Trends in the Nematic–Isotropic Liquid Transition Temperatures for the Homologous Series of 4-n-Alkoxy- and 4-n-Alkyl-4'-cyanobiphenyls

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The lower homologues of the series of 4-n-alkoxy- and 4-n-alkyl-4'-cyanobiphenyls have been prepared and their liquid crystal transition temperatures determined. The trends in the nematic–isotropic liquid (N–I) transition temperatures along the series are compared with observed trends for other homologous series. These results reveal deficiencies in the theoretical treatments that have been proposed to explain trends in N–I transition temperatures in such series. However, the results may be explained by the existence, in the case of the higher homologues, of certain alkyl chain conformations which are especially favourable to the stability of the nematic phase.

WE report the nematic–amorphous isotropic liquid (N–I) transition temperatures of the lower members of the homologous series of 4-n-alkyl- and 4-n-alkoxy-4'-cyanobiphenyls. These compounds give unexpectedly high values for the N–I transition temperatures compared with those for the higher homologues.[1] Before discussing the new results, we shall present views on the observed variation in N–I transition temperatures on ascending other homologous series of mesogens.

Studies of many homologous series of mesogens have shown that the temperatures for mesophase–mesophase and mesophase–amorphous isotropic liquid transitions show regular trends as the series are ascended.[2,3] For series of nematogens, a regular alternation of N–I transition temperatures occurs and when these are plotted against the number of carbons in the terminal alkyl chain, the points lie on two curves. When the alkyl group is directly attached to a ring, the upper curve is for the odd members and the lower curve for the even members. When the terminal group is an n-alkoxy-group, the reverse situation occurs because the oxygen is geometrically equivalent to a CH_2 group. A common behaviour for the two separate curves for a series is that both either rise or fall initially and then level out, the alternation becoming less pronounced as the series is ascended. Alternatively, the upper curve may sometimes fall and level out, while the lower curve rises slightly or stays almost level as the series is ascended.

At one time, most series gave the types of curve which fall for both odd and even members, the initial slopes being greatest for series involving high N–I transition temperatures. Later,[4] series were found for which both curves rise as the chain is lengthened. These series involve rather low N–I transition temperatures, and the quest for mesogens of low m.p. has increased the number of examples of series giving this type of N–I curve.[5,6]

Attempts have been made to explain the shapes of N–I curves in terms of the effects of increasing chain length on the anisotropy of molecular polarisability.[7] Assuming a rigid, extended zig-zag chain, the axial polarisability is increased about twice as much as the polarisability at right angles to the molecular long axis on passing from an even to an odd member of an alkyl-substituted series. On passing from an odd to an even member, the polarisabilities along and perpendicular to the long axis are increased almost equally. The anisotropy of molecular polarisability at comparable molecular weights is therefore greater for odd members of an alkyl substituted series and their N–I transition temperatures are higher than those for even members. The opposite will of course apply in the case of alkoxy-substituted mesogens.

Although it seems unreasonable to assume that an alkyl chain adopts a regular, extended, zig-zag conformation in the fluid nematic phase, the alternation in the N–I temperatures can only be explained if some preference for such an extended conformation in fact occurs. Damping of the N–I alternation is then explained in terms of the statistical increase in the number of non-extended conformations possible for the longer alkyl chains giving a progressive decrease in the differences in the anisotropies of molecular polarisability between odd and even members.

It has been pointed out[7] that such arguments lead to an explanation only for the rising types of curve, since they assume that the anisotropy of molecular polarisability increases along the series.

Although the Maier–Saupe theory[8] of the nematic state considers only attractive dispersion forces when considering the free energy difference (ΔF) between the nematic and isotropic phases, recent studies[7] suggest that the entropy contribution to ΔF due to steric intermolecular repulsions (repulsive forces) is also important and an expression which considers both contributions is (1) where S is the order parameter, $-AS^2$ is the

$$\Delta F = -AS^2 - BTS^2 - T\Sigma(S) \qquad (1)$$

internal energy arising from dispersion forces (A being approximately proportional to the anisotropy of molecular polarisability), BS^2 is the packing entropy, and Σ is the orientational entropy.

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

[2] G. W. Gray, ' Molecular Structure and the Properties of Liquid Crystals,' Academic Press, London and New York, 1962.

[3] G. W. Gray, ' Liquid Crystals and Plastic Crystals,' eds. G. W. Gray and P. A. Winsor, Ellis Horwood, Chichester, 1974, vol. 1, ch. 5.

