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## Liquid Crystals

Publication details, including instructions for authors and subscription information:

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### Columnar phases from semi-discoid molecules. Phase induction via hydrogen bonding and charge transfer interactions

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**To cite this Article** Paulus, W. , Ringsdorf, H. , Diele, S. and Pelzl, G.(1991) 'Columnar phases from semi-discoid molecules. Phase induction via hydrogen bonding and charge transfer interactions', *Liquid Crystals*, 9: 6, 807 – 819

**To link to this Article:** DOI: 10.1080/02678299108055003

**URL:** <http://dx.doi.org/10.1080/02678299108055003>

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## Columnar phases from semi-discoid molecules

### Phase induction via hydrogen bonding and charge transfer interactions

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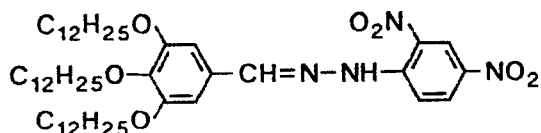
(Received 6 April 1990; accepted 27 December 1990)

To investigate the non-linear optical properties of nitrophenylhydrazones, a series of 4-nitro- and 2,4-dinitrophenylhydrazones of substituted aromatic aldehydes were synthesized. It was found that many of the dinitrophenylhydrazone derivatives are liquid-crystalline and X-ray investigations show that the mesophase corresponds to a hexagonal columnar structure. To explain this unusual behaviour it is necessary to assume that a mesogenic structure is formed by intramolecular hydrogen bonding of the dinitrophenylhydrazones. Charge transfer induced antiparallel alignment of these molecular dipoles leads to discoid structures, forming the columnar phases.

#### 1. Introduction: induction of mesophases

In the past few years, there has been a growing interest in the induction of mesogenic structures and phases. Recently Diele *et al.* [1] found that a smectic phase can be induced by mixing two different compounds, which form a mesogenic core by a proper steric arrangement. To induce discotic liquid-crystalline properties, it is necessary to mix electron rich molecules, like substituted triphenylenes, which do not form liquid-crystalline phases by themselves, with compounds with a high electron deficiency like trinitrofluorenone [2, 3]. The induction of mesogenic structures by interactions other than covalent bonding is long known to be possible for certain substituted benzene carboxylic acids, which form a mesogenic core via two intermolecular hydrogen bonds [4, 5]. There are also some systems known to form liquid-crystalline melts where the mesogenic units contain intramolecular hydrogen bonded, six membered rings [6, 7, 8]. These enamine-ketones show a liquid-crystalline phase, whereas molecules without the intramolecular hydrogen bond are only crystalline.

In order to improve the non-linear optical properties of nitrophenylhydrazones [9, 10] a series of benzaldehyde derivatives with electron donating substituents was recently synthesized, for example



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It was surprising to find that some of the dinitro derivatives have liquid-crystalline properties. Furthermore X-ray investigations show that these compounds do not only have mesophases, but even form columnar phases with a hexagonal structure. To explain these data, we assume that intramolecular hydrogen bond and intermolecular charge transfer interactions, with an alternating antiparallel dipole orientation, play a crucial part in forming these mesophases. To avoid the introduction of a new nomenclature and supported by the obtained results the phases under discussion are designated by the term discotic ( $D_h$ ).

## 2. Synthesis and characterization of substituted nitrophenylhydrazones

The principal way of synthesis of alkyloxy substituted 4-nitro- and 2,4-dinitrophenylhydrazones is shown in the following reaction scheme:

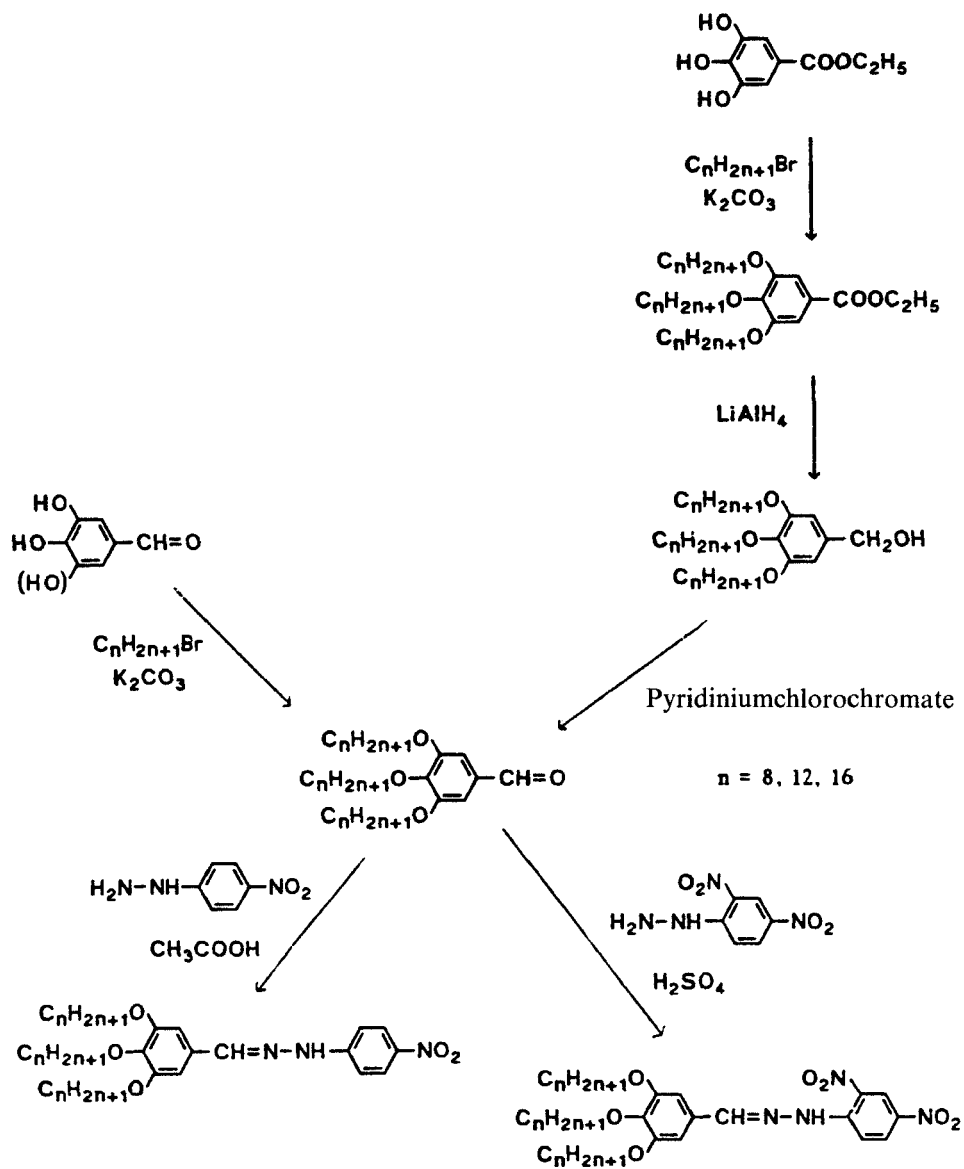
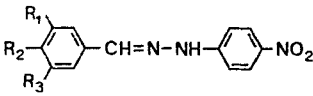
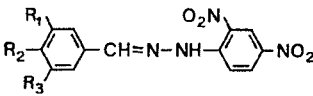
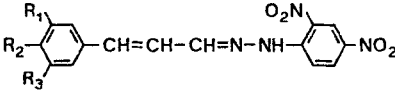


