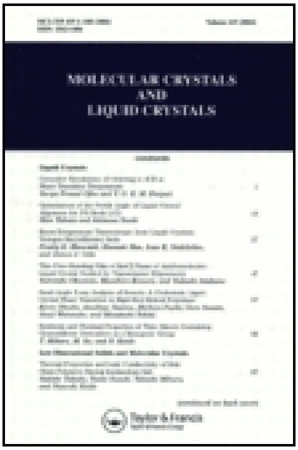


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

Synthesis of Isocyano and (Haloalkynyl)Biphenyls: New Thermotropic Liquid Crystals

A. L. Bailey [a] & Gordon S. Bates [b]

[a] Dow Chemical Canada Inc., Modeland Rd, Sarnia, ON, Canada, N7T 7K7

[b] Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC, Canada, V6T 1Y6

Version of record first published: 24 Sep 2006.

To cite this article: A. L. Bailey & Gordon S. Bates (1991): Synthesis of Isocyano and (Haloalkynyl)Biphenyls: New Thermotropic Liquid Crystals, Molecular Crystals and Liquid Crystals, 198:1, 417-428

To link to this article: http://dx.doi.org/10.1080/00268949108033417

Mol. Cryst. Liq. Cryst., 1991, Vol. 198, pp. 417–428
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Synthesis of Isocyano and (Haloalkynyl)Biphenyls: New Thermotropic Liquid Crystals

A. L. BAILEY†

†Dow Chemical Canada Inc., Modeland Rd, Sarnia, ON, Canada, N7T 7K7

and

GORDON S. BATES‡,[1]

‡Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC, Canada, V6T 1Y6

(Received August 20, 1990)

4-*n*-Alkyl-4′-cyanobiphenyls (**1**) have achieved widespread application as stable thermotropic liquid crystals with mesophases at room temperature. The importance of the cyano functional group in the liquid-crystalline behaviour of these compounds is not clearly defined. By modifying this functional group with minimal changes in molecular geometry, we have found two new classes of mesomorphs. 4-*n*-Alkyl-4′-isocyanobiphenyls (**2**) and 4-*n*-alkyl-4′-(haloalkynyl)biphenyls (**3**). The synthesis of these compounds is described. Compound **2a** (R = *n*-butyl) is non-mesomorphic, whereas compound **2b** (R = *n*-pentyl) is a virtual liquid crystal melting at 34–5°C and supercooling to a nematic phase at 30°C, and **2c** (R = *n*-hexyl) is a nematic liquid crystal from 9 to 19°C. Compounds of structure **3** (R = *n*-pentyl, X = $Si(CH_3)_3$, H, CH_3, Cl) are not liquid crystals. The corresponding bromo- and iodoalkynes (**3**, R = *n*-pentyl, *S* = Br, I) are liquid crystals with mesomorphic ranges of 88–108°C and 110–119°C, respectively.

Keywords: thermotropics, synthesis, isocyanides, biphenyl, haloalkynes

INTRODUCTION

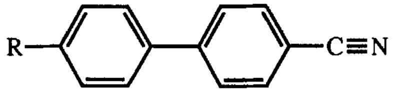
The discovery of room-temperature nematic liquid crystals in the early 1970's was fundamental to the advancement of technological applications of liquid crystals. Since that time, the tremendous increase in the use of these materials for electronic displays has been the most obvious and perhaps the most commercially important result of this discovery. From a chemical perspective, the effect of these developments has been a widespread interest in the nature of the liquid-crystalline phenomenon at the molecular level. The physical interactions between liquid crystal

---

[1] Author to whom correspondence should be addressed.

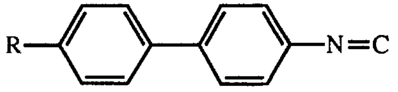
molecules and the molecular components responsible for these interactions are not well understood.

The 4-*n*-alkyl-4′-cyanobiphenyls (**1**), prepared in 1974,[1] were the first mesogenes to be discovered with such short molecular lengths and low molecular weights. Since their discovery, little work has been published on modification of the simple biphenyl system to determine the role or importance of the cyano group's contribution to the liquid-crystalline behaviour of these compounds. Of note are Gray's work on nitro compounds,[1] and an extensive study by Dabrowski and Zytynski.[2] In neither case was the room-temperature nematic behaviour of the cyanobiphenyls simulated by other functional groups. In the present study, the concept of replacing the cyano group with minimal changes in molecular geometry led to two classes of target compounds, isocyanides **2** and haloalkynes **3**. The synthesis of these compounds and their properties are discussed below.

