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# Hydrogen-bonded polycatenar mesogens

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The tricatenaar, hydrogen-bonded complexes formed between alkoxy stilbazoles and an imine were found to be mesomorphic. Subsequently, related tetracatenar complexes were also investigated and found to be non-mesomorphic. We report the transition temperatures of these complexes and discuss structural modifications.

## 1. Introduction

Intermolecular hydrogen bonding is now accepted as a useful strategy for the construction of liquid crystalline materials [1]. Work primarily by Kato and Fréchet [2], and then by Lehn [3], ourselves [4] and others [5] has shown how it may be used in both polymeric and low molar mass systems to form mesomorphic complexes between proton acceptors (usually pyridines or other nitrogen heterocycles) and proton donors (often benzoic acids or phenols). In the archetypal 'pyridine acceptor/benzoic acid donor' system, the hydrogen bond region may be likened in a structural sense to an ester function (figure 1), albeit one which is slightly longer and possessed of much greater flexibility. Thus, comparisons between hydrogen-bonded systems and their covalent analogues are instructive in delineating the rôle of the hydrogen bond.

Polycatenar mesogens are a relatively new class of mesogen [6]. A polycatenar liquid crystal may crudely be considered as an intermediate situation between a rod-like and a disc-like molecule in that in certain cases, different members of a homologous series may show either columnar or lamellar phases, or sometimes both. Polycatenar liquid crystals generally consist of a long, rigid aromatic core, with alkoxy chains at both ends, and they have aroused great interest due to their unusual structure and also due to the mesomorphism they exhibit. Malthête *et al.* suggested a nomenclature [6] for compounds of this structural type, which is related to the number of aliphatic chains so that those having three, four, five or six chains are termed tri-, tetra-, penta- and hexa-catenar, respectively. Thus, hexacatenar and

pentacatenar mesogens behave similarly to columnar liquid crystals as they exhibit nematic and columnar mesophases. Tricatenaar and forked mesogens [7] (bicatenar with two chains on the same side) show nematic and smectic phases and in some cases cubic phases, similar to calamitic mesogens [6]. Tetracatenars [8] are by far the most interesting class of polycatenar systems when the terminal chains are in the 3- and 4-positions as they can show nematic, smectic C, cubic, and columnar mesophases in the same series at differing chain lengths [6]. A rather good example is given by the phase diagram which we found for tetracatenar bipyridines [9]. In figure 2, we have drawn the schematic diagrams of the polycatenars which are the subject of this study and have labelled them using the same proposed nomenclature.

Previous studies on hydrogen-bonded liquid crystals have concentrated mainly on mesogens showing either nematic/smectic or columnar mesophases, in the latter case including studies of carbohydrate mesogens [1]. More recently, however, Praefcke [10], Lattermann [11] and Percec [12] have investigated mesomorphic, hydrogen-bonded, polycatenar systems. These have been found to exhibit similar mesomorphism to that of the

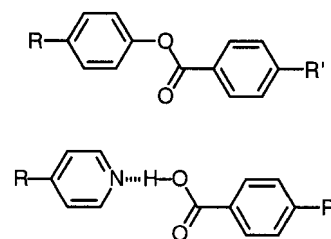


Figure 1. Analogy between H-bonded complex and related covalent ester.

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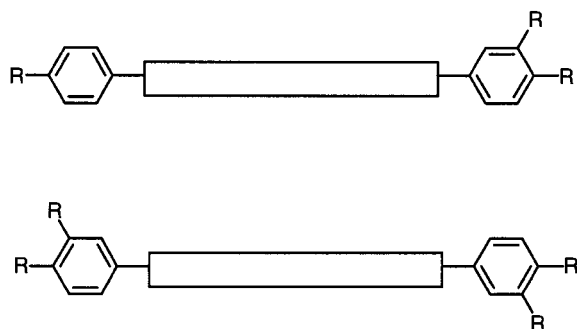


Figure 2. Schematic representation of two examples of polycatenar liquid crystals (tricatenaar and tetracatenaar).

covalently bonded polycatenar systems, namely nematic and columnar mesophases. For example, the 2,3,4-trialkoxycinnamic acids (figure 3:  $R = C_nH_{2n+1}$ ) show monotropic ( $n = 4$  and  $8$ ) and enantiotropic ( $n = 6$ ) nematic phases [10]. Longer chain homologues have not been investigated; such homologues may be the key to finding the columnar phase. It appears that for these compounds the *ortho*-substitution destroys the tendency for lateral interaction; therefore the smectic C phase is destabilized and does not occur.

