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Liquid Crystals

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The synthesis and characterization of a new class of liquid crystals based on bis-triazinic compounds

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The synthesis and characterization of a new class of liquid crystals based on symmetrical bis-triazine rings connected by a flexible alkyl spacer is reported. A mechanism to account for the liquid-crystallinity in this system has been proposed. Slow kinetics for the formation of the mesophase from the isotropic phase and the crystalline phase from the mesophase make the melting transitions virtually irreversible. Potential areas of application have been identified.

1. Introduction

Thermotropic liquid-crystalline compounds have, in recent years, gained importance, due to their increased utilization in display devices. At present about 20 000 thermotropic liquid-crystalline compounds are known. Most are closely related to a characteristic geometric molecular shape consisting of a rigid rod-like core where two or more aromatic or aliphatic rings are linked together by means of a rigid linking group. In the past 10 years several new classes of substances have been synthesized which are derived more or less from this classical model: twin, polycatenar, discotic, pyramidal compounds and metal complexes [1-4]. The lack of a generally accepted quantitative theory to predict mesogenic behaviour precludes a rational approach to molecular design. Consistent with qualitative expectations, however, very few low-molar mass mesogenic compounds possessing an internal flexible linking group are reported in the literature. A flexible linking group can join two mesogenic units to act as a decoupling spacer, as in the case of twins, for example [5].

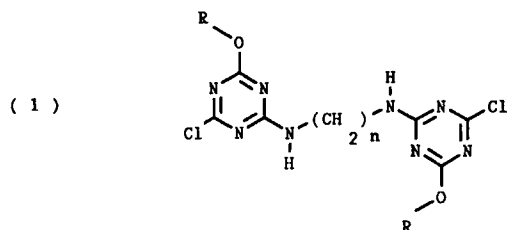
In this paper we present evidence for a new class of mesomorphic materials based on two *s*-triazine units and an alkyl flexible spacer as shown in formula (1). This structure completely lacks the conventional rod-like core, in as much as the triazine unit lacks the geometrical anisotropy, i.e. the aspect ratio, to give it the character of a mesogenic sub-unit. These compounds none the less surprisingly possess mesomorphic behaviour over a relatively wide temperature range. An alternative explanation for liquid-crystallinity in these systems must therefore be proposed since the traditional picture of a mesogenic unit, separated by a flexible spacer does not apply. In the following, the synthesis, characterization and mesophase characterization of this new class of liquid crystals are presented.

2. Experimental

2.1. Synthesis

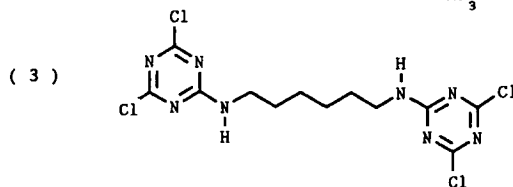
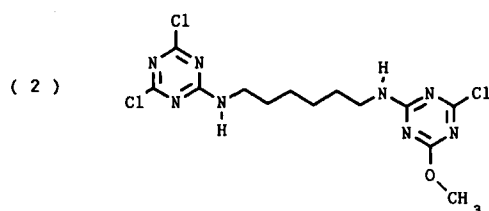
Substituted triazines were prepared according to the method of Thurston *et al.* [6] and recrystallized from heptane (purity > 99 per cent, GC analysis). Alkyldiamines

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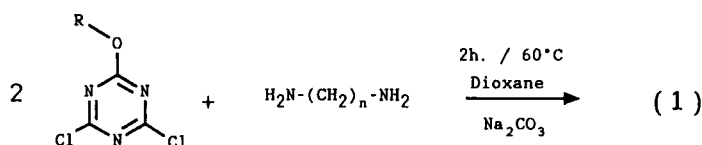
$n = 6$ to 12
 $R = -CH_3$ or $-C_2H_5$

Symbols used: $NnNClO1$ for $R = -CH_3$
 $NnNClO2$ for $R = -C_2H_5$



Formulae.

were purified by crystallization from hexane. Products of general formula (1) were obtained by reacting 2,4-dichloro-6-alkoxy-1,3,5-triazine with a stoichiometric amount of an alkyldiamine in the presence of a proton acceptor such as sodium carbonate, according to the reaction scheme.