Table 1. Compounds synthesized.

			
1-5		6, 7, 9-14	
			
8			
1	R <sub>1</sub> = H	R <sub>2</sub> = OC <sub>18</sub> H <sub>37</sub>	R <sub>3</sub> = H
2, 7, 8	R <sub>1</sub> = OC <sub>16</sub> H <sub>33</sub>	R <sub>2</sub> = OC <sub>16</sub> H <sub>33</sub>	R <sub>3</sub> = H
9	R <sub>1</sub> = OC <sub>12</sub> H <sub>25</sub>	R <sub>2</sub> = OC <sub>12</sub> H <sub>25</sub>	R <sub>3</sub> = H
10	R <sub>1</sub> = OC <sub>6</sub> H <sub>13</sub>	R <sub>2</sub> = OC <sub>6</sub> H <sub>13</sub>	R <sub>3</sub> = H
3, 11	R <sub>1</sub> = OC <sub>16</sub> H <sub>33</sub>	R <sub>2</sub> = OC <sub>16</sub> H <sub>33</sub>	R <sub>3</sub> = OC <sub>16</sub> H <sub>33</sub>
4, 12	R <sub>1</sub> = OC <sub>12</sub> H <sub>25</sub>	R <sub>2</sub> = OC <sub>12</sub> H <sub>25</sub>	R <sub>3</sub> = OC <sub>12</sub> H <sub>25</sub>
13	R <sub>1</sub> = OC <sub>8</sub> H <sub>17</sub>	R <sub>2</sub> = OC <sub>8</sub> H <sub>17</sub>	R <sub>3</sub> = OC <sub>8</sub> H <sub>17</sub>
5, 14	R <sub>1</sub> = H	R <sub>2</sub> = N(C <sub>16</sub> H <sub>33</sub> ) <sub>2</sub>	R <sub>3</sub> = H
6	R <sub>1</sub> = H	R <sub>2</sub> = OC <sub>11</sub> H <sub>21</sub>	R <sub>3</sub> = H

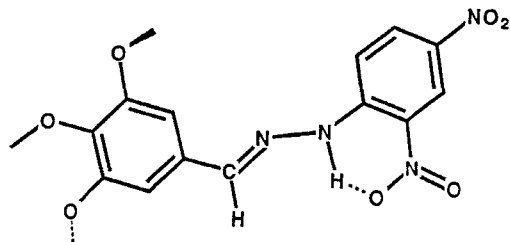
The highly substituted aldehydes can be made in two different ways, depending on the degree of substitution. The two chain alkyloxy compounds are made by alkylation of the analogue dihydroxybenzaldehydes. The three chain derivatives are better made by alkylation of the ethyl gallate followed by a reduction and an oxidation to the aldehyde. Direct alkylation of the 3,4,5-trihydroxybenzaldehyde was also tried but the yields were very low. The synthesis of the dihexadecylaminobenzaldehyde is described elsewhere [10]. All of the compounds synthesized are shown in table 1.

All of the compounds were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy (<sup>13</sup>C NMR data are given as examples for compounds **2** and **8**) using a 400 MHz NMR spectrometer (Aspect 3000, Bruker). To study the thermal properties of the compounds, a Perkin-Elmer DSC-2 differential scanning calorimeter and a Leitz Ortholux Microscope equipped with a Mettler FP5 hot stage were used. To characterize the mesophase of some of the 2,4-dinitrophenylhydrazones, X-ray measurements and miscibility experiments were performed.