[4] D. J. Byron, G. W. Gray, A. Ibbotson, and B. M. Worrall, *J. Chem. Soc.*, 1963, 2246.

[5] J. Van der Veen, W. H. de Jeu, A. H. Grobben, and J. Boven, *Mol. Cryst. Liquid Cryst.*, 1972, **17**, 291; W. H. de Jeu and J. Van der Veen, *Philips Res. Reports*, 1972, **27**, 172.

[6] 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, vol. 2, p. 617.

[7] W. H. de Jeu, J. Van der Veen, and W. J. A. Goossens, *Solid State Comm.*, 1973, **12**, 405.

[8] W. Maier and A. Saupe, *Z. Naturforsch.*, 1958, **13a**, 564; 1959, **14a**, 822; 1960, **15a**, 287.

For a phase transition at constant volume ($\Delta F = 0$), the expression for the N–I transition temperature T_c is (2) where k is Boltzmann's constant.

$$T_c = 2A/4.54k - 2B \qquad (2)$$

It is considered [7] that B is in some way proportional to the effective molecular length : breadth ratio, and from the work of Stenschke,[9] who reasons that reductions in effective length : breadth ratio for a molecule due to alkyl chain bending are proportional to temperature and
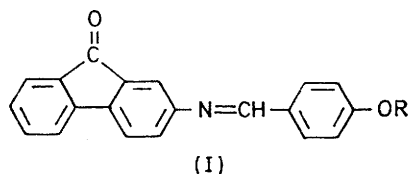
molecular length, de Jeu *et al.*[7] conclude that, as the chain lengthens, so B will assume smaller values. The effect of B is thought to be small at lower temperatures, and so the change in T_c with chain length is expected to be determined mainly by variations in A. Chain motions will become more important when higher T_c values are involved and the decrease in B may become predominant

plete answer. The N–I temperatures of the 2-(*p*-n-alkoxybenzylideneamino)fluorenones(I) (even after exhaustive purification) do not conform [10] to the trends discussed above. Both curves fall initially to minima, then rise slightly and fall again. A regular effect still occurs, but of a more complex kind than those so far treated theoretically. Curves involving maxima and minima have also been reported for other series.[11,12]

Interest in the homologous series of 4-n-alkyl- and 4-n-alkoxy-4′-cyanobiphenyls[1,6,13] led us to examine the lowest members of both these series. When the new transition temperatures and those obtained earlier for some higher homologues are plotted against the number of carbons in the alkyl chains, behaviour similar to that of the series of 2-(*p*-n-alkoxybenzylideneamino)fluorenones (I) is found for both series (see Figure 1). The results now discussed therefore confirm that present theories are not adequate to explain the shapes of N–I curves in all their experimentally observed forms.

Transition temperatures for the compounds reported in the present work are given in Table 1. The variation in the N–I transition temperatures with (i) n (the number of carbons in the alkyl chain) for the series of 4-n-alkyl-4′-cyanobiphenyls and (ii) $n + 1$ (to include the oxygen in
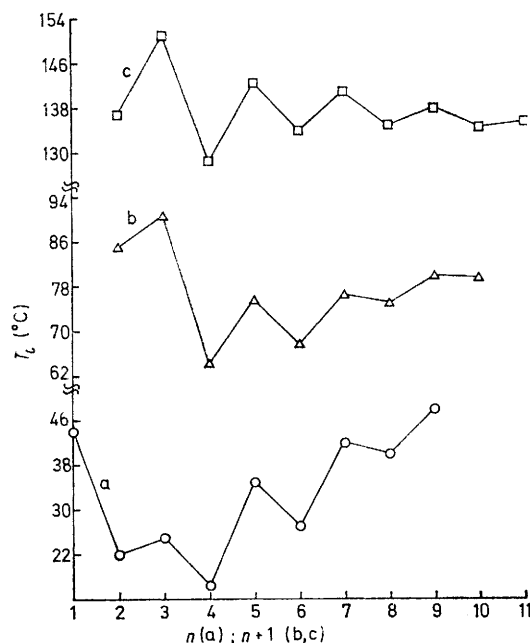
TABLE 1

Thermodynamic data for 4-n-alkyl- and 4-n-alkoxy-4′-cyanobiphenyls

Compound	C–I (°)	ΔH(C–I)/ kcal mol^{-1}	I–N (°)
4-Cyano-4′-methylbiphenyl	109	5.4	(45 ± 3) *
4-Cyano-4′-ethylbiphenyl	75	4.1	(22 ± 1) *
4-Cyano-4′-propylbiphenyl ¶	68	6.4	(25) * (25.5) †
4-Cyano-4′-nonyloxybiphenyl	65 ‡	9.4 ‡	79.5
4-Cyano-4′-methoxybiphenyl	104	5.5	(85.5) †
4-Cyano-4′-ethoxybiphenyl §	102	5.9	(90.5) †

C = crystal; I = isotropic liquid; N = nematic.

