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Synthesis and mesomorphic properties of some asymmetrical pyrimidinylphenyldiacetylenes

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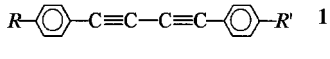
1. Introduction

Mesogenic materials having a large optical birefringence (Δn) are of interest for IR and radio applications, as well as for PDLC and cholesteric devices. Materials with large, positive dielectric anisotropies ($\Delta\varepsilon$) are useful for almost any application that involves electric fields. Asymmetric dialkyldiacetylenes of the type



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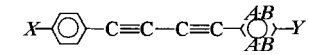
were reported to have low temperature, wide range nematic phases with low viscosities and Δn values of 0.285 in the IR region [1]. This makes them useful for modulating infrared radiation. However, their dielectric anisotropies are rather small, *c*. 1. We are interested in modifying this diacetylene structure to obtain mesogens having wide range nematic phases, but with large Δn and/or $\Delta\varepsilon$. Large Δn is expected for the molecules of **1** as they have two sets of delocalized π electrons in the diacetylene structure, along the long axis of the molecule. Similarly, small $\Delta\varepsilon$ is expected as large $\Delta\varepsilon$ in nematic liquid crystals results primarily from the re-orientation of fixed electrical dipoles in the structure. These molecules are essentially symmetric, and therefore have very small dipoles. Thus, $\Delta\varepsilon$ is likely to result primarily from the asymmetric molecular polarizability, as does Δn, rather than from molecular re-orientation, and is therefore small.

Replacing one of the benzene rings of structure **I** with a nitrogen-containing ring seemed appropriate, since the resulting compounds would have delocalized dipoles. Such nitrogen-containing aromatic rings should also be more electronegative and would therefore be expected to conjugate better with the electronegative diacetylene group than does the benzene ring, resulting in larger molecular polarizabilities and therefore larger Δn. Electron density calculations using the GAMESS program with the AM1 and 631G* bases confirmed these ideas and that these structures would be worth investigating. Quantum chemistry calculations on these molecules were performed using first the AM1 semi-empirical basis set for geometry optimization. All alkyl chains were replaced by a simple hydrogen. After an optimum geometry was obtained using AM1, this geometry and the corresponding hessian were used in a restricted Hartree–Fock 631G* *ab initio* calculation. The dipole moment was calculated, which is important for estimates of the dielectric anisotropy. The polarizability was assessed by calculating the dipole moment in the presence of a finite electrical field. This was then compared with the polarizability calculated in this way for the parent compound. More qualitative or intuitive issues—such as the greater conjugation in electron deficient rings and the diacetylenes—were also examined. It seems possible that localized charges in such highly polarizable molecules may decrease mesogenicity and increase reactivity. Thus both the Mulliken and Lowdin charge densities were examined.

One such nitrogen-containing ring is the pyrimidine one which has the nitrogen atoms *meta* to each other:



2. B=N **a**. X=C_6H_{13}, Y= CN; **b**. X=C_6H_{13}, Y= RC≡C– and **c**. X=C_6H_{13}, Y= OBu

3. A=N X=CN, Y=C_7H_{15}

The pyrimidine **2** with Y=CN, X = R would be expected to have both larger dipole moments and dielectric anisotropies than the corresponding analogue with A=N. However, this latter compound was calculated to have larger Δn values. The opposing dipoles in the nitrogen-containing aromatic and cyano groups may also lead to better mesogenic properties. Another possibility would be to place the cyano group on the benzene ring, **3**. This compound should have the largest dipole of these three