Reaction scheme.

The general synthetic procedure is described as follows: a solution of 0.05 mol of alkyldiamine in 50 ml of dioxane was added under stirring at 5–10°C to a mixture of 0.1 mol of 2,4-dichloro-6-alkoxy-1,3,5-triazine in 100 ml of dioxane in which was suspended 0.1 mol of sodium carbonate. The mixture was stirred for 30 min at room temperature and then for 1 hour at 50–60°C. The product was precipitated by pouring the cooled slurry into 600 ml of iced water under vigorous stirring. The solid white product was filtered off, washed with cold water and dried under vacuum.

Compounds of general formula (1) have been synthesized with n ranging from 0 to 12 and the alkoxy group being methoxy, ethoxy, propoxy, butoxy and isopropoxy. Derivatives with alkyl amino groups (methylamine, ethylamine, dimethylamine,

diethylamine, hexylamine, tert-octylamine, morpholine, piperidine and pyrrolidine) instead of the alkoxy groups have also been synthesized.

The chemical structure of these compounds has been confirmed by characterization utilizing: IR spectroscopy, proton NMR spectroscopy and EI mass spectroscopy.

2.2. Purification and analysis

TLC analysis of compound N6NC1O1 (formula (1)), using a 95/5 (v/v) mixture of chloroform/acetone as eluent revealed a principal spot and traces of impurities for the crude product. Their separation was achieved by column chromatography (silica gel; same eluent as in the TLC analysis) yielding a high purity product (> 99 per cent determined by HPLC analysis: column-Rosil C 18, UV detector at 254 nm). The principal impurities were identified by EI mass spectroscopy (electronic impact, 70 eV source) their structures being shown in formulae (2) and (3). The effects of impurities on liquid-crystalline behaviour consist of a broadening of the mesogenic range and a lowering of the melting point; therefore, thermal data obtained on the impure compounds are not reproducible. A chromatographic purification step followed by crystallization from a chloroform/hexane mixture was required to obtain reproducible data.

Thermogravimetric analysis (TGA) showed that all of the pure samples had good thermal stability up to 250°C, at which temperature, decomposition began. The onset of decomposition was most likely due to the presence of the alkoxy groups.

2.3. Optical microscopy

All compounds were observed with a polarizing microscope equipped with a controlled hot stage plate (Mettler FP 80 and FP 82).

2.4. Differential scanning calorimetry

Differential scanning calorimetry measurements were performed on a Perkin-Elmer DSC 7 with a Perkin-Elmer Professional computer 7700 using heating/cooling rates of 2–10°C/min.

2.5. X-ray diffraction

X-ray diffraction patterns of samples in the powdered form were collected with a Philips PW 1011/00 apparatus using Cu-K_α radiation and a Ni filter. Spectra of quenched mesophases were obtained using a Debye-Scherrer chamber with the sample in a Lindemann capillary 1 mm in diameter. In order to obtain these spectra, Lindemann capillaries were prepared by filling them with the compounds in their powdered form and heating them in the FP 80 hot stage to the liquid-crystalline state, as observed with the polarizing microscope. The capillaries were then removed for rapid cooling after which the X-ray spectra were obtained. The cloudy appearance of the quenched samples and their birefringence indicated the presence of the quenched mesomorphic state.