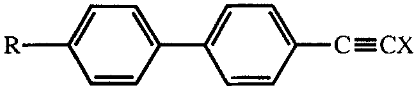


R = *n*-alkyl

1



2

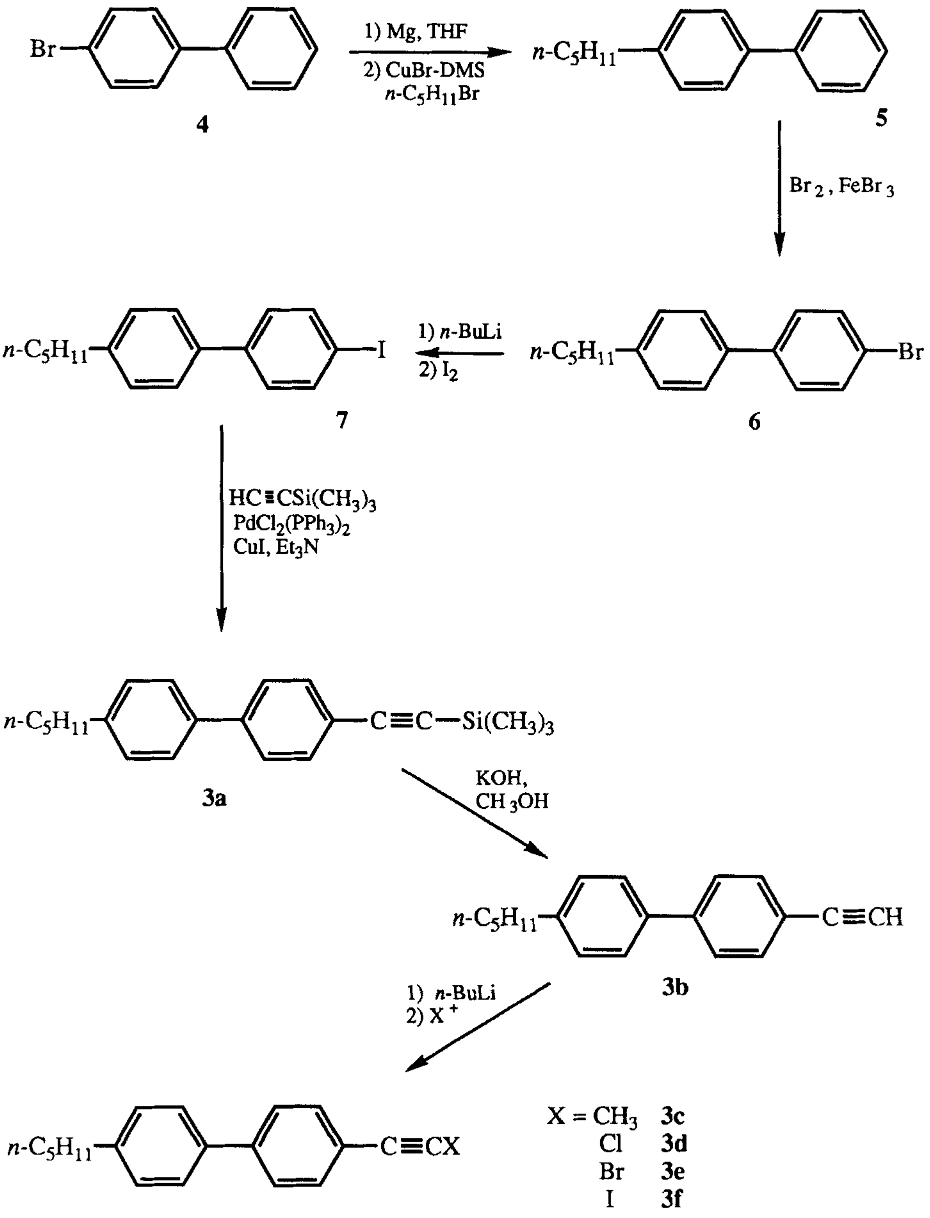


3

RESULTS AND DISCUSSION

The 4-*n*-alkyl-4′-(haloalkynyl-biphenyls (**3a–f**) were prepared from 4-bromobiphenyl (**4**) as depicted in Scheme 1. A Grignard coupling with 1-bromopentane, *para*-bromination of the unsubstituted aromatic ring, and transhalogenation to the iodide (**7**) were achieved with an overall yield of 52%. Compound **7** was then conveniently coupled with ethynyltrimethylsilane by a reaction involving *in situ* generation of Pd(0) catalyst as described by Sonogashira *et al.*[3] With copper(I) iodide as a co-catalyst, this reaction proceeds at room temperature and provides an efficient alternative to organozinc reactions for alkynyl-aryl coupling. The yield from this reaction was 81%. The trimethylsilyl group of **3a** was removed with methanolic potassium hydroxide to give the terminal alkyne (**3b**). Substitutions of the alkyne by deprotonation with *n*-butyllithium and reaction of the resulting anion with methyl benzenesulphonate, *N*-chlorosuccinimide, *N*-bromosuccinimide, or iodine gave the (haloalkynyl)biphenyls **3c–f**.

The melting behaviours of these compounds are summarized in Table I. Compounds **3a–d** have only crystal-isotropic transitions with no evidence of mesomorphism. The bromo- and iodoalkynes (**3e, f**) have liquid crystal phases at 88–108°C and 110–119°C, respectively. At these elevated temperatures, the haloalkyne functionality is reactive, and the compounds gradually turn yellow, orange, and

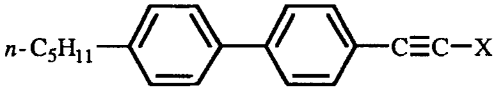


SCHEME 1 Synthesis of 4-alkyl-4′-(haloalkynyl)biphenyls **3a–f**

eventually brown. In spite of this instability, the observed mesophases indicate that the alkyne moiety will support mesomorphism in the biphenyl system when substituted with an appropriately polar group. Substitution of the alkyne with other small, polar groups which maintain an overall linear structure may give stable nematic liquid crystals.