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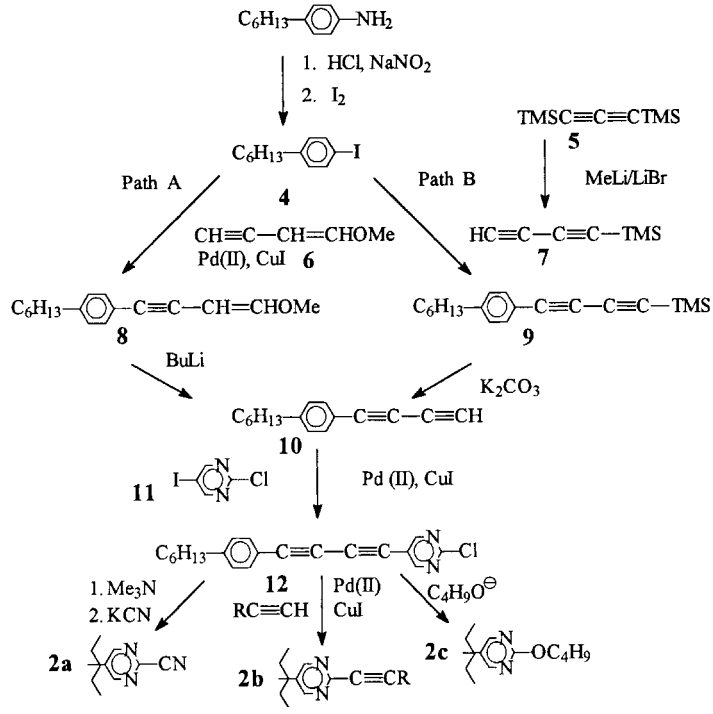
analogues, with Δn values between the two. We chose to synthesize several of the diacetylenes **2** and **3** and determine their mesomorphic properties. Our initial targets included **2** with Y a simple alkyl chain, but this proved difficult to synthesize. Hence, we chose to synthesize mesogens in which Y had a triple bond adjacent to the heterocyclic ring, **2b**. No quantum chemistry calculations were performed on this molecule. However, it is expected that it should have a larger conjugation length and, in consequence a larger polarizability. Yet, it is also more rigid and, in consequence, would be expected to have higher transition temperatures.

Another possibility would be to place the cyano group on the benzene ring **3**. This compound should have the largest dipole of these three analogues with Δn values between the two. We chose to synthesize several of the diacetylenes **2** and **3** and determine their mesomorphic properties.

