso-2-naphthol 98 per cent (Aldrich); piperidine puriss (Fluka); 2-butanone (BDH), 4-heptylbenzoic acid (Aldrich); 10 per cent Pd/c (Fluka); 12-hydroxydodecanoic acid (Aldrich); trans-cyclohexane-1,4-dicarboxylic acid (Aldrich); *N*,*N*-dicyclohexyl carbodiimide (Merck). Amino spiropyran was prepared according to [3].

2.2. *Synthesis*

5′-Hydroxy-1′,3′,3′-trimethyl-6-nitro-spiro [2H-1-benzopyran-2,2′-indoline] (5′-hydroxy spiropyran IV) and 5-hydroxy-1,3,3-trimethyl-spiro [indoline-2,3′-[3H]-naphtho[1,2-b]-1,4-oxazine] (5-hydroxy spirooxazine, V) were synthesized as shown in figure 1.

5-Methoxy-2,3,3-trimethyl indolenine (*I*) (*see* [7]): A solution of 4-methoxyphenylhydrazine hydrochloride (10 g, 0·057 mole) and methyl isopropyl ketone (6·2 ml, 0·057 mole) and abs. ethanol was refluxed for 4 hrs. After filtration the solvent was evaporated to give the product [TLC: R_f = 0·3 (yellow spot), kieselgel 60F 254, eluent

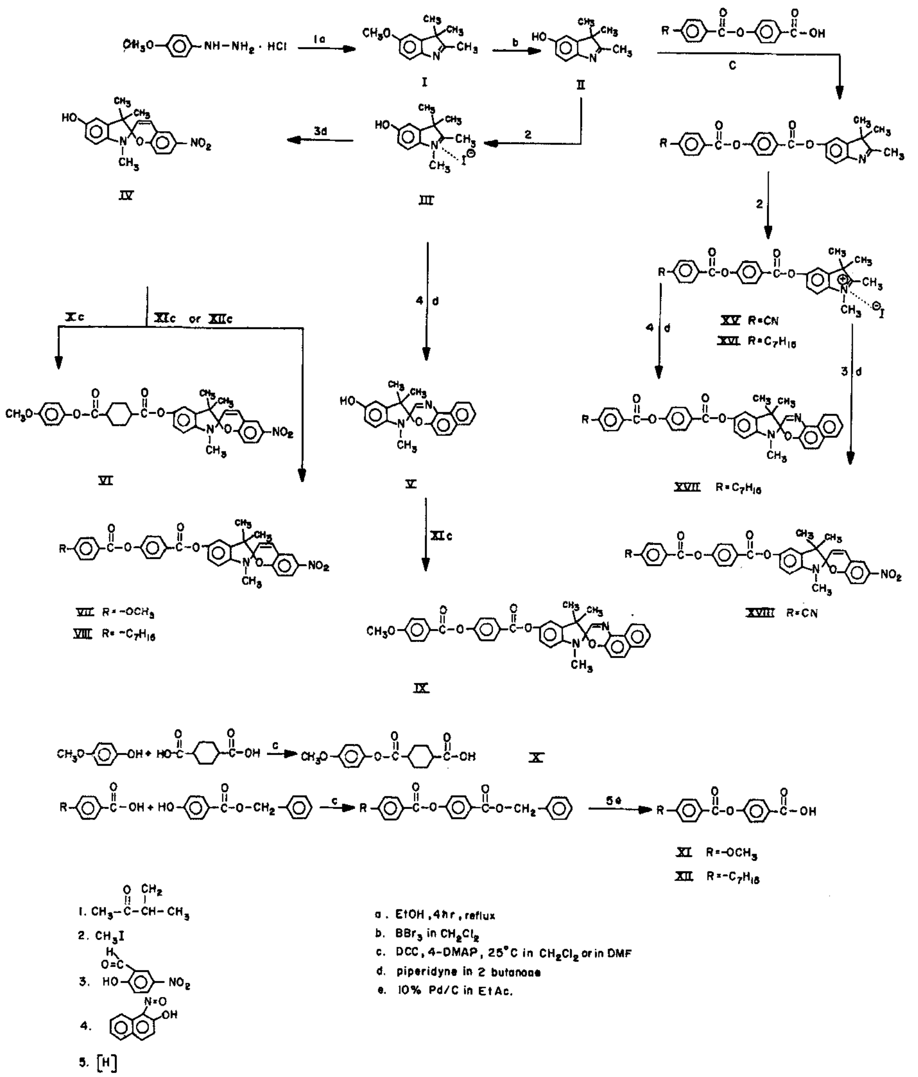


Fig. 1. Reaction scheme for the synthesis of spiropyrans and naphtospirooxazine containing mesogenic groups.

ethyl acetane/hexane, 1 : 2]. This product was used directly in the following step without further purification.