### 3. Results and discussion

The thermotropic behaviour of substituted 4-nitro- and 2,4-dinitrophenylhydrazones **1-14** have been investigated. 4-nitro- and 2,4-dinitrophenylhydrazones are known to crystallize well with a defined melting point, and are therefore often used in organic chemistry to characterize ketones and aldehydes [11]. It was found that only the 2,4-dinitrophenylhydrazones **7-13** exhibit liquid-crystalline phases whereas the 4-nitrophenylhydrazones **1-5** crystallize without a mesophase. To explain the liquid-crystalline behaviour of the 2,4-dinitrophenylhydrazones we have to consider that an

intramolecular hydrogen bond exists between the *o*-NO<sub>2</sub>- and the NH-group. This intramolecular hydrogen bond makes the molecule flat and rigid and the result is a mesogenic structure



This is strongly supported by the results of Etter *et al.* [12] who have shown that in the crystalline phase, 4-nitroanilines form only intermolecular hydrogen bonds whereas 2,4-dinitroanilines form intramolecular and intermolecular hydrogen bonds. The formation of dimers due to four centre interactions of intermolecular hydrogen bonds (as found for the crystalline 2,4-dinitro-4'-N,N-diethylaminodiphenylamine) can be ruled out, because the transition enthalpies of the clearing process are too low (see table 2). Furthermore, in solution the <sup>1</sup>H NMR spectroscopy showed a strong shift of the NH-proton (see data shown in the Experimental) of the dinitro derivatives compared to the mononitro analogues, which also indicates a strong intramolecular hydrogen bond.

The thermotropic behaviour of the 2,4-dinitrophenylhydrazones was investigated by polarizing microscopy and DSC (see table 2). To exhibit liquid-crystalline behaviour, it is necessary that the aldehyde moiety has more than one substituent **7–13** otherwise the compound is only crystalline **6**. Hydrazones with only two alkyloxy substituents (**7–10**) have, compared to the tris substituted hydrazones **11–13**, only very small mesophase ranges. This can be explained by the high tendency of 2,4-dinitrophenylhydrazones to crystallize because of the high dipole–dipole interactions. To disturb the tight packing of the molecules it is necessary to introduce large alkyloxy substituents. The optimum chain length of the tris substituted compounds is about

Table 2. DSC data for the 2,4-dinitrophenylhydrazones **6–14**.

Compound	Thermotropic behaviour <i>T</i> /°C	Transition enthalpies/kJ mol <sup>-1</sup> C→D <sub>n</sub> →I	
<b>6</b>	C135I		
<b>7</b>	C124D <sub>n</sub> 130I	59.4	3.9
<b>8</b>	C(85D <sub>n</sub> )115I	52.4	2.3
<b>9</b>	C(94D <sub>n</sub> )130I	48.5	3.0
<b>10</b>	C(100S116N)133I		
<b>11</b>	C106D <sub>n</sub> 134I	65.3	5.1
<b>12</b>	C97D <sub>n</sub> 137I	43.2	4.6
<b>13</b>	C96D <sub>n</sub> 136I	29.2	3.8
<b>14</b>	C57C <sub>2</sub> 81C <sub>3</sub> 92I		

C = crystalline; S = smectic; I = isotropic; N = nematic; D<sub>n</sub> = discotic hexagonal; C<sub>1</sub> = C<sub>2</sub> = C<sub>3</sub> = crystalline modifications; ( ) = compounds exhibit a monotropic transition. Phase transitions at a cooling rate of 20°C/min. All other compounds recorded at a heating and cooling rate of 10°C/min.

eight to twelve carbon atoms (**12**, **13**). If the chain length is increased the broadness of the mesophase is decreased, probably due to the crystallization tendency of the alkyl chains. Compared to this, the di-substituted dinitrophenylhydrazones **7–10** behave differently. They exhibit their broadest mesophase if the chain length is at least sixteen carbon atoms long. Below that, the di-substituted compounds are only monotropic. On further decrease of the chain length (to the dihexyloxy derivative **10**) only a monotropic nematic and a smectic phase can be observed. The dinitrophenylhydrazone **8** of the 3,4-dihexadecyloxycinnamic aldehyde is only monotropic, in contrast to the hydrazone **7** of the analogous benzaldehyde. This is probably due to a mixture of the *cis* and *trans* isomers, which narrows the mesophase.

Under the polarizing microscope, the low viscosity liquid-crystalline phase shows a texture reminiscent of a  $D_{ho}$  phase (see figure 1). Therefore miscibility experiments have been performed with typical  $NO_2$  and  $NH$  containing compounds, which show conventional smectic and nematic phases (see table 3). In no case could complete miscibility be observed which indicates that the liquid-crystalline phase is not a smectic. On the other hand contact preparations of the different dinitrophenylhydrazones with each other, e.g. **7** and **11**, **11** and **13**, show that all observed liquid-crystalline phases (except compound **10**) belong to the same phase type (see figure 3).

Oriented samples were not obtained in any case, but X-ray studies using the Guinier film method were performed to give the final proof of a columnar phase. There are one or two reflections at small angles and up to three diffuse scattering maxima in the wide angle region (see figure 2). Within the liquid-crystalline phase the patterns were found to be identical regardless of temperature. For the dodecyl **12** and hexadecyl homologues **11** a conventional layer structure can be excluded. Because of the complete miscibility of the liquid-crystalline phases between the octyl **13** and the hexadecyl