Lattermann [11] has investigated poly(alkoxy)-benzamides (figure 4:  $R = C_nH_{2n+1}$ ,  $X = H$  or  $Br$ ). For the di-3,4- and di-3,5-alkoxybenzamides, the identification of the mesophases is still under investigation. The hexacatenar compounds show columnar phases similarly to the non-H-bonded systems.

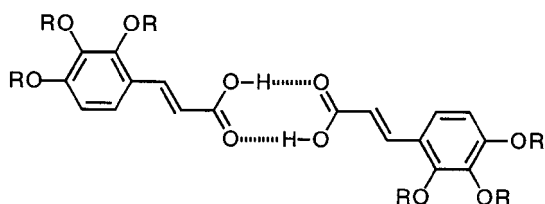


Figure 3. Dimeric 2,3,4-trialkoxycinnamic acids.

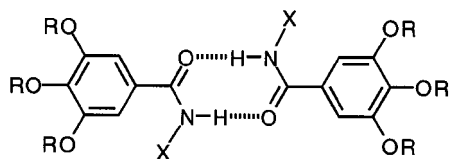


Figure 4. Dimeric 3,4,5-trialkoxybenzamides.

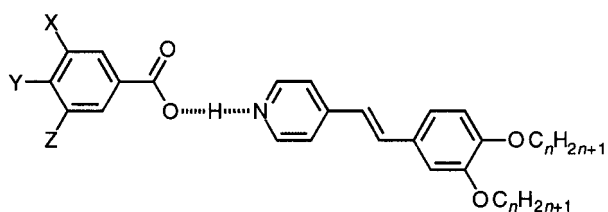


Figure 5. Benzoic acid/stilbazole complex structure.

Table 1. Transition temperatures for the complexes 1–10 of general structure given in figure 5.

Complex	$X$	$Y$	$Z$	$n$	Melting point/ $^{\circ}C$
1	H	$OC_{10}H_{21}$	H	2	117
2	H	$OC_{10}H_{21}$	H	4	101
3	H	$OC_{10}H_{21}$	H	8	90
4	H	$OC_{10}H_{21}$	H	11	92
5	H	$OC_7H_{15}$	H	8	91
6	H	$OC_7H_{15}$	H	11	89
7	H	CN	H	8	115
8	H	CN	H	11	108
9	$OC_{12}H_{25}$	$OC_{12}H_{25}$	$OC_{12}H_{25}$	8	54
10	$OC_{12}H_{25}$	$OC_{12}H_{25}$	$OC_{12}H_{25}$	11	58

We are interested in studying the mesomorphism of both hydrogen-bonded and metal complexes formed by mono- and poly-alkoxystilbazoles [4, 13]. In this paper, we report on the investigation of polycatenar, hydrogen-bonded complexes containing a three- or four-ring aromatic core and a pyridyl-benzoic acid hydrogen bond, in order to effect a comparison with related, covalently-bonded systems.

## 2. Experimental

Alkoxystilbazoles [14] and dialkoxystilbazoles [13] were prepared as described earlier. The imines were simply prepared in a condensation reaction [15] of the relevant alkoxybenzaldehyde with 4-aminobenzoic acid.

The complexes were all prepared from pure components. They were made by separately dissolving the correct molar amounts in freshly distilled tetrahydrofuran and then mixing. The solvent was removed by slow evaporation and the complex was subsequently annealed and slowly cooled to yield the final product.