5-Hydroxy-2,3,3,-trimethyl indolenine (*II*) (*see* [*8*]): A solution of 5-methoxy-2,3,3-trimethyl indolenine (0·057 mole) in 30 ml of methylene chloride was cooled in an ice bath. Boron tribromide (11 ml, 0·11 mole) in 20 ml methylene chloride was added dropwise while stirring. The mixture was left at room temperature overnight and neutralized by saturated sodium carbonate solution (pH 7–8) carefully. Methylene chloride layer was separated, dried, solvent was evaporated to yield 9 gr (90 per cent) of brown material. Anal Calcd. for $C_{11}H_{13}NO$: C, 75·4; H, 7·48; N, 7·99. Found: C, 68·3; H, 7·54; N, 7·17. ^{1}H-NMR (CD_3CN) δ = 1·53 (S, 6 H); 2·46 (S, 3 H); ABX system: 6·99 (dd, H, J = 8, 2 Hz); 7·10 (*d*, H, J = 2 Hz); 7·54 (*d*, H, J = 8 Hz).

5-Hydroxy-1,2,3,3-tetramethyl-3H-indolium iodide (*III*) (*see* [7]): To 3 gr (0·017 mole) of 5-hydroxy-2,3,3-trimethyl indolenine 6 ml of methyl iodide and 1 ml of methylene chloride were added. The mixture was refluxed overnight, the precipitated product was filtered, washed with benzene and crystallized from ethanol to yield 3 g (58 per cent) of pale brown solid. Anal. Calcd. for $C_{12}H_{16}INO$: C, 45·44; H, 5·08; N, 4·42; I, 40·0. Found: C, 46·31; H, 4·79; N, 4·35; I, 35·29. ^{1}H-NMR (DMSO) δ = 1·49 (S, 6 H); 2·69 (S, 3 H); 3·91 (S, 3 H); 6·95 (dd, H, J = 8·6, 2·2 Hz); 7·13 (*d*, H, J = 2·2 Hz); 7·68 (*d*, H, J = 8·6 Hz).

5'-Hydroxy-1',3','3'-trimethyl-6-nitro-spiro [*2H-1-benzopyran-2,2'-indoline*] (*5'-hydroxy spiropyran IV*) (*see* [*9*]): Iodide salt III 1·5 g (4·7 mmole) and 5-nitrosalicylaldehyde 0·79 g (4·7 mmole) were dissolved in 15 ml of 2-butanone in the presence of 0·46 ml (4·7 mmole) of piperidine. After the reaction mixture was refluxed for 1 h, solvent was evaporated. Material was dissolved in chloroform and benzene was added. Solution was concentrated to give a solid which was filtered. Yield, 1·5 g (68 per cent).

5-Hydroxy-1,3,3-trimethyl-spiro [*indoline-2,3'-*[*3H*] *naphtho* [*2,1-b*]*-1,4-oxazine*] (*5-hydroxy spirooxazine V*) (*see* [*9*]) was synthesized in a similar way to that described for spiropyran IV. Material was purified by flash chromatography (eluent ethyl acetate/hexane, 1 : 5). The yield of green solid was 200 mg (20 per cent), mp 102–103°C. Anal. Calcd. for $C_{22}H_{20}N_2O_2$: C, 76·72; H, 5·85; N, 8·13. Found: C, 77·01; H, 5·97; N, 8·24.

5'-[*4*(*4-Methoxyphenoxycarbonyl*) *cyclohexylcarboxy*]*-1',3',3'-trimethyl-6-nitro-spiro*[*2H-1-benzopyran-2,2'-indoline*] (*VI*): Material was synthesized by direct esterification of acid *X* with 5'-hydroxy spiropyran IV. Purification by flash chromatography (eluent ethyl acetate/hexane 1 : 3), mp 230°C (yellow crystals).