3. Results and discussion

Of the compounds studied and described in the experimental section, only those having the structure of formula (1) with n ranging from 6 to 12 and R being methoxy

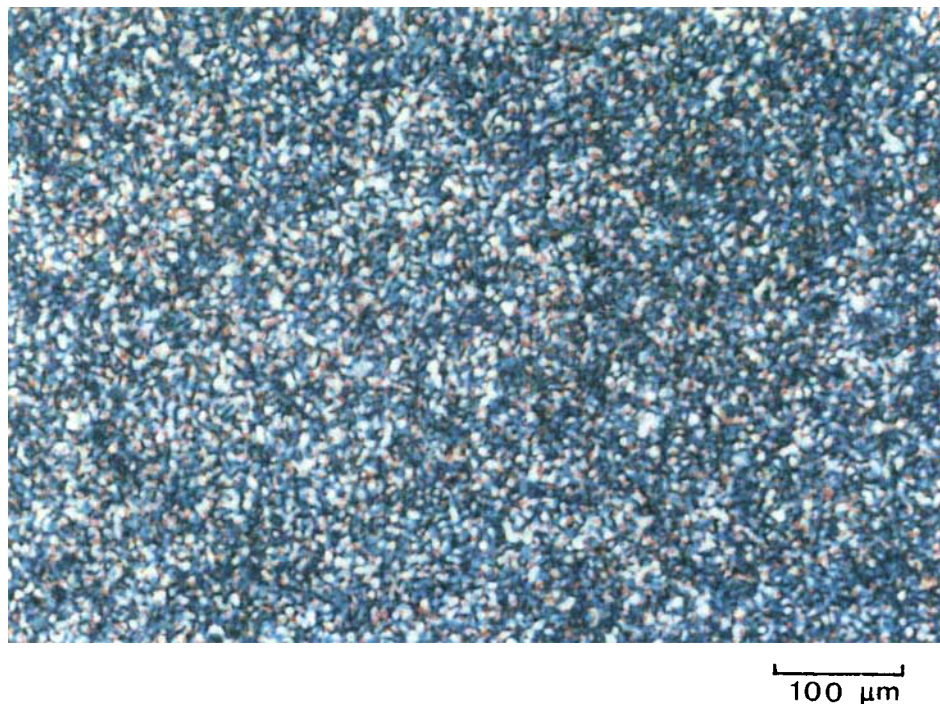


Figure 1. A typical mesophase texture as shown by the polarized photomicrograph of N12NCIO2 at 90°C.

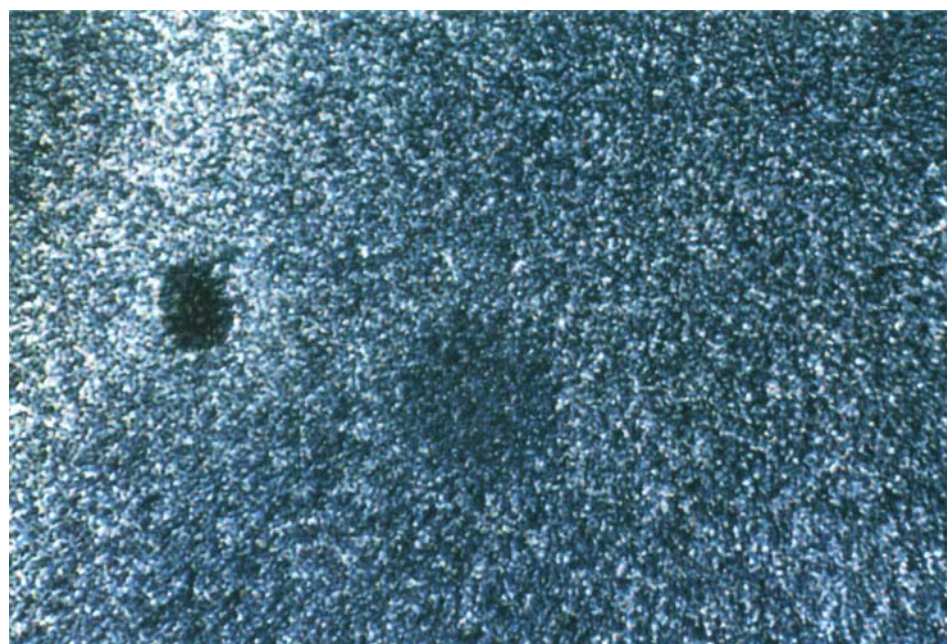
Transition data for the liquid-crystalline compounds as obtained by thermal analysis.