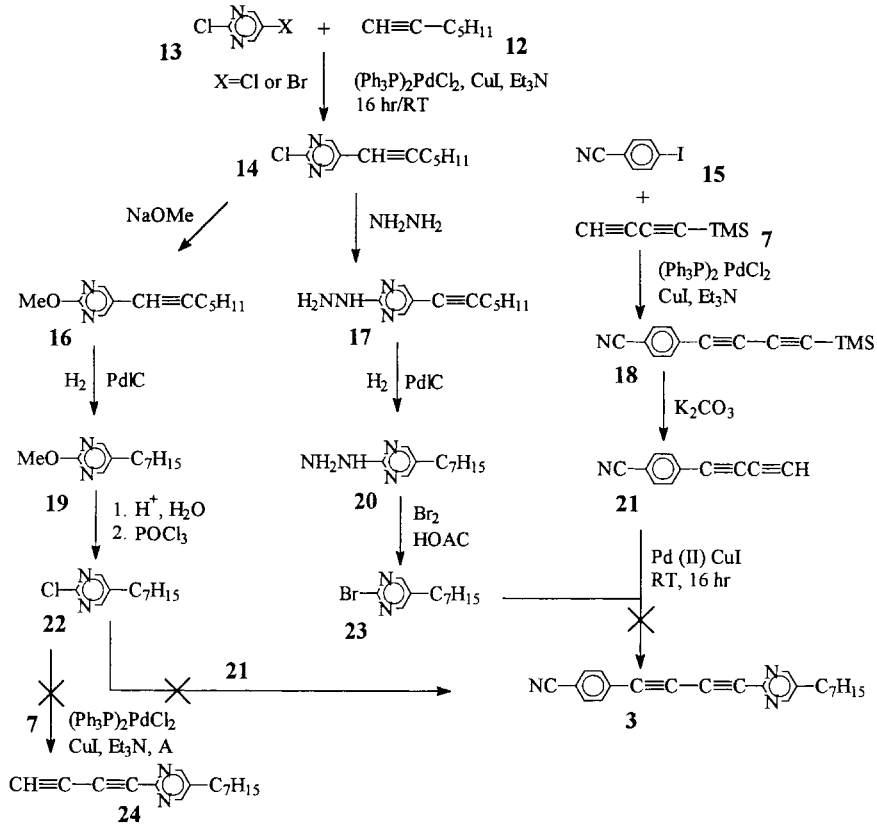
2. Synthesis

Two pathways to the synthesis of the diacetylenes **2** were tried as shown in scheme 1. In path A, the iodide **4** prepared from the corresponding aniline was coupled with the diacetylene **6** in the presence of a Pd (II) catalyst, followed by elimination of methanol from the product **8** with *n*-butyllithium to form the terminal diacetylene **10** [2, 3]. A major problem with this approach was the instability of the eyne-yne compound **8** which hydrolyzed to the corresponding aldehyde if not used immediately. Thus, path B was designed to replace path A. Path B involved converting the diTMS protected butadiyne **5** to the monoprotected compound **7**, reacting this with the iodide **4** and removing the protecting group with K_2CO_3 to give the acetylene **10** [4, 5]. This terminal diacetylene was unstable even in the dark at room temperature. However, the crude material isolated from path B was sufficiently pure to use immediately in the next coupling step with the chloropyrimidine **11** [6] to obtain the diacetylene **12**. Initial attempts to displace the chlorine atom with an alkyl group using a Ni(O) catalysed Grignard reaction [7] to obtain the diacetylene **2** with $X = Y = R$ led to a complete decomposition of the starting diacetylene as determined by ^{1}H NMR. To confirm the presence of the chlorine atom, a small amount of the diacetylene **12** was treated with lithium butoxide. Isolation of the alkoxypyrimidinyldiacetylene **2c** confirmed the structure **12**. The desired cyano compound **2a** was isolated by converting the chloride **12** to the trimethylammonium salt, followed by treatment with potassium cyanide in DMSO. Reacting the chloride **12** with an alkylacetylene in the presence of Pd (II) and CuI gave the pyrimidinyl acetylene **2b** (R=C_5, C_{10}).

The pyrimidinyldiacetylene series **3** proved to be more difficult to synthesize (scheme 2). Although the chloropyrimidine **22** was successfully prepared in a multistep synthesis from the chloride **13** and 1-heptyne, coupling with the diacetylene **21** to give the cyano compound **3** was unsuccessful. This was also the case in an attempt to couple this chloride with the TMS protected diacetylene **7** to obtain compound **24**. The recovery of a high



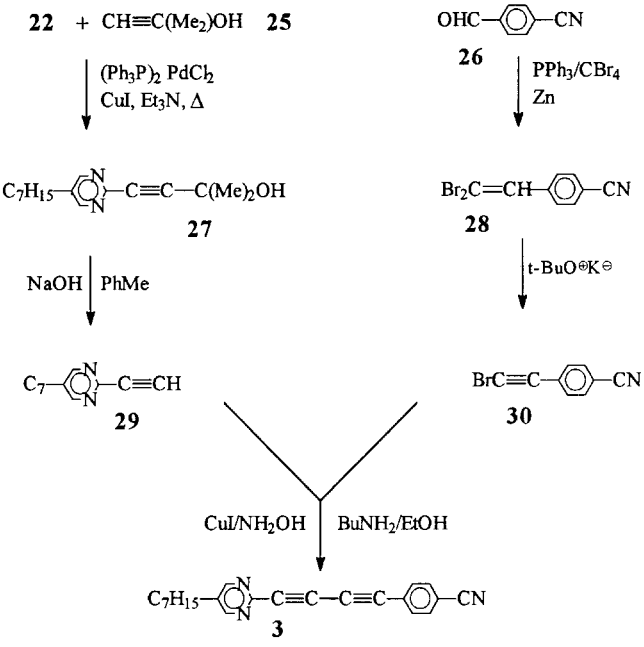
Scheme 1.