5'-(*4*(*4-Methoxybenzoyloxy*) *benzoyloxy*]*-1',3',3'-trimethyl-6-nitro-spiro* [*2H-1-benzopyran-2,2'-indoline*] (*VII*) (*see* [*10*]): 4(4-methoxy benzoyloxy)benzoic acid 200 mg (0·75 mmole) and 5'-hydroxy spiropyran IV 254 mg (0·74 mmole) were dissolved in DMF/methylene chloride 1 : 1 (2 ml) in the presence of 4-dimethylaminopyridine 10 mg. The solution was cooled (0°C) and 155 mg (0·78 mmole) of *N,N'*-dicyclohexylcarbodiimide was added. The reaction mixture was stirred at room temperature overnight, filtered and solvent evaporated. The residue was redissolved in methylene chloride, washed with water, dried over anhydrous sodium sulphate and evaporated. Purification by chromatography (eluent methylene chloride), mp 205°C.

5'-[*4*(*4-Heptylbenzoyloxy*) *benzoyloxy-1',3',3'-trimethyl-6-nitro-spiro* [*2H-1-benzopyran-2,2'-indoline*] (*VIII*) (*see* [*10*]) was prepared according to method described for material VII. Purification by flash chromatography (eluent ethyl acetate/hexane 1 : 4), mp 178°C. Anal. Calcd. for $C_{40}H_{40}N_2O_7$: C, 72·72; H, 6·10; N, 4·24. Found: C, 72·28; H, 5·98; N, 4·31.

5-[*4*(*4-Methoxybenzoyloxy*) *benzoyloxy*]*-1'3',3'-trimethyl-spiro* [*indoline 2,3'-*[*3H*]*-naphtho*[*2,1-b*]*-1,4-oxazine*] (*IX*): 5-hydroxy spirooxazine V and acid XI were dissolved in a minimum amount of methylene chloride. A catalytic amount of 4-dimethylaminopyridine and then *N,N'*-dicyclohexylcarbodiimide were added. Purification by flash chromatography (eluent methylene chloride/hexane, 4 : 1), yield 50 per cent, mp 195°C. Anal. Calcd. for $C_{36}H_{30}N_2O_6$: C, 73·71; H, 5·15; N, 4·77. Found: C, 75·2; H, 5·31; N, 4·35.

4-(*4-Methoxyphenoxycarbonyl*) *cyclohexylcarboxylic acid* (*X*) (*see* [*10*]) was prepared according to Hassner's method. Reaction was carried out in DMF for 3$\frac{1}{2}$ h;

crystallization from toluene. Anal. Calcd. for $C_{15}H_{18}O_5$: C, 64·73; H, 6·52. Found: C, 65·00; H, 6·82. ^{1}H-NMR ($CDCl_3$) δ = 1·66, 2·25 (m, 10H cyclohexane ring); 3·79 (S, 3H); 6·91 (m, 4H aromatic ring).

4-(4-Methoxybenzoyloxy) benzoic acid (XI) (see [10]) and 4-(4-heptylbenzoyloxy) benzoic acid (XII) were synthesized as shown in figure 1. Coupling was performed according to Hassner's method. Hydrogenation was carried out in ethyl acetate in the presence of 10 per cent Pd/C overnight. Crystallization from toluene gave product as white crystals. XI: Yield 80 per cent. Anal. Calcd. for $C_{15}H_{12}O_5$: C, 66·17; H, 4·44. Found: C, 66·19; H, 4·54. XII: Yield 89 per cent. Anal. Calcd. for $C_{21}H_{24}O_4$: C, 74·09; H, 7·11. Found: C, 73·3; H, 7·15.

5-[4(4-(Hepthylbenzoyloxy) benzoyloxy]-1,3,3-trimethyl-spiro [indoline-2,3′-[3H] naphtho[2,1-b]-1,4-oxazine] (spirooxazine XVII) was synthesized in the way described in figure 1. Material was purified by flash chromatography. Structures were verified by NMR, mp 159°C. XVII: Anal. Calcd. for $C_{42}H_{42}O_5N_2$: C, 77·04; H, 6·47; N, 4·28. Found: C, 77·05; H, 6·24; N, 4·26.

5′-[4(4-Cyanobenzoyloxy) benzoyloxy]-1′,3′,3′-trimethyl-6-nitro-spiro [2H-1-benzopyran-2,2′-indoline] (spiropyran XVIII): Material was prepared as shown in figure 1. Purification by flash chromatography (eluent ethyl acetate/hexane 1 : 3), mp 203°C (off white solid; purple melt). Anal. Calcd. for $C_{34}H_{25}N_3O_7$: C, 69·5; H, 4·29; N, 7·15. Found: C, 69·51: H, 4·22; N, 6·86.

