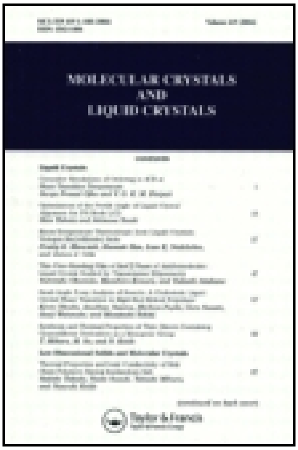

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Synthesis and Liquid Crystal Properties of Dimethylene Linked Compounds Incorporating the Cyclobutane or Spiro[3.3]heptane Rings

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To cite this article: L K. M. Chan , P. A. Gemmell , G. W. Gray , D. Lacey & K. J. Toyne (1989): Synthesis and Liquid Crystal Properties of Dimethylene Linked Compounds Incorporating the Cyclobutane or Spiro[3.3]heptane Rings, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 168:1, 229-245

To link to this article: http://dx.doi.org/10.1080/00268948908045974

Mol. Cryst. Liq. Cryst., 1989, Vol. 168, pp. 229–245
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Printed in the United States of America

Synthesis and Liquid Crystal Properties of Dimethylene Linked Compounds Incorporating the Cyclobutane or Spiro[3.3]heptane Rings

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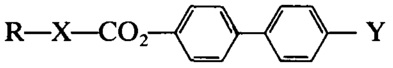
(Received July 10, 1988)

The preparation of sixteen dimethylene linked compounds is described [14 incorporating the cyclobutane ring and 2 incorporating the spiro[3.3]heptane ring], and a comparison is made between the transition temperatures of these compounds and those of the corresponding esters.[1] This comparison once again highlights the fact that the cyclobutane ring should be regarded, in terms of its ability to promote nematic thermal stability, as a "chain stiffener" rather than as a ring system.

A comparison is also made of the nematic thermal stabilities of the *trans*-cyclobutane and the spiro[3.3]heptane systems and of the *trans*-cyclohexane and the spiro[5.5]undecane systems.

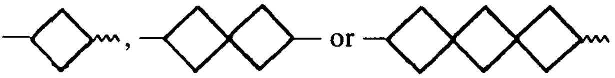
INTRODUCTION

One of the major conclusions drawn from our earlier work on the liquid crystalline properties of esters of general structure (I), incorporating the cyclobutane and related ring systems, was that the cyclobutane ring was a poor core component in promoting nematic thermal stability when compared with larger rings.[1] However, if the cyclobutane ring were viewed as part of an alkyl chain, then it is more effective in enhancing nematic thermal stability than a —$(CH_2)_3$— unit of a terminal alkyl chain and so it would be regarded as an alkyl "stiffener,"



(I)

where R = *n*-alkyl, H

X = 

Y = *n*-alkyl or CN.

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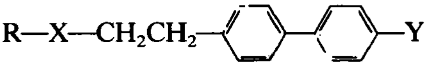
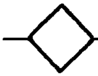
† Author to whom all correspondence is to be sent.

The low melting points and wide nematic ranges of the esters (I), either as the *trans*-isomer [(I) R = C_5H_{11}, X = —◇— and Y = CN; C–N 35.5°C, N–I 139.5°C] or as the isomeric mixture [(I), R = C_3H_7, X = —◇∿ and Y = CN; C–N 42.0°C, N–I 103.0°C], led to the possibility of producing interesting cyclobutane analogues of the commercially successful 4-*n*-alkyl-4'-cyanobiphenyls (CB) in which three carbons of the *n*-alkyl chain have been replaced either by a cyclobutane or by a spiro(3.3)heptane ring [see general structure (II)]. These new analogues of CBs would have the advantage of higher T_{N-I} values and wider nematic ranges,


(II)

where R = *n*-alkyl or H

X = , Y = C_3H_7, C_5H_{11} or CN

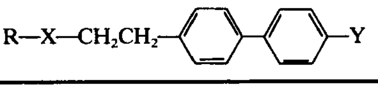
X = , Y = CN.

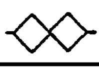
RESULTS AND DISCUSSION

Altogether 14 dimethylene linked compounds were prepared [12 incorporating the cyclobutane ring as *cis*/*trans* mixtures and 2 incorporating the spiro[3.3]heptane ring], and the transition temperatures for these are given in Table I.

TABLE I

Transition temperatures for the dimethylene linked compounds of structure (II).[a]


(II)

R	X	Y	Transition temperatures (°C) C–S_x, S_B, S_A, N, I	S_x–S_B	S_A–N	S_B–I	S_A–I	N–I
H	 *cis-/trans-*	CN	62.0	–	–	–	–	[16.5]
CH_3		CN	48.0	–	–	–	–	(39.0)
C_2H_5		CN	20.0	–	–	–	–	51.1
C_3H_7		CN	22.0	–	38.6	–	–	57.1
C_4H_9		CN	22.5	–	50.0	–	–	56.5
C_5H_{11}		CN	27.0	–	53.8	–	–	55.0
C_6H_{13}		CN	26.0	–	–	–	60.6	–
H		C_5H_{11}	49.0	–	–	–	–	–
CH_3		C_5H_{11}	56.5	–	–	–	–	–
C_4H_9		C_5H_{11}	30.0	41.5†	–	61.6	–	–
C_6H_{13}		C_5H_{11}	57.0	–	–	62.0	–	–
C_6H_{13}		C_3H_7	45.0	–	–	53.0	–	–
C_3H_7		CN	67.0	–	84.5	–	–	107.0
C_4H_9		CN	63.5	–	97.0	–	–	106.4

[a] [ ] Virtual value obtained from miscibility studies with E7; ( ) monotropic transition; †the S_x phase has not yet been classified.

Dimethylene linked compounds incorporating the cyclobutane ring

Like the cyclobutane esters,[1] these dimethylene linked compounds were also prepared by a non-stereospecific route (see Experimental Section for details) and they exist as mixtures of *cis*- and *trans*-isomers.

When the transition temperatures of the cyano-substituted, cyclobutyl compounds (II) (isomeric mixtures only) are compared to the transition temperatures of the corresponding cyclobutane esters,[1] it is seen that the dimethylene linked compounds have the lower mps (10–20°C) and T_{N-I} values (40–50°C) (except for the hexyl dimethylene linked homologue which is not nematogenic), and greater smectic tendencies than the corresponding cyclobutane esters.