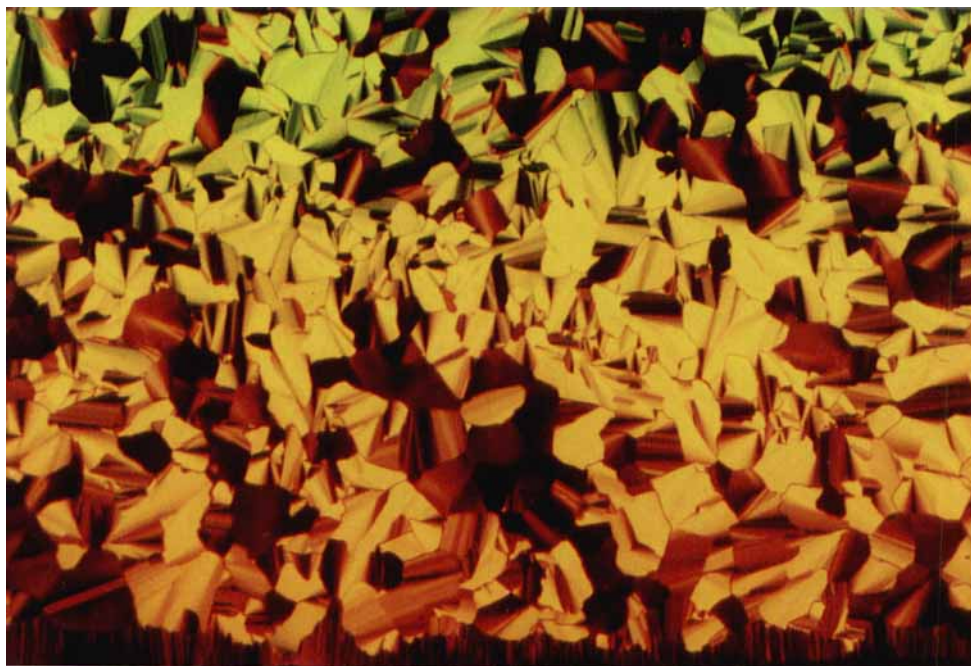


Figure 1. Compound **11** observed under the polarization microscope at 125°C.

Table 3. Compounds used for miscibility experiments.

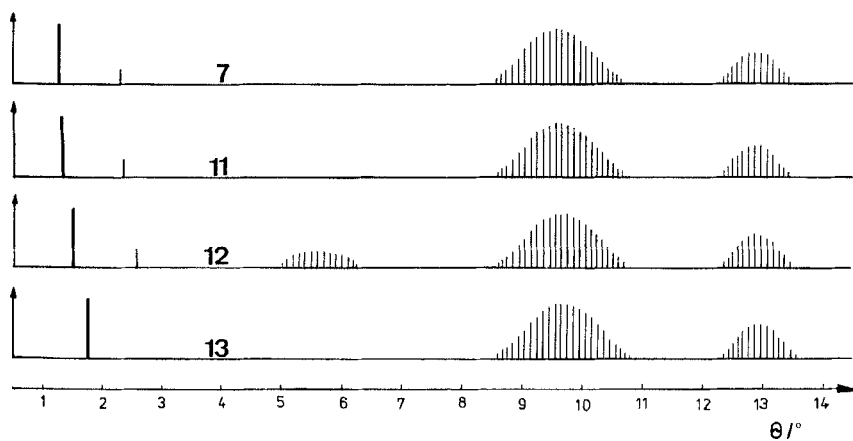
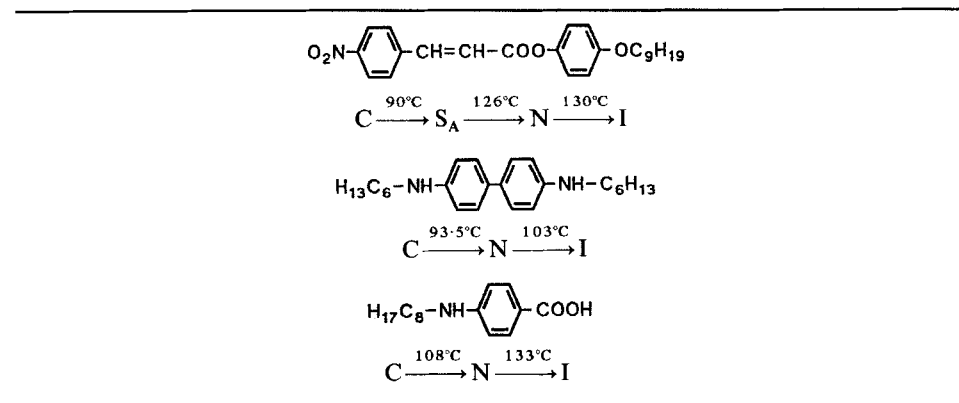


Figure 2. Schematic representation of the X-ray reflections of compounds 7, 11, 12, and 13.

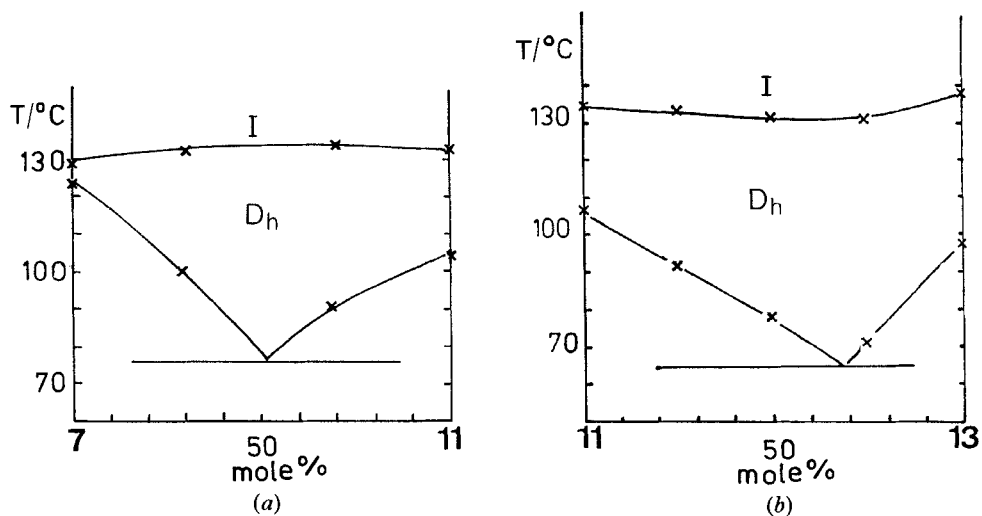


Figure 3. Miscibility diagrams of compounds (a) 7 and 11 (b) 11 and 13.

Table 4. X-ray measured Bragg angles and calculated lattice parameters; the length of the molecules were estimated using CPK models.

