Properties of the Liquid Crystals formed by Some 4′-Substituted 4-(β-*p*-Substituted Arylethyl)biphenyls

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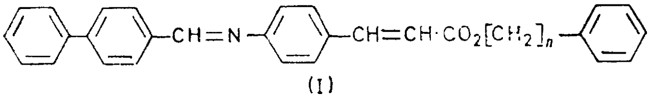
The C_2—C_8 ethers of 4-(β-4-cyanophenylethyl)-4′-hydroxybiphenyl and the C_3—C_8 ethers of 4-cyano-4′-(β-4-hydroxyphenylethyl)biphenyl have been prepared and found to exhibit liquid crystal phases of wide range. The differences between the two sets of compounds with regard to their m.p.s, and their smectic and nematic properties are discussed. Eutectic mixtures of these compounds with one another are capable of giving very wide range nematic phases. When the compounds are mixed together with other low melting nematogens such as 4-cyano-4′-n-pentylbiphenyl, low melting, nematic, eutectic mixtures are obtained; an unusual elevation of the N–I transition temperature relative to the predicted value is found for the latter mixtures.

THE effects which are observed on the liquid crystal properties of the n-alkyl 4-(4-phenylbenzylideneamino)-cinnamates when a hydrogen of the terminal methyl group of the n-alkyl chain is replaced by a phenyl ring have already been reported.[1] The resulting ω-phenylalkyl esters (I) have nematic-amorphous isotropic liquid (N–I) transition temperatures which decrease generally as the alkylene chain is increased in length. However, the most striking feature of the series is the very large alternation in nematic phase thermal stability which is observed on moving from members having odd (low N–I values) to members having even (high N–I values) numbers (*n*) of methylene units in the alkylene chain. The higher N–I values for even *n* values are similar to the N–I values found for the n-alkyl analogues;[1] the lower N–I values for odd *n* values are very considerably lower than those of the n-alkyl analogues. This very large alternation in nematic phase thermal stability was accounted for in terms of the phenyl ring of the ω-phenylalkyl group either lying in (high N–I values, even *n* values) or out (low N–I values, odd *n* values) of the volume of a cylinder defined by rotation of the rest of the molecule about its long molecular axis. More recently,[2,3] it has been shown that when the ω-phenyl ring contains a 4-substituent (CH_3 or Cl), the N–I values are increased by *ca.* 40°, provided that the 4-substituted ω-phenyl ring lies along the long molecular axis, *i.e.*, if *n* is odd, the N–I values are decreased by the 4-substituent, and the results are understandable in terms of the stereochemistry of the system and the greater deviation from linearity resulting from the 4-substituent.



(I)

Bearing these results in mind, we considered whether certain of the factors involved could be used to produce structurally modified materials similar to 4-cyano-4′-n-pentylbiphenyl (5CB)[3] in chemical–photochemical stability but having higher N–I values and wider nematic ranges. We first examined 4-cyano-4′-β-phenylethylbiphenyl (II) which has the constants C–I, 122°; N–I,

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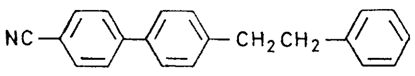
[1] G. W. Gray and K. J. Harrison, Symposium of the Chemical Society, Faraday Division No. 5, 1971, p. 54.

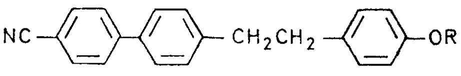
[2] D. Coates and G. W. Gray, *J. de Physique*, 1975, **36**, C1, No. 3, 365.

[3] G. W. Gray, *J. de Physique*, 1975, **36**, C1, No. 3, 337.