* Virtual I–N transition temperature for the monotropic transition obtained by extrapolation (see Experimental section). † I–N Transition temperature for the monotropic transition obtained directly by optical microscopy. ‡ Data for the crystal–smectic phase transition; smectic A–nematic, 77°. § Differential thermal analysis indicated that this compound produced an unstable crystal form when crystallised from ethanol. On melting, this unstable crystal form (C–I 100°) reverted to a more stable form (C–I 102°). ¶ Differential thermal analysis indicated that this compound produced an unstable crystal form when solidification occurred *via* the nematic phase. On heating, this unstable crystal form reverted to the more stable form at *ca.* 32°.

in its effect and lead to a fall in T_c with increase in chain length.

Important as these theoretical attempts are in explaining the shapes of N–I curves, they do not provide a com-

FIGURE 1 The variation in N–I transition temperatures, T_c, with the number of carbon atoms (n) in the alkyl chain for a, 4-n-alkyl-4′-cyanodiphenyls; and with $n + 1$ for b, 4-n-alkoxy-4′-cyanobiphenyls and c, 2-(*p*-n-alkoxybenzylidene-amino)fluorenones

the case of the alkoxy-group) for both the series of 4-n-alkoxy-4′-cyanobiphenyls and 2-(*p*-n-alkoxybenzylidene-amino)fluorenones(I) are shown in Figure 1. The three plots are similar, particularly for the lower homologues.

[9] H. Stenschke, *Solid State Comm.*, 1972, **10**, 653.
[10] G. W. Gray, J. B. Hartley, A. Ibbotson, and F. Marson, *J. Chem. Soc.*, 1955, 4359.
[11] H. Kelker and B. Scheurle, *J. Physique*, 1969, **30**, C4, No. 11—12, 104.
[12] J. A. Castellano, J. E. Goldmacher, L. A. Barton, and J. S. Kane, *J. Org. Chem.*, 1968, **33**, 3501.
[13] G. W. Gray, K. J. Harrison, and J. A. Nash, *Electronic Letters*, 1973, **9**, 130.

Prior to this work the fluorenone derivatives [10] were considered to be unique because of the manner in which the N–I temperatures varied along the series. However, since none of the series shown in Figure 1 exhibits either one of the two types of expected behaviour mentioned earlier, the generalisations made previously become suspect and the fluorenones can no longer be regarded as exceptional.

With the omission of the first two members of each series, the 4-n-alkyl- and 4-n-alkoxy-4'-cyanobiphenyls do in fact show the behaviour expected for series with low N–I values. For the series of fluorenones(I) omission of the first two members gives an upper curve (even homologues) which falls with increasing chain length, thus conforming to the behaviour of series with high N–I values, and a lower curve (odd homologues) which conforms to that for series with low N–I values. This dual behaviour within a series is not unusual, and occurs with intermediate N–I values, i.e. at the change-over between the two extreme types of expected behaviour. The apparently anomalous behaviour of the homologous series shown in Figure 1 appears therefore to be attributable in each case to the properties of the first two members. In this context it must be remembered that for many homologous series giving rising N–I curves, values for the N–I transition temperatures of the lower homologues have not been obtained either because of their high m.p.s (C–I temperatures) and the fact that the means of obtaining ' virtual ' N–I transition temperatures) are comparatively novel, or because the earlier homologues were not prepared. It is possible that further investigations of such series will reveal similar trends to those shown in Figure 1. The behaviour of the three homologous series shown in Figure 1 would then be of a general and not of an anomalous kind.