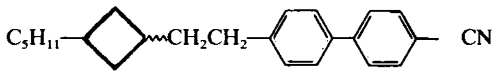
For the dialkyl homologues, this trend is continued with the dimethylene linked compounds again having lower mps and T_{S_B-I} values ($\simeq$ 20°C) than the corresponding cyclobutane esters (an additional unknown smectic phase is given by the butyl/pentyl dimethylene linked compound).

In order to allow a more valid comparison between the dimethylene linked compounds (II) and the cyclobutane esters,[1] it was important, at least for one of the dimethylene linked compounds, to obtain pure *cis*- and *trans*-isomers. Attempts to separate the *cis*- and *trans*-isomers of the pentyl homologue (see Experimental Section for details) were unsuccessful however, and only mixtures enriched in either the *cis*-isomer or the *trans*-isomer were obtained. The transition temperatures for these mixtures are given in Table II. Nevertheless, by plotting the transition temperatures given in Table II against mixture composition, and assuming fairly linear transition lines, the extrapolated transition temperatures for the pure *cis*- and *trans*-isomers were obtained (Figure 1).

The extrapolated values for the pentyl homologue of the *cis*- and *trans*-cyclobutane dimethylene linked compound are given in Table III, along with the transition temperatures for the corresponding *cis*- and *trans*-cyclobutane esters. As can be seen from results shown in Table III, the *cis*-isomers of both the cyclobutane ester and the dimethylene linked compound have lower mesophase thermal stabilities and are more predominantly smectic than the corresponding *trans*-isomers.

TABLE II

Transition temperatures and isomeric ratios for *cis*-/*trans*-mixtures of compounds (III).



(III)

Mixture[a]	C–S_A	Transition temperatures (°C) S_A–N	S_A–I	N–I	Ratio of *cis*-/*trans*-isomers
A	27.0	53.8	–	55.0	66:34
B	24.0	–	48.0	–	86:14
C	28.5	66.5	–	72.2	35:65
D	–	56.5	–	58.5	60:40

[a] A: Mixture obtained from the original synthesis (see Table I). B and C: Enriched isomeric mixtures obtained from reactions carried out on the corresponding precursor nitrile (see Experimental Section): D: Prepared from mixtures of B (50 wt %) and C (50 wt %).

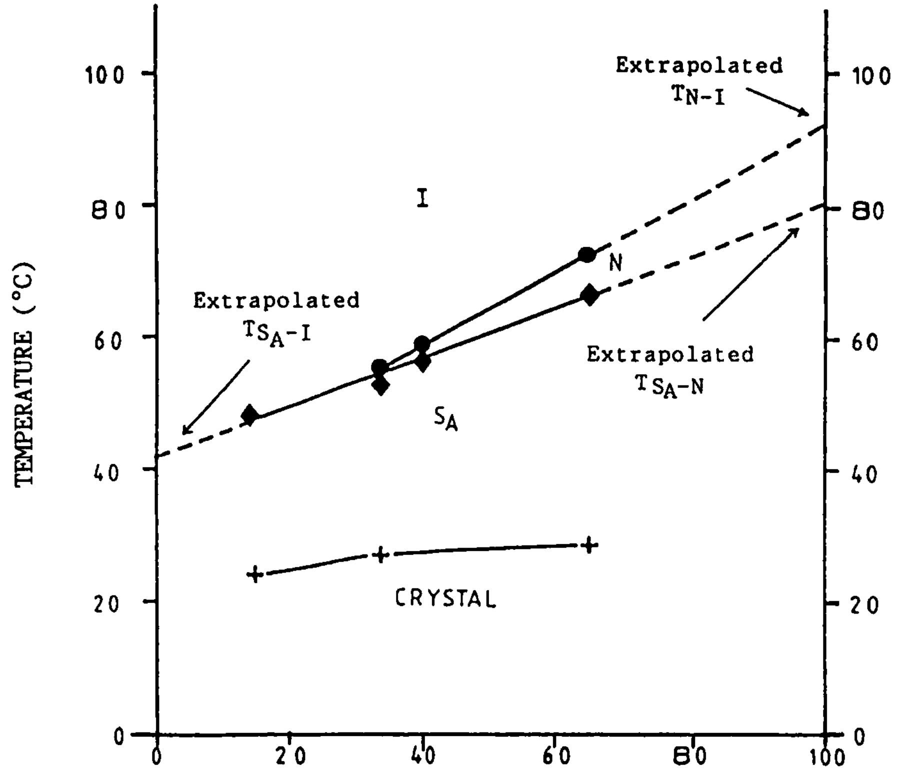
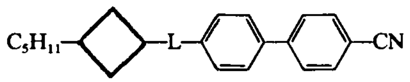


FIGURE 1 Plot of transition temperatures (°C) vs. *trans*-isomer composition (wt %) for *cis*-/*trans*-isomers of compounds (III). (●, N–I; ◆, S_A–N/I; +, mps).

It can also be seen that when the ester linkage is replaced by the dimethylene unit, the clearing points for both the *cis*- and the *trans*-isomers are decreased; in the former case, the decrease is 21.5°C and in the latter case the decrease is 48.5°C. The main reason for the lower mesophase thermal stability of the dimethylene bridged compound relative to that of the corresponding ester is that in the former,

TABLE III

Comparison of the transition temperatures for isomeric compounds of structure (IV).



(IV)

Isomer	L	Transition temperatures (°C) C–S_A/N	S_A–N	S_A–I	N–I
cis-	CO_2	40.0	47.5	–	63.5
cis-[a]	CH_2CH_2	–	–	42.0	–
trans-	CO_2	35.5	–	–	139.5
trans-[a]	CH_2CH_2	–	81.0	–	91.0

[a] The transition temperatures quoted for the *cis*- and *trans*-isomers were obtained from a diagram of state for the two isomers (see Figure 1).

the —CH_2CH_2— linkage unit does not contribute any π-conjugation toward that already present in the cyanobiphenyl core; in the latter case, however, the molecule now has an extension of its π-conjugation through the —CO_2— linkage.