Compound	$T_{CN}/^{\circ}\text{C}$	$T_{Cl}/^{\circ}\text{C}$	$T_{Ni}/^{\circ}\text{C}$	$T_g/^{\circ}\text{C}$
N5NCIO1	—	35	—	—
N6NCIO1	148	—	153	—
N7NCIO1	131	—	137	23
N8NCIO1	116	—	132	19
N9NCIO1	91	—	100	16
N10NCIO1	66	—	83	9
N12NCIO1	81	—	91	5
N12NCIO2	76	—	104	1

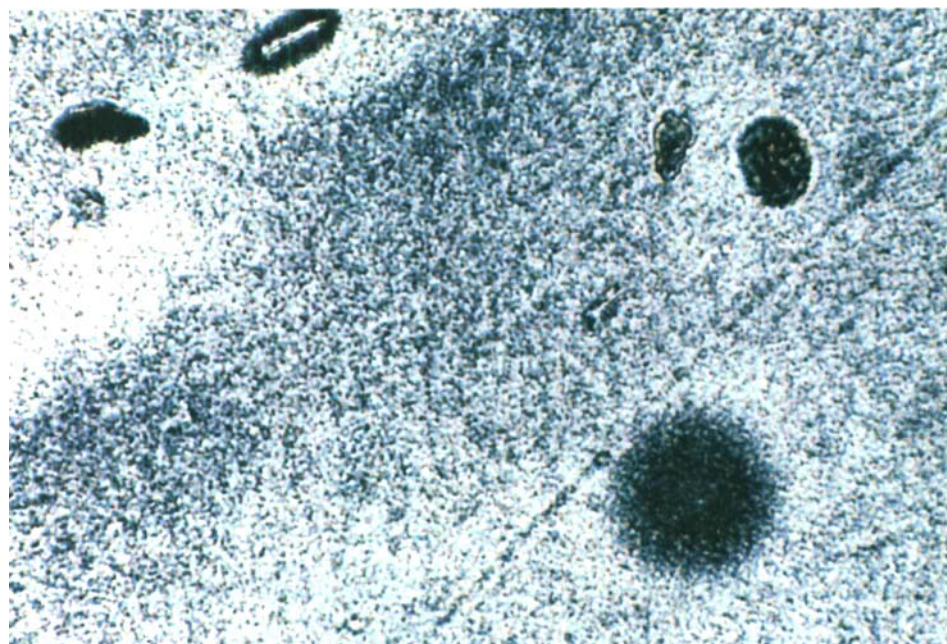
or ethoxy exhibited liquid-crystalline behaviour. The transition data are summarized in the table.

The liquid-crystalline textures were the same for all mesogenic compounds examined and typified by the photomicrograph shown in figure 1. The first transition, from the crystalline to the mesomorphic state occurred slowly and it was necessary to shear the microscope slides in order to obtain a uniform organization. The second transition to the isotropic state also occurred over a broad temperature range, independently of the heating rate. Upon cooling from the isotropic state, the sample recovered neither the mesomorphic nor the crystalline state. Similarly, on cooling from the mesophase the sample did not crystallize, even at the slowest cooling rates. The cooled samples were either extremely viscous liquids or hard glasses; isotropic if cooled from the isotropic state or mesomorphic if cooled from the mesomorphic state.

It was possible to align uniaxially most of these compounds by the application of mechanical stress in the mesophasic state. This can be achieved by sliding the two



(a)



(b)

100 μm

Figure 2. As in figure 1 but after being subjected to mechanical shearing. (a) Parallel to the polarizer axis. (b) at 45° to the polarizer axis with an exposure time equal to 10 per cent of that for (a).

microscope glasses sandwiching the sample along their principal axis. In this way the sample appears dark when the glasses are oriented with the sliding direction parallel to one of the polarizers in a crossed polar configuration, but exhibits a very large and uniform birefringence (without any texture) when the glasses are oriented at 45° . Polarized photomicrographs of the texture, for compound N12NCIO2 (with $n = 12$ and $R = -OC_2H_5$, formula (1)) in the mesomorphic state, are shown before and after orientation by mechanical shearing in figures 1 and 2, respectively. The N12NCIO2 compound, with the longest inter-triazinic chain (C_{12}) and the ethoxy substituent, will subsequently be the candidate of choice for more in depth evaluation, since most of the observations and measurements performed on the other compounds resulted in similar observations and conclusions.