Scheme 2.

percentage of the starting chloropyrimiidine **22**, but very little of the diacetylenes **21** or **7** from these reactions, suggests that this is probably due to a combination of low reactivity of the chloride and the instability of the terminal diacetylenes. However, the more reactive bromide **23** also failed to couple with the diacetylene **21**. Either the iodide **13** (X =I) or the bromide (X =Br) [8] could be used to prepare the acetylene **14**, with the iodide giving a slightly better yield (86% versus 73%). Although the isolated bromide contained a pyrimidine impurity as shown by ^{1}H NMR which could only be removed by chromatography followed by distillation, it was easier to prepare than the iodide and thus became the preferred starting material. No problems were encountered in the synthesis of the diacetylene **18** [5] used in these coupling reactions, except that the purified material usually contained some of the deprotected material **21**.

To avoid using a terminal diacetylene in the final coupling step, a new approach was designed (scheme 3). Synthesis of the bromoacetylene **30** was described earlier [9, 10]. The acetylene **29** was synthesized by coupling the chloropyrimidine **22** with the acetylene **25** and treating the product **27** with sodium hydroxide in toluene. The two acetylenes **29** and **30** were coupled using the Cadiot–Chodleiewicz method [11].



Scheme 3.

Attempts to improve the reactivity of the chloropyrimidine **22** by replacing the chlorine with an iodine atom (by treating the chloride with hydrogen iodide [12]) led to the formation of the reduced pyrimidine,

5-heptylpyrimidine. Treatment of the chloride with sodium iodide in acetone gave no reaction.

3. Mesomorphic properties

Transition temperatures, as determined by hot-stage polarizing microscopy, are given in the table, along with some melting enthalpy values determined by DSC. Only compounds **2a** with *Y*=CN and OBu showed nematic phases. Both the pyrimidines **2a** and **3** decomposed at the clearing temperatures and became yellow when exposed to light at room temperature (r.t.). Still, they seemed to be more stable than the dialkyldiphenyldiacetylenes. Physical properties, such as Δn and $\Delta \varepsilon$, will be reported in a later paper.

4. Conclusions

Several new pyrimidinylphenyldiacetylenes have been prepared as potential new mesogens having large birefringence values, but were found to have poor mesomorphic properties. Compounds containing the nitrile group, like many others containing dipoles rigidly connected to an aromatic ring system, such as a nitro group, often have high transition temperatures. Attaching a triple bond directly to the aromatic ring system increases the length of the rigid core of the diacetylenes. Such a modification usually leads to higher transition temperatures and longer mesophase ranges in mesogens with various other core groups. However, in the diacetylenes the transition temperatures increase, but the mesophase ranges decrease.

One compound, **2c** and its homologues, however, seem to merit further study. This compound is predicted to be marginally more birefringent than the useful diphenyldiacetylenes. It has a significant dipole (3.3 D in 631G* in 'gas phase') along the long axis of the molecule, although there is also a large dipole (2.2 D) perpendicular to the long axis. This dipole is diffuse, which may in part explain the relatively good mesogenic properties. Thus, it would also be expected to have a significantly higher dielectric anisotropy than the diphenyldiacetylenes. Its mesogenic properties are somewhat poorer than, but still comparable to, those of diphenyldiacetylenes; its predicted polarizability/birefingence is somewhat better than that of the diphenyldiacetylenes.

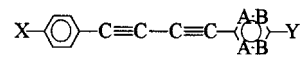
5. Experimental

All temperatures reported are in °C. Degassed solvents were obtained by sonification for 5–10 min. All organic extracts were dried over anhydrous $MgSO_4$ unless otherwise indicated. Commercially available starting materials were used without purification. Flash column chromatography was done using Mallinckrodt silica gel (230–400 mesh). TLC data were obtained using Anal-Tech silica gel GHLF Uniplates with UV light and I_2 as the detectors. Melting points were determined using a Hoover–Thomas melting point apparatus and are corrected. These were not taken for compounds for which transition temperatures were determined.