TABLE I

Melting behaviour of 4-alkyl-4'-(haloalkynyl)biphenyls **3a–f**



Compound	X	Melting range / °C
3a	-Si(CH$_3$)$_3$	85-86
3b	H	79-80
3c	CH$_3$	82-83
3d	Cl	115-116
3e	Br	88-108*
3f	I	110-119*

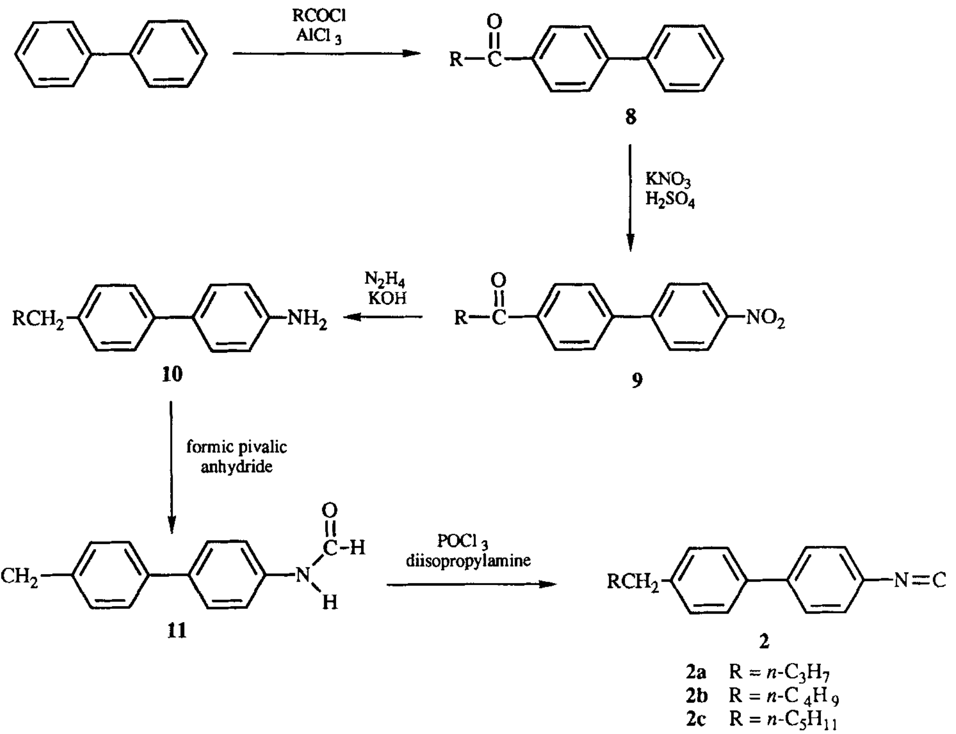
* Mesomorphic compound.

The synthesis of the 4-*n*-alkyl-4'-isocyanobiphenyls was attempted by two routes.* The preferred route to these compounds, illustrated in Scheme 2, involved the acylation of biphenyl, nitration of the unsubstituted ring, simultaneous reduction of the ketone and the nitro group by the Huang-Minlon modification of the Wolff-Kishner reduction to give the amine **10**, formylation with formic pivalic anhydride, and dehydration with phosphoroyl chloride and diisopropylamine to yield the isocyanobiphenyls **2**.

Isocyanobiphenyls with three different alkyl chain lengths were synthesized by this method. The *n*-butyl compound (**2a**) exhibits a crystal-isotropic transition at 36°C with no evidence of a liquid crystal phase. While the *n*-pentyl compound (**2b**) also melts sharply to an isotropic phase at 34°C, the melt supercools to a nematic phase at 30°C and remains nematic at room temperature for several hours. The *n*-hexyl derivative (**2c**) is a true nematic liquid crystal between 9 and 19°C. Unfortunately, the isocyanobiphenyls are also unstable. When exposed to the air they decompose to brown tars. In the absence of air, the solid materials and dilute dichloromethane solutions are relatively stable, but the liquid phases develop a blue-green colour indicative of arylisocyanide tetramerisation.[5] Nevertheless, the mesogenic properties of these compounds make them interesting candidates for metal-centered complexes in which the isocyano functional group may be stabilised. The formation of discotic mesophases in such complexes is a potential application.

---

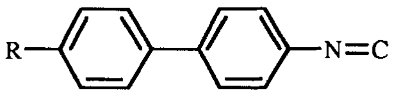
* The first and less successful route began with carboxylation of the Grignard reagent derived from 4-*n*-alkyl-4'-bromobiphenyl (**6**). Conversion to the acyl azide via the acid chloride and subsequent Curtius rearrangement yielded the corresponding isocyanate in an overall yield of 80% from **6**. However, reduction of the isocyanate using trichlorosilane and triethylamine[4] gave an unexpectedly complex mixture of products from which the isocyanides **2** could not easily be isolated.