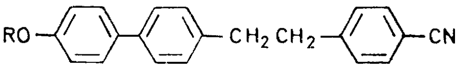
[93.6°]; * the alkyl analogue (4-cyano-4′-ethylbiphenyl) has the constants[4] C–I, 75°; N–I, [22°]. The nematic phase thermal stability had therefore been increased by 71.6°. This is a very large effect compared with the results found for the esters (I) with even n values; the ω-phenylalkyl and n-alkyl esters have similar N–I values. The difference can probably be accounted for in terms of the much larger relative increase in anisotropy of polarisability on moving from 4-cyano-4′-ethylbiphenyl to structure (II) compared with that when a phenyl ring is added to the much larger ester to give a molecule of the structure shown in (I).



(II)



(III)



(IV)

As can be seen from structure (II), the stereochemistry of the alkylene chain (number of methylene units = n = 2) positions the terminal β-phenyl ring along the line of the long molecular axis. A longer alkylene chain consisting of an even number of methylene units would however lower the overall nematic thermal stability because, by analogy with the general trend for the series of ω-phenylalkyl esters (I), the alkylene chain as a whole becomes more out of line as its length is increased and the rigidity of the molecule is diminished.

The most rigid situation is of course when $n = 0$, *i.e.*, when no alkylene chain exists between the biphenyl system and the phenyl ring. The compounds are then derivatives of *p*-terphenyl. Materials such as the 4″-n-alkyl-4-cyano-*p*-terphenyls have already been investigated[5] and they do have high N–I transition temperatures and chemical–photochemical stabilities which are comparable with 5CB and its analogues. Even 4-cyano-*p*-terphenyl has a virtual N–I value of 188°, and this is higher than the N–I value for 4-cyano-4′-β-phenylethylbiphenyl (n = 2). 4-Cyanobiphenyl on the other hand has[4] a virtual N–I value of —40°. These results reflect the importance of (1) the greater molecular rigidity of *p*-terphenyl compounds compared with that of the compound (II) and (2) the greater anisotropy of molecular polarisability of *p*-terphenyl compounds compared with that of their biphenyl analogues. The terphenyl mesogens named above have of course quite high m.p.s (C–N values), but their importance relates to their use in conjunction with biphenyl mesogens such as 5CB as eutectic compositions with low C–N values (<—10°) and quite high N–I values (>60°).[5]

If materials based on structure (II) having useful liquid crystal properties were to be obtained, it was clearly necessary to modify the structure in some way. By analogy with the earlier results obtained by 4-substituting the ω-phenylalkyl ester (I) and because of the high position of the methoxy-group in the nematic efficiency order for terminal substituents,[6] it was decided to introduce a range of n-alkoxy-groups into the β-phenyl ring of 4-cyano-4′-β-phenylethylbiphenyl (II) in order to increase as far as possible the N–I value of 93.6° for the parent system, and hopefully also, to lower the melting point. The effects of most small structural changes on m.p. are very unpredictable, but low values are often found in homologous series for the butyl(oxy) to heptyl(oxy) members.

Therefore, the C_2–C_8 series of ethers of 4-cyano-4′-(β-4-hydroxyphenylethyl)biphenyls (III) was prepared and the transition temperatures of the compounds were measured. These results are given in Table 1 and Figure 1.

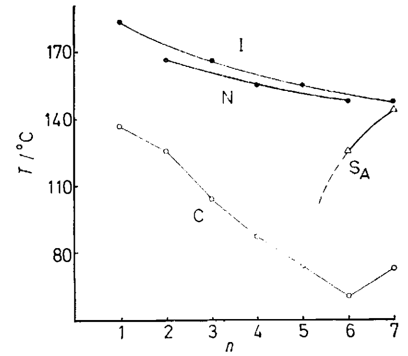


FIGURE 1 Transition temperatures plotted against the number of methylene units (n) in the alkylene chain (R) for 4-NCC_6H_4-$C_6H_4(CH_2CH_2C_6H_4OR$-4)-4 (III): ○ = crystal (C)–nematic (N) or –smectic A (S_A); △, S_A–N; ●, N–isotropic liquid (I)