## 3. Results and discussion

### 3.1. Three-ring systems

Initially, we undertook the formation of three-ring complexes formed between 3,4-dialkoxystilbazoles and either 4-alkoxybenzoic acids, 4-cyanobenzoic acid or 3,4,5-trialkoxybenzoic acid (figure 5). Unfortunately, none of these complexes was mesomorphic, unlike some related, covalent tricatenaar mesogens (figure ) [7], and all simply melted directly to isotropic liquids (table 1). For the putative pentacatenar mesogens, 9 and 10, the core of the mesogen is simply insufficiently long to stabilize a mesophase, but for complexes 1–8, by analogy with the covalent analogues, it is clearly the presence of the hydrogen-bonded function which suppresses mesomorphism due to its flexibility.

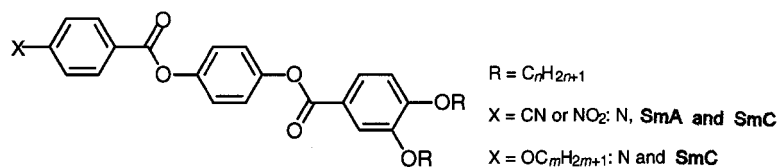


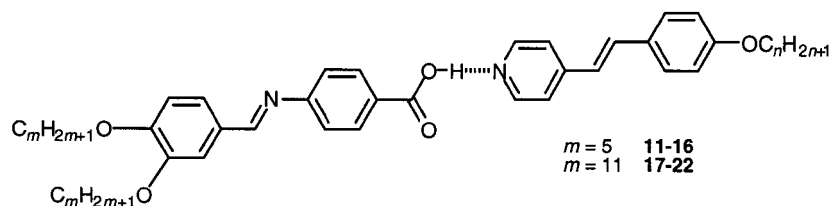
Figure 6. Examples of some related mesomorphic, three-ring systems.

Table 2. Transition temperatures for the complexes **11–22** of general structure given in figure 7.

Complex	$n$	Transition	Temperature/ $^{\circ}C$
$m = 5$			
<b>11</b>	3	Cr–SmC	116
		SmC–N	120
		N–I	159
<b>12</b>	6	Cr–SmC	120
		SmC–N	138
		N–I	162
<b>13</b>	8	Cr–SmC	124
		SmC–N	144
		N–I	159
<b>14</b>	10	Cr–SmC	125
		SmC–N	148
		N–I	159
<b>15</b>	12	Cr–SmC	106
		SmC–N	148
		N–I	154
<b>16</b>	14	Cr–SmC	109
		SmC–N	147
		N–I	150
$m = 11$			
<b>17</b>	3	Cr–N	95
		N–I	118
<b>18</b>	6	Cr–SmC	98
		SmC–N	112
		N–I	124
<b>19</b>	8	Cr–SmC	103
		SmC–N	116
		N–I	147
<b>20</b>	10	Cr–SmC	120
		SmC–N	128
		N–I	140
<b>21</b>	12	Cr–SmC	89
		SmC–I	145
<b>22</b>	14	Cr–SmC	96
		SmC–I	148

Table 3. Transition temperatures for the complexes **23–34** of general structure given in figure 9.

Complex	$m$	Transition	Temperature/ $^{\circ}C$
$n = 2$			
23	3	Cr–N	111
		N–I	163
24	6	Cr–N	142
		N–I	191
25	10	Cr–N	140
		N–I	185
26	15	Cr–N	138
		N–I	166
$n = 6$			
27	3	Cr–N	151
		N–I	198
28	6	Cr–SmC	111
		SmC–N	134
28	6	N–I	182
		Cr–SmC	103
29	10	SmC–N	175
		N–I	184
30	15	Cr–SmC	117
		SmC–I	190
$n = 14$			
31	3	Cr–SmC	117
		SmC–N	178
		N–I	197
32	6	Cr–SmC	107
		SmC–N	147
		N–I	180
33	10	Cr–SmC	105
		SmC–N	138
		N–I	171
34	15	Cr–SmC	98
		SmC–I	165

Figure 7. Schematic diagram of the tricatener complexes **11–22**.

