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Liquid Crystals

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A study of the stability and phase behaviour of some smectic liquid crystalline biphenyl derivatives

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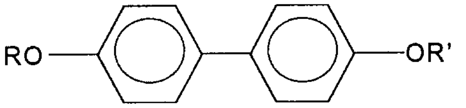
The syntheses and liquid crystalline phase behaviour of a series of alkylated dihydroxybiphenyl derivatives of type (**1**) are reported. In particular, these materials were designed in order to study the effect on phase behaviour of the location of an (*S*)-2-methylbutyloxy substituent along the lateral alkyl chain and also of the number of oxygen atoms substituted into the chain.



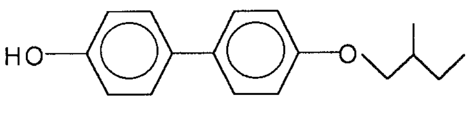
(1)

1. Introduction

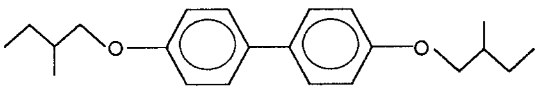
Chirality is of great interest in the field of liquid crystals and many investigations have been made to study chirality-related effects and properties that are dependent on the molecular structure and more specifically the nature and environment of the asymmetric centre.

In the present study, earlier investigations [1] were continued into a series of biphenyl ethers with chiral centres. In particular, the effect on the mesomorphic behaviour was examined by altering the number and position of oxygen atoms in the ether chains. Also the results were compared with those obtained for the non-chiral analogues.

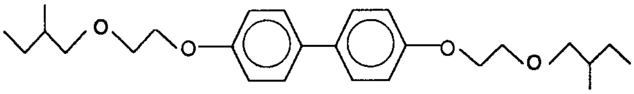
It is well known that molecular structure may be varied to control chirality-related effects on the phase properties of biphenyl derivatives [1]. In this work we have investigated the effect of the chiral substituent (*S*)-2-methylbutyloxy on phase transitions of compounds (**7**–**13**) as a function of its position relative to the biphenyl core and also the effect of oxygen introduced into the terminal alkyl chain whereby it becomes a polyether. Detailed studies were performed also on both chiral and racemic examples of 4-alkyl-4′-(2-methylbutyloxy)-biphenyls and of di-substituted (2-hydroxyethoxy)biphenyls.



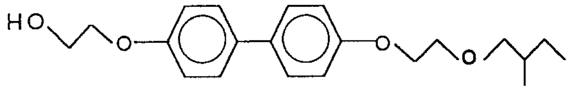
(**7a/7b**) 4-Hydroxy-4′-(2-methylbutyloxy)biphenyl



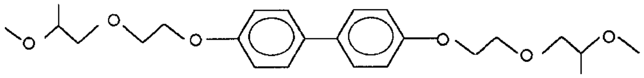
(**8a/8b**) 4,4′-Bis(2-methylbutyloxy)biphenyl



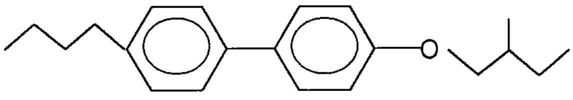
(**9a/9b**) 4,4′-Bis[2-(2-methylbutyloxy)ethoxy]biphenyl



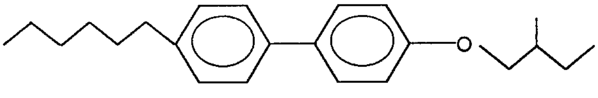
(**10**) 4-(2-Hydroxyethoxy)-4′-[2(2-methylbutyloxy)ethoxy]biphenyl



(**11**) 4,4′-Bis[(*S*-(+)-2-methoxypropyloxy)ethoxy]biphenyl



(**12**) 4-Butyl-4′-(2-methylbutyloxy)biphenyl



(**13**) 4-Hexyl-4′-(2-methylbutyloxy)biphenyl

2. Experimental

Syntheses of the biphenyl ethers were carried out by successive alkylations of 4,4′-dihydroxybiphenyl. The

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following procedures are typical. Yields given refer to crude products.