Compound	$\Theta_1/^\circ$	$\Theta_2/^\circ$	$\Theta_2/\Theta_1$	$\bar{a}_{\text{hex}}/\text{\AA}$	$L/\text{\AA}$
13	1.77	—	—	28.8	27.6
12	1.56	2.65	1.70	33.0	32.8
11	1.36	2.38	1.75	37.3	37.6
7	1.31	2.23	1.70	39.4	37.6

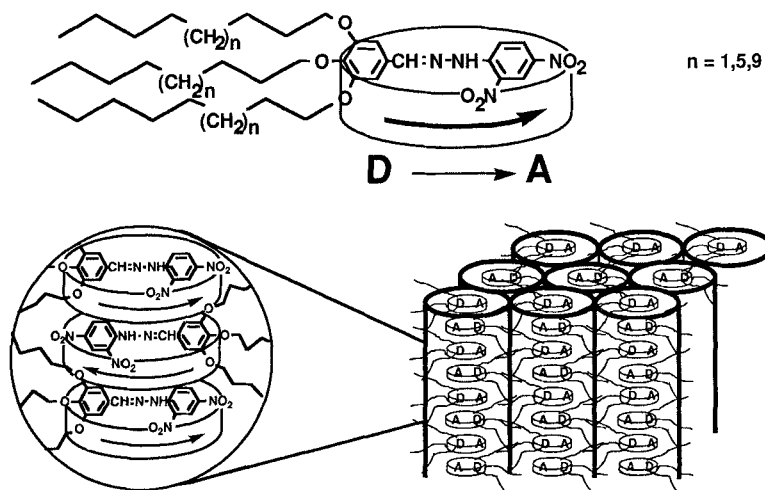


Figure 4. Antiparallel alignment of the dinitrophenylhydrazones and induction of a hexagonal columnar mesophase.

derivative **11** (see figure 3) we can assume the same phase structure for both substances. The ratios of the Bragg angles (see table 4) indicate a hexagonal structure. The difference of the observed ratio from the theoretical value of 1.732 is within error limits if a conventional film method is used. If a hexagonal structure is assumed, the lattice parameter  $a$  is almost the same value as the maximum length of the molecule.

In agreement with these observations, we can assume that the molecules aggregate alternately in a strong antiparallel fashion which leads to a columnar structure. The formation of dimers due to four centre interactions of two intermolecular hydrogen bonds would lead to a higher lattice parameter  $a$ . Though the obtained results indicate that the columns are formed because of charge transfer interactions between the molecules. A hint for this interaction is the colour change from orange to deep red when forming the columnar phases. The low clearing enthalpies of the 2,4-dinitrophenylhydrazones (see table 2) are in agreement with the results obtained with doped discotic liquid crystals, which also exhibit a decrease in the clearing enthalpy due to charge transfer interactions [3]. The columns have cylindrical shapes with nearly circular cross-sections as shown schematically in figure 4. These molecular structures form a dense cylinder packing because the molten alkyl chains fill the space between the aromatic moieties of the molecules. This reasoning would also explain why the trisubstituted dinitrophenylhydrazones have their broadest mesophase at shorter chain



lengths than the di-substituted ones. If the di-substituted derivatives have only short chain lengths, the mesophases become smaller (9) and even their phase behaviour changes (10). In fact, the compound with the shortest carbon chain (10) is only monotropic, and we can only observe a smectic and nematic texture. The compound 6 with only one alkenyloxy-substituent shows no mesophase. The alkylamino-substituted dinitrophenylhydrazone 14 has too high a dipole moment and crystallizes too well to show a low viscosity liquid-crystalline phase. There is some evidence that there could be some highly ordered phases, but this has not been proven so far.

#### 4. Experimental

The synthetic pathway is shown for 3,4-dihexadecyloxycinnamic aldehyde-2',4'-dinitrophenylhydrazone.

50 g (0.36 mole) of powdered and dried  $K_2CO_3$ , 0.2 g (1.2 mmole) of KI and 15 g (0.1 mole) of 3,4-dihydroxybenzaldehyde were suspended in 76 g (0.25 mole) 1-hexadecylbromine and 250 ml acetone. The reaction was refluxed for one week under an argon atmosphere. The inorganic residue was filtered and extracted several times with hot hexane. The organic phase was washed with water and dried with  $Na_2SO_4$ . The substance was purified by flash chromatography with dichloromethane. Yield: 33.4 g (52 per cent), mp 73°C.

##### 4.1. Preparation of 3,4-dihexadecyloxycinnamic acid

5.3 g (0.033 mole) of malonic acid was dissolved in 100 ml dried pyridine. 23.5 g (0.04 mole) of the aldehyde dissolved in 50 ml pyridine was added slowly together with 5 ml of piperidine. The solution was refluxed for four hours and then poured into cooled hydrochloric acid. The white crystals were sucked off and the aqueous phase extracted twice with diethylether. The purification was done by recrystallisation with hexane/diethylether 1:1. Yield: 23.4 g (93 per cent), mp 120°C.

##### 4.2. Preparation of 3,4-dihexadecyloxycinnamic alcohol

5.0 g (8 mmole) of the acid was dissolved in 150 ml dry diethylether and a solution of 0.8 g (21 mmole)  $LiAlH_4$  in 20 ml diethyl ether was added slowly. The mixture was stirred overnight and then refluxed for five hours. After addition of water, the organic phase was separated, washed with water and dried with  $Na_2SO_4$ . After this the ether was removed. Yield: 2.2 g (45 per cent).

##### 4.3. Preparation of 3,4-dihexadecyloxycinnamic aldehyde

6.0 g (60 mmole)  $CrO_3$  was mixed with 9.5 g pyridine dissolved in 150 ml dichloromethane. After 15 min, 2.2 g (3.6 mmole) of the alcohol dissolved in a small amount of dichloromethane was added. The mixture was stirred for another 15 min and then the organic phase was separated from the black residue which was extracted twice with diethyl ether. The organic solutions were poured together and the solvent removed. Yield: 0.6 g crude product (27 per cent).