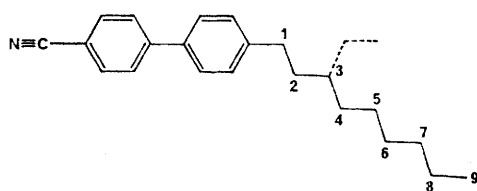A study of the molecular geometry, see Figure 2, of

FIGURE 2   The idealised molecular geometry of 4-n-alkyl-4'-cyanobiphenyls

the 4-n-alkyl- and 4-n-alkoxy-4'-cyanobiphenyls can lead to qualitative predictions about the relationship between the N–I values of adjacent homologues (C_3 and C_4, C_4 and C_5, etc.). For a homologous series of nematogens with low N–I transition temperatures, the low values reflect a low inherent tendency of the unalkylated parent compound to form a nematic phase. In the case of the 4-n-alkyl-4'-cyanobiphenyls, the parent compound, 4-cyanobiphenyl has a ' virtual ' I–N temperature of ca. −45°, 135° below the m.p. (see Figure 3). That is, the relatively short lath-shaped molecules have little tendency to form a stable, parallel molecular orientation of the

nematic type. The addition of a 4'-methyl group to 4-cyanobiphenyl causes an increase in the length and the anisotropy of polarisability of the molecule. This produces a large increase (ca. 90°) in nematic thermal
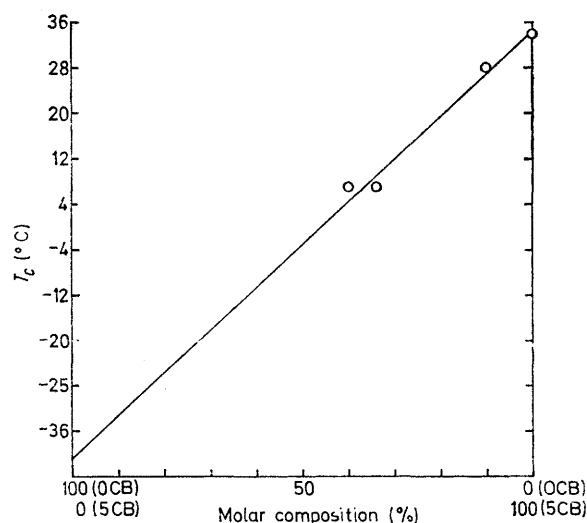

FIGURE 3   N–I Transition temperatures, T_c, of binary mixtures of 4-cyanobiphenyl (OCB) and 4-cyano-4'-n-pentylbiphenyl (5CB); virtual I–N transition of OCB, ca. −45°

stability, i.e. the methyl group assists in retaining a parallel orientation of the cyanobiphenylyl groups.

The formation of the 4'-ethyl derivative leads to a small increase in the width of the molecule, giving a deviation from the strict lath-like shape of the methyl compound, but does not have a significant effect on the anisotropy of polarisability. These effects produce a decrease in nematic thermal stability with respect to the methyl derivative. This behaviour is reversed in the homologous series of the 4-n-alkoxy-4'-cyanobiphenyls and the fluorenones(I) because of the geometrical effect of the ether oxygen.

By extending the above principles, it is possible to predict the qualitative relationship between the N–I values of adjacent homologues in each of the three series given in Figure 1. Quantitative predictions are, however, required to explain the overall shapes of the plots shown in Figure 1. Although equation (2)[7] gives an expression for T_c, the N–I transition temperature, it is not possible to determine the values of the variables A and B. Equation (2) merely predicts that N–I values will increase with increasing anisotropy of molecular polarisability and with increasing molecular length : breadth ratio. The anisotropy will tend to increase with chain length, while the length : breadth ratio will tend to decrease with chain length, assuming that the carbon chain adopts the more stable, planar, zig-zag conformation. A predominance of the anisotropy over the length : breadth ratio will lead to a progressive increase in N–I values, whereas if the length : breadth ratio predominates, a progressive decrease in N–I values will be observed.

We can use the above ideas to make some tentative

suggestions about the conformations of the alkyl chains in the nematic phases of the homologous series under discussion.

The most energetically favoured conformation for a free alkyl chain is the fully extended, all-*trans*, zig-zag conformation. In the solid phase, the carbon chain of an n-alkane is exclusively in this conformation. This is thought to occur because of the external constraints imposed upon the chain in producing efficient molecular packing in the crystal lattice. In the liquid phase of an n-alkane the carbon chain is essentially free to adopt a distribution of conformations depending upon temperature and the chain length. In the intermediate nematic phase, there may be small residual constraints on the alkyl chain of a nematogen to adopt extended conformations. Although there will probably be a distribution of conformers, there may be a predominance of a conformer which is most favourable to the formation and maintenance of the nematic order. The proportion of the most favourable conformer will, however, tend to decrease with increasing temperature and chain length.

