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The crystal K phase of 4,4′-di-(2-methoxyethoxy)biphenyl

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Detailed studies of 4,4′-di-(2-methoxyethoxy)biphenyl have shown that it displays the first recorded incidence of the crystal K phase forming directly on cooling from the isotropic phase.

1. Introduction

This work was carried out as part of a project to find novel thermotropic low temperature liquid crystals [1]. The biphenyl based material was chosen so as to confirm or deny the widely held belief that addition of a second oxygen in a terminal chain destabilizes the mesophase. The results were unexpected as they yielded the first recorded incidence of the formation of the crystal K phase directly on cooling from the isotropic melt.

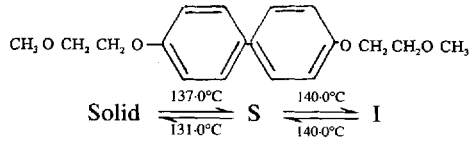
2. Preparation

4,4′-Di-(2-methoxyethoxy)biphenyl was synthesized by a Williamson ether reaction between 4,4′-dihydroxybiphenyl and 2-bromoethyl methyl ether under mildly basic conditions. Purification was carried out by flash chromatography until TLC confirmed purity.

3. Results and discussion

3.1. *Optical studies*

These were carried out using a Leitz optical microscope fitted with a hot-stage. The phase sequence for 4,4′-di-(2-methoxyethoxy)biphenyl can be written as:



Photomicrographs of the mesophase(s) are shown in figure 1. Those in figure 1 (*a*) were taken as the mesophase formed from the isotropic liquid (black regions) and those in figure 1 (*b*) were taken at various regions of the sample, held at a temperature a few degrees into the mesophase, but well above crystallization. Miscibility studies were carried out on the mesophase, which showed that it was not S_A or S_C. Phase S was considered to be a mesophase for the following reasons: (i) the transition between the S phase and the isotropic phase was reversible without detectable supercooling. (ii) The texture merged as it grew from the isotropic phase. (iii) The texture showed no change on holding the sample at 138°C for 2 h.

3.2. *Differential scanning calorimetry studies*

These were carried out using a Perkin–Elmer DSC 2C. On heating, the material shows two endothermal transitions (see figure 2, peaks 1 and 2). The transition temperatures and enthalpy values for the transitions are shown in table 1. On cooling two exothermal transitions (see figure 2, peaks 3 and 4) were found; data are given in table 1. The DSC data clearly show the failure of the S phase to undergo significant supercooling. The large ΔH value on cooling from the isotropic phase confirms the existence of an ordered phase as suggested by the textures of figure 1 (*a*).

3.3. *X-ray diffraction studies*

Low and wide angle diffraction studies were carried out, but only the wide angle studies were made out under a magnetic field. Alignment of the sample was achieved by heating it just above the mesophase to isotropic transition and holding it there overnight while applying a 0·6 T magnetic field. The sample was then allowed to cool down into the mesophase region at 8°C per hour. Exposure was carried out over a 3 h period. A typical X-ray photograph

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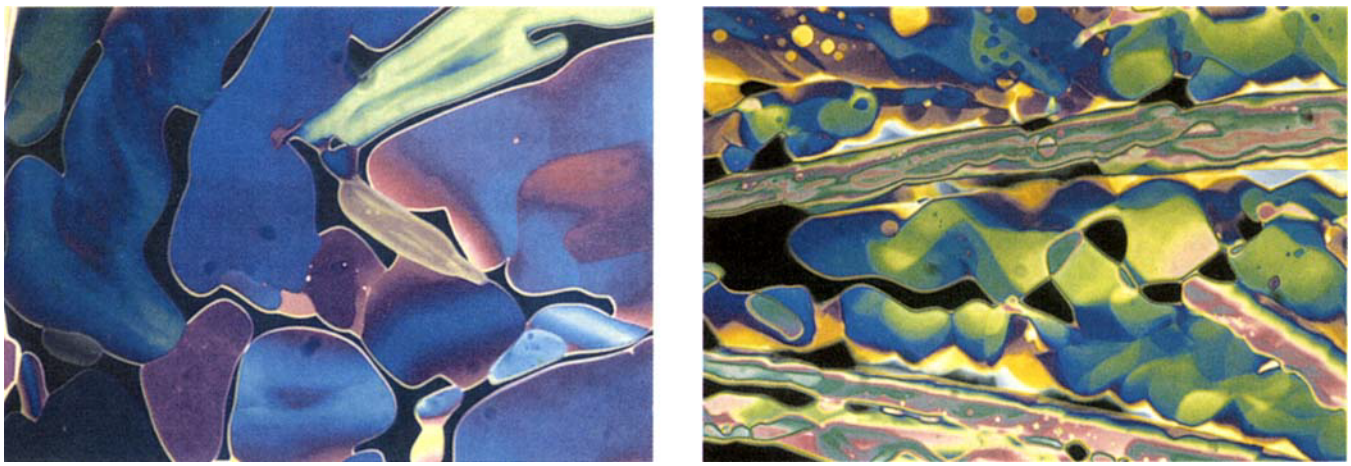