2.1. *Method 1: symmetrical 4,4′-dialkylated biphenyldiols*

2.1.1. *4,4′-Bis(2-methylbutyloxy)biphenyl, (8) [2] and 4-hydroxy-4′-(2-methylbutyloxy)biphenyl (7)*

To 4,4′-dihydroxybiphenyl (**1**) (3·5 g, 0·02 mol) in 2-butanone (10 ml) was added potassium carbonate (8·5 g, 0·06 mol) with stirring and the mixture heated to reflux. 1-Bromo-2-methylbutane (6·9 g, 0·05 mol) was added and heating continued. The progress of the reaction was monitored by TLC using ether:pentane (1:1 v/v) as eluant. The order of elution was: dialkyl ether > monoalkyl ether > biphenyldiol. On completion, the reaction was quenched by adding water and the two layers were separated. The organic phase was washed with water (4 × 25 ml) and then dried over magnesium sulphate and filtered. The solvent was removed *in vacuo*. The remaining solid, an approximately 1:1 mixture of **7** and **8**, 6·0 g, was purified by flash chromatography on silica using as eluant ether:pentane (1:1 v/v).

2.1.2. *4-Alkyl-4′-(2-methylbutyloxy)biphenyls*

4-Butyl-4′-[*S*-(+)-2-methylbutyloxy]biphenyl (**12**) and 4-hexyl-4′-[*S*-(+)-2-methylbutyloxy]biphenyl (**13**) were prepared by the same method, but using the respective 4-alkyl-4′-hydroxybiphenyl in place of (**1**).

Analogously, using 2-bromoethanol in place of bromo-2-methylbutane, 4,4′-bis(2-hydroxyethoxy)biphenyl (**2**) was prepared. 4-(2-Methylbutyloxy)-4′-hydroxybiphenyl and 4-(2-hydroxyethoxy)-4′-hydroxybiphenyl were also prepared analogously, but using half quantities of potassium carbonate and 1-bromo-2-methylbutane or 2-bromoethanol, respectively. These were produced as by-products and not studied. Unsymmetrical dialkoxybiphenyls were synthesized analogously by means of two sequential monoalkylations.

2.2. *Method 2: alkylations of the hydroxyethyl side chain*

2.2.1. *4-(2-Hydroxyethoxy)-4′-[2-(2-methylbutyloxy)-ethoxy]biphenyl (10) and 4,4′-bis[2-(2-methylbutyloxy)ethoxy]biphenyl (9)*

4,4′-Bis(2-hydroxyethoxy)biphenyl (**2**) (5·5 g, 0·02 mol) was added to a solution of sodium hydride (1·0 g, 0·042 mol) in anhydrous DMSO (25 ml) followed by 1-bromo-2-methylbutane (6·0 g, 0·04 mol). The mixture was allowed to stand until it became neutral. Water was added and the product extracted into ether (5 × 20 ml). The ether solution was dried ($MgSO_4$), the solvent removed and the product purified by column chromatography. This yielded a mixture of 4,4′-bis-[2-(2-methylbutyloxy)ethoxy]biphenyl (**9**) and 4-(2-hydroxyethoxy)-4′-[2-(2-methylbutyloxy)ethoxy]biphenyl (**10**) in either chiral or racemic forms. The yield was 7·1 g of an approximately 1:1 mixture of **9** and **10**.

2.3. *Method 3: preparation of 4,4′ bis-[(S-(+)2-methoxypropyloxyethoxy]biphenyl (11)*

To *S*(+)-ethyl lactate (**3**) (12·0 g, 0·1 mol) was added methyl iodide (15·6 g, 0·11 mol) and sodium hydride (2·6 g, 0·11 mol) in anhydrous DMSO (925 ml). The mixture was then washed with water and the product extracted into ether (4 × 20 ml). The ether solution was dried ($MgSO_4$), filtered and the solvent removed to yield ethyl *S*(+)-2-methoxypropionate (**4**), which was purified by distillation under vacuum. Ethyl 2-methoxypropionate (**4**) (13·4 g, 0·1 mol) was treated with lithium aluminium hydride (3·8 g, 0·11 mol) in a solution of THF (25 ml) at 0°C. The mixture was quenched in water and the product extracted into ether (4 × 25 ml). The ether extract was dried ($MgSO_4$), filtered and the solvent removed to yield *S*(+)-2-methoxypropanol (**5**).

