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Mesomorphic Transition Temperatures and Viscosities for Some Cyano-biphenyls and -p-terphenyls with Branched Terminal Alkyl Groups

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Mesomorphic Transition Temperatures and Viscosities for Some Cyano-biphenyls and -*p*-terphenyls with Branched Terminal Alkyl Groups

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A number of 4-alkyl- and 4-alkoxy-4′-cyanobiphenyls and 4-alkyl-4″-cyano-*p*-terphenyls with branched chains have been prepared. Marked depressions in the liquid crystal transition temperatures have been observed relative to those for the corresponding *n*-alkyl derivatives, although the melting points are affected to a smaller extent. The viscosities of 10 wt% solutions of the individual branched-chain materials in the commercial mixture E7 have been determined at 0 °C and 25 °C and substantial increases in the measured bulk viscosities have been recorded.

INTRODUCTION

Because of the commercial importance of the 4-alkyl- and 4-alkoxy-4′-cyanobiphenyls and related *p*-terphenyls[1,2] stemming from their high stability and suitability for applications in electro-optical displays, it was considered that a survey should be made of the effects of branching of the terminal alkyl chains of these compounds upon certain of their physical properties—notably their liquid crystal transition temperatures and viscosities.

Some years ago, Gray and Harrison[3] established the effects of branching of terminal alkyl chains (by a lateral methyl substituent)

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upon the liquid crystal transition temperatures of a range of Schiff's bases derived from alkyl 4-aminocinnamates, including those with a terminal cyano substituent in the benzylidene moiety. A few other types of mesogen containing similarly branched terminal alkyl groups have been studied,[4,5] and the general pattern of effect on the liquid crystal transition temperatures was consistent with that established for the cinnamate esters. However, it was considered important to verify, by a systematic experimental study, that methyl branching of the alkyl chains of the cyano-biphenyls and -*p*-terphenyls did result in the same behavioural trends. Moreover, we wished to obtain data on the effects of different locations of the methyl branching group upon the viscosities of the systems.

RESULTS AND DISCUSSION

Effects of chain-branching on transition temperatures

Fourteen branched-chain materials were prepared; these include seven 4-alkoxy- and five 4-alkyl-4′-cyanobiphenyls, and two 4-alkyl-4″-cyano-*p*-terphenyls. Transition temperatures for these compounds and the corresponding *n*-alkyl analogues are recorded in Table I. It is immediately clear that the effects of the chain-branching on the nematic–isotropic liquid transition temperatures approximate to those that might have been expected on the basis of the earlier results[3-5] using different types of mesogen.

Reference to Table I reveals that methyl branching of the alkyl chain of a 4-*n*-alkyl- or 4-*n*-alkoxy-4′-cyanobiphenyl results in each case in a severe depression of the nematic clearing point of that material. 1-Methylation in the alkoxy series and 2-methylation in the alkyl series produce by far the greatest depressions in the clearing points, and there is a gradual diminution of this effect as the branching methyl group is moved away from the aromatic core. The depressions in the transition temperatures of the ethers are usually greater than those for the corresponding materials with the terminal alkyl substituents directly attached to the aromatic ring. Melting points are affected by methyl branching in a less regular manner than the clearing points, and when melting-point decreases do occur, they are smaller than the corresponding decreases in clearing point. In three cases, chain-branching raises the melting points, compared with those for the analogous mesogens with *n*-alkyl chains.

Turning to the actual T_{N-I} values, it is noted that an alkoxy compound branched at the 1-carbon exhibits a lower clearing point than the alkyl compound branched at the 2-position and containing

TABLE I

Comparison of transition temperatures for some compounds containing branched or unbranched terminal alkyl chains