SCHEME 2 Synthesis of 4-alkyl-4′-isocyanobiphenyls **2a–c**

TABLE II

Melting behaviour of 4-alkyl-4′-isocyanobiphenyls **2a–c**



R	Compound	Melting range / °C
n-C_4H_9	**2a**	36-37
n-C_5H_{11}	**2b**	34-35†
n-C_6H_{13}	**2c**	9-19*

* Mesomorphic compound.

† Supercools to nematic at room temperature and clears with warming, T_{NI} = 30°C.

CONCLUSIONS

Both the isocyanobiphenyls and haloalkynylbiphenyls have been found to exhibit liquid-crystalline behaviour. These compounds are closely related to the cyanobiphenyl series, differing only in the nature of the polar functional group. While the polarity of the functional group obviously plays an important role in determining the existence of mesomorphism in the biphenyl system, the magnitude and direction of the dipole seem to be less relevant than simply the presence of an appropriately polar group.

EXPERIMENTAL

All air-sensitive manipulations were carried out under an atmosphere of dry nitrogen. For reactions requiring anhydrous conditions, glassware was oven-dried overnight. Stirring was achieved by teflon-coated magnetic stirring bars. Cold temperature baths used were as follows: −24°C, carbon tetrachloride/dry ice; −78°C, acetone/dry ice.

Anhydrous tetrahydrofuran was obtained by distillation over sodium and benzophenone, methanol for recrystallisations was dried over Linde 3Å molecular sieves, and dichloromethane was dried by passing through a column of alumina. All reaction and extraction solvents were distilled prior to use. The low-boiling (35–60°C) fraction of petroleum ether was used. Practical grade 4-bromobiphenyl (90%) was purchased from Aldrich Chemical Company and was not purified before use. Ethynyltrimethylsilane was prepared by the method of Westmijze and Vermeer.[6] Copper(I) bromide dimethylsulphide complex was prepared according to House *et al.*[7] Hexane solutions of *n*-butyllithium were purchased from Aldrich and were standardized by titration against diphenylacetic acid. Pivaloyl chloride, phosphoroyl chloride, diisopropylamine, and the straight-chain acid chlorides were all distilled prior to use. All other reagents were commercially available and were used without further purification.

Melting points (m.p.) were determined with a Gallenkamp capillary melting point apparatus and are uncorrected. Apparent mesomorphic transitions are expressed as wide melting ranges.

Infrared (IR) spectra were recorded as solutions in special grade chloroform, unless otherwise specified, using a Perkin-Elmer 1710 Fourier Transform spectrophotometer. Prominent signals are reported with units of cm^{-1}. Proton magnetic resonance (^1H-NMR) spectra were recorded on a Varian XL-300 spectrometer. Unless otherwise specified, samples were dissolved in deuteriochloroform, and chemical shifts were determined relative to internal tetramethylsilane. The signals are reported as chemical shifts (δ) in parts per million, followed by multiplicity and relative peak integration in parentheses: s = singlet, d = doublet, t = triplet, m = multiplet. Low and high-resolution electron impact mass spectral analyses were performed on a Kratos MS-50 mass spectrometer. The mass to charge ratio (m/z) of the molecular ions (M^+) and the base peaks are reported with their relative intensities. The measured exact masses are also compared to calculated values.

Thin-layer chromatography (TLC) was performed on Merck silica gel 60 F_{254} pre-coated aluminum sheets. Visualization was achieved by irradiation with ultraviolet light. Column chromatography was carried out on Merck flash silica, 230–400 mesh, unless otherwise specified. Gas chromatographic (GC) analysis was performed on a Hewlett-Packard 5830A chromatograph with a 1.8 m × 3 mm column packed with 3% OV-17.

4-n-Pentylbiphenyl (**5**). A mixture of 4-bromobiphenyl **4** (3.5 g, 15 mmol) and magnesium turnings (0.36 g, 15 mmol) in 20 mL of tetrahydrofuran was refluxed for 90 minutes to give the Grignard reagent indicated by a golden colour and the disappearance of the metal. Copper(I) bromide dimethylsulphide complex (0.3 g, 1.5 mmol) was added at 0°C to give a bright yellow-green mixture. Addition of 1-bromopentane (2.0 mL, 16 mmol) and heating to reflux produced a dark green solution which slowly turned turbid. Refluxing was continued for 20 hours resulting in a grey and purple mixture. The solvent was removed by rotary evaporation and 100 mL of petroleum ether was used to extract the hydrocarbon. The mixture was filtered through a short plug of silica gel which was then washed with a further 100 mL of petroleum ether. Removal of the solvent and column chromatography using petroleum ether as eluant yielded 3.2 g (95%) of colourless, liquid product. GC analysis showed the presence of the original 10% biphenyl impurity. No purification or further analysis was carried out before the next step in the synthesis.