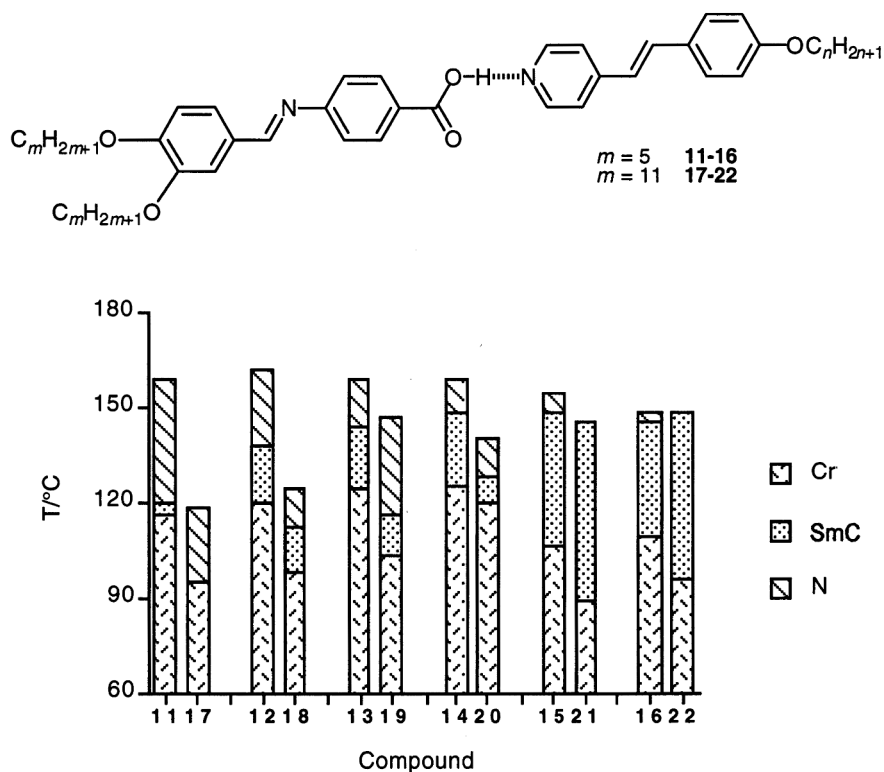


Figure 8. Phase behaviour of complexes 11–22.

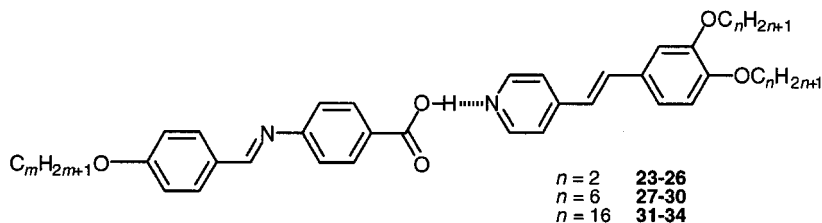


Figure 9. Schematic diagram of the tricatenaar complexes 23–34.

### 3.2. Four-ring tricatenaar systems

As the three-ring systems had proved to be non-mesomorphic, we modified the complexes to include an additional phenyl ring, thus enhancing the structural anisotropy. The complexes now comprised a stilbazole and a two-ring imine which terminated in a carboxylic acid group. The first series to be considered carried one chain on the stilbazole and two chains on the imine (figure 7). A number of complexes of differing chain lengths were studied; their transition temperatures are collected in table 2 and their mesomorphism is displayed in figure 8).

These asymmetric tricatenaar mesogens were found to exhibit stable enantiotropic mesophases and are interesting because neither of the mesophases exhibited, nematic and smectic C, is shown by either of the two components; the imine is non-mesomorphic while the stilbazole shows a smectic B and a crystal E phase [14].

Thus, from non-mesomorphic components it has been possible to assemble mesogenic moieties which show a mesomorphism characteristic of a simple tricatenaar mesogen, namely nematic and smectic C phases.