The m.p.s, which show a trend downwards from 136.3 at C_2 to a minimum of 61.3° at C_7, rise again at C_8. The N–I values lie on two smooth curves, the upper curve for those compounds having an even number of carbons in the alkyl chain. The N–I values, ranging from 183.6 (C_2) to 147.8° (C_7), show a large increase over that of the unsubstituted compound (II). Smectic properties are first encountered for the C_7 and C_8 members; the smectic phase is unusually mobile and miscibility studies with n-butyl 4-(4-phenylbenzylideneamino)cinnamate[1] showed it to be smectic A in type. The steeply rising thermal stability of the smectic phase on moving along the series is shown in Figure 1, and it is likely that the C_9 analogue will be purely smectogenic, whereas the C_6 analogue is purely nematogenic.

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* Square brackets indicate a monotropic transition.

[4] G. W. Gray and A. Mosley, *J.C.S. Perkin II*, 1976, 97

[5] G. W. Gray, K. J. Harrison, and J. A. Nash, *J.C.S. Chem. Comm.*, 1974, 431.

[6] G. W. Gray, 'Liquid Crystals and Plastic Crystals,' eds. G. W. Gray and P. A. Winsor, Ellis Horwood Publishers, Chichester, Sussex, 1974, vol. 1, ch. 4.1.

Thus, taking the 4-n-hexyloxy-substituent in the β-phenyl ring as an example, this has increased the N–I transition temperature by 61.4° and lowered the m.p. by 47.5° compared with the parent unsubstituted compound (II). The total enthalpies of fusion to the nematic phase are also given in Table 1; these are fairly high at *ca.* 8 kcal mol^{-1} on average.

TABLE 1

Thermodynamic data for
$4\text{-NCC}_6H_4C_6H_4(CH_2CH_2C_6H_4OR\text{-}4)\text{-}4$ (III)

R	C–N or S_A [a] (°)	S_A–N [a] (°)	N–I [a] (°)	Enthalpy of fusion [b] ΔH/ kcal mol^{-1}
Et	136.3		183.6	6.6 *
Pr	127		166.4	8.6
Bu	105		166.0	8.4
C_5H_{11}	87.5		155.5	9.29 *
C_6H_{13}	74.5		155.0	8.1
C_7H_{15}	61.3	125.8	147.8	8.2
C_8H_{17}	72.5	144	148.0	8.3

C = crystal; S_A = smectic A; N = nematic; I = isotropic liquid.

[a] Transition temperatures were measured using a Mettler FP52 hot stage. [b] Total enthalpies of fusion to the nematic phase were measured using a Stanton–Redcroft differential thermal analyser, model 71.

* Crystal–crystal change occurs, detected on heating the sample from room temperature.

The effect on the liquid crystal properties of reversing the terminal groups (CN and RO) was next examined by preparing the series of 4-alkoxy-4′-(β-4-cyanophenylethyl)biphenyls (IV). The liquid crystal transition temperatures for these compounds are presented in Table 2 and Figure 2.

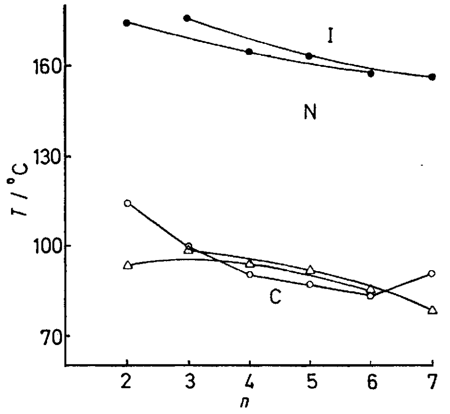

FIGURE 2 Transition temperatures plotted against the number of methylene units (*n*) in the alkylene chain (*R*) for $4\text{-ROC}_6H_4C_6H_4(CH_2CH_2C_6H_4CN\text{-}4)\text{-}4$ (IV); ○, C–N or C–S_A; △, S_A–N; ●, N–I