Compound	C–N or I (°C)	S–N or I (°C)	N–I (°C)	ΔT(N–I) (°C)
$MeCH_2CH_2CH_2BipCN$	46.5	—	(16.5)	
$MeCH_2CHMeCH_2BipCN$	12	—	(−28)	−44.5
$MeCHMeCH_2CH_2BipCN$	55.5	—	(9)*	−7.5
$MeCH_2CH_2CH_2OBipCN$	78	—	(75.5)	
$MeCH_2CH_2CHMeOBipCN$	46	—	(−42)*	−117.5
$MeCH_2CHMeCH_2OBipCN$	57	—	(12)*	−63.5
$MeCHMeCH_2CH_2OBipCN$	74	—	(44)*	−31.5
$MeCH_2CH_2CH_2CH_2BipCN$	22.5	—	35	
$MeCH_2CH_2CHMeCH_2BipCN$	[a]	—	−16	−51
$MeCH_2CHMeCH_2CH_2BipCN$	9	(−19)	(−8)	−43
$MeCHMeCH_2CH_2CH_2BipCN$	50	—	(−1)*	−36
$MeCH_2CH_2CH_2CH_2OBipCN$	53	—	67.5	
$MeCH_2CH_2CH_2CHMeOBipCN$	10	—	(−63)*	−130.5
$MeCH_2CH_2CHMeCH_2OBipCN$	21	(−5)	—	−72.5[b]
$MeCH_2CHMeCH_2CH_2OBipCN$	45	—	(21.5)	−46
$MeCHMeCH_2CH_2CH_2OBipCN$	86.5	—	(47.5)*	−20
$MeCH_2CH_2TerCN$	182	—	275.5	
$MeCHMeCH_2TerCN$	154.5	—	226	−49.5
$MeCH_2CH_2CH_2TerCN$	154	—	242	
$MeCHMeCH_2CH_2TerCN$	150	—	216	−26

KEY:

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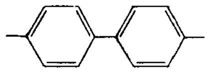

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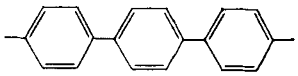

[a] It has not been possible to freeze this material.

[b] Based on T_{S-I}.

( ) Represents a monotropic transition.

( )* Represents a virtual transition determined by extrapolation of results obtained with mixtures.

the same total number of atoms in the chain. This is exemplified by the clearing-point difference between 4-cyano-4′-(2″-pentyloxy)biphenyl (−42°) and 4-cyano-4′-(2″-methylpentyl)biphenyl (−16°) (see Table I). The nematic–isotropic transition temperature of the former compound (an ether) is therefore *lower* than that of the latter compound (a substituted alkane). The same result is obtained if we compare the 1-methylalkoxy compounds with the 2-methylalkyl analogues having the same number of *carbon* atoms in the chains. Special factors (possibly intramolecular steric effects) seem to be involved here as the nematic–isotropic liquid transition temperatures of the alkoxy compounds branched at the 2- and 3-carbons are higher than those of the corresponding alkyl compounds branched at the 3- and 4-carbons and containing the same total number of atoms in the chain.

In order to explain the general decreases in clearing point upon incorporation of a lateral methyl group in the terminal alkyl chain of these systems, it is envisaged that the branching methyl group protrudes from the normal rotation volume of the parent unsubstituted molecule.

Intermolecular interactions will result in an increased separation between neighbouring molecules with attendant decreases in attractive molecular interactions and in T_{N-I}. The extent of the depression decreases gradually as the branching methyl group is moved towards the end of the carbon chain, see Table I, although the clearing point of the parent, open-chain material is not reattained by any branched-chain material studied here. As the position of branching is moved away from the central aromatic core, the branching methyl group occupies a position on more flexible parts of the chain. This may permit the methyl group to be accommodated more readily in the normal rotation-volume, thereby causing less serious intermolecular steric effects. Thus, as the methyl group is moved towards the end of the chain, there will be a consequent minimising of its disadvantageous effect on the clearing points.

The two branched-chain derivatives of cyano-*p*-terphenyl, ie, 4-cyano-4″-(2‴-methylpropyl)-*p*-terphenyl and 4-cyano-4″-(3‴-methylbutyl)-*p*-terphenyl, exhibit transition temperatures consistent with the previous results (see Table I), and thus similar arguments can be advanced for them. These materials are both terminally branched and as now expected, the depression in the N–I transition temperature is less for the 3-methylbutyl compound (−26°) than for the 2-methylpropyl material (−49.5°).

Effects of chain-branching on viscosities

Because

(a) viscosity measurements consume considerable quantities of materials, even when these are used as relatively low concentration solutions in a nematic host, and

(b) available quantities of the branched chain material were limited, the scope and range of viscosity measurements that might have been desirable could not be achieved. We had to chose between:

(1) testing the materials (dissolved in a commercially important host) under the types of condition that might be relevant to their use

in display devices, ie, at a fixed wt% composition and at two significant fixed temperatures (25 °C and 0 °C);

(2) carrying out the viscosity measurements at temperatures governed by two fixed values of a reduced temperature factor and using equimolar concentrations. Since the T_{N-I} values of the host plus solute would differ from one material to another, the viscosity values would then relate to a range of real temperatures. Whichever conditions were chosen, it was desirable to measure the viscosity for each solution at each temperature using duplicate or even triplicate samples (see experimental section) to ensure reliability of the data. Availability of material therefore precluded our employing both types of experimental conditions, and we decided to select (1) as giving a more ready guide to the effects of chain-branching when employing conditions relevant to those under which liquid crystals are used and assessed for applications.