A Nicolet Magna FTIR spectrophotometer was used to record IR spectra using NaCl plates. ^1H and ^{13}C NMR spectra were determined in $CDCl_3$ with TMS as the internal standard, using a Varian Gemini-200 spectrometer equipped with a VXR-400 data station at 200 and 50 MHz, respectively. Coupling constants are in Hz units. ^{13}C NMR chemical shifts were compared with those values calculated using a softshell ^{13}C NMR Module. DSC scans were run using a Perkin-Elmer DSC7 equipped with a TAC 7/PC instrument controller at a rate of $5°C\,min^{-1}$ which had been calibrated using indium. Capillary GC analysis was obtained using a Hewlett-Packard mode 5890 instrument equipped with an HP3395 integrator, an FID detector and a Hewlett Packard 5 m methylsilicone gum column.

Transition temperatures (°C) were determined using a Leitz Laborlux 12 POL polarizing microscope fitted with a modified and calibrated Mettler FP-2 heating stage at a heating rate of $2°C\,min^{-1}$. Crystallization temperatures were obtained by cooling the melt at $2°C\,min^{-1}$ until crystals were formed, to ensure that all

Table. Transition temperatures (°C) and melting enthalpies ($kJ\,mol^{-1}$) for



A	*B*	*X*	*Y*	K[a]	N	I	ΔH_m
C	N	C_6H_{13}	CN	125.7[b]	128.6–129.2	142.2–142.7 dec	21.9
C	N	C_6H_{13}	$C_5H_{11}C{\equiv}C$	152.8	—	158.3–159.1	39.0
C	N	C_6H_{13}	$C_{10}H_{21}C{\equiv}C$	141.7	—	146.3	—
C	N	C_6H_{13}	OC_4H_9	80.4	90.7	99.4	—
N	C	NC	C_7H_{15}	—	—	~200 dec	—

[a] K = crystallization temperature obtained on cooling at $2°\,min^{-1}$; N = nematic phase and I = isotropic liquid.
[b] A crystal-to-crystal change was observed at 124.9°C on cooling.

mesophases had been observed before this temperature. These crystals were reheated to obtain the melting temperatures and to confirm that these were not mesophases.

5.1. *4-Hexyliodobenzene (**4**)*

A solution of 6.2M $NaNO_2$ in H_2O (1.0 ml) was added dropwise to a stirred solution of 4-hexylaniline (1.0 g, 5.6 mmol) and 5M HCl (15 ml) in 1,4-dioxane (3 ml), initially at 5°C, while maintaining the reaction temperature at 6°C. A solution of 4M KI (1.8 ml) was then added cautiously to avoid foaming (especially on a large scale). The reaction mixture was heated in a 90° water bath for 20 min, cooled to r.t. and extracted with Et_2O (2 × 30 ml). The organic extract was washed with a saturated aqueous Na_2SO_3 solution (25 ml), dried, filtered and the filtrate concentrated *in vacuo* to give the crude product. This material was chromatographed to give 1.35 g (83.8%) of the iodobenzene **3** as a colourless liquid: TLC (hexane) $R_f = 0.55$, IR (film) 2955, 2927, 2861, 1485, 1465 and 1007 cm^{-1}; ^1H NMR δ 7.57 (d, 2, $J = 8.1$, ArH *ortho* to I), 6.91 (d, 2, $J = 8.1$, ArH *ortho* to C_6), 2.53 (t, 2, $J = 7.6$, α-CH_2Ar), 1.65–1.50 (m, 2, β-CH_2), 1.40–1.20 (6, m, $3CH_2$) and 0.87 (t, 3, $J = 5.68$, CH_3); ^{13}C NMR 142.44, 137.16, 130.49, 90.48, 35.40, 31.63, 31.22, 28.83 and 14.07.