The m.p.s again trend downwards from 114.7 at C_3 to a minimum of 83.5° at C_7 and then rise again to C_8. The results are similar to those for compounds (III), except that the overall change in m.p. along the series is smaller. The N–I values again lie on two smooth curves, the upper curve for compounds with even numbers of carbons in the alkyl chain. The N–I values for compounds (IV) are generally *ca.* 10° higher than those of compounds (III). A significant difference in the smectogenic properties of compounds (III) and (IV) is also found. *All* type (IV) compounds showed a smectic phase which miscibility studies with n-butyl 4-(4-phenylbenzylideneamino)cinnamate [1] proved to be smectic A in type. An interesting feature of the smectic A to nematic (S_A–N) transition temperatures is that not only do they alternate between members with odd and even numbers of carbons in the alkyl chain, but also a maximum in the S_A–N transition value apparently occurs at 98.8° for the C_4 compound. This contrasts with the smectic properties of the compounds (III) for which no smectic phase can be detected until the C_7 compound. The smectic properties of the compounds (IV) as a whole are therefore more marked than those in series (III) for the earlier members of the series up to C_6, but the dramatic increase in smectic thermal stability of the compounds (III) as the alkyl chain is extended beyond C_6, coupled with the decrease in smectic thermal stability with increasing alkyl chain length for the analogous members of series (IV), leads to a reversal of the relative thermal stabilities of the two series.

TABLE 2

Thermodynamic data for
$4\text{-ROC}_6H_4C_6H_4(CH_2CH_2C_6H_4CN\text{-}4)\text{-}4$ (IV)

R	C–N or S_A [a] (°)	S_A–N [a] (°)	N–I [a] (°)	Enthalpy of fusion [b] ΔH/ kcal mol^{-1}
Pr	114.7	[93.9]	173.6	8.15 *
Bu	99.5	[98.8]	175.4	7.91 *
C_5H_{11}	91.0	93.5	164.7	6.77 **
C_6H_{13}	88.3	91.3	163.2	5.93
C_7H_{15}	83.5	85.1	157.4	6.43 *
C_8H_{17}	91.8	[<80]	155.9	6.7

C = crystal; S_A = smectic A; N = nematic; I = isotropic liquid; [ ] = monotropic transition.

[a] Transition temperatures were measured using a Mettler FP52 hot stage. [b] Total enthalpies of fusion to the nematic phase were measured using a Stanton–Redcroft differential thermal analyser, model 71.

* Each asterisk indicates the occurrence of a crystal–crystal change detected on heating the sample from room temperature.

The precise temperature of the monotropic S_A–N transition of the C_8 compound in series (IV) could not be obtained due to the onset of crystallisation. However, it is certainly only just below 80°, and has therefore been placed on the smooth curve connecting the points for the earlier members of the series with even alkyl chains (see Figure 2).

Compared with compounds (III), compounds (IV) with the same alkyl chain length therefore have higher N–I values (*ca.* 10°), are more smectogenic before C_7, are much less smectogenic above and including C_7, and have higher m.p.s except for the C_4 and C_3 members which are slightly lower melting. Repeated heating and cooling of samples of these compounds did not affect the transition temperatures and their reversibility, showing their stability to heat to be good.

The effects of reversing the end groups of the molecule, although marked as regards smectic thermal stability, are not as significant in the case of nematic thermal stability. The reasons for such differences are not clearly understood. However, if the biphenyl part of the molecule is regarded as the most significant rigid, polarisable core part of the molecule, then the results indicate that the alkoxy-group of compounds (IV) conjugates more with biphenyl (by a $+M$ effect) than the cyano-group of compounds (III) conjugates with the biphenyl system (by a $-M$ effect). That is, compounds (IV) have the higher anisotropy of molecular polarisability.