Measurements of viscosities were therefore made using 10 wt% solutions of the individual branched-chain materials in the commercial nematic mixture E7.[6] The temperatures used were 25 °C and 0 °C, and the results are recorded in Table II.

As can be seen from the results in Table II, the viscosity of E7 at either 0 °C or 25 °C is increased in every case by the addition of a branched chain solute. If a fixed reduced temperature factor had been used to define the two temperatures used, the relative viscosity values would have been higher, except in the case of the terphenyls (System 5, Table II), since in all other cases the T_{N-I} of E7 is *reduced* by the solute, ie, the present measurements relate to temperatures closer to the N–I transition than that in the case of pure E7. Therefore, the use of fixed reduced temperatures would have increased the magnitude of the observed enhancements of viscosity.

Considering next the results within any given system (1–5) in Table II, the molar masses are constant, and molarity effects do not perturb the argument. For example, for System 3, the viscosity falls as the methyl group is moved away from the ring system towards the end of the chain. At the same time, T_{N-I} of the solute and consequently the T_{N-I} of the solution in E7 *rises* and the measurements at 0 °C or 25 °C are being made further from T_{N-I}. As a result, the viscosity decreases would be even greater if the experiments had been done at temperatures determined by a fixed reduced temperature factor. The movement of the branching methyl group towards the free end of the molecule therefore decreases the effect of the methyl group on the viscosity and it may be argued again that as the branching point moves to more flexible parts of the chain, the protruding effect of the group is diminished. The drag on molecular movement will therefore

TABLE II

Viscosity data for some branched-chain materials

System	Material	Viscosity 25 °C (cSt)	Viscosity 0 °C (cSt)	Clearing Point (°C)
	E7 (508607)	32.0	160.7	60
1	$\mathrm{MeCH_2CHMeCH_2BipCN}$	32.8	164.7	(−28)
	$\mathrm{MeCHMeCH_2CH_2BipCN}$	32.7	163.8	(9)*
2	$\mathrm{MeCH_2CH_2CHMeOBipCN}$	39.4	202.5	(−42)*
	$\mathrm{MeCH_2CHMeCH_2OBipCN}$	38.3	193.2	(12)*
	$\mathrm{MeCHMeCH_2CH_2OBipCN}$	34.95	175.4	(44)*
3	$\mathrm{MeCH_2CH_2CHMeCH_2BipCN}$	36.4	180.3	−16
	$\mathrm{MeCH_2CHMeCH_2CH_2BipCN}$	35.7	176.6	(−8)
	$\mathrm{MeCHMeCH_2CH_2CH_2BipCN}$	34.3	167.8	(−1)*
4	$\mathrm{MeCH_2CH_2CH_2CHMeOBipCN}$	40.7	223.7	(−63)*
	$\mathrm{MeCH_2CH_2CHMeCH_2OBipCN}$	40.0	218.7	−5
	$\mathrm{MeCH_2CHMeCH_2CH_2OBipCN}$	39.3	199.1	(21)
	$\mathrm{MeCHMeCH_2CH_2CH_2OBipCN}$	38.3	192.4	(47)*
5	$\mathrm{MeCHMeCH_2TerCN}$	41.7	228.3	226
	$\mathrm{MeCHMeCH_2CH_2TerCN}$	43.8	248.5	216

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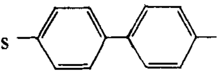

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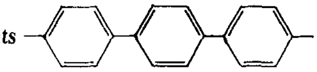

( ) Represents a monotropic transition.
( )* Represents a virtual transition.

fall, the viscosity will diminish and (as reasoned earlier) T_{N-I} of the solute will rise. Similar arguments apply to all the individual systems 1 to 5.

If we separately compare either alkyl systems or ethers that involve an increase in chain length, but chain-branching at the same point in the chain, the viscosity consistently rises. At the same time, the T_{N-I} values of the solutes sometimes rise and sometimes fall, and therefore, if the reduced temperature effect were taken into account, the viscosity increase with chain length would appear sometimes greater and sometimes smaller. Such compositions are also influenced by molarity effects.