##### 4.4. Preparation of 3,4-dihexadecyloxycinnamic aldehyde-2',4'-dinitrophenylhydrazone

1.2 g (6 mmole) of 2,4-dinitrophenylhydrazine was dissolved in 6 ml concentrated sulphuric acid and 9 ml of water. 30 ml of ethanol were added slowly. 0.6 g (1 mmole) of aldehyde dissolved in a little ethanol was poured into the warm solution and at once a red precipitate was formed. The solution was sucked off and the residue was

recrystallized from dioxane and acetic acidethylester. Then the product was purified by flash chromatography (dichloromethane/hexane 2:1). Yield: 0.11 g (14 per cent), mp 115.3°C.

The corresponding 4-nitrophenylhydrazones were synthesized using acetic acid/water 1:1 instead of concentrated sulphuric acid.

### 5. Analysis

All NMR measurements were done in CDCl<sub>3</sub>.



4-octadecyloxybenzaldehyde-4'-nitrophenylhydrazone (**1**): mp 110°C.

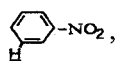

C<sub>31</sub>H<sub>47</sub>N<sub>3</sub>O<sub>3</sub> Calc. C: 73.05 per cent, H: 9.29 per cent, N: 8.24 per cent.  
(F.W. 509.7) Found C: 73.36 per cent, H: 9.21 per cent, N: 7.77 per cent.

3,4-dihexadecyloxybenzaldehyde-4'-nitrophenylhydrazone (**2**): mp 100°C.

C<sub>45</sub>H<sub>75</sub>N<sub>3</sub>O<sub>4</sub> Calc. C: 74.85 per cent, H: 10.47 per cent, N: 5.82 per cent.  
(F.W. 722.1) Found C: 75.08 per cent, H: 10.10 per cent, N: 5.63 per cent.

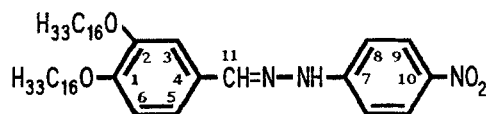
<sup>1</sup>H NMR: 0.9 t (CH<sub>3</sub>-), 1.3 m (CH<sub>3</sub>-(CH<sub>2</sub>)<sub>13</sub>), 1.8 m (-CH<sub>2</sub>-CH<sub>2</sub>-O-),

4.0 m (-CH<sub>2</sub>-O-), 6.8 s , 7.0 d ,

7.1 d , 7.3 d , 7.7 s (-CH=N-),

7.9 s (-NH-), 8.2 d .


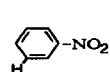
<sup>13</sup>C NMR: (1) 149.6, (2) 149.7, (3) 113.2, (4) 127.1, (5) 121.3, (6) 110.9, (7) 151.1, (8) 111.6, (9) 126.2, (10) 140.2, (11) 141.8.

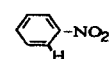


3,4,5-trihexadecyloxybenzaldehyde-4'-nitrophenylhydrazone (**3**): mp 86°C.

C<sub>61</sub>H<sub>107</sub>N<sub>3</sub>O<sub>5</sub> Calc. C: 76.12 per cent, H: 11.20 per cent, N: 4.37 per cent.  
(F.W. 962.6) Found C: 76.90 per cent, H: 10.59 per cent, N: 3.98 per cent.

<sup>1</sup>H NMR: 0.9 t (CH<sub>3</sub>-), 1.3 m (CH<sub>3</sub>-(CH<sub>2</sub>)<sub>13</sub>), 1.8 m (-CH<sub>2</sub>-CH<sub>2</sub>-O-),

4.0 m (-CH<sub>2</sub>-O-), 6.8 s , 7.1 d ,

7.7 s (-CH=N-), 8.0 s (-NH-), 8.2 d .

3,4,5-tridodecyloxybenzaldehyde-4'-nitrophenylhydrazone (**4**): mp 74°C.

C<sub>49</sub>H<sub>83</sub>N<sub>3</sub>O<sub>5</sub> Calc. C: 74.10 per cent, H: 10.53 per cent, N: 5.29 per cent.  
(F.W. 794.2) Found C: 74.05 per cent, H: 10.70 per cent, N: 5.18 per cent.

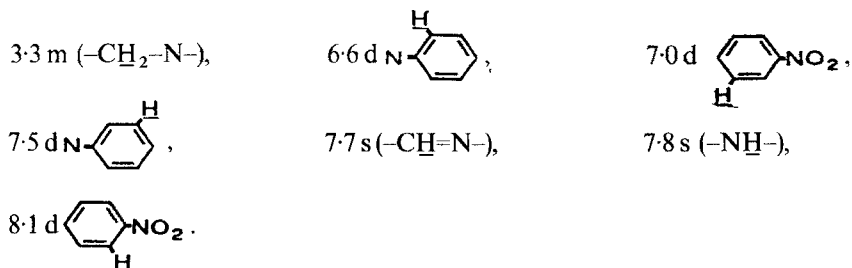
<sup>1</sup>H NMR: identical values as compound **3**.

4-N,N-dihexadecylaminobenzaldehyde-4'-nitrophenylhydrazone (5): mp. 47°C.

$C_{45}H_{76}N_4O_2$  Calc. C: 76.65 per cent, H: 10.86 per cent, N: 7.95 per cent.

(F.W. 705.1) Found C: 76.23 per cent, H: 10.83 per cent, N: 7.94 per cent.