5.2. *4-(p-Hexylphenyl)-1-methoxy-1-butene-3-yne (**8**)*

A degassed solution of the iodide **4** (2.50 g, 8.68 mmol) and Et_3N (20 ml) in the freshly distilled olefin **6** was added dropwise to a mixture of CuI (0.08 g, 0.42 mmol) and $(PPh_3)_2PdCl_2$ (0.12 g, 0.17 mmol) under N_2. This mixture was stirred for 2 h in a water bath at 35°C. The insoluble solids were removed by filtration and washed thoroughly with Et_2O; the Et_2O was removed from the filtrate *in vacuo*. The remaining liquid was extracted with Et_2O (3 × 50 ml) and the organic layer dried over anhydrous K_2CO_3, filtered and the filtrate concentrated *in vacuo* to give the crude product. This material was purified by chromatographing through 50 g of silica gel that was slurry packed with a 1% solution of Et_3N in hexane. A gradient elution from 100% hexane to 10% Et_2O/hexane gave 1.80 g (85.7%) of the purified ene-yne compound **8** as a yellow liquid: TLC (10% Et_2O/hexane) $R_f = 0.42$; IR (film) 2967, 2930, 2861, 1633, 1510, 1275 and 1262 cm^{-1}; ^1H NMR δ 7.35 (d, 2, $J = 8.2$, ArH *ortho* to C≡C), 7.09 (d, 2, 8.1, ArH *ortho* to CH_2), 6.30 (d, 1, $J = 6.4$, CH=C), 4.73 (d, 1, $J = 6.4$, CHO), 3.80 (s, 3, OMe), 2.57 (t, 2, $J = 7.7$, α-CH_2), 1.65–1.54 (m, 2, β-CH_2), 1.34–1.24 (m, 6, 3 CH_2) and 0.87 (t, 3 $J = 6.45$, CH_3); ^{13}C NMR ($CDCl_3$) δ 155.81, 142.77, 131.24, 128.23, 120.93, 92.84, 85.58, 82.85, 60.64, 35.84, 31.67, 31.17, 28.89, 22.57 and 14.06.

5.3. *1-(p-Hexylphenyl)-1,3-butadiyne (**10**)*

A 1.6M solution of *n*-BuLi in hexane (9.2 ml, 14.7 mmol) was added dropwise to a stirred solution of the ene-yne compound **8** (1.76 g, 7.27 mmol) in THF at − 78° under N_2. This mixture was then allowed to warm to − 40°C over 20 min, stirred for 1 h and cautiously poured into ice/H_2O with stirring. The THF was removed *in vacuo* and the remaining liquid extracted with CH_2Cl_2 (3 × 50 ml). The organic layer was dried over anhydrous K_2CO_3, filtered and the filtrate concentrated *in vacuo* to give the crude product. This material was chromatographed through 40 g silica gel that was packed using a 1% solution of Et_3N in hexane. Elution with hexane gave 1.38 g (90.2%) of the diacetylene **10** as a brown liquid which was unstable at r.t. even in the absence of light: TLC (10% Et_2O in hexane) $R_f = 0.65$; IR (film) 3304, 2956, 2929, 2855, 2207, 1605, 1508, and 1466 cm^{-1}; ^1H NMR δ 7.42 (d, 2, $J = 8.1$, ArH *ortho* to C≡C), 7.13 (d, 2, 8.1, ArH *ortho* to CH_2), 2.60 (t, 2, $J = 7.7$, α-CH_2), 2.45 (s, 1, CH), 1.70–1.58 (m, 2, β-CH_2), 1.34–1.24 (m, 6, $3CH_2$) and 0.87 (t, 3, $J = 6.4$, CH_3); ^{13}C NMR δ 144.96, 132.70, 128.55, 118.02, 75.66, 72.87, 70.89, 68.29, 35.98, 31.64, 31.08, 28.89, 22.56 and 14.06.