Spiropyran XXII was synthesized stepwise as described in figure 2. The product was purified by flash chromatography (eluent methylene chloride), yield 55 per cent, mp 65°C (yellow solid; purple melt). Anal. Calcd. for $C_{46}H_{48}N_4O_8$: C, 70·39; H, 6·16; N, 7·14. Found: C, 69·34; H, 6·05; N, 6·96.

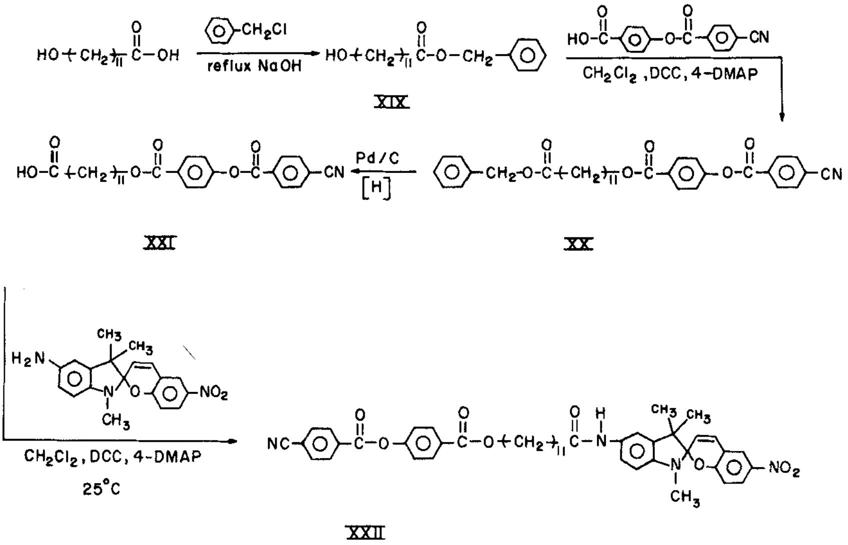


Figure 2. Reaction scheme for the synthesis of spiropyran connected to a mesogenic group by a spacer.

2.3. *Material characterization*

The transition temperatures of the crystals and quasi-mesophases were determined by polarization microscopy and differential scanning calorimetry (DSC).

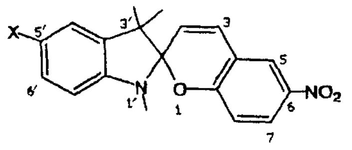
A Wild-M8 polarizing microscope with an Ernst Leitz Wetzlar hot stage was used. The DSC measurements were performed with a Mettler TA3000 instrument. Optical absorption and kinetic measurements were performed with a Varian 2200 spectrophotometer with a heating-cooling attachment [11]. Flash photolysis was conducted as it is described in [12].

Film preparation: the spirooxazine XVII mesophase films were prepared by fast cooling of the melted crystals (to the appropriate temperature). Spiropyran films were prepared as described in [3, 4]. Each sample was vacuum-dried before spectroscopic investigation. The film thickness varied from 2 to 6 μm.