$^1H$  NMR: 0.9 t ( $CH_3-$ ), 1.2 m ( $CH_3(-CH_2-)_{13}$ ), 1.6 m ( $-CH_2-CH_2-N-$ ),

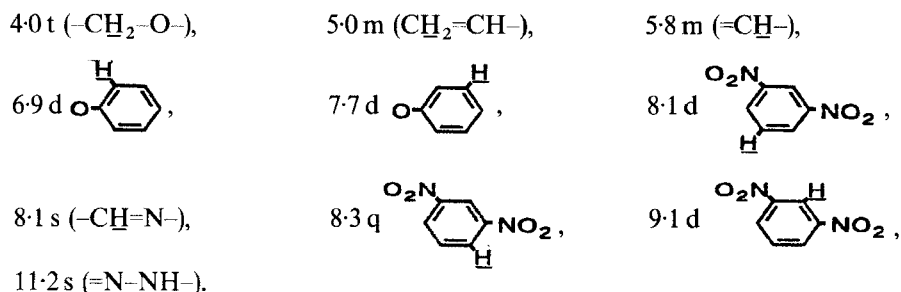


4-(10-undecenyloxy)benzaldehyde-2',4'-dinitrophenylhydrazone (6): mp 136°C.

$C_{24}H_{30}N_4O_5$  Calc. C: 66.92 per cent, H: 6.02 per cent, N: 11.15 per cent.

(F.W. 454.5) Found C: 66.64 per cent, H: 6.56 per cent, N: 11.00 per cent.

$^1H$  NMR: 1.3 m ( $=CH-CH_2(-CH_2-)_6$ ), 1.8 m ( $-CH_2-CH_2-O-$ ), 2.0 m ( $=CH-CH_2-$ ),

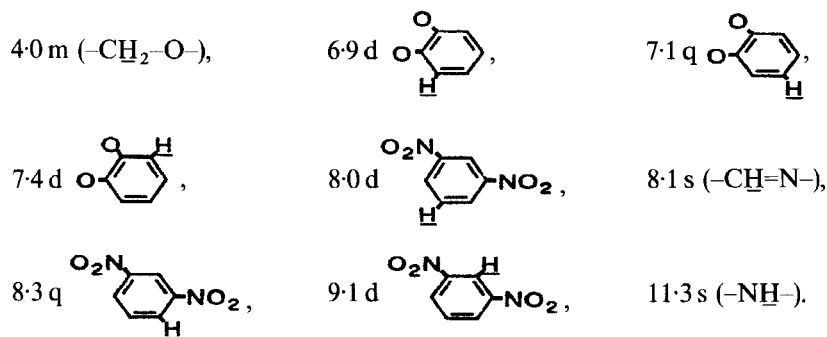


3,4-dihexadecyloxybenzaldehyde-2',4'-dinitrophenylhydrazone (7): mp 124°C.

$C_{45}H_{74}N_4O_6$  Calc. C: 70.46 per cent, H: 9.72 per cent, N: 7.30 per cent.

(F.W. 767.1) Found C: 70.03 per cent, H: 9.69 per cent, N: 7.09 per cent.

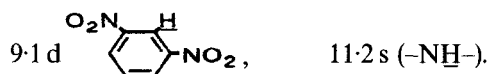
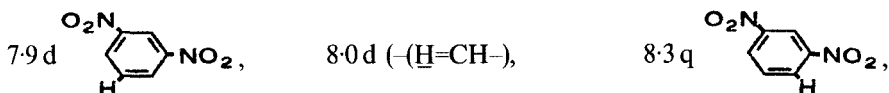
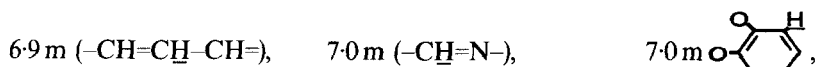
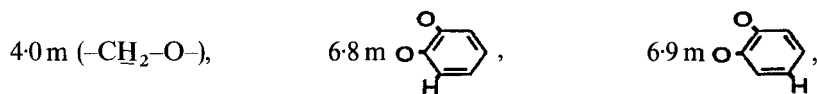
$^1H$  NMR: 0.9 t ( $CH_3-$ ), 1.3 m ( $CH_3(-CH_2-)_{13}$ ), 1.8 m ( $-CH_2-CH_2-O-$ ).



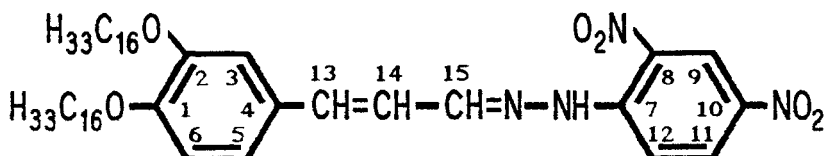
3,4-dihexadecyloxycinnamic aldehyde-2',4'-dinitrophenylhydrazone (9/8):  
mp, 115°C.

$C_{45}H_{74}N_4O_6$  Calc. C: 70.46 per cent, H: 9.72 per cent, N: 7.30 per cent.  
(F.W. 767.1) Found C: 70.03 per cent, H: 9.69 per cent, N: 7.09 per cent.

$^1H$  NMR: 0.9 t ( $CH_3-$ ), 1.3 m ( $CH_3(-CH_2-)_{13}$ ), 1.8 m ( $CH_2-CH_2-O-$ ),



$^{13}C$  NMR: (1) 151.1, (2) 149.5, (3) 113.5, (4) 128.6, (5) 123.5, (6) 112.0, (7) 144.5, (8) 129.3,  
(9) 129.9, (10) 138.1, (11) 131.8, (12) 116.6, (13) 141.5, (14) 121.7, (15) 150.3.



3,4-didodecyloxybenzaldehyde-2',4'-dinitrophenylhydrazone (9): mp 130°C.

$C_{37}H_{58}N_4O_6$  Calc. C: 67.86 per cent, H: 8.93 per cent, N: 8.56 per cent.  
(F.W. 654.9) Found C: 67.72 per cent, H: 8.92 per cent, N: 8.67 per cent.

$^1H$  NMR: identical values as compound 7.

3,4-dihexyloxybenzaldehyde-2',4'-dinitrophenylhydrazone (10): mp 133°C.