The influence of molecular structure on smectic properties is very dependent on how the molecules pack into the smectic layers. Although many smectogens form smectic A phases consisting of layers which are one molecular length thick, others, notably the series of 4-n-alkyl-4′-cyanobiphenyls, form smectic A phases which consist of interdigitated bilayers,[7] in which the cyano-groups of the molecules are probably towards the centre. It is possible that the compounds under study behave in a similar way. If this is the case, and the alkoxy-groups form the lamellar surfaces, then in one case, (III), we have the cyano-groups on the rod-like biphenyl residues in the middle of each layer and in the other, the cyano-groups on a single phenylene ring which is attached to the flexible $CH_2{\cdot}CH_2$ unit in the middle of each layer. Therefore, without firm knowledge of how the molecules actually pack, any assessment of the smectic properties would be purely speculative.

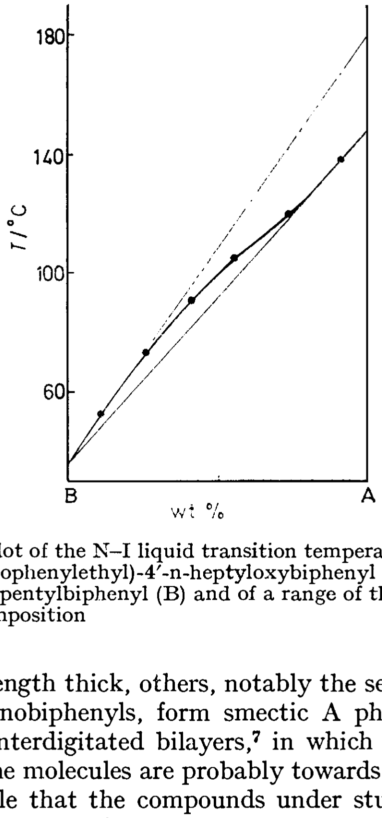

FIGURE 3 Plot of the N–I liquid transition temperatures of pure 4-(β-4-cyanophenylethyl)-4′-n-heptyloxybiphenyl (A) and 4-cyano-4′-n-pentylbiphenyl (B) and of a range of their mixtures against composition

In view of the wide nematic ranges and the fact that the compounds, which are of positive dielectric anisotropy, share the good stability characteristics of 5CB and its analogues, the possibility of obtaining mixtures with high N–I values and lower m.p.s than those of the pure materials was examined.

One of the best nematic, eutectic, binary mixtures contained 74.5 wt % of the C_7 member of series (III) and 25.5 wt % of the C_5 member of series (III). The constants for this mixture, which were calculated on a Digico Micro 16V computer using the technique of Hulme *et al.*[8] were C–N, 53.5; N–I, 150°; the experimental values were C–N, 53—53.5; N–I, 149.7°. Therefore a substantial depression in the m.p.s of the pure components was obtained, with a consequent widening of the nematic range. Mixtures containing more components have lower m.p.s. For example, a mixture of the C_5 member (12.4 mol %), the C_6 member (24.0 mol %), and the C_7 member (38.0 mol %) of series (III) and the C_7 member (25.6 mol %) of series (IV) has the calculated constants C–N, 36.7; N–I, 153.2°. From these two examples the scope and limitations of these compounds for producing mixtures with high N–I temperatures (*ca.* 150°) and fairly low C–N temperatures (*ca.* 30—50°) can be seen. Mixtures having such nematic ranges are of interest for some specialised types of electro-optical displays and also for g.l.c.