3. Results

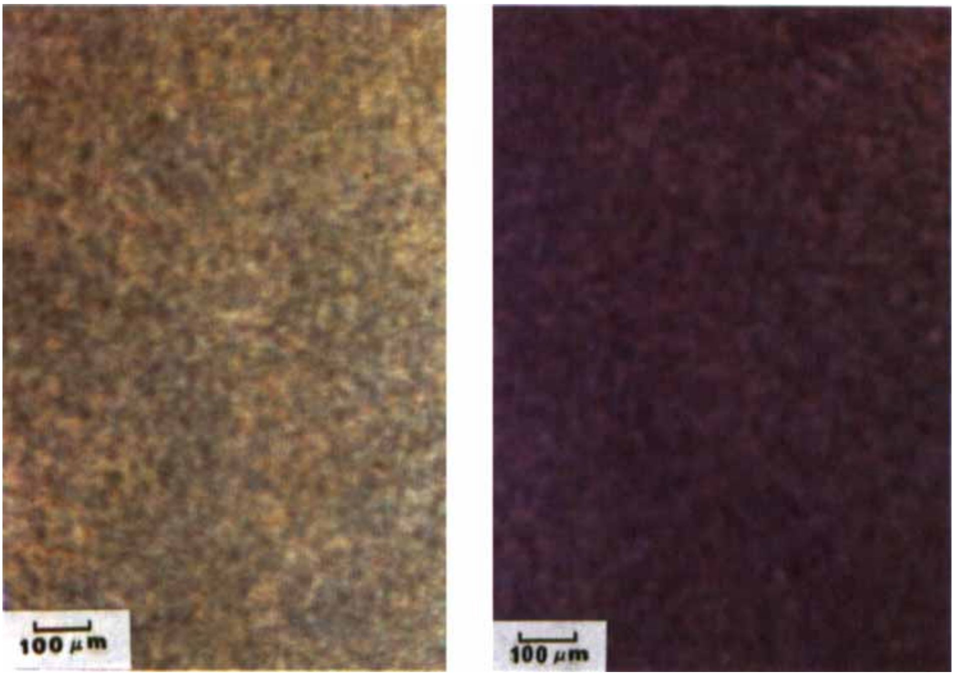
Description of photo- and thermochromism and of the phase transitions of spiropyran and spirooxazine molecules with mesogenic substituents is given in tables 1 and 2. Spiropyrans, giving a QLC-phase which were synthesized earlier are also listed in table 1. One can see that all spiropyrans synthesized up to now are thermochromic and with the exception of three of them, they are also photochromic. However, it is just these three spiropyrans which form a QLC-phase and are differentiated from the others by the 'bridging' Schiff-base group. This group, unlike other investigated bridging groups, enables conjugation between the aromatic mesogenic and the indoline units and makes the molecular structure less flexible and straighter. This apparently promotes the mesophase formation; yet these conjugated molecules are not photoactive. Explanation of this fact involves some difficulties because very little is known as yet about the effects of the molecular structure on the stability of the spiropyran and mercocyanine forms in the ground and excited states (see for example [13, 14], and references therein).

Table 2. Characteristics of spironaphthoxazines containing a mesogenic group.



No.	Substituent *X*	T_c °C	T_m (m.p.) °C	Photo-chromism	Thermo-chromism
1	CH_3O-Ph-OOC-C_6H_{10}-COO-	–	230	+	+
2	CH_3O-Ph-COO-Ph-COO-	–	205	+	+
3	C_7H_{15}-Ph-COO-Ph-COO-	–	178–180	+	+
4	NC-Ph-COO-Ph-COO-	–	203	+	+
5	NC-Ph-COO-Ph-COO$(CH_2)_{11}$-CONH-	–	65	+	+
6	$C_6H_{13}O$-Ph-COO-Ph-CH=N-	110	165–168	–	+
7	CH_3O-Ph-COO-Ph-CH=N-	130	198–203	–	+
8	NC-Ph-COO-Ph-CH=N-	170	210–214	–	+

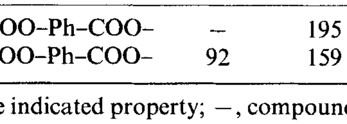
+, compound exhibits the indicated property; –, compound does not exhibit the indicated property.



(*a*) (*b*)

Figure 3. Film of photochromic spirooxazine observed between cross polarizers; (*a*) before irradiation, (*b*) after UV-irradiation.

Table 2. Characteristics of spironaphthoxazines containing a mesogenic group



No.	No. at Fig. 1	Substituent *X*	T_c °C	T_m (m.p.) °C	Photo-chromism	Thermo-chromism
1	IX	CH_3O-Ph-COO-Ph-COO-	–	195	+	+
10	XVII	C_7H_{15}-Ph-COO-Ph-COO-	92	159	+	+

+, compound exhibits the indicated property; –, compound does not exhibit the indicated property.

The first successful preparation of a photochromic mesophase resulted from the synthesis of 5-[4(4-heptylbenzoyloxy)benzoyloxy]-1,3,3-trimethylspiro [indoline-2,3'-[3H]-naphtho[2,1-b]-1,4-oxazine] (compound XVII in figure 1). The mesomorphic films of the compound acquire a deep colour on UV-irradiation at room temperature (figure 3). The colour decays spontaneously, its decay can be accelerated by irradiation with visible light. The process is reversible and can be repeated without marked fatigue. An investigation of the thermodynamic, spectral and kinetic properties of the compound is reported below.