A comparison of the transition temperatures for the *trans*-isomer of dimethylene linked compound (IV) with those for similar dimethylene linked compounds in which the cyclobutane ring has been replaced by other rings or by a —$(CH_2)_3$— unit (i.e., the cyanobiphenyls) is given in Table IV.

It can be clearly seen, not only from these results, but also from our results on the cyclobutane esters,[1] that the cyclobutane ring, when linked to a π-system by an ester group, or by a dimethylene group, is very poor at promoting nematic thermal stability compared with larger ring systems. This substantiates the idea developed in our earlier paper that a cyclobutane ring system is best regarded, in terms of its ability to support nematic thermal stability, as a "chain stiffener" rather than as a ring.

Dimethylene linked compounds incorporating the spiro[3.3]heptane system

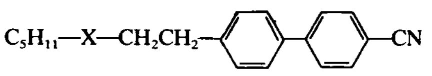
A comparison of the transition temperatures for the propyl and butyl homologues of the dimethylene linked compounds (VI) and their corresponding ester homologues is given in Table V.

The dimethylene linked compounds incorporating the spiro[3.3]heptane system again have lower nematic thermal stabilities (average decrease of 45.7°C), lower mps and greater smectic tendencies than the corresponding esters; indeed the situation is very similar to that found for the cyclobutane systems given in Table III.

Finally, it is interesting to note the effect on the thermal stability of the nematic phase of replacing a ring system with its spiro analogue. A comparison of the liquid

TABLE IV

Comparison of the transition temperatures for compounds of structure (V).



(V)

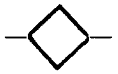
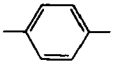
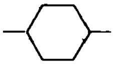
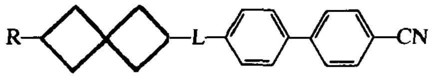
—X—	Transition temperatures (°C) C-S_A,N	S_A-N	S_A-I	N-I	Reference
trans 	-	81.0	-	91.0	
	60.0	-	-	136.0	2
trans 	79.0	86.0	-	184.0	2
—$(CH_2)_3$—	44.0	-	50.5	-	3

TABLE V

Comparison of the transition temperatures for compounds of structure (VI).



(VI)

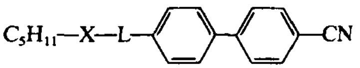
		Transition temperature (°C)		
R	L	$C-S_A,N$	S_A-N	N-I
C_3H_7	CO_2	82.0	-	154.7
C_3H_7	CH_2CH_2	67.0	84.5	107.0
C_4H_9	CO_2	78.2	-	150.1
C_4H_9	CH_2CH_2	63.7	97.0	106.4

crystal properties of mesogens incorporating the spiro[3.3]heptane, spiro[5.5] undecane,[5] *trans*-cyclobutane and *trans*-cyclohexane[4] units is given in Table VI.

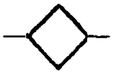
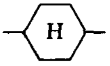
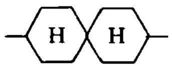
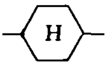
The results presented in Table VI show that the T_{N-I} value for the *trans*-cyclohexane ester is some 100°C higher than that for the *trans*-cyclobutane ester. However, when each of the two rings becomes part of a spiro-ring system, the situation

TABLE VI

Comparison of the transition temperatures for compounds of structure (VII).



(VII)

		Transition temperature (°C)		
—X—	—L—	$C-S_A,N$	S_A-N	N-I
trans- 	$-CO_2-$	35.5	-	139.5
racemic 		64.5	129.5	150.0
trans- 		85.2	-	240.8[4]
racemic 		87.0	163.0	178.0[5]
trans- 	$-CH_2CH_2-$	-	81.0[a]	91.0[a]
racemic  [b]		67.0	84.5	107.0
trans- 		79.0	86.0	184.0[3]

[a]These transition temperatures are extrapolated values (see Figure 1).
[b]The values for the spiro[3.3]heptane compound refer to the propyl homologue.

is different. Replacement of a *trans*-cyclobutane ring by spiro[3.3]heptane leads to an *increase* in the nematic thermal stability of the system, albeit quite small (10.5°C), whereas replacement of cyclohexane by spiro[5.5]undecane *decreases* the nematic thermal stability by a large amount, i.e., 62.8°C.

The reason for the differences in nematic thermal stabilities between the two ester series with monoalicycles and related spiro-ring systems can readily be understood on the basis of the different geometries of the molecule. Thus, despite the fact that the molecular length of the spiro[5.5]undecane is much greater than that of the cyclohexane system, the influence of the 90° twist between the planes of the bulky cyclohexane rings in the spiro-compounds appears to have the overriding effect in depressing the nematic thermal stability.

Although the spiro[3.3]heptane system makes a smaller contribution to the length of the molecule, it has a smaller volume of rotation. Thus, the 90° twist between the planes of the cyclobutane rings in the spiro[3.3]heptane has far less effect on the nematic thermal stability. The spiro[3.3]heptanes presumably have slightly higher T_{N-I} values than the corresponding cyclobutanes because the increased molecular length effect predominates over the molecular broadening effect.

This reasoning seems to apply to the dimethylene linked compounds when the cyclobutane ring is replaced by the spiro[3.3]heptane ring, although in this series of compounds there are no values available for dimethylene linked analogues corresponding to the esters containing the spiro[5.5]undecane ring.

EXPERIMENTAL

Physical measurements

All final products were shown to be pure by various standard techniques (tlc, glc, hplc). Structural confirmation for these products (and, where necessary, for any of the intermediates) was obtained by ^{1}H NMR spectroscopy (Jeol JNMPM × 60 spectrometer), infrared spectroscopy (Perkin-Elmer 457 grating spectrometer), and mass spectrometry (AEI MS902 mass spectrometer).

Transition temperatures were measured using a Mettler MP5 hot stage and control unit, in conjunction with an Olympus BPSP 753 polarizing microscope.

The differential scanning calorimetric measurements were carried out using a Perkin-Elmer DSC 2C with data station.