The mesogenic compounds showed broad melting peaks and broad isotropization peaks in the DSC as noted previously by optical microscopy. Recrystallization rarely occurred at a cooling rate of $10^\circ\text{C}/\text{min}$. Subsequent thermal scans did not show any endothermic or exothermic peaks. Measurements performed after a few hours or a few days showed that these compounds could remain in the metastable glassy state for prolonged periods but would always recrystallize, given sufficient time, varying from days to months. The data reported in the table are, therefore, given for the first scan on the virgin powder with a heating rate of $10^\circ\text{C}/\text{min}$. The melting behaviour was virtually independent of heating rate and, scans at slower heating rates (5 and $2^\circ\text{C}/\text{min}$), gave very similar results.

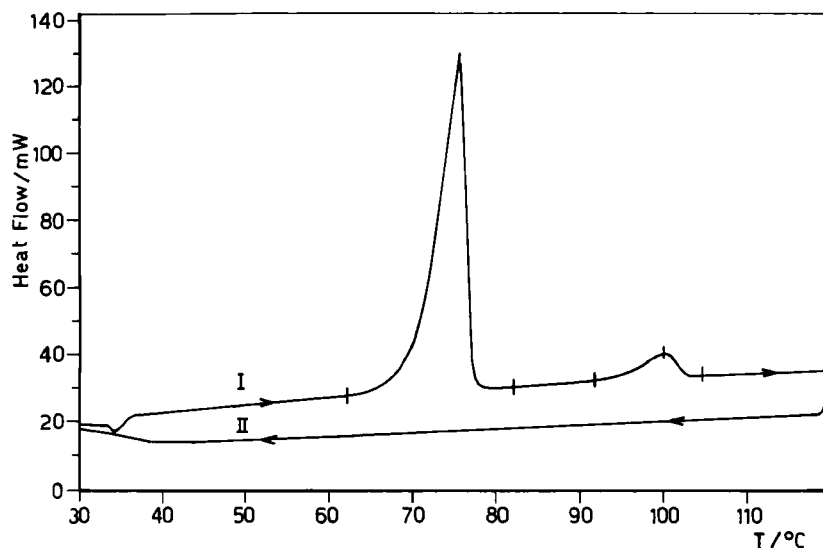


Figure 3. The DSC pattern for N12NCIO2 with heating and cooling rates of $5^\circ\text{C}/\text{min}$. (I—First heating; II—Cooling).

The DSC scan of N12NCIO2, typical of many samples, is shown in figure 3. The first peak ($\Delta H = 74.4 \text{ J/g}$) corresponds to melting, while the second peak ($\Delta H = 6.2 \text{ J/g}$) to isotropization. On cooling, no transitions have been observed. The second scan for the same compound (see figure 4) shows the supercooled mesophasic state with its T_g at 0°C . The DSC results are thus largely in accord with microscope observations.