We shall now consider the homologous series of 4-n-alkyl-4'-cyanobiphenyls as a typical example of a series of nematogens with low N–I values. The methyl and ethyl homologues exist as distinct conformers, assuming free rotation of the terminal methyl group. The most favourable conformer of the propyl derivative, from the points of view of both nematic phase and conformer stabilities, is the all-*trans* form. The possible existence of other conformers will lower the N–I transition temperature. The alkyl chain of the butyl homologue should also have a preference for the all-*trans* conformation in the nematic phase, for although other conformations are possible, these would again be either detrimental to the stability of the nematic phase and/or energetically unfavourable.

If these assumptions are correct, then the tendency for the alkyl chain to adopt the planar zig-zag conformation produces a downward trend in the N–I transition temperatures of the first four homologues. Therefore, if this trend was continued we would expect the pentyl derivative to have a lower nematic thermal stability than the propyl derivative. However, Figure 1 illustrates that there is a large increase in nematic thermal stability on passing to the pentyl homologue. This behaviour may be due to the predominance of a conformer which though energetically less favourable than the planar zig-zag conformer, is especially favourable to the stability of the nematic phase. This conformer is obtained by taking the all-*trans* conformation of the pentyl chain and rotating the plane of the C-3 ,-4, and -5 carbon atoms through 135—180° about the C-2–C-3 axis; the effect of a rotation through 180° is shown in Figure 2 (dotted line). The corresponding rotation about the C-2–C-3 axis is not favourable in the case of the butyl derivative because of the freely rotating, terminal methyl group.

It is suggested that the presence of other similar conformers is responsible for the progressively increasing N–I values which are observed for the homologues higher

than butyl in the series of 4-n-alkyl-4'-cyanobiphenyls and higher than propoxy in both the series of 4-n-alkoxy-4'-cyanobiphenyls and 2-(*p*-n-alkoxybenzylideneamino)-fluorenones.

In series with higher N–I transition temperatures, the thermal fluctuations of the alkyl chain will reduce the proportions of those conformers which are especially favourable for nematic thermal stability and so the falling type of N–I curve will be observed. The proportion of these favourable conformations will also depend
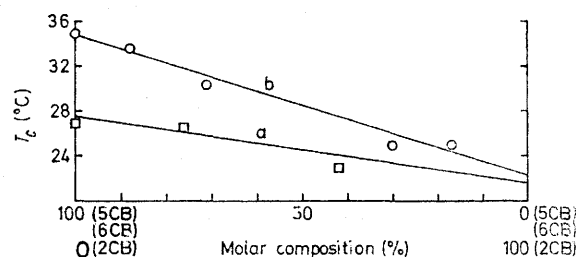
FIGURE 4 N–I Transition temperatures, T_c, of binary mixtures of a, 4-cyano-4'-ethylbiphenyl (2CB) and 4-cyano-4'-n-hexyl-biphenyl(6CB); and b, 2CB and 4-cyano-4'-n-pentylbiphenyl (5CB) (see Table 1)
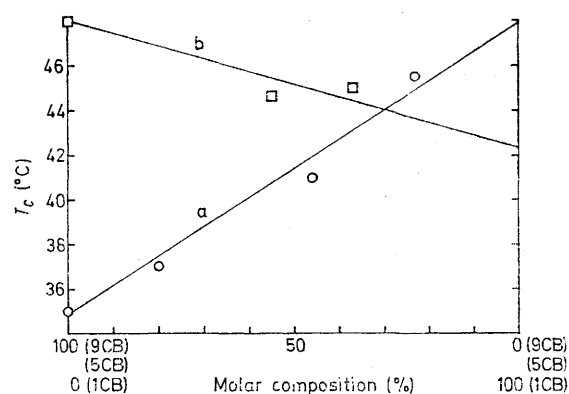
FIGURE 5 N–I Transition temperatures, T_c, of binary mixtures of a, 4-cyano-4'-methylbiphenyl (1CB) and 4-cyano-4'-n-pentylbiphenyl (5CB); and b, 4-cyano-4'-nonylbiphenyl (9CB) and 1CB (see Table 1)

on the ability of the lath-like aromatic parts of the nematogenic molecules to force the alkyl chains into approximately coaxial conformations in order to preserve the nematic order of the system.