S(+)-2-methoxypropan-1-ol (9·9 g, 0·1 mol) was added to a solution of *p*-toluene sulphonyl chloride (20·7 g, 0·11 mol) in pyridine (50 mL) and stirred at −5°C for 2 h. On standing a precipitate formed, which was washed in water and extracted into ether (5 × 25 ml). The ether solution was dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. This yielded the precursor *S*(+)-2-methoxypropyl *p*-toluene sulphonate (**6**), 18 g, 75% yield.

4,4′-Bis[*S*-(+)2-methoxypropyloxyethoxy]biphenyl (**11**) was prepared by the reaction of *S*(+)-2-methoxypropyl *p*-toluene sulphonate (**6**) following method 2.

3. Characterization of products

Products were purified using flash column chromatography over silica gel using a mixture of diethyl ether and pentane (1:1 v/v) as solvent. Purity of final products was assessed by thin layer chromatography (Kieselgel 60 F_{254}), detecting spots by UV. Structure assignments of the products were made by IR (Perkin-Elmer 1420), ^{1}H NMR (Perkin Elmer 34B 220 MHz) and mass spectrometry using both chemical and electron ionization.

3.1. *4-Hydroxy-4′-(2-methylbutyloxy)biphenyl (7a)*

R_f (ether:pentane, 1:1 v/v) 0·47; IR ν/cm^{-1} (film) 3343 (O–H) 1249, 1169 (C–O); ^{1}H NMR ($CDCl_3$) 1·06 (d, 3H, CH_3, $J = 8$ Hz), 1·12 (t, 3H, CH_3, $J = 8$ Hz), 1·35 (m, 2H, CH_2), 1·60 (m, 2H, –CH–), 3·92 (oct, 4H, –CH_2OPh, $J = 4·5$ Hz), 7·00–7·52 (2 × d, 8H, 2 × Ph); mass spectrum *m/z*: 256 (M+). Calc. for $C_{17}H_{20}O_2$: C 79·68, H 7·81%. Found: C 79·37, H 7·86%.

3.2. *4-Hydroxy-4′-[S-(+)-2-methylbutyloxy]biphenyl (7b)*

R_f (ether:pentane, 1:1 v/v) 0·43; IR ν/cm^{-1} (film) 3336 (O–H) 1249, 1155 (C–O); ^{1}H NMR ($CDCl_3$) 1·06 (t, 3H,

CH_3, $J = 8$ Hz), 1·14 (t, 3H, CH_3, $J = 8$ Hz), 1·35 (m, 2H, CH_2), 1·65 (m, 2H, –CH–), 3·86 (oct, 4H, $–CH_2OPh$, $J = 4·5$ Hz), 4·82 (s, 1H, O–H) 6·95–7·48 (2 × d, 8H, 2 × Ph); mass spectrum *m/z*: 256 (M+). Calc. for $C_{17}H_{20}O_2$: C 79·68, H 7·81%. Found: C 79·43, H 7·69%. $[\alpha]_D^{20} = +0·6°$ ($CHCl_3$).

3.3. *4,4′-Bis-(2-methylbutyloxy)biphenyl (**8a**)*

R_f (ether : pentane, 1 : 1 v/v) 0·75; IR ν/cm^{-1} (film) 1242, 1171 (C–O); ^{1}H NMR ($CDCl_3$) 0·98 (t, 3H, CH_3, $J = 8$ Hz), 1·06 (d, 3H, CH_3, $J = 7$ Hz) 1·32 (qt, 4H, CH_2, $J = 6·5$ Hz), 1·65 (m, 2H, CH–), 4·06 (t, 4H, $–CH_2O$, $J = 6·5$ Hz), 6·95–7·48 (2 × d, 8H, 2 × Ph); mass spectrum *m/z*; 326 (M+). Calc. for $C_{22}H_{30}O_2$: C 80·98, H 9·20%. Found: C 81·08, H 9·41%.

3.4. *4,4′-Bis-(S-(+)-2-methylbutyloxy)biphenyl (**8b**)*

R_f (ether : pentane, 1 : 1 v/v) 0·69; IR ν./cm^{-1} (film) 1242, 1171 (C–O); ^{1}H NMR ($CDCl_3$) 1·04 (t, 3H, CH_3, $J = 8$ Hz), 1·14 (d, 3H, CH_3, $J = 7$ Hz) 1·35 (qt, 4H, CH_2, $J = 6·5$ Hz), 1·65 (m, 2H, CH–), 3·96 (dqt, 4H, $–CH_2O$, $J = 6·5$ Hz), 7·00–7·50 (2 × d, 8H, 2 × Ph); mass spectrum *m/z*: 326 (M+). Calc. for $C_{22}H_{30}O_2$: C 80·98, H 9·20%. Found: C 80·84, H 9·14%. $[\alpha]_D^{20} = +0·4°$ ($CHCl_3$).