3.1. *Formation of mesophase and phase transitions of mesogenic spirooxazine XVII*

The crystals melt at 159°C, according to DSC (curve 1 in figure 4 gives an isotropic fluid). Fast cooling of the fluid film led to the appearance of a birefringent texture of about 100°C which is preserved on further cooling of the film, without crystallization. Phase transition peaks with a low ΔH (about 0·5 J/g) were also observed at ~ 100°C on the DSC thermograms (curves 2, 3 in figure 4) which seems to indicate a mesophase–isotropic phase transition. The glassy birefringent films are stable at room temperature, but prolonged heating of the films, especially above the clearing point (120°C) induced crystallization of this material. The spirooxazine mesophase was stabilized by alignment in an electrostatic field, just as reported for spiropyran QLCs [3, 4].

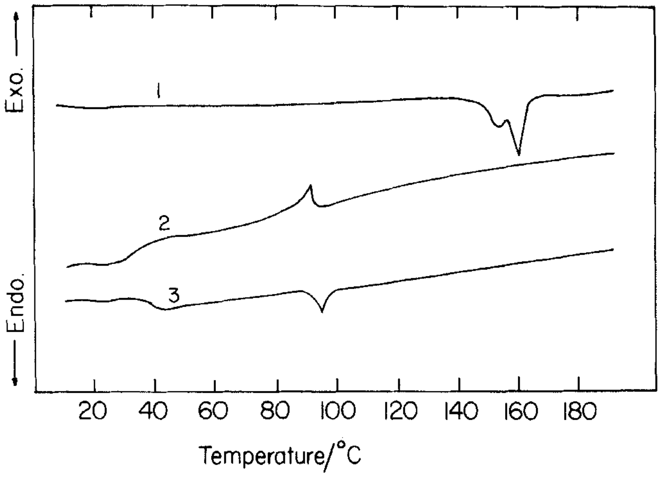


Figure 4. DSC thermograms of compound XVII: (1) crystal heating; (2) melt cooling; (3) the second heating cycle and the nematic–isotropic transition (T_c).

3.2. *Spectra and colour decay kinetics*

The absorption spectra resulting from the UV irradiation of spirooxazine XVII in the mesomorphic phase and in tetrahydrofuran solution are similar (figures 5, 6). In the visible region they have an absorption maximum at ~610 nm and a pronounced shoulder around 580 nm that apparently indicates two overlapping bands. According to [14] these bands relate to two merocyanine isomers which are in thermal equilibrium with each other. The fact that the shape of the spectra remains unchanged during UV irradiation and the thermal colour decay of the irradiated mesogenic glass (figures 5 (*a*) and (*b*)) is in line with this assumption. However, in liquid THF solution at low temperature a red shift of the absorption band was observed (figure 6).

Typical kinetics of decoloration processes of an UV-irradiated glassy mesomorphic film and of a solution of the spirooxazine XVII in THF are shown in figures 5 and 6. The colour decay both in solution and in the mesophase deviates markedly from first order kinetics. It is therefore very difficult to compare the rate constants in these media. Some impression about the decay rate is given by the decoloration