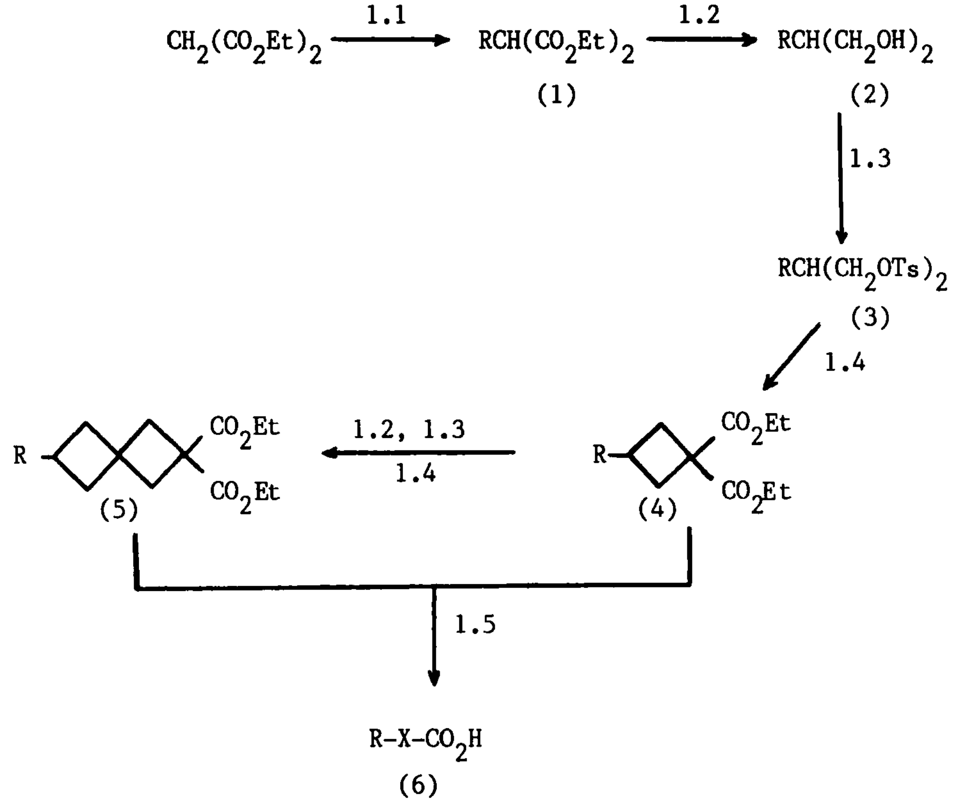
The compounds containing the cyclobutane ring are mixtures of *cis*- and *trans*-isomers. In this case, the purities (where given) relate to the isomeric mixtures. In one case [(13), R = C_5H_{11}, X = —◇—] enriched isomeric mixtures containing either the *cis*- or *trans*-isomer as the major component were obtained. The isomeric purity (%) was obtained by using ^{1}H NMR (400 MHz, University of Sheffield).

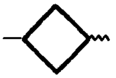
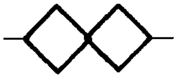
In the case of the spiro[3.3]heptanes, the purity (where given) relates to the racemic system and no attempt has been made to resolve these into their enantiomeric forms.

Materials

The reaction pathways used in the preparation of the dimethylene linked compounds of structure (II) are given in Schemes 1 and 2. Experimental details for the synthetic steps used in Scheme 1 can be found in Reference 1. Small-scale distillations were accomplished by using a modified sublimation apparatus in which a cup has been fitted to the lower end of the "cold-finger." This so-called "short-path" (SP) distillation apparatus is especially useful for handling small amounts of suitably volatile materials, ranging from 0.1 to 5 g. When this technique has been used to purify a compound, the symbol (SP) is inserted after the temperature and pressure, e.g., 60°C/0.5 mmHg (SP). The temperature here does not refer to the boiling point of the liquid, but to the temperature of the surrounding oil bath.

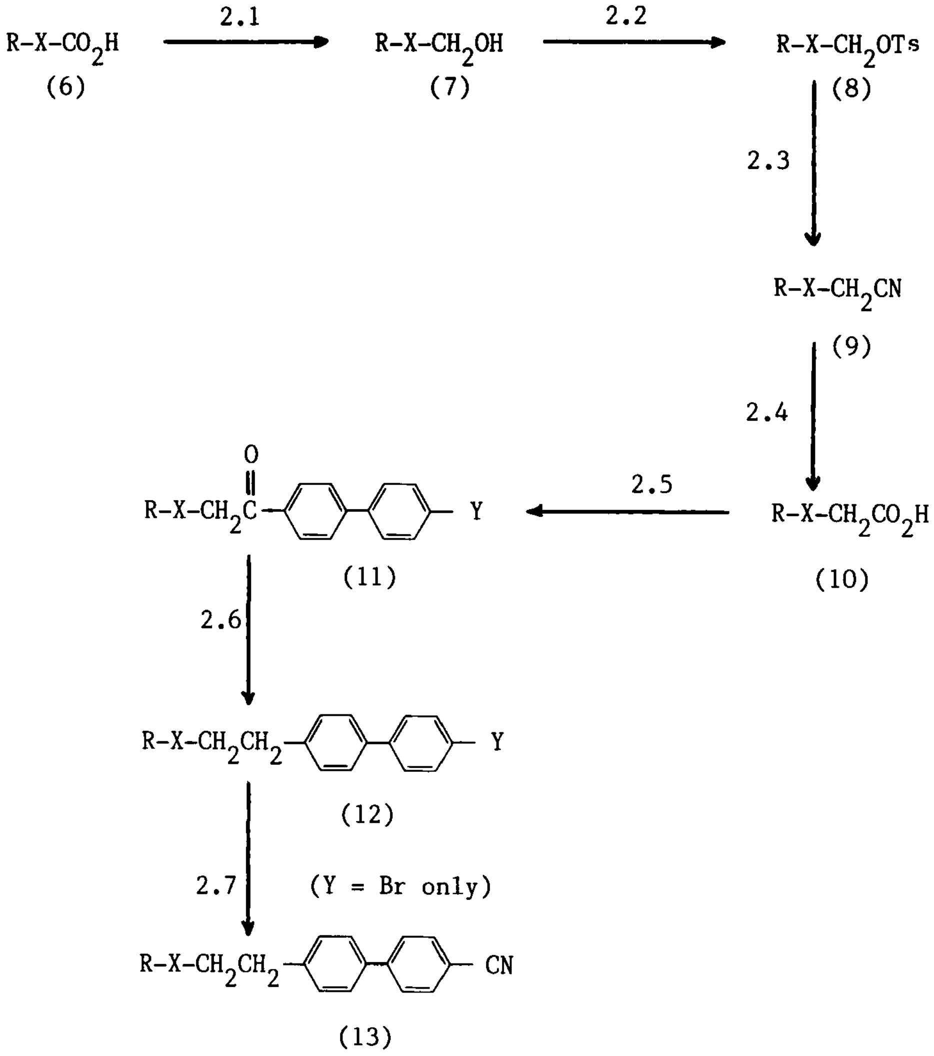
SCHEME 1 The experimental details for the synthetic steps 1.1 to 1.5 can be found in Reference 1.