5.4. *2-Chloro-5-(4-p-hexylphenylbuta-1,3-diynyl)-pyrimidine (**12**)*

To a stirred, degassed solution of the diacetylene **10** (5.7 g, 207 mmol) in Et_3N (8 ml) under N_2 were added the chloropyrimidine **11** (0.68 g, 2.8 mol), CuI (0.04 g, 0.23 mmol) and $(PPh_3)_2PdCl_2$ (0.07 g, 0.10 mmol). The reaction mixture was stirred for 30 min in a water bath at 35°C and filtered. The solids were washed thoroughly with H_2O and Et_2O, and the Et_2O removed from the filtrate *in vacuo*. The remaining liquid was extracted with CH_2Cl_2 (3 × 50 ml) and the organic layer dried, filtered and the filtrate concentrated *in vacuo* to give the crude product. This material was chromatographed through 30 g of silica gel that was slurry packed with a 1% solution of Et_3N in hexane. Gradient elution from 100% hexane to 20% Et_2O/hexane gave 0.57 g (65.5%) of the chloropyrimidinyldiacetylene **12** as a colourless solid: m.p. 145.1–146.1°; TLC (20% EtOH/hexane) $R_f = 0.61$; IR (Nujol) 2228, 1517, 1409 and 1159 cm^{-1}; ^1H NMR δ 8.74 (s, 2, pyrim H), 7.47 (d, 2, $J = 8.3$, ArH *ortho* to C), 7.19 (d, 2, $J = 8.3$, ArH *ortho* to CH_2), 2.63 (t, 2, $J = 7.7$, α-CH_2), 1.61–1.57 (m, 2, β-CH_2), 1.33–1.27 (m, 6, $3CH_2$) and 0.88 (t, 3, $J = 6.4$, CH_3); ^{13}C NMR δ 161.67, 159.60, 145.57, 132.61, 128.67, 117.67, 117.58, 85.30, 82.20, 72.49, 72.11, 35.99, 31.60, 31.02, 28.85, 22.52 and 14.02.

5.5. *5-(4-p-Hexylphenylbuta-1,3-diynyl)-2-pyrimidinecarbonitrile (**2a**)*

Trimethylamine gas was slowly bubbled through a stirred solution of the diacetylene **12** (0.38 g, 1.8 mmol)

in benzene (50 ml) for 5 min and this solution stirred at r.t. for 30 min. The insoluble solids were removed by suction filtration and the filtrate treated again in the same manner. The insoluble solids were combined (0.44 g), dissolved in DMSO (25 ml) and treated with KCN (0.31 g, 4.8 mmol) at r.t. for 1 h under N_2. The resultant dark brown reaction mixture was slowly poured into H_2O and the mixture extracted with Et_2O (3×50 ml). The organic layer was washed with H_2O (50 ml), dried, filtered and the filtrate concentrated *in vacuo* to give the crude product. This material was chromatographed through 25 g silica gel using a gradient elution from 100% hexane to 20% Et_2O/hexane to give 0.15 g (62.5%) of the cyanodiacetylene **2a** as a pale yellow solid. Further purification by recrystallization from hexane gave a colourless, analytical material: TLC (10% Et_2O/hexane) $R_f = 0.37$; IR (Nujol) 2208, 1607, 1530 and 1428 cm^{-1}; ^1H NMR δ 8.88 (s, 2, pyrim H), 7.47 (d, 2, $J = 8.3$, ArH *ortho* to C), 7.19 (d, 2, $J = 8.3$, ArH *ortho* to CH_2), 2.63 (t, 2, $J = 8.3$, α-CH_2), 1.61–1.57 (m, 2, β-CH_2), 1.33–1.27 (m, 6, $3CH_2$) and 0.88 (t, 3, $J = 6.4$, CH_3); ^{13}C NMR δ 160.12, 146.03, 141.99, 132.72, 128.76, 121.71, 117.29, 115.28, 87.27, 85.22, 72.53, 72.00, 36.02, 31.59, 31.01, 28.85, 22.52, 14.02. Elemental analysis: calcd for $C_{21}H_{19}N_3$, C 80.46, H 6.11, N 13.42; found C 80.24, H 5.97, N 13.22%.