The data do not allow clear comparisons to be made either between alkyl compounds and ethers of the same chain length (including oxygen) and with branching at the same number of atoms from the ring. The viscosities in fact fall at a given temperature (0 °C or 25 °C) from ether to alkyl compound, eg, at 25 °C, System 2 Compound 3 to

System 3 Compound 3, from 34.95 to 34.3; System 2 Compound 2 to System 3 Compound 2 from 38.3 to 35.7. The alkyl compounds however have the lower T_{N-I}. Consequently, the reduced temperature effect should increase the viscosity of the alkyl compound, so bringing the pairs of viscosity closer, or even raising that of the alkyl compound above that of the ether at the same effective reduced temperature. In comparing ethers and alkyl compounds in this way, molarity effects will be very small because of the similar weight contributions of CH_2 and oxygen.

Under the conditions of measurement at 0 °C and 25 °C, the terphenyls have by far the greatest effect on the viscosity of E7. Practical considerations apart, however, it must be remembered that because of the high T_{N-I} values of the terphenyls, the viscosity effect would be diminished if a reduced temperature factor were used. Contrarily, the higher molar mass means that the terphenyls were studied at a reduced molarity which would lead to under-estimates of the viscosity effect.

As mentioned earlier, the main aim was to obtain information about the effects of branched-chain solutes on the viscosity of a nematic host under conditions that would affect the use of the liquid crystal mixture in a display device. Clearly, in all cases, the adverse viscosity effect would diminish the response time of E7 in a twisted nematic device. It is also worth pointing out that the viscosity enhancements brought about by the relatively low concentrations (10 wt%) of the solutes are appreciable. The viscosities of the *pure* nematic solutes must therefore be very high and it is possible that the viscosity effects of chain branching may be of practical interest in the area of two-frequency switching materials. Since chain branching is a simple, effective way of introducing chirality into a system, the viscosity data obtained are also relevant in the context of cholesteric materials, eg, the best twisting effects are achieved by chain branching close to the aromatic ring system, under which circumstances, the viscosity effects will be greatest.

EXPERIMENTAL

Physical measurements

All liquid crystal transition temperatures were recorded using a Mettler FP52 hot stage or a Kofler cold stage in conjunction with a suitable polarising microscope (Nikon L-Ke). In those cases where direct observations of liquid crystal transitions were not possible, virtual clearing-point values were determined assuming a linear clearing-point relationship across the phase diagram for mixtures of varying composition of the test material in E8.[6] Linear extrapolation of the transition temperature line (over as short a composition range as possible, in order to be as certain as possible that no curvature of the line occurred) to 100% of the test material gave the value of the virtual clearing-point.

Viscosity evaluations were obtained using 10 wt% solutions of the branched-chain 4-alkyl- and 4-alkoxy-4′-cyanobiphenyls and 4-alkyl-4″-cyano-*p*-terphenyls in the commercial liquid crystal mixture E7.[6] The low melting point (−9 °C), high clearing point (60 °C), and ability to supercool rendered this a good nematic solvent to use.

The viscosity experiments involved the use of two glass viscometers (types CMSM, sizes 200 and 350) supplied by Poulten, Selfe, and Lee Limited. The viscometers were calibrated, and the constants C at 25 °C were determined as 0.1160 and 0.5124 cSt^{-1}. The kinematic viscosity of a liquid may be calculated from an observed time of flow (t sec) by means of the formula V (viscosity in cSt) = Ct.

Determinations of viscosity of the solutions were made at 0 °C and 25 °C, and often evaluations of the viscosity of a given solution were made using both viscometers at each of the two temperatures. At least three separate timings were recorded in all cases; any unusual results were discounted and the observations repeated. Good agreement and reproducibility were obtained for the great majority of the timings taken, and it is estimated that the degree of error was within ±1%. An average value of the viscosity of each solution of a branched-chain cyanobiphenyl or cyano-*p*-terphenyl at both 0 °C and 25 °C was then calculated from these recordings.

Preparation of materials

When not commercially available, starting materials such as branched-chain alkanols, halogenoalkanes, carboxylic acids and acyl chlorides were prepared by standard methods and used to make the branched-chain 4-alkyl- and 4-alkoxy-4′-cyanobiphenyls and 4-alkyl-4″-cyano-*p*-terphenyls.

The branched-chain 4-alkyl-4′-cyanobiphenyls were produced[1,2] by using branched-chain acyl chlorides. Friedel–Crafts acylation of commercially available 4-bromobiphenyl gave the ketones which were reduced, using a mixture of lithium aluminium hydride and anhydrous aluminium chloride, to the 4-alkyl-4′-bromobiphenyls. (The formation of alkene was avoided in all but one case, and this impurity was removed in the purification of the subsequent nitrile.) Cyanation then yielded the required branched-chain 4-alkyl-4′-cyanobiphenyls (see Table I for the liquid crystal transition temperatures).