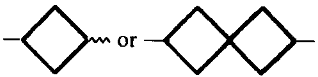


For compounds (6), —X— =  or 

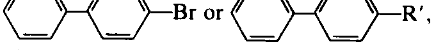
1.1 : *n*-RBr, NaOEt, EtOH.
1.2 : (i) $LiAlH_4$, Et_2O; (ii) dilute HCl.
1.3 : 4-Toluenesulphonyl chloride (TsCl), C_5H_5N.
1.4 : $CH_2(CO_2Et)_2$, NaH, dioxan.
1.5 : (i) KOH, EtOH, H_2O; (ii) H^+; (iii) heat (decarboxylation).

SCHEME 2



For compounds (6) to (13), --X— =  or

For compounds (11) and (12), —Y = —Br or *n*-alkyl (R').

2.1 : (i) $SOCl_2$; (ii) $LiAlH_4$, Et_2O.
2.2 : TsCl, C_5H_5N.
2.3 : NaCN, DMSO.
2.4 : (i) KOH, EtOH, H_2O; (ii) 18% w/v HCl.
2.5 : (i) $SOCl_2$; (ii) $AlCl_3$,  —Br or —R', $CHCl_2CHCl_2$.
2.6 : $NH_2NH_2.H_2O$, KOH, $(HOCH_2CH_2)_2O$.
2.7 : CuCN, N-methylpyrrolidin-2-one.

In the following text, whenever analytical hplc was used in checking the purity of a sample, the mobile phase employed was a mixture of methanol:water (80:20). The analytical hplc was carried out on a Whatman Partisil ODS II column.

*3-*n*-Alkylcyclobutyl- or 6-*n*-alkylspiro[3.3]hept-2-yl-methanols (7).* The appropriate compound (6a–i) (0.038 mol) was initially converted into the corresponding acid chloride by treatment with thionyl chloride. The acid chloride obtained was then dissolved in sodium-dried ether (40 cm^3) and added dropwise to a vigorously stirred mixture of lithium aluminum hydride (1.78 g, 0.047 mol) in sodium-dried ether (60 cm^3). After the addition, the reaction mixture was heated under reflux for 2 h. When cooled, the unreacted lithium aluminum hydride was destroyed by the dropwise addition of ethyl ethanoate (10 cm^3), followed by water (20 cm^3) and then 5% wt/vol hydrochloric acid solution (20 cm^3). The aqueous phase was shaken with ether (2 × 200 cm^3) and the combined extracts were washed with water (50 cm^3) and dried ($MgSO_4$). After removal of the solvent, the oily residue was distilled under reduced pressure to give the product (7) as a colorless liquid.

Results for compounds prepared are given in Table VII.

The IR data for these compounds are exemplified by the data given below for compounds (7e) and (7i).

For compound (7e): IR (neat) 3330 (broad), 2959, 2920, 2856, 1460, 1035, 1015 cm^{-1}.

For compound (7i): IR (neat) 3330 (broad), 2940, 2918, 2844, 1468, 1045, 1015 cm^{-1}.

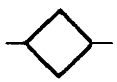
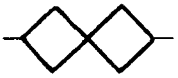
The purity of compounds (7) was >97% by glc.

*Tosylates of 3-*n*-alkylcyclobutyl- or 6-*n*-alkylspiro[3.3]hept-2-yl-methanols (8).* The tosylates (8a–i) were prepared by using compound (7) (0.030 mol) and 4-toluenesulphonyl chloride (6.30 g, 0.033 mol) in dry pyridine (15 cm^3). The crude products were used in the next stage of the synthesis without purification. Yields were in the range 85–95%.

TABLE VII

Yields (%) and bps for 3-*n*-alkylcyclobutyl- and 6-*n*-alkylspiro[3.3]hept-2-yl-methanols (7).

R—X—CH_2OH (7)

Compound no.	R	—X—	Yield (%)	bp (°C/mm Hg)
(7a)	H		74	51/20[a]
(7b)	CH_3		74	68/20 (SP)
(7c)	C_2H_5		84	100/20 (SP)
(7d)	C_3H_7		79	65/0.1
(7e)	C_4H_9		85	110/20
(7f)	C_5H_{11}		92	115/20
(7g)	C_6H_{13}		88	80/0.1 (SP)
(7h)	C_3H_7		82	110/1.0 (SP)
(7i)	C_4H_9		83	130/20 (SP)

[a]Lit[6] 85°C/30 mm Hg.

The IR data below for the tosylates of 3-*n*-butylcyclobutyl-(8e) and 6-*n*-butylspiro[3.3]hept-2-yl-methanol (8i) exemplify the two series.

For compound (8e): IR (neat) 2960, 2930, 2856, 1598, 1360, 1178, 955, 840, 815 cm^{-1}.

For compound (8i): IR (neat) 2958, 2920, 2844, 1600, 1365, 1180, 955, 830, 816 cm^{-1}.

3-n-Alkylcyclobutyl- or 6-n-alkylspiro[3.3]hept-2-yl-ethanonitriles (9). To a stirred solution of sodium cyanide (1.50 g, 0.030 mol) in sieve-dried dimethyl sulphoxide (25 cm^3) at 80°C was added, dropwise, a solution of the appropriate compound (8a–i) (0.0275 mol) in dry dimethyl sulphoxide (25 cm^3). The reaction mixture was then heated at 130°C for 1.5 h. When cooled, the reaction mixture was diluted with water (100 cm^3) and the nitrile extracted into ether (3 × 100 cm^3). The combined extracts were washed with water (100 cm^3) and dried ($MgSO_4$). After removal of the solvent, the residue was distilled under reduced pressure to give the nitrile (9) as a colorless pungent liquid.