4-Bromo-4'-n-pentylbiphenyl (**6**). 4-*n*-Pentylbiphenyl **5** (9.0 g, 40 mmol), 0.2 g of iron filings, and 50 mL of 1 M bromine solution in carbon tetrachloride were stirred for 1.5 hours. Concentrated aqueous $NaHSO_3$ was added to quench the excess bromine, and the mixture was filtered. The organic phase was washed with 2 × 50 mL of water and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure to yield 12.3 g of a crude yellow product. Recrystallisation from 100 mL of methanol gave 8.4 g (69%) of white crystals of the biphenyl **6**: m.p. 94–95°C (lit. 95°C[2]); ^{1}H-NMR δ 7.54 (d, 2H), 7.47 (d, 2H), 7.43 (d, 2H), 7.24 (d, 2H), 2.64 (t, 2H), 1.65 (m, 2H), 1.36 (m, 4H), 0.90 (t, 3H); and IR 3012, 2931, 1484 cm^{-1}.

4-Iodo-4'-n-pentylbiphenyl (**7**). To a solution of 4-bromo-4'-*n*-pentylbiphenyl **6** (3.0 g, 10 mmol) in 50 mL of tetrahydrofuran at −78°C was added *n*-butyllithium (6.6 mL 1.5 M in hexane, 10 mmol) giving a pale yellow solution, which turned turbid after a few minutes. After 30 minutes of stirring, iodine crystals (2.51 g, 10 mmol) were added, and the mixture was left, slowly warming overnight. The solvent was removed from the clear yellow solution by rotary evaporation, and the residue was extracted with 50 mL of petroleum ether and filtered. Washing with 50 mL of water, drying over anhydrous $MgSO_4$, and removal of the solvent gave 3.9 g of a crude, off-white product. Recrystallisation from methanol yielded 2.8 g (80%) of white crystals: m.p. 111–112°C (lit. 112°C[2]); ^{1}H-NMR δ 7.75 (d, 2H), 7.47 (d, 2H), 7.32 (d, 2H), 7.24 (d, 2H), 2.64 (t, 2H), 1.65 (m, 2H), 1.36 (m, 4H), 0.90 (t, 3H); and IR 3012, 2931, 1484 cm^{-1}.

4-n-Pentyl-4'-(2-trimethylsilyl)ethynylbiphenyl (**3a**). 4-Iodo-4'-*n*-pentylbiphenyl **7** (1.0 g, 2.85 mmol), ethynyltrimethylsilane[6] (4.0 mL 0.85 M in tetrahydrofuran, 3.4 mmol), triphenylphosphine (0.16 g, 0.6 mmol), palladium dichloride (0.05 g, 0.3 mmol), triethylamine (3 mL), and copper(I) iodide (0.03 g, 0.15 mmol) were combined and stirred at room temperature. After five minutes, a black mixture formed, and stirring was continued for a further 15 minutes. Removal of the volatiles followed by extraction with 50 mL of petroleum ether, filtering, washing with 50 mL of water, drying over anhydrous $MgSO_4$, and removal of the solvent gave 1.02 g of a light brown product. Column chromatography with petroleum ether as eluant yielded 0.74 g (81%) of white crystals: m.p. 85–86°C; ^{1}H-NMR δ 7.53 (s, 4H), 7.49 (d, 2H), 7.24 (d, 2H), 2.63 (t, 2H), 1.65 (m, 2H), 1.35 (m, 4H), 0.90 (t, 3H), 0.25 (s, 9H); IR 3011, 2960, 2931, 2155 (strong, sharp), 1494 cm^{-1}; and MS m/z 320 (89.5, M+), 305 (100, M^+-CH_3), exact mass measured 320.1962 (calc'd 320.1960).

4-Ethynyl-4'-n-pentylbiphenyl (**3b**). A solution of 4-*n*-pentyl-4'-(2-trimethylsilyl)ethynylbiphenyl **3a** (1.0 g, 3.1 mmol), potassium hydroxide (10 mL 1 N in methanol), and 20 mL of dichloromethane was stirred for 45 minutes. The solvents were removed under reduced pressure, and the residue was extracted with 50 mL of petroleum ether, washed with 50 mL of aqueous 0.1 M HCl, 50 mL of water, and dried over anhydrous $MgSO_4$. Removal of the solvent gave 0.76 g of a light yellow product. Column chromatography with petroleum ether as eluant gave 0.72 g of pure compound (94%): m.p. 79–80°C (lit. 80°C[2]); ^{1}H-NMR δ 7.55 (s, 4H), 7.50 (d, 2H), 7.25 (d, 2H), 2.64 (t, 2H), 1.65 (m, 2H), 1.35 (m, 4H), 0.90 (t, 3H); IR 3303, 3015, 2932, 2108 (med., sharp), 1493 cm^{-1}; and MS m/z 248 (53.2, M+), 191 (100, M^+-C_4H_9), exact mass measured 248.1563 (calc'd 248.1565).