3.5. *4,4′-Bis-[2-(2-methylbutyloxy)ethoxy]biphenyl (**9a**)*

R_f (ether : pentane, 1 : 1 v/v) 0·81; IR ν/cm^{-1} (film) 1271, 1172 (C–O); ^{1}H NMR δ_H ($CDCl_3$) 1·06 (d, 6H, CH_3, $J = 7$ Hz), 1·12 (t, 6H, CH_3, $J = 8$ Hz), 1·30 (qt, 4H, CH_2, $J = 6$ Hz), 1·60 (m, 2H, –CH–), 1·92 (qt, 4H, CH_2O, $J = 7$ Hz), 3·94 (s × t, 4H, $O–CH_2CH_2–O$, $J = 5$ Hz), 4·06 (s, 4H, $–CH_2OPh$), 7·00–7·54 (2 × d, 8H, 2 × Ph); mass spectrum *m/z*: 414 (M+). Calc. for $C_{26}H_{38}O_4$: C 75·36, H 15·46%. Found: C 75·25, H 15·27%.

3.6. *4,4′-Bis-[2-(S-(+)-2-methylbutyloxy)ethoxy]biphenyl (**9b**)*

R_f (ether : pentane, 1 : 1 v/v) 0·90; IR ν/cm^{-1} (film) 1277, 1171 (C–O); ^{1}H NMR ($CDCl_3$) 1·06 (d, 6H, CH_3, $J = 7$ Hz), 1·12 (t, 6H, CH_3, $J = 8$ Hz), 1·35 (qt, 4H, CH_2, $J = 6$ Hz), 1·68 (m, 2H, –CH–), 1·96 (qt, 4H, CH_2O, $J = 7$ Hz), 3·56 (s × t, 4H, $O–CH_2CH_2–O$, $J = 5$ Hz), 3·92 (oct, 4H, $–CH_2OPh$, $J = 7$ Hz), 7·04–7·52 (2 × d, 8H, 2 × Ph); mass spectrum *m/z*; 414 (M+). Calc. for $C_{26}H_{38}O_4$: C 75·36, H 15·46%. Found: C 75·21, H 15·13%. $[\alpha]_D^{20} = +1·1°$ ($CHCl_3$).

3.7. *4-[2-(2-Methylbutyloxy)ethyloxy]-4′-(2-hydroxyethoxy)biphenyl (**10a**)*

R_f (ether : pentane, 1 : 1 v/v) 0·46; IR ν/cm^{-1} (film) 3342 (O–H) 1247, 1171 (C–O); ^{1}H NMR ($CDCl_3$) 1·06 (d, 3H, CH_3, $J = 5$ Hz), 1·12 (t, 3H, CH_3, $J = 9$ Hz), 1·36 (qt, 2H, CH_2, $J = 6$ Hz), 1·6–1·8 (m, 1H, –CH–), 1·96 (qt, 2H, CH_2O, $J = 5$ Hz), 3·8–4·0 (s × t, 4H, $O–CH_2CH_2–O$) 5·26 (s, 2H, CH_2OH), 7·00 (dd, 4H, Ph), 7·52 (qt, 4H, Ph); mass spectrum *m/z*: 344 (M+). Calc. for $C_{21}H_{28}O_4$: C 73·25, H 8·14%. Found: C 73·09, H 8·07%.

3.8. *4-[2-(S-(+)-2-Methylbutyloxy)ethoxy]-4′-(2-hydroxyethoxy)biphenyl (**10b**)*

R_f (ether : pentane, 1 : 1 v/v) 0·46; IR ν/cm^{-1} (film) 3343 (O–H) 1274, 1173 (C–O); ^{1}H NMR ($CDCl_3$) 1·06 (d, 3H, CH_3, $J = 5$ Hz), 1·12 (t, 3H, CH_3, $J = 8$ Hz), 1·38 (qt, 2H, CH_2, $J = 6$ Hz), 1·68 (m, 1H, –CH–), 1·98 (qt, 2H, CH_2O, $J = 7$ Hz), 3·8–4·0 (s × t, 4H, $O–CH_2CH_2–O$) 5·24 (s, 2H, CH_2OH), 7·00 (dd, 4H, Ph), 7·52 (qt, 4H, Ph); mass spectrum *m/z*: 344 (M+). Calc. for $C_{21}H_{28}O_4$: C 73·25, H 8·14%. Found: C 73·29, H 7·98%. $[\alpha]_D^{20} = +0·6°$ ($CHCl_3$).