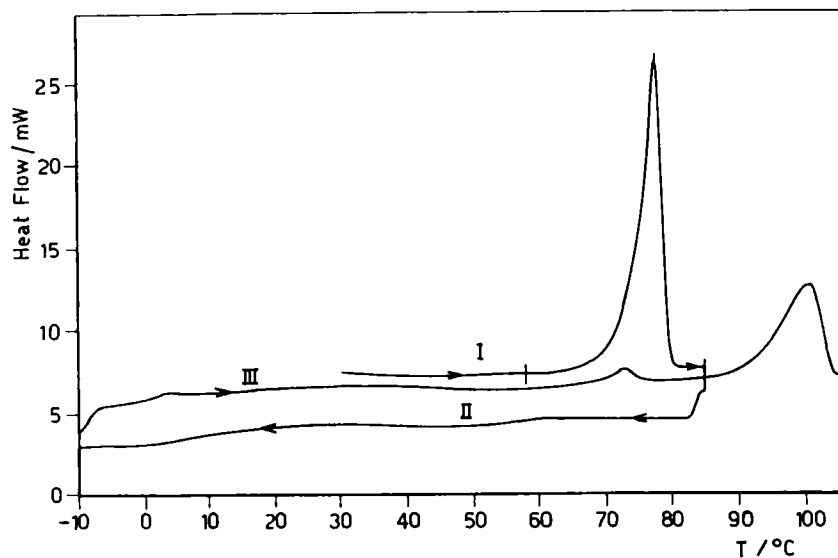


Figure 4. The DSC scan for N12NC102 but with heating-cooling-heating cycles as indicated at 10°C/min. (I, first heating; II, cooling; III, second heating.)

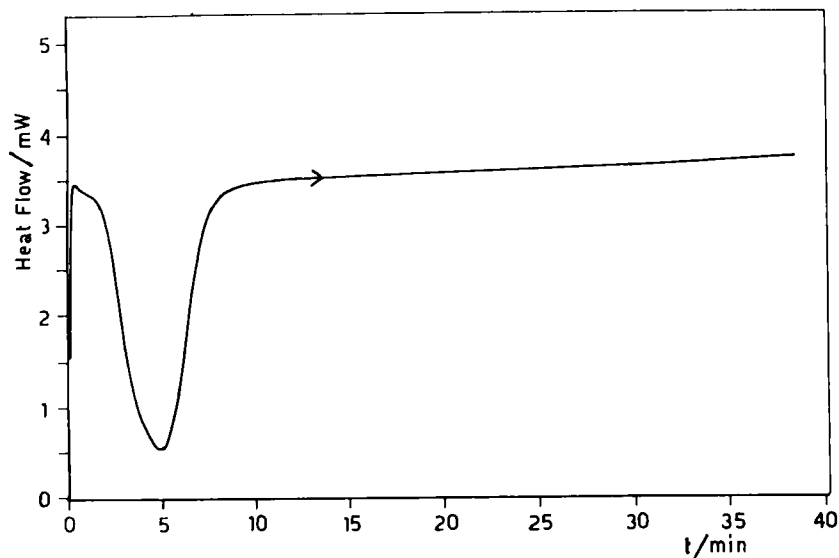


Figure 5. The isothermal DSC scan for N8NC101 showing the kinetics of crystallization at 80°C.

Thermograms also showed some anomalies for the various samples. For example, the thermogram for compound N8NC101 shows slightly different behaviour: during cooling an exothermic peak can be observed at 80°C, the enthalpy of which depends on the cooling rate. Figure 5 shows the same compound run isothermally at 80°C, where it appears that crystallization takes approximately 10 min at that temperature.

All of the pure compounds, after recrystallization in a hexane-chloroform mixture, exhibit a diffraction spectrum typical of the microcrystalline state. The X-ray