Figure 1 (*a*)

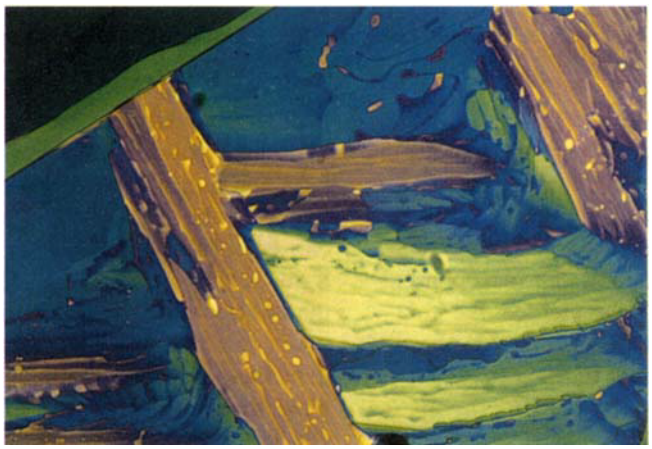

Figure 1 (*b*)

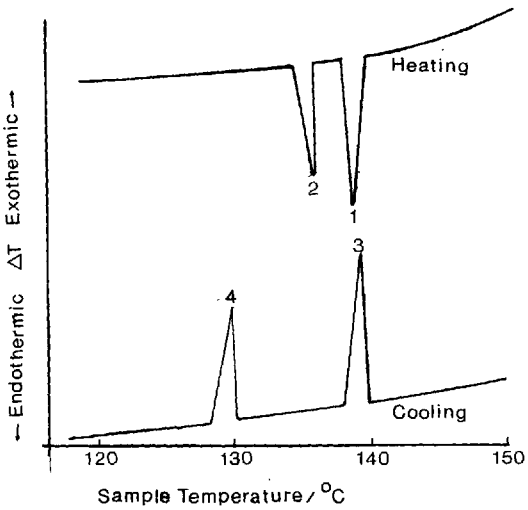

Figure 2. DSC scans (heating and cooling) for 4,4′-di-(2-methoxyethoxy)biphenyl.

Table 1. DSC results for 4,4′-di-(2-methoxyethoxy)biphenyl.

Peak number†	Transition temperature/°C	Transition	ΔH/kJ mol^{-1}
1	139·17	S–I	22·67
2	136·27	Solid–S	17·53
3	139·39	I–S	22·44
4	128·76	S–Solid	16·65

† See figure 2.

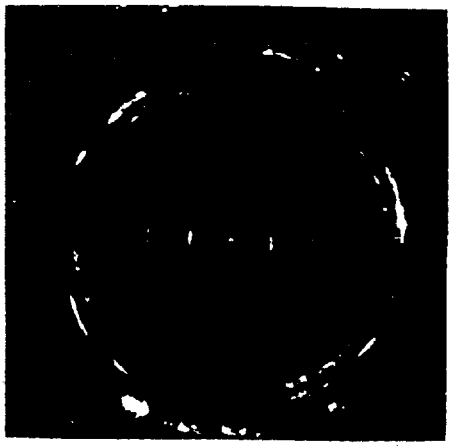

Figure 3. X-ray diffraction photographs of 4,4′-di-(2-methoxyethoxy)biphenyl.