3.9. *4,4′-Di-[(S-(+)-2-methoxypropyloxy)ethoxy]-biphenyl (**11**)*

R_f (ether : pentane, 1 : 1 v/v) 0·63; IR ν/cm^{-1} (film) 1245, 1174 (C–O); ^{1}H NMR ($CDCl_3$), 1·32 (d, 6H, CH_3, $J = 5$ Hz), 3·50 (s, 6H, CH_3O), 3·75 (m, 2H, –OCH–) 4·00 (m, 8H, $–OCH_2CH_2O$), 6·95–7·45 (2 × d, 8H, Ph); mass spectrum *m/z*: 418 (M+). Calc. for $C_{24}H_{34}O_6$: C 68·90, H 8·13%. Found: C 68·82, H 8·08%. $[\alpha]_D^{20} + 2·3°$ ($CHCl_3$).

3.10. *4-Butyl-4′-[S-(+)-2-methylbutyloxy]biphenyl (**12**)*

R_f (ether : pentane, 1 : 4 v/v) 0·88; IR ν/cm^{-1} (film) 1248, 1173 (C–O); ^{1}H NMR ($CDCl_3$), 0·98 (d, 3H, CH_3, $J = 7$ Hz), 1·02 (t, 3H, CH_3, $J = 8$ Hz) 1·08 (t, 3H, CH_3, $J = 7·5$ Hz), 1·25–1·50 (m, 4H, butyl CH_2), 1·35 (m, 2H, CH_2), 1·88–1·98 (m, 1H, –CH–), 2·68 (t, 2H, $Ph–CH_2$, $J = 7$ Hz), 3·86 (oct, 2H, $–CH_2O$), 7·00–7·24 (2 × d, 4H, 2 × Ph), 7·52 (t, 4H, Ph); mass spectrum *m/z*: 296 (M+). Calc. for $C_{21}H_{28}O$: C 85·13, H 9·46%. Found: C 84·94, H 9·53%. $[\alpha]_D^{20} + 0·25°$ ($CHCl_3$).

3.11. *4-Hexyl-4′-[S-(+)-2-methylbutyloxy]biphenyl (**13**)*

R_f (ether : pentane, 1 : 4 v/v) 0·85; IR ν/cm^{-1} (film) 1271, 1175 (C–O); ^{1}H NMR ($CDCl_3$), 0·98 (d, 3H, CH_3, hexyl), 1·04 (t, 3H, CH_3, $J = 8$ Hz), 1·12 (t, 3H, CH_3, $J = 6$ Hz), 1·40 (m, 8H, hexyl CH_2), 1·70 (m, 2H, CH_2), 1·95 (m, 1H, –CH–), 2·70 (t, 2H, $Ph–CH_2$, $J = 7$ Hz), 3·88 (oct, 2H, $–CH_2O$), 7·00–7·28 (2 × d, 4H, 2 × Ph), 7·52 (t, 4H, Ph); mass spectrum *m/z*: 324 (M+). Calc. for $C_{23}H_{34}O$: C 85·18, H 9·87%. Found: C 85·08, H 9·76%. $[\alpha]_D^{20} + 0·6°$ ($CHCl_3$).

4. Results

4.1. *Phase observations*

The phase assignments and transition temperatures for the products were first determined by thermal optical microscopy using a Leitz polarizing microscope with a hot stage and photographic facility. The transition temperatures and enthalpies were then determined using a Perkin-Elmer series 2 differential scanning calorimeter (DSC). This instrument was calibrated using a sample of indium, the measured latent heat of 28·38 J g^{-1} comparing well with the standard value of 28·55 J g^{-1}. Materials were studied at a scanning rate of 5° min^{-1} in both heating and cooling cycles.