Results for compounds (9a–i) prepared are given in Table VIII.

The purities of these nitriles were in all cases >97% (glc). The IR data for these compounds are exemplified by the results given below for compounds (9e) and (9i).

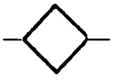
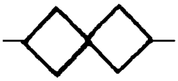
For compound (9e): IR (neat) 2960, 2928, 2858, 2243, 1460, 1423, 1280 cm^{-1}.

For compound (9i): IR (neat) 2960, 2935, 2842, 2244, 1468, 1422, 1282 cm^{-1}.

2-(3-n-Alkylcyclobutyl)- or 2-(6-n-Alkylspiro[3.3]hept-2-yl)-ethanoic acids (10). The appropriate compound (9a–i) (0.024 mol) was added to a solution of potassium hydroxide (6.7 g, 0.12 mol) in water (25 cm^3) and ethanol (50 cm^3), and the mixture was heated under reflux for 24 h. When cooled, the ethanol was removed by distillation under reduced pressure. Water (20 cm^3) was then added to the residue and while being cooled in an ice bath, the potassium salt was acidified with 18% wt/vol hydrochloric acid solution. The free carboxylic acid was extracted

TABLE VIII

Yields (%) and bps for 3-*n*-alkylcyclobutyl- and 6-*n*-alkylspiro[3.3]hept-2-yl-ethanonitriles (9).

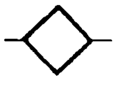
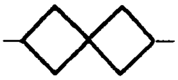
		$R—X—CH_2CN$ (9)		
(9a)	H		82	57/20[a]
(9b)	CH_3		80	68/20
(9c)	C_2H_5		80	85/20 (SP)
(9d)	C_3H_7		88	92/20 (SP)
(9e)	C_4H_9		89	56/0.2
(9f)	C_5H_{11}		89	124/20
(9g)	C_6H_{13}		87	140/20 (SP)
(9h)	C_3H_7		71	60/0.1 (SP)
(9i)	C_4H_9		85	75/0.1 (SP)

[a] Lit[6] 95–100°C/45 mm Hg.

TABLE IX

Yields (%) and bps for 2-(3-*n*-alkylcyclobutyl)- and 2-(6-*n*-alkylspiro[3.3]hept-2-yl)-ethanoic acids (10).

R—X—CH_2CO_2H (10)

Compound no.	R	—X—	Yield (%)	bp (°C/mm Hg)
(10a)	H		90	109/20
(10b)	CH_3		93	115/20
(10c)	C_2H_5		85	120/20 (SP)
(10d)	C_3H_7		89	65/0.01 (SP)
(10e)	C_4H_9		90	145/20 (SP)
(10f)	C_5H_{11}		88	116/20
(10g)	C_6H_{13}		88	105/0.2 (SP)
(10h)	C_3H_7		81	100/0.1 (SP)
(10i)	C_4H_9		71	90/0.1 (SP)

into ether (3 × 50 cm^3) and the combined extracts were washed with water (50 cm^3) and dried ($MgSO_4$). After removal of the solvent, the crude acid was distilled under reduced pressure to afford compounds (10a–i) as colorless liquids.

Results for compounds (10a–i) are given in Table IX.

The purities of these carboxylic acids were in all cases >98% (glc). The IR data below for the cyclobutane and spiroheptane compounds (10e and 10i) exemplify the two series.

For compound (10e): IR (neat) 2960, 2925, 2858 (broad), 2685, 1710, 940 cm^{-1}.

For compound (10i): IR (neat) 2958, 2920, 2844 (broad), 2630, 1710, 935 cm^{-1}.

*4-[(3-*n*-Alkylcyclobutyl)ethanoyl]- or 4-[(6-*n*-alkylspiro[3.3]hept-2-yl)ethanoyl]-4'-*n*-alkyl- or -4'-bromo-biphenyls (11).* The carboxylic acids (10a–i) (0.015 mol) were converted into the acid chlorides using an excess of thionyl chloride (5 cm^3) and by boiling the reaction mixture for 2 h with the exclusion of moisture. The unreacted thionyl chloride was then removed by distillation under reduced pressure, and the residual acid chloride was dissolved in sieve-dried 1,1,2,2-tetrachloroethane (10 cm^3).

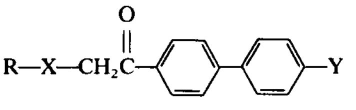
The solution of the acid chloride was added dropwise to a cooled, stirred mixture of finely powdered anhydrous aluminum chloride (0.016 mol) and the appropriate 4-bromobiphenyl or 4-*n*-alkylbiphenyl (0.015 mol) in sieve-dried 1,1,2,2-tetrachloroethane (30 cm^3). After the addition, the reaction mixture was stirred for 16 h at room temperature. Each crude product was purified by column chromatography on silica gel, using chloroform:petroleum fraction (bp 60–80°C) (1:1) as eluent. The appropriate fractions were collected and the product was crystallized from ethanol. The yields, mps, and transition temperatures for the compounds prepared are given in Table X.

The purities of the compounds (11a–n) prepared above were checked by hplc and shown to be >99.5%. The IR and ^1H NMR data for these compounds are exemplified by the data given below for compounds (11e), (11n) and (11h).

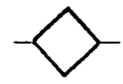
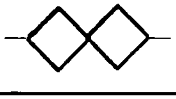
For compound (11e): IR (KCl) 2958, 2920, 2850, 1678, 1601, 1397, 805 cm^{-1};

TABLE X

Yields (%) and transition temperatures for 4-[(3-*n*-alkylcyclobutyl)ethanoyl]- and 4-[(6-*n*-alkylspiro[3.3]hept-2-yl)ethanoyl]-4′-*n*-alkyl- and 4′-bromo-biphenyls (11).