Various spectroscopic and chemical investigations are now being planned in an attempt to confirm (or otherwise) the existence of the postulated conformers.

EXPERIMENTAL

Thermodynamic Measurements (*see Table* 1).—Transition temperatures [crystal–isotropic liquid (C–I) and isotropic liquid–nematic (I–N)] were determined by optical microscopy (Nikon L-Ke polarising microscope) with the aid of a Mettler FP52 heating stage and FP5 control unit.

The I–N transitions for 4-cyano-4'-ethoxy-, -4'-methoxy-, and -4'-n-propyl-biphenyls were monotropic, but the transition temperatures could be measured directly. The 'virtual' I–N temperatures of 4'-methyl- and 4'-ethyl-4-cyanobiphenyls and of 4-cyanobiphenyl were obtained by

extrapolation from the measured I–N transition temperatures of various mixtures of known composition of each of these compounds with a suitable mesomorphic compound. The results of these extrapolations are shown in Figures 3—5. The validity of this method is supported by the agreement between the values for the I–N transition temperature of 4-cyano-4'-n-propylbiphenyl obtained by this method and by direct optical microscopy (Table 1).

Enthalpies of the C–I transitions were measured using a Stanton Redcraft model 671 low temperature differential thermal analyser. Indium was used as a calibration standard, and the accuracy of the enthalpies is estimated as ±10%.

Preparation of Materials.—The 4'-ethyl and 4'-n-propyl derivatives of 4-cyanobiphenyl were prepared by the route used by Gray *et al.*[6] However, different reagents or solvents were employed in some of the reactions. The ketone obtained by Friedel–Crafts acylation of 4-bromobiphenyl was

4-Bromo-4'-methylbiphenyl was prepared by the method of Gomberg and Pernet.[16]

The final cyano-derivatives were purified by column chromatography (silica gel; chloroform) and/or crystallisation from ethanol. Each of the products had a purity of >99% by g.l.c. and gave the expected mass ion when analysed by mass spectrometry. Further data on these compounds and their precursors are given in Table 2.

We are grateful to D. Coates and D. G. McDonnell of this laboratory, who, in the course of other work, prepared 4-cyano-4'-n-propylbiphenyl and 4-cyano-4'-n-nonyloxybiphenyl.

4-Bromo-4'-ethylbiphenyl.—A solution of anhydrous aluminium trichloride (7 g, 0.053 mol) in anhydrous ether (20 ml) was added dropwise to a mixture of lithium aluminium hydride (1 g, 0.026 mol) and anhydrous ether (20 ml). A solution of 4-acetyl-4'-bromobiphenyl (3 g, 0.011 mol) in anhydrous chloroform (40 ml) was then added over 30 min.

TABLE 2

M.p.s. and analytical data for 4-n-alkyl- and 4-n-alkoxy-4'-cyanobiphenyls and their precursors

Compound	M.p. (°C)	Found (%)				Formula	Required (%)			
		C	H	Br	N		C	H	Br	N
4-Bromo-4'-methylbiphenyl	133 [135] [a]									
4-Cyano-4'-methylbiphenyl	109	86.6	5.8		7.6	$C_{14}H_{11}N$	87.0	5.7		7.3
4-Acetyl-4'-bromobiphenyl	129 [129—130] [b]									
4-Bromo-4'-ethylbiphenyl	125	64.6	4.9	30.5		$C_{14}H_{13}Br$	64.3	5.0	30.7	
4-Cyano-4'-ethylbiphenyl	75	86.6	6.0		6.8	$C_{15}H_{13}N$	87.0	6.3		6.8
4-Bromo-4'-propionylbiphenyl	121	62.5	4.7	28.0		$C_{15}H_{13}BrO$	62.3	4.5	27.7	
4-Bromo-4'-propylbiphenyl	107	65.5	5.6	29.2		$C_{15}H_{15}Br$	65.5	5.5	29.1	
4-Cyano-4'-propylbiphenyl	68	86.8	6.6		6.1	$C_{16}H_{15}N$	86.9	6.8		6.3
4-Bromo-4'-nonyloxybiphenyl	120	67.6	7.3	21.0		$C_{21}H_{27}BrO$	67.4	7.2	21.3	
4-Cyano-4'-nonyloxybiphenyl	65 †	82.4	8.4		4.5	$C_{22}H_{27}NO$	82.2	8.4		4.4
4-Bromo-4'-methoxybiphenyl	146 [145] [c]									
4-Cyano-4'-methoxybiphenyl	104	80.0	5.7		6.7	$C_{14}H_{11}NO$	80.4	5.3		6.7
4-Bromo-4'-ethoxybiphenyl	139 [139] [c]									
4-Cyano-4'-ethoxybiphenyl	100	80.7	5.8		6.2	$C_{15}H_{13}NO$	80.7	5.8		6.3

* Where good agreement with literature m.p.s. was obtained, elemental analyses were not carried out, but each product was shown to give the correct mass ion. † Crystal–smectic A transition temperature.