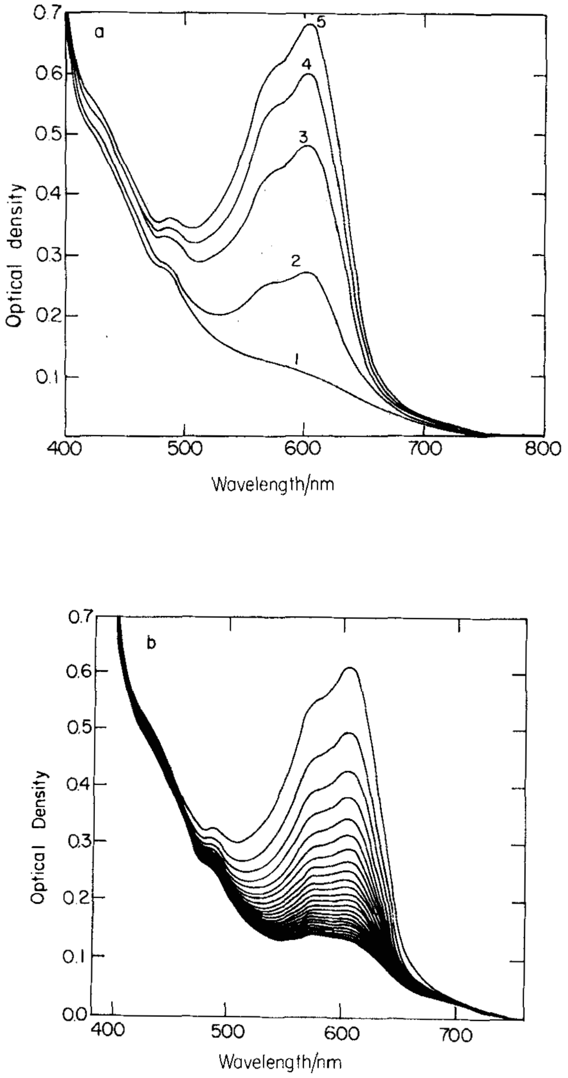


Figure 5. Absorption spectra of XVII glassy mesomorphic film at room temperature. (*a*) (1) Before irradiation; Successive exposures to UV light (λ = 365 nm) for (2) 1 min; (3) 3 min; (4) 5 min; (5) 10 min. (*b*) Thermal decay of the visible absorption band measured in 2 min time intervals.

half-lives in the glassy state and in solution. These are 470 and 1·5 s, respectively. The decoloration kinetics in solution at room temperature was measured by the flash photolysis technique [12]. The temperature dependence of the colour decay rates in solution does not obey the Arrhenius equation.

3.3. *Order parameter*

Alignment of a mesomorphic film in an electrostatic field between two metal electrodes on a glass slide and cooling to room temperature provided a possibility to estimate an order parameter (S) of the merocyanine dye formed on UV-irradiation

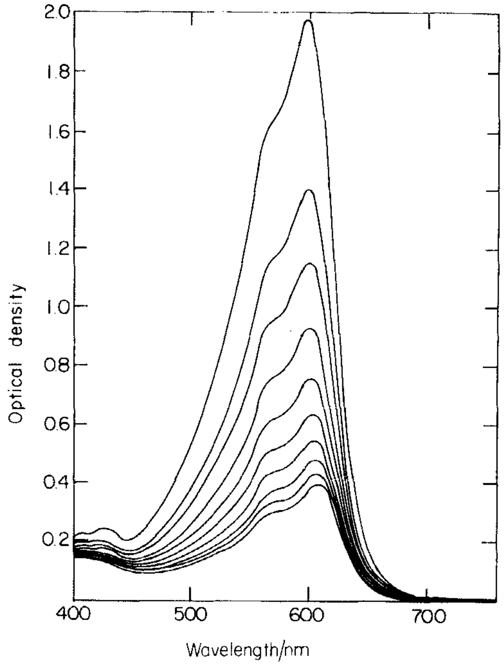


Figure 6. Absorption spectra of 10^{-5} M XVII in THF at −18°C. Thermal decay of the photo-induced absorption band measured in 1 min time intervals.

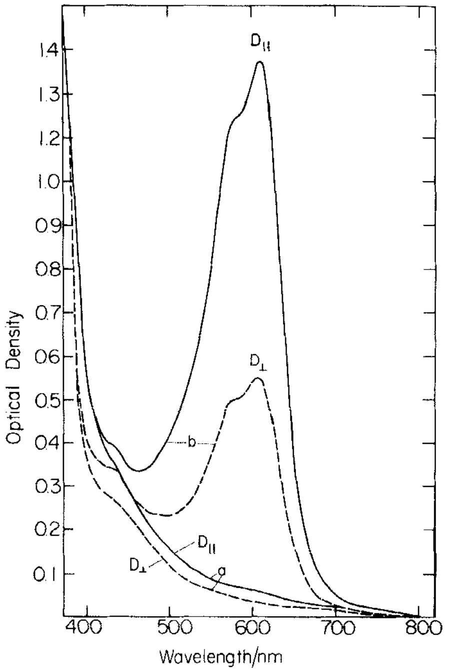


Figure 7. Polarization absorption spectra of XVII, aligned in the electric field (0·5 kV/mm) measured at −20°C. $D_{\parallel}$ and $D_{\perp}$ correspond to the measurements in light polarized parallel and perpendicular to the mesophase director. (*a*) Before irradiation; (b) after 5 min UV irradiation. Merocyanine order parameter $S = 0{\cdot}32$.

of the film. The order parameter of the merocyanine is given by

$$S = (D_{\|} - D_{\perp})/(2D_{\perp} + D_{\|})$$

where $D_{\|}$ and $D_{\perp}$ are, respectively the absorption parallel and perpendicular to the electric field (figure 7). At the electric field strength ~ 1 kV/mm the order parameter was about 0·3.