(11)

Compound no.	R	—X—	Y	Yield (%)	Transition temperatures (°C)				
					C-S/S_A/I	S_x-S_A	S_A-N	S_A-I	N-I
(11a)	H		Br	45	121	-	-	-	-
(11b)	CH_3		Br	63	97	-	-	-	-
(11c)	C_2H_5		Br	60	107	-	-	-	-
(11d)	C_3H_7		Br	59	99	-	φ[a]	-	φ
(11e)	C_4H_9		Br	58	84	-	(80)[a]	-	(82)
(11f)	C_5H_{11}		Br	64	92	-	-	(80)	-
(11g)	C_6H_{13}		Br	63	83	-	-	(74)	-
(11h)	H		C_5H_{11}	41	95	-	-	-	-
(11i)	CH_3		C_5H_{11}	40	99	-	-	-	-
(11j)	C_4H_9		C_5H_{11}	56	65	89.5	-	104	-
(11k)	C_6H_{13}		C_5H_{11}	55	49	83.5	-	99	-
(11l)	C_6H_{13}		C_3H_7	50	80.5	86.5	-	95	-
(11m)	C_3H_7		Br	56	116	-	(99)	-	(114)
(11n)	C_4H_9		Br	60	97	-	103	-	112.5

[a]φ, Not determined, strongly monotropic; ( ) monotropic transition. The S_x smectic phase has not been classified.

^{1}H NMR ($CDCl_3$) δ 0.70–1.64 (10 H,m), 1.70–3.00 (5 H,m), 3.00–3.40 (2 H,m), 7.20–8.50 (8 H,m).

For compound (11n): IR (KCl) 2956, 2918, 2842, 1682, 1602, 1390, 808 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.70–2.94 (19 H,m), 2.94–3.20 (2 H,d), 7.04–8.18 (8 H,m).

For compound (11h): IR (KCl) 2958, 2920, 2850, 1677, 1600, 1398, 806 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.72–1.08 (3 H,m), 1.08–2.86 (15 H,m), 2.86–3.20 (2 H,m), 7.08–8.12 (8 H,m).

*1-(3-*n*-Alkylcyclobutyl)- or 1-(6-*n*-alkylspiro[3.3]hept-2-yl)-2-(4′-*n*-alkylbiphenyl-4-yl)- or 2-(4′-bromobiphenyl-4-yl)-ethanes (12).* The appropriate compound (11) (0.0070 mol) was added to a stirred mixture of diethylene glycol (50 cm^3), hydrazine hydrate (1.75 g, 0.035 mol) and potassium hydroxide (0.98 g, 0.0175 mol). The reaction mixture was then heated at 130°C for 2 h. The excess of hydrazine hydrate and water formed in the reaction were distilled off and the temperature of the reaction mixture was raised and then maintained at 180°C for 4 h. On being cooled to room temperature, the mixture was poured into water (100 cm^3) and the product was extracted into ether (3 × 100 cm^3). The combined ether extracts were washed with water (100 cm^3) and dried ($MgSO_4$). After removal of the solvent, the residue was purified by column chromatography on silica gel, using chloroform:petroleum fraction (bp 60–80°C) (1:5) as eluent. The appropriate fractions were concentrated and the product was crystallized from ethanol. The yields, mps and transition temperatures are given in Table XI. The purity of compounds (12) was checked by hplc and shown to be >99.5%. These compounds are exemplified by the data given below for compounds (12e), (12i) and (12j).

For compound (12e): IR (KCl) 2956, 2918, 2850, 1607, 1587, 1480, 810 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.70–2.36 (17 H,m), 2.40–2.76 (2 H,t), 7.10–7.72 (8 H,m).

For compound (12i): IR (KCl) 2940, 2910, 2840, 1605, 1587, 1482, 808 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.68–2.33 (21 H,m), 2.33–2.67 (2 H,t), 6.77–7.67 (8 H,m).

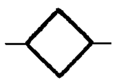
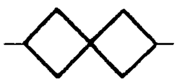
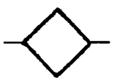
For compound (12j): IR (KCl) 2958, 2920, 2850, 1500, 809, 798 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.80–2.36 (18 H,m), 2.40–2.90 (4 H,m), 7.08–7.64 (8 H,m).

*1-(3-*n*-Alkylcyclobutyl)- or 1-(6-*n*-alkylspiro[3.3]hept-2-yl)-2-(4′-cyanobiphenyl-4-yl)ethanes (13).* A stirred mixture of the appropriate compound (12, Y = Br) (0.0050 mol), anhydrous copper(I)cyanide (0.90 g, 0.010 mol) and redistilled *N*-methylpyrrolidin-2-one (35 cm^3) was heated at about 200°C for 6 h. On being cooled, the dark reaction mixture was poured onto a mixture of hydrated iron(III)chloride (1.7 g), concentrated hydrochloric acid (0.6 cm^3), and water (25 cm^3) and the resultant mixture was stirred at 60–70°C for 20 min. The organic material was then extracted into chloroform (3 × 50 cm^3) and the combined chloroform extracts were washed successively with cold dilute hydrochloric acid (50 cm^3), water (50 cm^3), 10% wt/vol sodium hydroxide solution (30 cm^3), and water (50 cm^3), and finally dried (MgSO$_4$).

TABLE XI

Yields (%) and transition temperatures for 1-(3-*n*-alkylcyclobutyl)- or 1-(6-*n*-alkylspiro[3.3]hept-2-yl)-2-(4′-*n*-alkylbiphenyl-4-yl)- or 2-(4′-bromobiphenyl-4-yl)-ethanes (12).

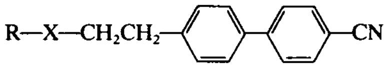
(12)

Compound no.	R	—X—	Y	Yield (%)	Transition temperatures (°C)		
					C–S$_x$,S$_B$,I	S$_x$–S$_B$	S$_B$–I
(12a)	H		Br	87	101	–	–
(12b)	CH$_3$		Br	67	102	–	–
(12c)	C$_2$H$_5$		Br	75	101	–	(99)
(12d)	C$_3$H$_7$		Br	79	97	–	98
(12e)	C$_4$H$_9$		Br	84	96.5	–	97
(12f)	C$_5$H$_{11}$		Br	80	94	–	95
(12g)	C$_6$H$_{13}$		Br	82	91	–	92.5
(12h)	C$_3$H$_7$		Br	76	100	–	101.5
(12i)	C$_4$H$_9$		Br	80	98	–	99
(12j)	H		C$_5$H$_{11}$	77	49	–	–
(12k)	CH$_3$		C$_5$H$_{11}$	60	56.5	–	–
(12l)	C$_4$H$_9$		C$_5$H$_{11}$	59	30	41.5[a]	61.6
(12m)	C$_6$H$_{13}$		C$_5$H$_{11}$	67	57	–	62
(12n)	C$_6$H$_{13}$		C$_3$H$_7$	66	45	–	53

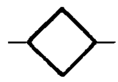
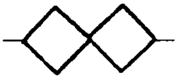
[a] The S$_x$ phase has not yet been classified; ( ) monotropic transition.