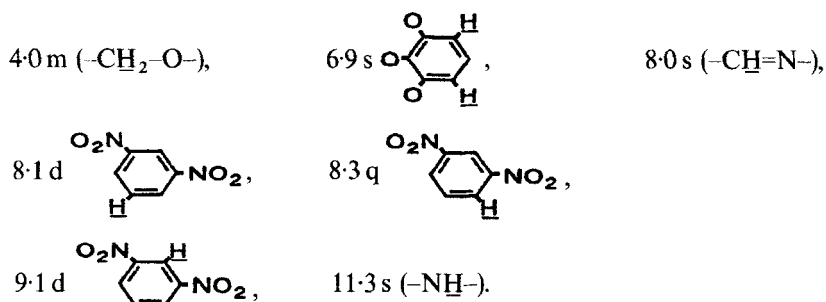
$C_{25}H_{34}N_4O_6$  Calc. C: 61.71 per cent, H: 7.04 per cent, N: 11.51 per cent.  
(F.W. 486.6) Found C: 61.69 per cent, H: 7.01 per cent, N: 11.62 per cent.

$^1H$  NMR identical values as compound 7.

3,4,5-trihexadecyloxybenzaldehyde-2',4'-dinitrophenylhydrazone (**11**): mp 106°C.

$C_{61}H_{106}N_4O_7$  Calc. C: 72.72 per cent, H: 10.60 per cent, N: 5.56 per cent.  
(F.W. 1007.6) Found C: 72.88 per cent, H: 10.63 per cent, N: 5.55 per cent.

$^1H$  NMR: 0.9 t ( $CH_3-$ ), 1.3 m ( $CH_3(-CH_2-)_{13}$ ), 1.8 m ( $-CH_2-CH_2-O-$ ),



3,4,5-tridodecyloxybenzaldehyde-2',4'-dinitrophenylhydrazone (**12**): mp 98°C.

$C_{49}H_{82}N_4O_7$  Calc. C: 70.13 per cent, H: 9.85 per cent, N: 6.68 per cent.  
(F.W. 839.2) Found C: 70.11 per cent, H: 9.85 per cent, N: 6.44 per cent.

$^1H$  NMR: identical values as compound **11**.

3,4,5-trioctyloxybenzaldehyde-2',4'-dinitrophenylhydrazone (**13**): mp 96°C.

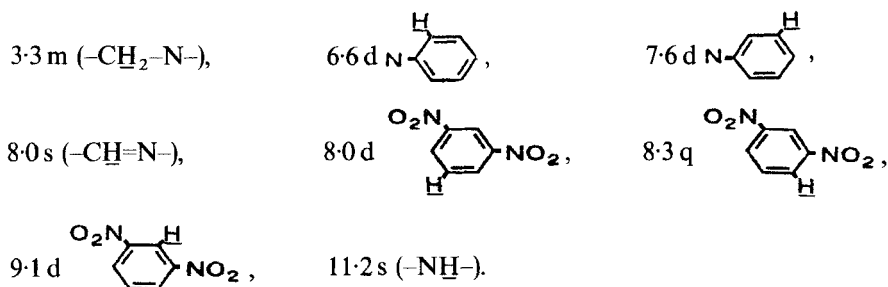
$C_{37}H_{68}N_4O_7$  Calc. C: 66.25 per cent, H: 8.71 per cent, N: 8.35 per cent.  
(F.W. 670.9) Found C: 66.33 per cent, H: 8.34 per cent, N: 8.53 per cent.

$^1H$  NMR: identical values as compound **11**.

4-N,N-dihexadecylaminobenzaldehyde-2',4'-dinitrophenylhydrazone (**14**): mp 92°C.

$C_{45}H_{75}N_5O_4$  Calc. C: 72.05 per cent, H: 10.08 per cent, N: 9.34 per cent.  
(F.W. 750.1) Found C: 71.96 per cent, H: 9.10 per cent, N: 9.32 per cent.

$^1H$  NMR: 0.8 t ( $CH_3-$ ), 1.3 m ( $CH_3(-CH_2-)_{13}$ ), 1.6 m ( $-CH_2-CH_2-N-$ ),



## References

- [1] DIELE, S., PELZL, G., WEISSFLOG, W., and DEMUS, D., 1988, *Liq. Crystals*, **3**, 1047.
- [2] RINGSDORF, H., WÜSTEFELD, R., ZERTA, E., EBERT, M., and WENDORFF, J. H., 1989, *Angew. Chem. Int. Ed.*, **28**, 914.
- [3] BENGES, H., EBERT, M., KARTHAUS, O., KOHNE, B., PRAEFCKE, K., RINGSDORF, H., WENDORFF, J. H., and WÜSTEFELD, R., 1990, *Adv. Mater.*, **2**, 3.
- [4] WEYGAND, C., and GABLER, R., 1940, *Z. phys. Chem. B*, **46**, 270.
- [5] WALTER, R., 1925, *Ber. dtsh. chem. Ges.*, **58**, 2303.
- [6] HARRIS, F. W., BELTZ, M., and SRIDHAR, K., 1989, *Polymer Preprints*, **29.2**, 308.
- [7] PAVLISTO, J. A., HUANG, S. J., and BENICEWICZ, B. C., 1982, *J. Polym. Sci. Polym. Chem. Ed.*, **20**, 3079.
- [8] DIELE, S., BRAND, P., and SACKMANN, H., 1972, *Molec. Crystals liq. Crystals*, **17**, 163.
- [9] PAULUS, W., and RINGSDORF, H., 1989, *18. Freiburger Arbeitstagung Flüssigkristalle*, p. 20.
- [10] LUPO, D., PRAB, W., SCHEUNEMANN, U., LASCHEWSKY, A., RINGSDORF, H., and LEDOUX, I., 1988, *Opt. Soc. Am. B*, **5**, 300.
- [11] ORGANIKUM, 15th Edn., VEB Verlag, p. 757.
- [12] PANUNTO, T. W., URBANCZYK-LIPKOWSKA, Z., JOHNSON, R., and ETTER, M. C., 1987, *J. Am. chem. Soc.*, **109**, 7786.