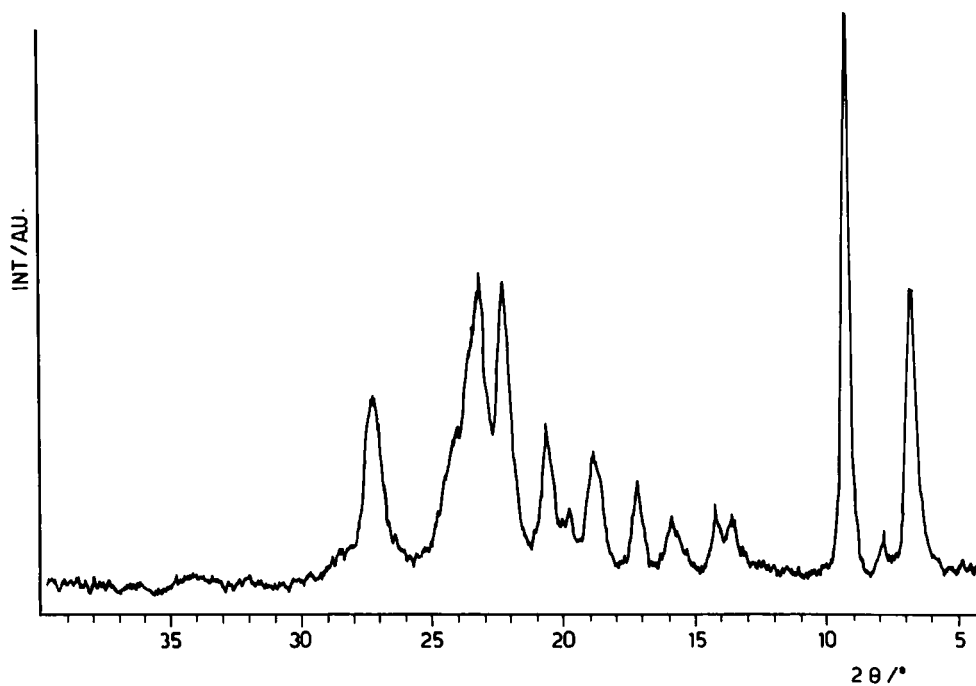


Figure 6. The X-ray powder diffraction pattern of N12NCIO2.

diffraction pattern of N12NCIO2 performed at room temperature is shown in figure 6 as a typical example. By contrast, the diffraction pattern of N12NCIO2 in its quenched mesomorphic state, as described in the previous section, is shown in figure 7 as a typical example.

The mesophase in the quenched glassy state, as well as the thermotropic state, exhibited a high degree of optical anisotropy and an X-ray diffraction pattern typical

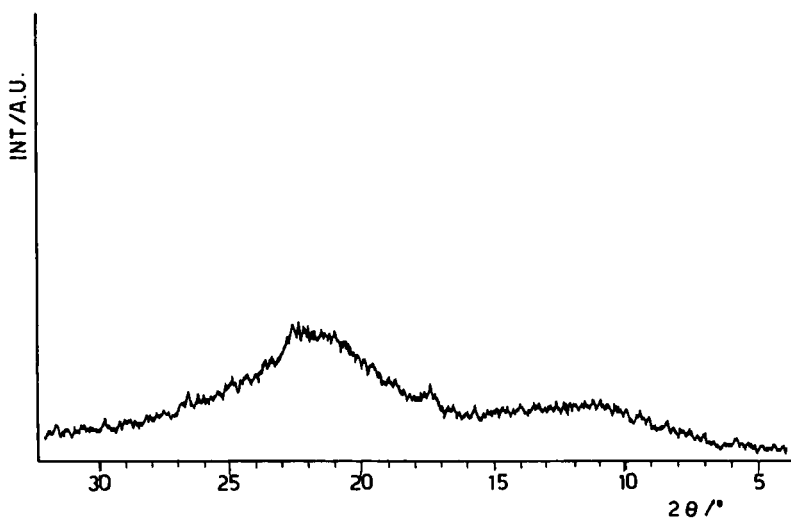


Figure 7. The X-ray diffraction pattern of N12NCIO2 in its quenched mesophasic state.

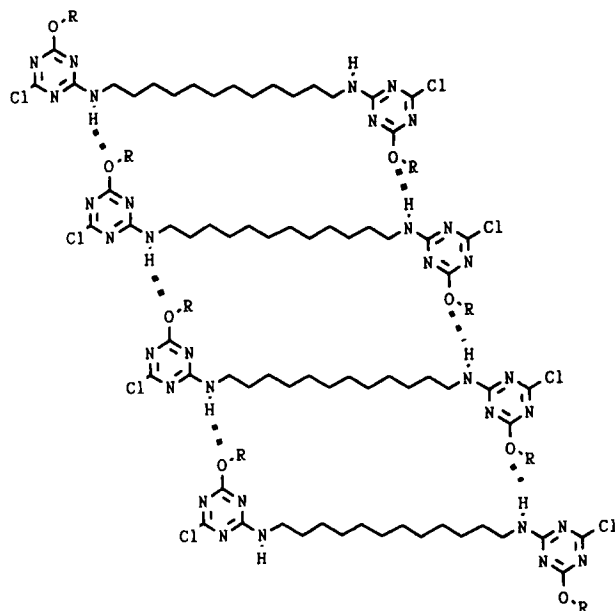


Figure 8. A schematic visualization of the organization promoted in the triazinic compounds by hydrogen bonding.

of the amorphous state in its thermotropic range indicating a lack of high symmetry organization. This mesophase, therefore, was tentatively assigned as a nematic pending further investigation. The nematic nomenclature for describing the nature of the phase transitions is used in the table.