For complexes 11–16, we can see that where there are two pentyloxy chains on the imine, increasing the alkoxy chain length on the stilbazole gently destabilizes the nematic phase while at the same time increasing the stability of the smectic C phase. The total destabilization of the nematic phase is only  $9^\circ C$  from propyloxy- to tetradecyloxy-stilbazole, while the smectic C phase is stabilized by nearly  $30^\circ C$ . Curiously, when there are two undecyloxy chains on the imine (17–22), the complex with propyloxystilbazole, 17, shows only a nematic phase, while for complexes 18–20, both smectic C and nematic phases are shown; the complexes with the longest stilbazole chains, 21 and 22, show only a smectic C phase. A general comparison of 11–16 with 17–22 shows

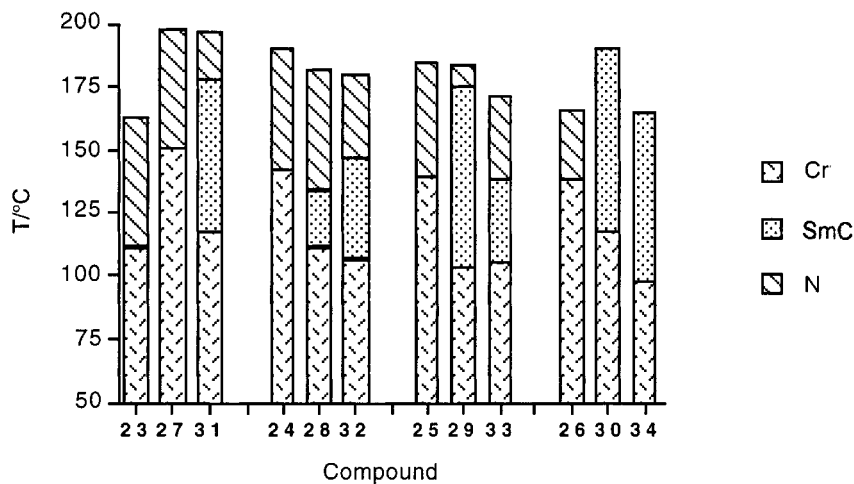
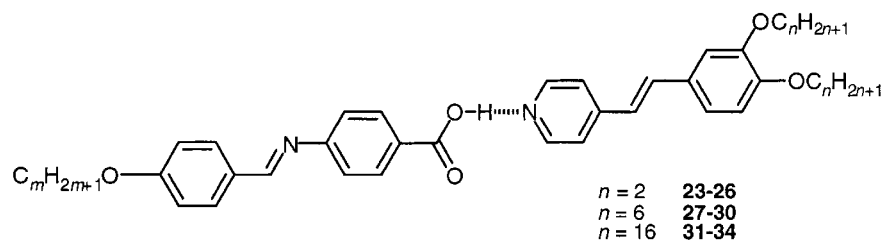


Figure 10. Phase behaviour of complexes **23–34**.

that for the longer chains on the imine, transition temperatures are generally lower.

We then examined a related series synthesized from a two-chain stilbazole and a single-chain imine (figure 9). Twelve derivatives were made based on three different chain lengths of the dialkoxystilbazole. The transition temperatures are collected in table 3 and the mesomorphism is displayed in figure 10.

As was the case with complexes **11–22**, once again materials with nematic and smectic C phases were found, only this time neither of the precursor components was mesomorphic, each simply melting to the isotropic state on heating. The differences in transition temperature as a function of chain length are now much less marked and the only definite trend is one of stabilization of the smectic C phase as the chain lengths get longer, with

the nematic phase eventually disappearing in **30** and **34**. Two other features are worthy of note. First, that there appears to be a particular island of stability for the smectic C phase in complex **29** which we attribute to particularly favourable relative lengths of  $n$  and  $m$ . Second, the transition temperatures are consistently higher in complexes **23–34** which possess two chains on the stilbazole, compared with complexes **11–22** which possess two chains on the imine; there is no ready explanation for this last observation.