Branched-chain 4-alkoxy-4′-cyanobiphenyls were prepared by the method of Gray, Harrison, and Nash[1,2] using branched-chain bromoalkanes in normal alkylation reactions. Cyanation of the bromoethers yielded the desired products (see Table I for the liquid crystal transition temperatures).

Branched-chain 4-alkyl-4″-cyano-*p*-terphenyls were prepared by a novel four-step synthesis, described below for 4-cyano-4″-(3‴-methylbutyl)-*p*-terphenyl.

4-(3‴-Methylbutanoyl)-p-terphenyl.—Freshly distilled 3-methylbutanoyl chloride (6.6 g, 0.049 mol) in sieve-dried nitrobenzene (20 cm^3) was added dropwise to a solution of *p*-terphenyl (9.4 g, 0.041 mol) and anhydrous aluminium chloride (6.2 g, 0.047 mol) in sieve-dried nitrobenzene (500 cm^3) under anhydrous conditions. The temperature of the solution was maintained at 30 °C throughout the addition and allowed to settle to room-temperature overnight while the solution was stirred.

The solution was added to a mixture of ice and 5M-hydrochloric acid and stirred for 30 min. The organic layer was separated off and steam-distilled to remove solvent and yield a solid residue. This was taken up in a minimum of chloroform and the resultant solution was dried over anhydrous magnesium sulphate. The crude product was eluted from a silica gel column using a 2 : 1 mixture of chloroform and hexane as eluent. Single-spot fractions containing product were collected and evaporated together to yield a solid residue which was crystallised from ethylene glycol monomethyl ether. The yield was 7.85 g (58.6%), mp 184–185 °C.

4-(3‴-Methylbutyl)-p-terphenyl.—The reduction was essentially the same as that already mentioned in the section on branched-chain 4-alkyl-4′-cyanobiphenyls. The yield was 87.7%, mp 165–166 °C.

4-bromo-4″-(3‴-methylbutyl)-p-terphenyl.—A solution of bromine (7.5 g, 0.047 mol) in sieve-dried chloroform (25 cm^3) was added in four equal portions at twenty-four hour intervals to a solution of 4-(3‴-methylbutyl)-*p*-terphenyl (5.5 g, 0.018 mol) in sieve-dried chloroform (150 cm^3) under anhydrous conditions and in the absence of ambient radiation. The reaction flask was maintained in a Dewar vessel, to which fresh ice-water was added as a coolant before each addition.

Twenty-four hours after the last addition of bromine, the solution was poured, with stirring, into saturated aqueous sodium metabisulphite (100 cm^3). The organic layer was separated off, and the aqueous layer shaken with chloroform (3 × 80 cm^3). The combined organic layers were washed with water (2 × 250 cm^3) and dried over anhydrous magnesium sulphate. The residue was crystallised from ethylene glycol monomethyl ether. The yield of 4-bromo-4″-(3‴-methylbutyl)-*p*-terphenyl was 5.3 g (77.2%), mp 222–223° C.

4-Cyano-4″-(3‴-methylbutyl)-p-terphenyl.—The cyanation step was carried out in the normal way[1,2] and the crude product purified by column chromatography using a 1.5 : 1 mixture of chloroform hexane as eluent. Single-spot fractions were collected as normal and the solid residue was crystallised from ethylene glycol monomethyl ether. The yield was 43.6% (see Table I for the liquid crystal transition temperatures).

The structures of all the final products and reaction intermediates were confirmed by ^{1}H nmr and infra-red spectroscopy, and by mass spectrometry. These techniques, in conjunction with thin layer chromatography, also indicated the product purity. Gas-liquid chromatographic checks on purity were also applied to each branched-chain 4-alkyl- and 4-alkoxy-4′-cyanobiphenyl and 4-alkyl-4″-cyano-*p*-terphenyl; these were established as > 99% pure.

CONCLUSIONS

Branching the terminal alkyl chains of alkyl- and alkoxy-cyanobiphenyls and alkyl-cyano-*p*-terphenyls consistently depresses the nematic–isotropic transition temperatures of the compounds and leads to enhanced viscosities of their solutions in E7 at both 0 °C and 25 °C. Both effects show that steric factors connected with the conformational identity of the terminal chain are important.

Although the T_{N-I} values of the branched chain cyanobiphenyls are undesirably low, a number of the melting points are also quite low, and the preparation of these materials has established the behaviour of a new range of colourless, stable materials of strong positive dielectric anisotropy, high viscosity and latent nematic character.

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