The specific rotation was measured for each chiral material using a polarimeter (Optical Activity Ltd) measuring to ±0·001°. It was found that the final products had approximately the same optical purity as the starting material, *S*(+)1-bromo-2-methylbutane.

Transition temperatures were obtained on cooling for all compounds studied for phase behaviour. The smectic B phase of compound **13** displayed a bâtonnet texture which on further cooling coalesced to give a typical mosaic texture. Compounds **8a**, **8b** (figure 1) and **9a** (figure 2) displayed mosaic platelet textures thus ruling out the presence of smectic A, B and C phases and suggesting a higher ordered smectic or crystal phases which could not be fully classified by this technique. The monosubstituted compounds were all crystalline and showed no mesophase behaviour.

The transition temperatures show as usual that substitution of a methylene group by oxygen adjacent to the phenyl ring increases the thermal stability of the phase. However on additional substitution, as with **11**, smectic phase behaviour can be lost totally, despite a relatively low melting point. Increasing chain length causes a decrease in thermal stability for all of the compounds studied.

Another effect concerns the carbon to oxygen ratio in the substituent chain [3] and in the studies here it appears that an increase in the ratio can raise the upper phase transition temperature, e.g. compare **8b** and **9b**.

4.2. *Differential scanning calorimetry*

For all compounds studied, the transition temperatures, enthalpies of the transitions and indications of the phase nature were given by DSC. The transition temperatures and related enthalpies are shown in tables 1 and 2. The results compared well with those obtained by microscopic techniques and often improved upon these in terms of accuracy and the range over which the phase behaviour was observed. The non-mesomorphic monosubstituted compounds all had large enthalpies of the Cr–I transition as would be expected for highly thermally stable crystalline compounds.

Table 1. Biphenyl ether derivatives: phase assignments and transition temperatures (°C). Transition temperatures on heating and (in parentheses) on cooling.

Compound	Cr$_1$–Cr$_2$	Cr–S	Cr–I	Sm–I
7a			137·8	
			(117·1)	
7b			135·6	
			(123·7)	
8a		83·6		87·0
		(79·6)		(85·3)
8b		73·2		76·7
		(58·4)		(76·7)
9a			74·7	
			(69·2)	
9b		68·9		72·0
		(56·4)		(71·7)
10a			137·4	
			(122·5)	
10b			135·2	
			(124·4)	
11			59·0	
			(54·2)	
12	38·38		46·4	
			(42·6)	
13		35·6		45·6
		(27·8)		(45·5)

Table 2. Biphenyl ether derivatives: cooling transition enthalpies and (in parentheses) entropies.

ΔH/kJ mol^{-1} (ΔS/kJ mol^{-1} C^{-1})	I–Sn	Sm–Cr	I–Cr
7a			91·64
			(0·78)
7b			114·3
			(0·92)
8a	36·29	8·43	
	(0·46)	(0·10)	
8b	51·45	20·96	
	(1·08)	(0·69)	
9a			68·54
			(0·99)
9b	71·47	26·79	
	(0·99)	(0·47)	
10a			165·1
			(1·34)
10b			167·1
			(1·34)
11			16·34
			(0·30)
12			17·05
			(0·40)
13	32·35	6·97	
	(0·71)	(0·25)	

The trends observed using polarizing microscopy were also supported by the results from DSC. For example (Neubert *et al.* [2]), comparing the Sm–I enthalpy of **13** with that of **8b** indicates that replacement of the methylene adjacent to the ring by an oxygen raises the enthalpy, suggesting a more ordered and stable phase for **8b**. Indeed this is the case, **8b** has a crystal E phase and **13** a SmB phase—see below. Similarly as the