Figure 1. Photomicrographs of the mesophase of 4,4′-di-(2-methoxyethoxy)biphenyl: (*a*) at the isotropic–crystal K transition temperature; (*b*) textures of different parts of the sample held at a temperature between the crystalline and isotropic liquid phases.

is shown in figure 3 and the data are given in table 2. The indexing of the data is shown in figure 4.

Thus the mesophase was identified as:

(i) A stacked hexagonally ordered phase, because of the relatively sharp bars of scattering centred at (110), (020) and extending approximately +/ − C* along the C direction;

(ii) A monoclinic unit cell with b (unique axis) $> a$, i.e., the molecules are tilted towards the apex of the hexagon;

(iii) As a crystal K phase because of the presence of reflections with $h + k = 2n + 1$ [2, 3].

It is interesting to note that the phase described in [2] as smectic K only has the order extending over 2 layers, while

Table 2. X-ray diffraction for 4,4′-di-(2-methoxyethoxy)biphenyl. All the d(calc) values are well within experimental error. The error for d(obs) is 2 per cent.

Arc no.	d(obs)/Å	Index	d(calc)/Å	d(deviation)/Å	
1	17·70	001	17·76	0·06	
2	8·93	002	8·88	0·05	
3	6·03	003	5·92	0·11	
4	4·87	111	4·87	0·00	
5	4·47	110	4·50	0·03	
6	3·98	020	4·00	0·02	
7	3·89	021	—	—	
8	3·64	022	3·65	0·01	
9	3·44	112	—	—	
10	3·35	121	3·35	0·00	
11	3·26	107	3·27	0·01	
12	3·11	121	—	—	
a/Å	b/Å	c/Å	α/°	γ/°	β/°
6·30	8·01	20·58	90	90	120·3

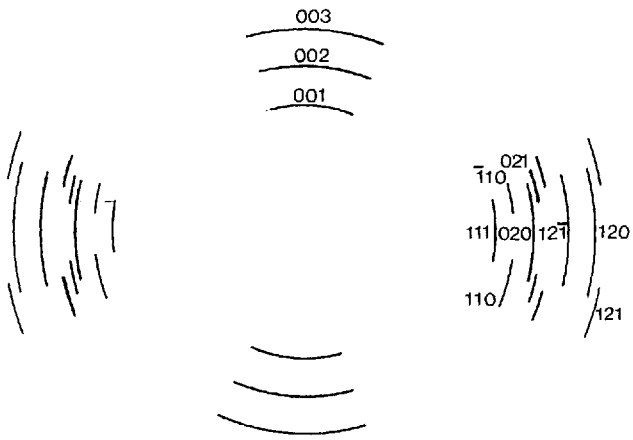

Figure 4. Indexing pattern for X-ray diffraction data.

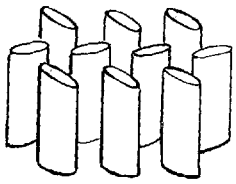

Figure 5. Packing of molecules within an untitled analogue of the crystal K phase.

the compound described here quite clearly shows ordering over 3 layers. If a density of $1{\cdot}2\,g\,cm^{-3}$ is taken for 4,4′-di-(2-methoxyethoxy)biphenyl, then each unit cell contains 2 molecules. Comparison of the area of the largest component of each molecule (the benzene ring) with the area of the unit cell shows clearly that rotation can only occur if it is cooperative in nature. Any other rotation would cause disruption of the unit cell/lattice planes which would be manifest as a degradation of the sharpness of the spots shown in figure 3. Figure 5 shows a typical packing arrangement of the molecules in an equivalent situation with an orthogonal orientation of the calamitic molecules, i.e., the tilt in the crystal K phase is not shown.

4. Conclusions

By the process of elimination of certain phase types (N– by optical methods; S_A, S_C– by miscibility techniques; S_B, S_C– by X-ray methods) and the positive results given by X-ray diffraction for the S phase of 4,4′-di-(2-methoxyethoxy)biphenyl, it has been identified as crystal K. The fact that this phase forms directly on cooling from the isotropic phase is of great interest and the photomicrographs should allow the positive identification of other crystal K phases from texture studies provided that no pseudomorphic textures are formed.

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