4-n-Pentyl-4'-(1-propynyl)biphenyl (**3c**). *n*-Butyllithium (1.5 mL 1.5 M in hexane, 2.25 mmol) was added slowly by syringe to a solution of 4-ethynyl-4'-*n*-pentylbiphenyl **3b** (0.5 g, 2.0 mmol) in 25 mL of tetrahydrofuran at −78°C to give a yellow solution which became opaque after a few minutes. The mixture was stirred for 30 minutes at −78°C and methyl benzenesulphonate (0.34 mL, 2.5 mmol) was added carefully. The mixture was then allowed to warm slowly, and a white precipitate formed which redissolved as room temperature was reached. The solvent was removed by rotary evaporation, and the solid residue was extracted with 50 mL of petroleum ether. Washing with 2 × 50 mL of water, drying over anhydrous $MgSO_4$, and removal of the solvent yielded 0.65 g of a crude yellow product. Column chromatography with petroleum ether as eluant gave 0.43 g (81%) of pure compound: m.p. 82–83°C; ^{1}H-NMR δ 7.6–7.4 (m, 6H), 7.24 (d, 2H), 2.63 (t, 2H), 2.06 (s, 3H), 1.65 (m, 2H), 1.35 (m, 4H), 0.90 (t, 3H); IR 3011, 2931, 1496 cm^{-1}; and MS m/z 262 (51.5, M+), 205 (100, M+-C_4H_9), exact mass measured 262.1719 (calc'd 262.1721).

4-Chloroethynyl-4'-n-pentylbiphenyl (**3d**). A solution of 4-ethynyl-4'-*n*-pentylbiphenyl **3b** (0.50 g, 2.0 mmol) in 15 mL of tetrahydrofuran was cooled to −78°C, and *n*-butyllithium (1.5 mL 1.5 M in hexane, 2.25 mmol) was added slowly to give a pale yellow solution. The solution was warmed to −25°C, and *N*-chlorosuccinimide (0.29 g, 2.2 mmol) was added to give initially a lime green, then yellow mixture. After 2 hours of stirring, the mixture was allowed to come to room temperature and poured into 50 mL of aqueous 2 M HCl and 50 mL of diethyl ether. The organic phase was separated and washed with 50 mL of aqueous 2 M NaOH and 50 mL of aqueous saturated NaCl, then dried over anhydrous $MgSO_4$ and filtered. The solvent was removed to give 0.69 g of a crude yellow product. Column chromatography with petroleum ether as the eluant gave 59 mg (12%) of starting material and 0.49 g (85%) of desired product as white needles: m.p. 115–116°C; ^{1}H-NMR δ 7.6–7.4 (m, 6H), 7.24 (d, 2H), 2.64 (t, 2H), 1.65 (m, 2H), 1.35 (m, 4H), 0.90 (t, 3H); IR 3012, 2931, 2221 (med., sharp), 1496 cm^{-1}; and MS m/z 282 (48.0, M+), 225 (100, M^+-C_4H_9), exact mass measured 282.1175 (calc'd 282.1175).

4-Bromoethynyl-4'-n-pentylbiphenyl (**3e**). The procedure followed was as above for **3d**, but *N*-bromosuccinimide (0.45 g, 2.5 mmol) was used in place of N-chlorosuccinimide. The amounts of other reagents and solvent were as given above. The crude product, 1.06 g of a flaky, brown solid, was chromatographed using petroleum ether as the eluant to give 40 mg (8%) of starting material and 0.45 g (68%) of desired product as white needles: m.p. range 88–108°C with an orange colour developing at 104°C; ^{1}H-NMR δ 7.6–7.4 (m, 6H), 7.24 (d, 2H), 2.64 (t, 2H), 1.65 (m, 2H), 1.35 (m, 4H), 0.90 (t, 3H); IR 3012, 2931, 2199 (weak, sharp), 1495 cm^{-1}; and MS m/z 326 (81.2, M+), 269 (100, M^+-C_4H_9), exact mass measured 326.0672 (calc'd 326.0671).

4-Iodoethynyl-4'-n-pentylbiphenyl (**3f**). To a solution of 4-ethynyl-4'-*n*-pentylbiphenyl **3b** (0.43 g, 1.7 mmol) in 20 mL of tetrahydrofuran at −78°C was added *n*-butyllithium (1.15 mL 1.5 M in hexane, 1.7 mmol). After 30 minutes of stirring, iodine crystals (0.44 g, 1.7 mmol) were added. As the mixture was allowed to slowly warm to room temperature, the dark brown colour disappeared resulting in a yellow solution. Stirring was continued overnight. The tetrahydrofuran was removed by rotary evaporation, and the residue was extracted with 50 mL of hexane. Filtration through silica gel and partial removal of the solvent resulted in the precipitation of the product as colourless needles. The starting material and product were indistinguishable by TLC, and the product was unstable to GC conditions. Analysis by ^{1}H-NMR showed less than 1% starting material. The product yellows quickly at room temperature: m.p. range 110–119°C; ^{1}H-NMR δ 7.6–7.4 (m, 6H), 7.25 (d, 2H), 2.63 (t, 2H), 1.65 (m, 2H), 1.35 (m, 4H), 0.90 (t, 3H); IR 3013, 2932, 1494 cm^{-1}; and MS m/z 374 (70.6, M^+), 317 (100, M^+-C_4H_9), exact mass measured 374.0533 (calc'd 374.0533).