The production of much lower m.p. mixtures can be achieved by mixing these compounds with nematogens of lower m.p. such as 5CB. The calculated constants for a eutectic mixture of 5CB (85 mol %) and the C_7 member of series (III) (15 mol %) are C–N, 16.4; N–I, 55°; the experimental constants were C–N, 13—14; N–I, 58.8°. The increase (3.8°) in the N–I value found relative to that calculated is unusual, and similar results were found for all compositions from *ca.* 5 up to *ca.* 70% of the β-phenylethyl compound (see Figure 3). This behaviour can be explained if it is assumed that the break up of the nematic order of the phases of the pure phenylethyl compounds is due to the onset of rotations about the C–C bond of the central $CH_2{\cdot}CH_2$ linkage as the temperature rises. At the lower N–I temperatures associated with these mixtures, these rotations may be less important and the β-phenylethyl compound behaves as if it had a much higher N–I value (*ca.* 180°, see the dotted line of extrapolation in Figure 3) characteristic of a more rigid molecule, such as a 4″-alkyl-4-cyano-*p*-terphenyl.

Lower melting mixtures may be obtained by mixing more compounds together. For example a eutectic mixture of the C_7 member (6.5 mol %), the C_8 member (4.2 mol %), and the C_6 member (4.2 mol %) of series (III) with 5CB (55.8 mol %) and 7CB (29.3 mol %) has the calculated constants C–N, 0.5; N–I, 54.2°. The actual N–I temperatures of such mixtures are again higher than the predicted values, so that even wider ranges than those calculated are obtained (see above).

The above results indicate that low melting mixtures with quite high N–I transition temperatures can be obtained from these compounds. Therefore, these

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[7] G. W. Gray and J. E. Lydon, *Nature*, 1974, **252**, 221.

[8] D. S. Hulme, E. P. Raynes, and K. J. Harrison, *J.C.S. Chem. Comm.*, 1974, 98.

materials are useful as stable additives of positive dielectric anisotropy which can be used to widen the ranges of lower melting, narrower range nematogens with which they are miscible. As such, the compounds fulfil a similar role to that of the 4″-alkyl-4-cyano-*p*-terphenyls and the esters of benzoyloxybenzoic acid.[9] However, it must be remembered that it is always uncertain, until rigorous experiments are carried out, whether high molecular weight additives will remain in solution (*i.e.*, below their solubility level) in the lower molecular weight compound(s) selected when a mixture is maintained at or below the temperature predicted for the eutectic m.p. If segregation should occur, corrections to the eutectic composition must be made to compensate for the immiscibility of a particular component.

EXPERIMENTAL

4-*n-Alkoxyphenylacetic Acids*.—4-Hydroxyphenylacetic acid was alkylated with the appropriate n-alkyl iodide, potassium hydroxide, water, and ethanol as described [10] for 5-n-alkoxy-1-naphthoic acids. After crystallisation from ethanol, the average yield of product was 80%; the m.p.s were Et, 59; Pr, 92; Bu, 88; pentyl, 83; hexyl, 81; heptyl, 78; octyl, 76°. Mass spectrometry gave the correct mass ion value in each case.

The corresponding 4-n-alkoxyphenylacetyl chlorides were prepared from the acids using thionyl chloride.

4-(4-*n-Alkoxyphenylacetyl*)-4′-*bromobiphenyls* (V).—A solution of 4-bromobiphenyl (0.05 mol) and the 4-n-alkoxyphenylacetyl chloride (0.057 mol) in dichloromethane (80 ml) was slowly added to a cooled mixture of anhydrous aluminium chloride (0.09 mol) in dichloromethane (60 ml). The solution was stirred at room temperature for 1 h, and heated under reflux for 3 h. When cool, the reaction mixture was poured over ice (30 g)–water (30 g)–concentrated hydrochloric acid (30 ml) and stirred for 0.5 h. The organic materials were extracted into chloroform, and the extract was washed well with water and dried ($MgSO_4$). The solid (or semi-solid) obtained on evaporation of the solvents was crystallised from toluene. Some samples required more than one crystallisation before they had a satisfactory purity. The yields were in the range 35—50%; a satisfactory combustion analysis and the correct mass ion values were obtained in each case. M.p. data are given in Table 3.