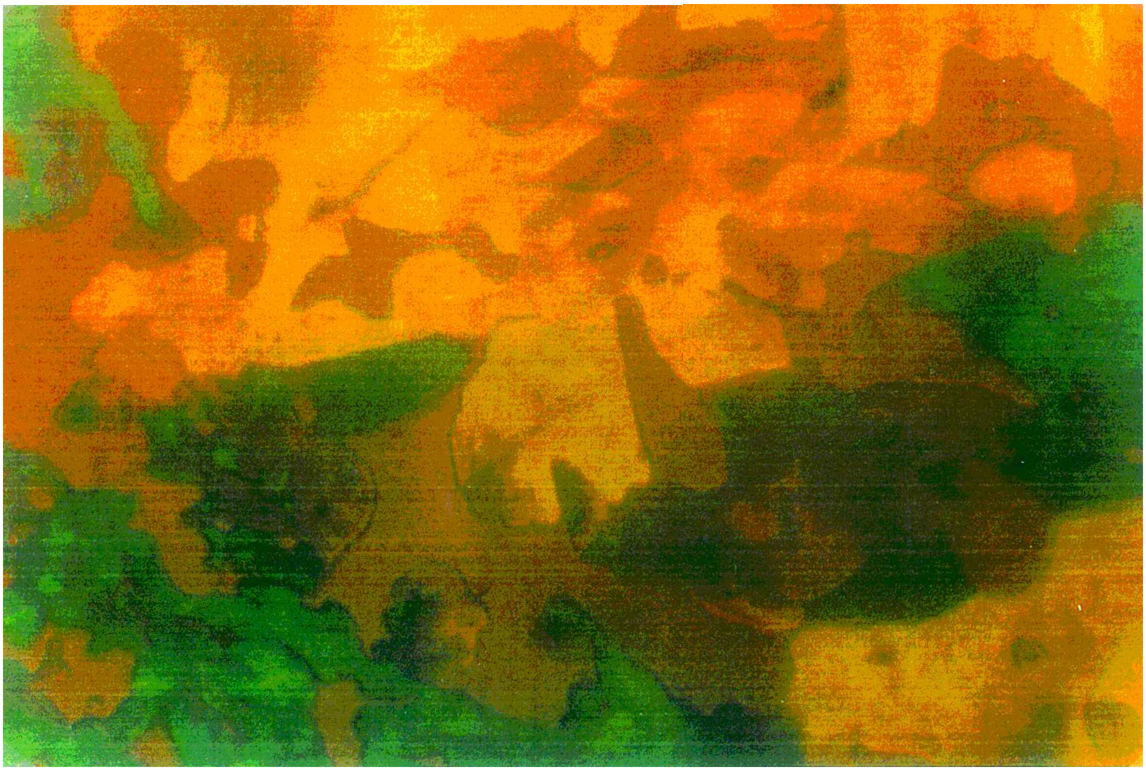

Figure 1. 4,4′-Di-[S-(+)-2-methylbutyloxy]biphenyl (**8b**); mosaic platelet texture of the E phase.