1-(4-Biphenyl)-1-pentanone (**8**). To a solution of biphenyl (5.0 g, 32 mmol) in 20 mL of carbon tetrachloride at 0°C was added anhydrous aluminum chloride (5.3 g, 40 mmol) in one portion. Immediately, the slow addition of a solution of pentanoyl chloride (4.0 mL, 33 mol) in 20 mL of carbon tetrachloride from a pressure-equalizing dropping funnel was begun and continued over 15 minutes. A further 10 mL of carbon tetrachloride was used to rinse the dropping funnel into the reaction mixture. The resulting blue solution was stirred overnight at room temperature and then refluxed for two hours. After cooling, the mixture was poured onto 50 g of ice and 20 mL of aqueous concentrated HCl to give a yellow mixture which was filtered into a separatory funnel. The organic layer was washed with 3 × 50 mL of water and dried over anhydrous $MgSO_4$. Rotary evaporation of the solvent gave a crude, brown product which by GC analysis contained a small amount of biphenyl. Recrystallisation from methanol yielded 5.1 g (68%) of a colourless crystalline product: m.p. 79°C (lit. 79°C[8]); ^1H-NMR δ 8.03 (d, 2H), 7.67 (d, 2H), 7.62 (d, 2H), 7.2–7.5 (m, 3H), 2.99 (t, 2H), 1.74 (m, 2H), 1.43 (m, 2H), 0.97 (t, 3H); IR 3017, 2961, 1678 (strong), 1605 cm^{-1}; and MS m/z 238 (15.3, M^+), 181 (100, M^+-C_4H_9), exact mass measured 238.1349 (calc'd 238.1358).

1-(4'-Nitro-1,1'-biphenyl-4-yl)-1-pentanone (**9**). To a stirred solution of 1-(4-biphenyl)-1-pentanone **8** (1.0 g, 4.1 mmol) in 5 mL of concentrated H_2SO_4 at 0°C was added potassium nitrate (0.45 g, 4.5 mol) over five minutes. After one hour the bright red solution was poured onto 50 g of ice with vigorous mixing. The mixture was allowed to come to room temperature, and the cream coloured solid was filtered and washed with 3 × 50 mL of water. Thin-layer chromatography with dichloromethane showed only one product with no starting material. However, GC indicated the presence of a second product. The pure material was obtained by recrystallisation from methanol which yielded 0.66 g (57%) of long, yellow needles: m.p. 122–123°C (lit. 123°C[8]); ^1H-NMR δ 8.33 (d, 2H), 8.09 (d, 2H), 7.78 (d, 2H), 7.72 (d, 2H), 3.01 (t, 2H), 1.75 (m, 2H), 1.43 (m, 2H), 0.97 (t, 3H); IR 3018, 2962, 1683, 1521, and 1347 cm^{-1} (strong); and MS m/z 283 (10.6, M^+), 226 (100, M^+-C_4H_9); exact mass measured 283.1201 (calc'd 283.1208).

4-Amino-4'-n-pentylbiphenyl (**10**). 1-(4'-Nitro-1,1'-biphen-4-yl)-1-pentanone **9** (1 g, 3.5 mmol), hydrazine hydrate (1 mL, 21 mmol), and 5 mL of diethylene glycol were refluxed (180°C) for two hours. A stream of dry nitrogen entering through a Claisen adapter was used to remove the small amount of water produced. To the cooled solution was added powdered potassium hydroxide (1.2 g, 21 mmol), and the mixture was refluxed overnight. The resulting brown solution was poured into 50 mL of aqueous 10% NaOH which was then extracted with 2 × 40 mL of benzene. The bright red organic solution was washed with 50 mL of water, dried over anhydrous $MgSO_4$ and filtered. Removal of the solvent by rotary evaporation yielded 0.82 g of crude orange product. Thin-layer chromatography using dichloromethane as the eluant indicated three products, the colourless compound with intermediate retention proving to be the desired amine. Column chromatography gave 0.53 g of a yellow powder which was further purified by sublimation to give 0.46 g (56%) of colourless needles: m.p. 72°C (lit. 72°C[8]); ^1H-NMR δ 7.44 (d, 2H), 7.39 (d, 2H), 7.20 (d, 2H), 6.72 (d, 2H), 3.57 (broad, exchanges, 2H), 2.62 (t, 2H), 1.64 (m, 2H), 1.34 (m, 4H), 0.90 (t, 3H); IR 3400 (broad), 3022, 2932, 1500 cm^{-1}; and MS m/z 239 (66.4, M+), 182 (100, M^+-C_4H_9); exact mass measured 239.1672 (calc'd 239.1674).

N-(4'-n-pentyl-1,1'-biphen-4-yl)formamide (**11**). To a solution of 4-amino-4'-*n*-

pentylbiphenyl **10** (0.55 g, 2.3 mmol) dissolved in 5 mL of dry dichloromethane at 0°C was added formic pivalic anhydride[9] (0.4 mL, approx. 3 mmol). After five minutes of stirring, thin-layer chromatography using dichloromethane as the eluant indicated that all of the starting material had reacted. Rotary evaporation followed by vacuum pumping to remove solvent traces and volatile products gave a white solid. Recrystallisation from methanol gave 0.58 g (96%) of a mixture of *cis* and *trans* isomers of the desired amide; m.p. 171°C; ^{1}H-NMR δ 8.74 (d, 0.5H), 8.40 (s, 0.5H), 7.83 (d, 0.5H), 7.7–7.0 (m, 8.5H), 2.65 (t, 2H), 1.65 (m, 2H), 1.35 (m, 4H), 0.90 (t, 3H); IR 3424 (sharp), 3014, 2931, 1695 (strong), 1505 cm^{-1}; and MS m/z 267 (72.2, M+), 210 (100, M^+-C_4H_9); exact mass measured 267.1623 (calc'd 267.1623).