4-(β-4-*n-Alkoxyphenylethyl*)-4′-*bromobiphenyls* (VI).—Huang-Minlon [11] reduction of the corresponding ketone (V) (0.014 mol) using 98% hydrazine hydrate (3.5 ml), potassium hydroxide (2.5 g), water (1 ml), and diethylene glycol (300 ml) gave an average yield of 82% of the phenylethyl compound (VI) after crystallisation from ethanol–toluene. A satisfactory combustion analysis and the correct mass ion values were obtained for each compound; m.p. data are given in Table 3.

4-(β-4-*n-Alkoxyphenylethyl*)-4′-*cyanobiphenyls* (III).—The corresponding bromo-compound (VI) (3.0 g) was heated under reflux and vigorously stirred with dry copper(I) cyanide (1.5 g) and dry *N*-methyl-2-pyrrolidone (6 ml) for 1.5 h. The cooled solution was poured into a solution of iron(III) chloride (4.7 g), water (90 ml), and concentrated hydrochloric acid (1.8 ml) and stirred at 60° for 0.5 h. After cooling the mixture, it was shaken with chloroform and the organic extracts were washed with water, dried ($MgSO_4$), and evaporated to dryness. The product was purified on a silicic acid column using chloroform as eluant, and then crystallised from ethanol until constant transition temperatures were obtained. In some cases an additional vacuum sublimation was carried out, but no alterations in the transition temperatures were found. Yields of *ca.* 60—65% were obtained. The thermodynamic constants and combustion analysis results are given in Tables 1 and 4, respectively. Mass spectrometry gave the correct mass ion value in each case.

TABLE 3

M.p.s (°) of 4-$BrC_6H_4C_6H_4(COCH_2C_6H_4OR$-4)-4 (V) and 4-$BrC_6H_4C_6H_4(CH_2CH_2C_6H_4OR$-4)-4 (VI)

R	(V)	(VI)
Et	205	156
Pr	214	160
Bu	205	152
C_5H_{11}	197	147
C_6H_{13}	195	147
C_7H_{15}	189	146
C_8H_{17}	182	150

TABLE 4

Combustion analysis results for 4-$NCC_6H_4C_6H_4(CH_2CH_2C_6H_4OR$-4)-4

	Found (%)				Required (%)		
R	C	H	N	Formula	C	H	N
Et	84.3	6.4	4.3	$C_{23}H_{21}NO$	84.4	6.4	4.3
Pr	84.2	6.8	4.3	$C_{24}H_{23}NO$	84.4	6.8	4.1
Bu	84.3	6.9	4.1	$C_{25}H_{25}NO$	84.5	7.1	3.9
C_5H_{11}	84.3	7.2	4.0	$C_{26}H_{27}NO$	84.5	7.4	3.8
C_6H_{13}	84.6	7.7	3.6	$C_{27}H_{29}NO$	84.6	7.6	3.7
C_7H_{15}	84.7	7.7	3.6	$C_{28}H_{31}NO$	84.6	7.9	3.5
C_8H_{17}	84.9	8.0	3.4	$C_{29}H_{33}NO$	84.6	8.1	3.4

4-*n-Alkoxybiphenyls*.—A mixture of cyclohexanone (170 ml), 4-hydroxybiphenyl (0.177 mol), the n-alkyl bromide (0.234 mol), and anhydrous potassium carbonate (65 g, 0.47 mol) was heated under reflux for 4 h. The mixture was filtered and the solvent evaporated under reduced pressure to give an oil which solidified on vacuum desiccation; the solid was crystallised from ethanol, in some cases with treatment with decolourising charcoal. The average yield was 85%; mass spectrometry gave the correct mass ion values and the m.p.s were Pr, 77; Bu, 76; pentyl, 63; hexyl, 68; heptyl, 74; octyl, 72°.