### 3.3. Four-ring tetracatenar systems

Having successfully generated mesogens in these two series of tricatener mesogens, we were now anxious to extend the studies to tetracatenar mesogens as these

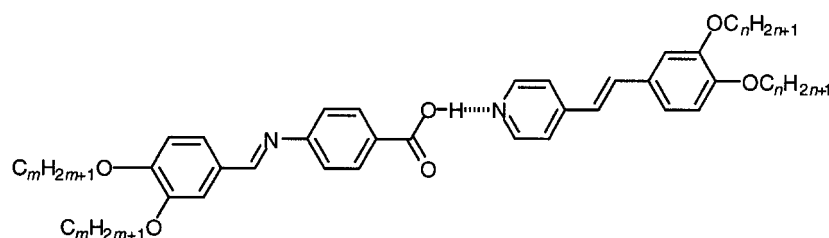


Figure 11. Schematic diagram of the tetracatenar complexes **35–40**.

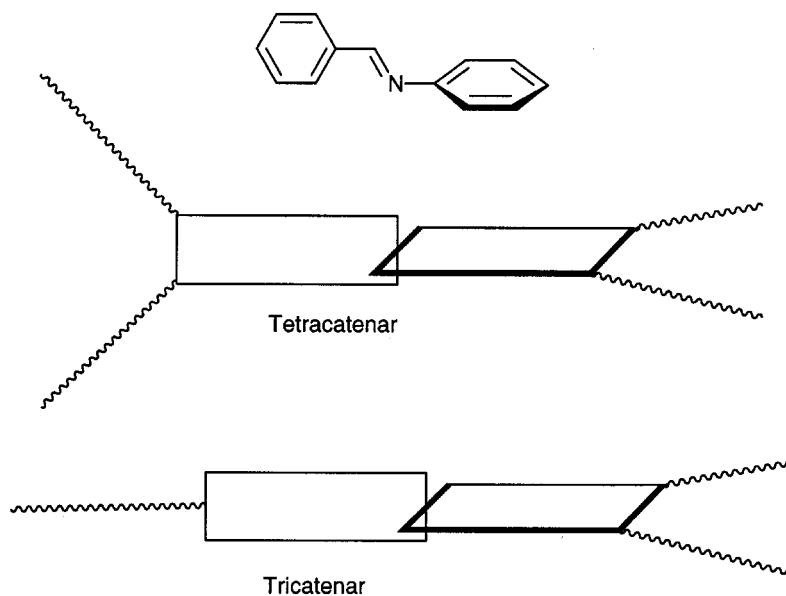


Figure 12. Schematic diagram to show the effects of the proposed 90° torsion angle in the imine bond of the tetracatenar mesogens.

could possess a more diverse and interesting mesomorphism. To this end, we prepared complexes **35–40** (figure 11) based on the dialkoxyimines and the dialkoxy-stilbazoles. Unfortunately, none of these complexes was mesomorphic, each melting straight to the isotropic state on heating; melting points are collected in table 4.

The reason for the lack of mesomorphism in these systems is not immediately obvious. Previously, it has been advanced that in cases where the chains of a mesogen constitute at least half of the molecular mass, then columnar phases are observed [16]; this condition is met here. Similarly, while we proposed that the flexibility in the centre of the molecule was a detrimental factor in the three-ring complexes **1–10**, it clearly did not adversely affect the mesomorphic properties of complexes **11–34** and so we can discount this factor, too. However, one possibility lies with the imine group. Thus, if the torsion angle in the imine group were 90°, the overall geometry of the complex including the chains would not be favourable to mesophase formation. However, in the case of the tricatenaar systems, such an orientation of the imine group would not adversely affect the mesomorphism at all (figure 12).

Table 4.

Complex	<i>m</i>	<i>n</i>	<i>T<sub>m</sub></i> /°C
<b>35</b>	8	2	137
<b>36</b>	14	2	134
<b>37</b>	8	6	125
<b>38</b>	14	6	116
<b>39</b>	8	11	126
<b>40</b>	14	11	120

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