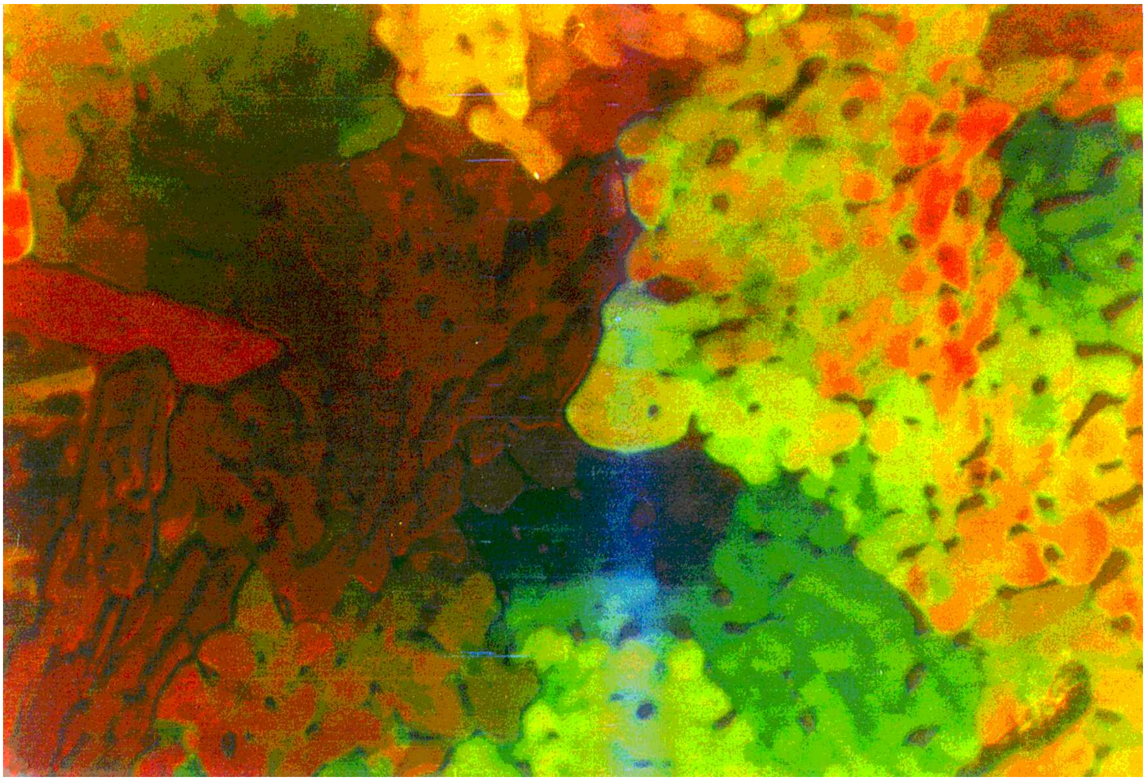

Figure 2. 4,4′-Bis[2-(2-methylbutyloxy)ethoxyl]biphenyl (**9a**); mosaic platelet texture of possible K phase.

Table 3. X-ray diffraction results.

Compound	Average *d*-spacing (Å) and index
8a	18·71 (0 0 1), 9·36 (0 0 2), 5·45 (1 1 1), 4·94 (1 1 0), 4·60 (0 2 0)
8b	19·7 (0 0 1), 9·66 (0 0 2), 4·98 (1 1 1), 4·59 (1 1 0), 3·83 (0 2 0)
9b	19·19 (0 0 1), 9·53 (0 0 2), 7·58 (1 1 1), 6·26 (0 0 3), 5·63 (1 1 0)
13	23·39 (0 0 1), 11·67 (0 0 2), 4·60 (1 1 1)

C/O ratio in the polyether chain increases, so does the upper phase transition enthalpy; compare **8b** and **9b** (table 2).

4.3. *X-ray diffraction studies*

The equipment used employed a monochromatic X-ray source, CuK_α (1·542 Å), which was diffracted by the sample held in a thin walled (0·1 mm) capillary tube. The diffracted beams were collected on a photographic film placed behind the sample. The sample tube was contained within an oven and the temperature was recorded by a thermocouple digital meter. Non-oriented samples were obtained by heating the compound to the isotropic state and then cooling into the mesophase region and holding at this temperature over a period of hours. For all compounds displaying mesomorphic behaviour, wide and low angle data were recorded.

5. Discussion

The smectic phase of **13** was confirmed as hex B, the results indicating a perpendicular phase with hexagonal packing [4]. Compounds **8a** and **8b** both display the characteristic patterns for a crystal E phase, there being two inner and three outer rings, the latter relating to the herringbone molecular packing [5]. This phase is not tilted. The assignment of the phase exhibited by **9b** is more difficult. There appears to be extensive ordering over the layers which excludes the possibility of lower ordered phases and it is evident that the phase is tilted. A tentative suggestion of crystal H or K is made [6].

6. Conclusions

By use of suitable techniques, the phases in four compounds have been identified: **13** (hex B), **8a** and **8b** (E) and **9b** (K).

From the observations made it is possible to define certain trends in the phase behaviour which are controlled by molecular structure. The results confirmed the belief that the addition of oxygen to the polyether chain reduces the mesophase thermal stability and the possibility of smectic behaviour in a compound [3]. This is shown by comparing the Sm–I transition temperatures for **8b**, **9b** and **11**, the final compound showing no phase behaviour.

It seems that the chirality of the 2-methylbutyl group causes disruption in the crystal structure, thus reducing thermal stability and encouraging smectic phase behaviour. This is supported when comparing **13** with the non-mesomorphic 4,4′-dipentyloxybiphenyl. Compound **13** behaves similarly to the analogous compound 4-pentyloxy-4′-hexylbiphenyl, which also displays a smectic B phase [7]. It is suggested that substituent protrusion and alkyl branching in the terminal chain actually enhances the stabilities of hex B and crystal K phases [8].

The smectic phase displayed by **9b** was tentatively assigned as K, and this is supported by the identification of a K phase for the analogous 4,4′-di(2-methoxyethoxy)-biphenyl [6].

The non-mesomorphic nature of compounds **7a**, **7b**, **10a**, **10b** and **12** probably arises from the unsymmetrical nature of the side chains which results in a highly ordered crystal state and the resulting high melting points inhibit observation of smectic phase formation in these compounds.

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