4-*n-Alkoxy*-4′-(4-*bromophenylacetyl*)*biphenyls* (VII).—A solution of the 4-n-alkoxybiphenyl (0.05 mol) and 4-bromophenylacetyl chloride (0.057 mol) in dichloromethane (80 ml) was slowly added to a mixture of anhydrous aluminium chloride (0.09 mol) in dichloromethane (60 ml) which was cooled in an ice–salt bath. The solution was then stirred in an ice-bath for 2 h, poured over ice (30 g)–water (30 g)–concentrated hydrochloric acid (30 ml), and stirred for

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[9] J. P. Van Meter and B. H. Klanderman, *Mol. Cryst. Liq. Cryst.*, 1972, **22**, 271, 285; D. Coates and G. W. Gray, *ibid.*, 1975, **31**, 275.

[10] G. W. Gray and Brynmor Jones, *J. Chem. Soc.*, 1954, 678.

[11] G. W. Gray, K. J. Harrison, J. A. Nash, J. Constant, D. S. Hulme, J. Kirton, and E. P. Raynes, ' Liquid Crystals and Ordered Fluids,' eds. J. F. Johnson and R. S. Porter, Plenum Press, New York, 1974, p. 617.

0.5 h. The mixture was shaken with chloroform and the organic layer washed with water and dried ($MgSO_4$). The solid obtained on evaporation of the solvents was crystallised from toluene. The yields were in the range 40—60%; a satisfactory combustion analysis and the correct mass ion values were obtained for each compound. The m.p.s and transition temperatures involving the smectic phases, identified by their microscopic textures as smectics A and B, are given in Table 5.

TABLE 5

M.p. (C–I or S) and liquid crystal transition temperatures (S_B–S_A and S_A–I) for $4\text{-ROC}_6H_4C_6H_4(COCH_2C_6H_4Br\text{-}4)\text{-}4$ (VII) and $4\text{-ROC}_6H_4C_6H_4(CH_2CH_2C_6H_4Br\text{-}4)\text{-}4$ (VIII)

R	C–I, S_B or S_A	(VII) S_B–S_A	S_A–I	(VIII) C–I
Pr	219°			158
Bu	210			165
C_5H_{11}	200	[189°]	[194°]	167
C_6H_{13}	189	[185]	194	168
C_7H_{15}	174	184	191	168
C_8H_{17}	172	182	195	169

[ ] = monotropic transition; C = crystal; S_A = smectic A; S_B = smectic B; I = isotropic liquid.

4-n-Alkoxy-4'-(β-4-bromophenylethyl)biphenyls (VIII).—These were prepared from the corresponding ketone (VII) in a similar manner to compounds (VI). In each case a satisfactory combustion analysis and the correct mass ion values were obtained; the m.p.s are given in Table 5.

4-n-Alkoxy-4'-(β-cyanophenylethyl)biphenyls (IV).—These were prepared from the bromo-compound (VIII) in a similar manner to compounds (III). The combustion analysis results and the thermodynamic constants are given in Tables 6 and 2, respectively. Mass spectrometry gave the correct mass ion value in each case.

TABLE 6

Combustion analysis results for $4\text{-ROC}_6H_4C_6H_4(CH_2CH_2C_6H_4CN\text{-}4)\text{-}4$

R	Found (%) C	H	N	Formula	Required (%) C	H	N
Pr	84.3	6.7	4.2	$C_{24}H_{23}NO$	84.4	6.8	4.1
Bu	84.7	7.0	3.9	$C_{25}H_{25}NO$	84.5	7.1	3.9
C_5H_{11}	84.3	7.2	4.0	$C_{26}H_{27}NO$	84.5	7.4	3.8
C_6H_{13}	84.3	7.5	3.7	$C_{27}H_{29}NO$	84.6	7.6	3.7
C_7H_{15}	84.8	7.8	3.4	$C_{28}H_{31}NO$	84.6	7.9	3.5
C_8H_{17}	84.6	8.0	3.5	$C_{29}H_{33}NO$	84.6	8.1	3.4

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