Examination of fluorescence polarization spectra of 4-dimethylamino 4′-nitrostilbene (DANS) dissolved in the spirooxazine XVII allowed to estimate an order parameter for the dissolved dye (figure 8). The fluorescence spectrum measured with exciting light polarized parallel to the sample alignment has two emission bands peaked at 600 and 660 mm, while with light polarized perpendicular to the alignment only one band peaked at 600 nm appears. Similar band splitting was observed by us for DANS dissolved in photochromic liquid crystal polyacrylates (see [15] where this effect was briefly discussed). The DANS order parameter estimated from fluorescence polarization spectra is 0·73, i.e. more than twice as the order parameter observed for merocyanine.

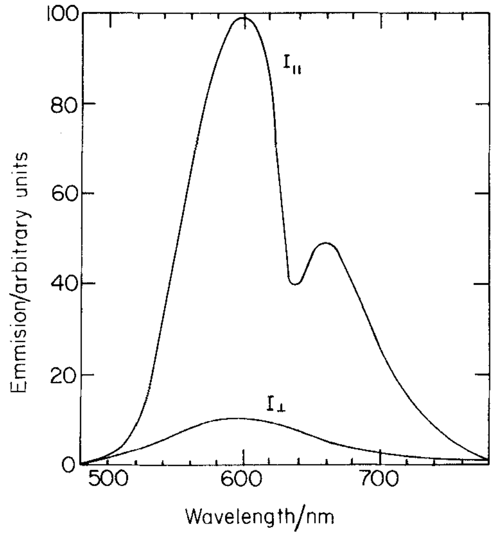


Figure 8. Polarization emission spectra of 1 per cent DANS in XVII after alignment in the electric field. $I_{\|}$ and $I_{\perp}$ correspond to the measurements with light polarized parallel and perpendicular to the mesophase director ($S = 0{\cdot}73$).

4. Discussion

Examination of different molecules resulting from the combination of a photochromic spiropyran or spirooxazine unit and a mesogenic unit indicates that in many cases such a combination impairs either the mesomorphic or photochromic properties characterizing the individual constituents. Presumably, among the factors leading to impairment of mesomorphic properties are deviation from cylindrical shape, distortion of the rigid structure of the molecule, and raise of the crystal melting point associated with the lattice energy growth. In the case of QLCs these factors were partially countered by connecting mesogenic and photochromic units by a bridging group with a double bond, and also by the preparation of amorphous films. However conjugation of the spiropyran unit with the aromatic mesogenic group led to vanishing photochromism of QLCs.

Unlike spiropyran QLCs, the spirooxazine mesophase can be obtained by supercooling of the crystal melt. Conceivably this occurs because the mesocyanine appearing on spirooxazine melting does not aggregate markedly as happens in the melt of spiropyrans. This aggregation prevents formation of the mesophase. Otherwise, the behaviour of mesomorphic spiropyrans and spirooxazine is rather similar; for instance the mesophase temperature range lies much below the melting point and the mesomorphic films are stabilized by alignment in an electrostatic field.

Supercooling itself stabilized the spirooxazine mesomorphic glass films sufficiently for these to be stored for months. Order parameters of merocyanine groups in the aligned spiropyran and spirooxazine mesomorphic films are about the same (0·3–0·4) while those of DANS molecules are markedly higher in the spirooxazine matrix (0·75 as opposed to 0·5).

Altogether these facts indicate that the structure of the spirooxazine mesophase is similar to the structure of spiropyran QLCs. An earlier, more detailed investigation [4] led us to the conclusion that the spiropyrans QLC mesophase consists of two sites —nematic domains embedded in a less organized amorphous-like site whose formation is promoted by bulky spiropyran units. The merocyanine or DANS molecules are distributed between the two sites and their order parameters reflect their penetration into the liquid crystalline site. Probably a substantial fraction of DANS molecules penetrates into the nematic domains since the DANS order parameter is rather high. We assumed also that the pleochroic dye molecules may play an active role, improving directional order in domains.

A distinguishing feature of the spirooxazine mesophase is photochromism. Earlier we reported photochromic mesophases formed by liquid crystal side chain copolymers, containing spiropyran side groups [15–17]. In the polymeric mesophases the merocyanine form of a photochrome was stabilized by aggregation or by interaction with a polar matrix. In the present work we found no spectral indication of aggregation of merocyanine formed from naphthyl-spirooxazine in solution or in the mesophase. We believe that the absence of an electron-accepting substituent in the naphthyl part of the molecule diminishes both the stability of the merocyanine form of the photochrome and its capacity to aggregate, resulting in relatively short lifetime of merocyanine both in isotropic and the anisotropic phases.

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