The compounds N12NCIO2 and N8NCIO1 were analysed by IR spectroscopy, NMR spectroscopy and EI mass spectroscopy in the quenched mesomorphic and melt-recrystallized states. After heat treatment, they showed the same pattern as before, indicating an unaltered chemical structure. From this fact we may infer that the lack of recrystallization, or formation of the mesophase, from the isotropic melt are kinetic phenomena and not indications of chemical modification.

Having established empirically the liquid-crystalline nature of these compounds, we can speculate as to how molecules possessing the general structure of formula (1) can exhibit mesomorphic behaviour. As noted previously, the rigid molecular core asymmetry, thought to be essential for liquid crystal formation, is lacking in these molecules. In fact, from work in progress it has been shown that mesogenic polymers may be formed from the structure in formula (1) by reacting the remaining Cl function on each triazine ring with a bifunctional flexible spacer such as alkylidene diamine. For such a polymer we have, therefore, an alternation between a 6-membered ring and a flexible spacer thus losing the identity of the original mesogenic unit shown in formula (1). Since it is generally accepted that the aspect ratio of a rigid mesogen must be 3–5, a single triazine ring is thus grossly insufficient.

It is proposed that the single H atom on the secondary amine can, through the action of hydrogen bonding, lead to intermolecular organization. This can be visualized schematically to occur along the lines shown in figure 8. Such a hydrogen bond can be visualized schematically to occur with the ether oxygen atom along the lines shown in figure 8.

The heteroatom of organic ethers (i.e. oxygen) and amines (i.e. nitrogen) is sufficiently basic to form hydrogen bonds with appropriate protic materials. The consequence of the hydrogen bond is to make the alkyl spacer group rigid and thus fulfil the rod-like approximation generally thought to be required for mesogenic properties. Alternatively such a hydrogen bond could form with the ring-nitrogen of the triazine ring. The resulting association of molecules could resemble a three dimensional domain of molecules similar to the swarm concept which was popular earlier in this century [7]. We emphasize that some intermolecular associations are necessary to make the structure rigid and so impart the observed liquid-crystalline properties in these otherwise flexible molecules.

The relatively high temperature of the mesophasic–isotropic transition precludes an infrared study aimed at looking for the loss of hydrogen bonding at the transition to the disordered fluid. Consistent with this concept, however, are experiments that substitute the hydrogen on the amine nitrogen with a CH_3 - group causing the molecule to lose its liquid-crystalline behaviour concurrently with the loss of hydrogen bonding capability.

Deuteration of the amino group could provide a useful probe to evaluate the significance of hydrogen bonding in forming the liquid-crystalline phase by NMR and neutron scattering techniques.

4. Device and applications

The irreversibility of the phase transitions could, in principle, make these materials candidates for optical storage media. The readily available and low cost starting materials combined with the ease of synthesis make these materials suitable for exploitation in device applications. The novel character of this class of compounds dictates that their electro-optical properties be determined as well.

5. Conclusions

A new class of thermotropic nematic liquid crystals, lacking the classical rigid core molecular structure, has been synthesized. The compounds form mesophases in a definite range of temperatures as evidenced by polarized microscopy, differential scanning calorimetry and X-ray diffraction. As the crystalline to mesophase and mesophase to isotropic state transitions are not reversible a simple interpretation of the results proved elusive. A mechanism for the formation of the liquid-crystalline phase for these molecules lacking a rigid molecular core has been proposed based on their ability to form intermolecular hydrogen bonds.

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