[a] Ref. 16. [b] D. J. Byron, G. W. Gray, and R. C. Wilson, *J. Chem. Soc.* (C), 1966, 840. [c] B. Jones and J. P. Sleight, *J. Chem. Soc.*, 1954, 1775.

reduced to the corresponding alkyl derivative by the method of Albrecht *et al.*,[14] which uses lithium aluminium hydride, aluminium trichloride, chloroform, and ether. This method is illustrated for the reduction of 4-acetyl-4'-bromobiphenyl; it was first used for the preparation of 4-bromo-4'-perdeuterio-n-pentylbiphenyl[15] and has since been found more convenient than the Huang-Minlon method.[6]

Cyanation of 4-n-alkyl- and 4-n-alkoxy-4'-bromobiphenyls was carried out using *N*-methyl-2-pyrrolidone as solvent. This is an improvement on the use of *NN*-dimethylformamide;[6] the reaction time is reduced from 18 to 1.5 h and the amount of amide formed is lowered. This method is illustrated for the preparation of 4-cyano-4'-ethylbiphenyl, and was used to prepare 4-cyanobiphenyl from 4-bromobiphenyl.

The 4'-ethoxy and 4'-methoxy derivatives of 4-bromobiphenyl were prepared by the alkylation of 4-bromo-4'-hydroxybiphenyl formed *in situ* by the alkaline hydrolysis of 4-phenylsulphonyloxy-4'-bromobiphenyl.

The reaction mixture was stirred and heated under reflux for 18 h. The excess of reducing agent was destroyed by the careful addition of water (30 ml). Concentrated hydrochloric acid (25 ml) was then added, followed by ether (100 ml). The ethereal layer was washed with water (3 × 100 ml) and dried (Na_2SO_4). The ether was removed, the residue crystallised from ethanol, and the required product (70%), m.p. 125—126°, obtained (see Table 2).

4-Cyano-4'-ethylbiphenyl.—Copper(I) cyanide (0.6 g 6.71 mmol) was added to a solution of 4-bromo-4'-ethylbiphenyl (1.1 g, 4.22 mmol) in *N*-methyl-2-pyrrolidone (5 ml). This mixture was stirred and heated under reflux for 1.5 h. The cooled reaction mixture was poured into a solution of iron(III) chloride (1.3 g) in water (20 ml) and concentrated hydrochloric acid (0.7 ml), and stirred at 60° for 30 min. The product was extracted into ether (1 × 30 ml, 2 × 20 ml). This solution was treated with animal charcoal, dried (Na_2SO_4), and then evaporated to dryness.

[14] W. L. Albrecht, D. H. Gustafson, and S. W. Horgan, *J. Org. Chem.*, 1972, **37**, 3355.

[15] G. W. Gray and A. Mosley, unpublished work.
[16] M. Gomberg and J. C. Pernet, *J. Amer. Chem. Soc.*, 1926, **48**, 1372.

The residue was crystallised from light petroleum (b.p. 40—60°) and the required product (46%), m.p. 75—76°, obtained (see Table 2).

In this case the crude product did not contain a significant amount of unchanged 4-bromo-4'-ethylbiphenyl as shown by t.l.c. If a larger amount of the bromo-compound is present, this is removed (first fraction) by column chromatography on silica gel (chloroform as eluant).

4-Bromo-4'-ethoxybiphenyl.—A mixture of 4-phenyl-sulphonyloxy-4'-bromobiphenyl (5 g, 0.013 mol), sodium hydroxide (1.2 g, 0.03 mol), dioxan (60 ml), and water (30 ml) was heated under reflux for 3 h. Ethyl iodide (3.5 g, 0.022 mol) was added and heating continued for a further 4 h. The crude product was isolated by filtration, washed with water, crystallised from ethanol, and dried. This gave the required product (76%), m.p. 139—140° (see Table 2).