TABLE XII

Yields (%) and bps or solvents for crystallization for 1-(3-*n*-alkylcyclobutyl)- or 1-(6-*n*-alkylspiro[3.3]hept-2-yl)-2-(4′-cyanobiphenyl-4-yl)ethanes (13).



(13)

Compound no.	R	—X—	Yield (%)	bp (°C)/Solvent (crystallization)
(13a)	H		64	MeOH
(13b)	CH_3		55	Hexane (− 15°C)
(13c)	C_2H_5		59	185/0.01 mm Hg (SP)
(13d)	C_3H_7		60	170/0.01 mm Hg (SP)
(13e)	C_4H_9		65	165/0.01 mm Hg (SP)
(13f)	C_5H_{11}		60	Propan-2-ol (− 78°C)
(13g)	C_6H_{13}		57	Hexane (− 78°C)
(13h)	C_3H_7		40	Ethanol (0°C)
(13i)	C_4H_9		34	Ethanol (0°C)

After removal of the solvent, the residue was purified by column chromatography on silica gel using chloroform:petroleum fraction (bp 60–80°C) (1:1) as eluent. The appropriate fractions were collected and distilled under reduced pressure or crystallized from a suitable solvent to give products (13). The yields, bps or solvents for crystallization for these compounds are given in Table XII, and the transition temperatures are given in Table I.

The purities of the compounds (13a–i), prepared by the above procedure, were shown (by hplc) to be >99.8%. The IR and ^{1}H NMR data for these compounds are exemplified by the results given below for compounds (13e) and (13i).

For compound (13e): IR (KCl) 2958, 2920, 2850, 2224, 1607, 1494, 818 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.70–1.44 (10 H,m), 1.44–2.38 (7 H,m), 2.42–2.78 (2 H,t), 7.12–7.76 (8 H,m).

For compound (13i): IR (KCl) 2958, 2918, 2840, 2226, 1604, 1495, 818 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.77–1.02 (3 H,t), 1.02–1.38 (6 H,m), 1.38–2.33 (12 H,m), 2.40–2.70 (2 H,t), 7.13–7.83 (8 H,m).

Attempted separation of cis- *and* trans-*isomers of 1-(4′-cyanobiphenyl-4-yl)-2-(3-*n-*pentylcyclobutyl)ethane (13f).* A number of attempts were initially made to isolate the pure *cis*- and *trans*-isomers of compound (13f) using a Gilson Autoprep hplc system in a similar way to that described for the separation of the *cis*-/*trans*-cyclobutane esters.[1] However, in this particular case, no separation was achieved.

From analytical glc on the precursor nitrile, (9) it seemed that it might be possible to separate this isomeric mixture into the component isomers. This would then enable the synthesis to proceed further to the preparation of the pure *cis*- and *trans*-ethanes (13) by using the latter part of Scheme 2.

However, only partial separation of the isomeric nitriles (9) was achieved using

TABLE XIII

The transition temperatures and isomeric purity (%) for enriched samples of compounds (11f), (12f), and (13f).

Compound no.		Transition temperatures (°C)						Isomeric purity (%)	
		C–S_B/S_A/I	S_C–S_A	S_A–N	S_B–I	S_A–I	N–I	*cis-*	*trans-*
(11f)	Component A[a]	91.0	–	–	–	(79.0)	–	85	15
	Component B	80.0	(61.0)[b]	87.0	–	–	89.0	32	68
(12f)	Component A	93.0	–	–	93.5	–	–	major *cis*-isomer[c]	
	Component B	95.5	–	–	96.5	–	–	major *trans*-isomer[c]	
(13f)	Component A[a]	24.0	–	–	–	48.0	–	86	14
	Component B	28.5	–	66.5	–	–	72.2	35	65

[a] The major isomeric component (A or B) of each of the isomeric systems [i.e., compounds (11f), (12f), and (13f)] was the same within a few percent as that of the enriched material used in the synthesis.

[b] ( ) Monotropic transition.

[c] Based on the results for compounds (11f) and (13f).

preparative glc [20 ft (30% polypropylene glycol on a 30/45 mesh Chromosorb P) column at 165°C at 250 cm³/min (N_2)].

The analytical results for the enriched isomeric mixtures (analytical glc) and the yields of each of the partially separated isomers (9) are given below (Table XIV).

Results for the mps and transition temperatures of the compounds prepared from partially separated mixtures of compound (9) and for their isomeric purities are given in Table XIII above.

TABLE XIV

(9f)

	Isomeric purity (%)		
	cis-	*trans-*	Yield[b]
Component A:			
cis-isomer[a] (retention time, 10 min)	88	12	0.46 g (30%)
Component B:			
trans-isomer[a] (retention time, 11 min)	32	68	0.42 g (28%)

[a] Identification of the *cis*- and *trans*-isomers of the starting material (9f) was based on spectroscopic evidence obtained for the final reaction product (13f).

[b] A total of 3.0 g of the isomeric nitriles (9f) was used, employing approximately 0.2 g samples for each separation.

ACKNOWLEDGMENTS

This paper is published by permission of the Director, HMSO, and the authors thank the UK Ministry of Defence for financial support (LKMC). They also thank BDH Limited, Poole, Dorset, UK, for supplying 4-bromo-, 4-propyl- and 4-pentyl-biphenyls under a MOD contract.

The authors are also grateful to Dr. I. Pickering and Dr. D. F. Ewing, of this department, for their most valuable assistance in preparative glc and the interpretation of the 400 MHz ^{1}H NMR spectra, respectively.

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