4-Isocyano-4'-n-pentylbiphenyl (**2b**). *N*-(4'-*n*-pentyl-1,1'-biphen-4-yl)formamide **11** (0.40 g, 1.5 mmol) and diisopropylamine (0.42 mL, 3 mmol) were dissolved in 6 mL of dichloromethane, and the solution was cooled to 0°C. Phosphoroyl chloride (150 μL, 1.6 mmol) was added dropwise. After five minutes of stirring at 0°C, thin-layer chromatography using dichloromethane as the eluant indicated a single product and no starting material. Ten millilitres of aqueous 20% Na_2CO_3 was added slowly, and the two-phase mixture was stirred at room temperature for five minutes before being poured into 40 mL of dichloromethane and 40 mL of water. The organic layer was separated and washed with another 40 mL of water, dried over anhydrous Na_2SO_4 and filtered to give a pale yellow solution. Column chromatography on alumina using dichloromethane as the eluant gave a colourless liquid product which was quickly transferred to a vacuum line and solidified by cooling. Failure to remove the residual solvent in the absence of air leads to the formation of brown tarry material. Under a dry nitrogen atmosphere the resulting white, crystalline solid 0.32 g (87%) melted at 34°C. The isotropic melt cooled to give a nematic liquid at approximately 30°C, which remained at room temperature but resolidified within 30 minutes. A blue-green colour slowly develops in the nematic liquid. The transition temperatures were determined by submerging the flask containing the material under nitrogen in a water bath which was slowly warmed. ^{1}H-NMR δ 7.59 (d, 2H), 7.47 (d, 2H), 7.42 (d, 2H), 7.27 (d, 2H), 2.65 (t, 2H), 1.65 (m, 2H), 1.35 (m, 4H), 0.90 (t, 3H); IR 3011, 2932, 2130 (strong, sharp) and 1496 cm^{-1}; and MS m/z 249 (20.6, M+), 192 (100, M^+-C_4H_9); exact mass measured 283.1201 (calc'd 283.1208).

4-Isocyano-4'-n-butylbiphenyl (**2a**). m.p. 36°C; ^{1}H-NMR δ 7.59 (d, 2H), 7.47 (d, 2H), 7.42 (d, 2H), 7.27 (d, 2H), 2.65 (t, 2H), 1.65 (m, 2H), 1.35 (m, 2H), 0.90 (t, 3H); IR 3013, 2929, 2121 (strong, sharp) and 1495 cm^{-1}; and MS m/z 235 (20.9, M+), 192 (100, M^+-C_3H_7).

4-Isocyano-4'-n-hexylbiphenyl (**2c**). m.p. range 9–19°C; ^{1}H-NMR δ 7.59 (d, 2H), 7.47 (d, 2H), 7.42 (d, 2H), 7.27 (d, 2H), 2.65 (t, 2H), 1.65 (m, 2H), 1.35 (m, 4H), 0.90 (t, 3H); IR (neat) 3011, 2931, 2129 (strong, sharp) and 1496 cm^{-1}; and MS m/z 263 (32.8, M+), 192 (100, M^+-C_5H_{11}).

Acknowledgment

We thank the Natural Sciences and Engineering Research Council (NSERC) of Canada for financial support.

References

1. G. W. Gray, K. J. Harrison, J. A. Nash, J. Constant, D. S. Hulme, J. Kirton and E. P. Raynes, *Liq. Cryst. Ord. Fluids*, **2**, 617 (1974).
2. R. Dabrowski and E. Zytynski, *Mol. Cryst. Liq. Cryst.*, **87**, 109 (1982).
3. K. Sonogashira, Y. Tohda and N. Hagihara, *Tetrahedron Lett.*, 4467 (1975).
4. J. E. Baldwin, J. C. Bottaro, P. D. Riordan and A. E. Derome, *J. Chem. Soc., Chem. Commun.*, 943 (1942).
5. C. Grundmann, *Chem. Ber.*, **91**, 1380 (1958).
6. H. Westmijze and P. Vermeer, *Synthesis*, 390 (1979).
7. H. O. House, C.-Y. Chu, J. M. Wilkins and M. J. Umen, *J. Org. Chem.*, **40,** 1460 (1975).
8. A. I. Pavlyuchenko, N. I. Smirnova, E. I. Kovshev, V. V. Titiv and G. V. Purvanetskas, *J. Org. Chem. U.S.S.R.*, **12**, 1066 (1976).
9. E. J. Vliestra, R. J. M. Nolte, J. W. Zwikker and W. Drenth, *Recueil, J. Roy. Netherlands Chem. Soc.*, **101**, 460 (1982).