5.6. *2-(Hept-1-ynyl)-5-(4-p-hexylphenylbuta-1-3-diynyl)-pyrimidine (**2b**, R = **1**-heptyne)*

To a degassed solution of the diacetylene **12** (0.32 g, 0.99 mmol) and 1-heptyne (0.12 g, 1.2 mmol) in Et_3N (12 ml) were added CuI (0.013 g, 0.07 mmol) and $(PPh_3)_2PdCl_2$ (0.02 g, 0.02 mmol). The reaction mixture was heated under reflux under N_2 for 3 h, cooled to r.t., filtered and the insoluble solids washed thoroughly with H_2O and Et_2O. The layers were separated from the filtrate and the aqueous layer extracted with Et_2O (3×25 ml). The organic layer was dried, filtered and the filtrate concentrated *in vacuo* to give the crude product. Chromatography of this material through 25 g silica gel using a 10% Et_2O/hexane solution gave 0.21 g (55.6% of the alkynyl diacetylene **2b**) as a pale yellow solid. Recrystallization of this material from hexane yielded the colourless diacetylene **2b**: TLC ($CHCl_3$) $R_f = 0.60$; (Nujol) 2234, 1505, 1441, 1242 cm^{-1}, ^1H NMR δ 8.76 (s, 2, Pyrim H), 7.46 (d, 2, $J = 8.3$, ArH *ortho* to C), 7.17 (d, 2, $J = 8.2$, ArH *ortho* to CH_2), 2.62 (t, 2, $J = 7.6$, $ArCH_2$), 2.49 (t, 2, $J = 7.1$, CCH_2), 1.80–1.26 (m, 14, $7CH_2$), 0.91 (t, 3, $J = 7.0$, CH_3 pyrim chain) and 0.88 (t, 3, $J = 6.4$, CH_3 benzene chain); ^{13}C NMR δ 159.62, 150.75, 145.42, 132.57, 128.66, 117.89, 116.81, 94.07, 85.26, 82.11, 80.01, 74.03, 72.34, 36.00, 31.61, 31.05, 28.85, 27.65, 22.53, 22.14, 19.39, 14.03 and 13.87.

The homologue with $R = C_{10}H_{21}$ was prepared in the same manner in a 61.9% yield and recrystallized from hexane to give a colourless solid. The structure was confirmed by IR, ^1H NMR and ^{13}C NMR.

5.7. *2-Butoxy-5-(4-p-hexylphenylbuta-1,3-diynyl)-pyrimidine (**2c**)*

To a stirred solution of *n*-BuOH (0.08 g, 1.1 mmol) in THF (1 ml) at $-78°C$ under N_2 was slowly added 1.6M *n*-BuLi in hexane (0.20 ml, 0.32 mmol). The reaction mixture was allowed to warm to r.t., stirred 5 min and cooled to $-78°$. A solution of the diacetylene **12** (0.05 g, 0.15 mmol) in THF (1 ml) was added; this mixture was stirred at r.t. for 64 h, diluted with H_2O and the THF removed *in vacuo*. The remaining liquid was washed with 5% aqueous KOH and H_2O, dried, filtered and the filtrate concentrated *in vacuo* to give the crude product. This was chromatographed through 20 g silica gel using 10% Et_2O/hexane to give 25 mg (52.0%) of recovered starting material **12** and 25 mg (46.3%) of the ether **2c** as a colourless solid. Further purification was achieved by recrystallization from MeOH: TLC ($CHCl_3$) $R_f = 0.58$; IR (Nujol) 2218, 2139, 1593, 1530 and 1346 cm^{-1}; ^1H NMR δ 8.62 (s, 2, pyrim H), 7.44 (d, 2, $J = 8.3$, ArH *ortho* to C≡C), 7.16 (d, 2, $J = 8.3$, ArH *ortho* to CH_2), 4.39 (t, 2, $J = 6.6$, OCH_2), 2.62 (t, 2, $J = 7.6$, $ArCH_2$), 1.85–1.75 (2, m, β-CH_2 on O), 1.64–1.40 (m, 4, β-CH_2 and δ-CH_2 on O), 1.36–1.27 (m, 6, $3CH_2$) 0.98 (t, 3, $J = 7.3$, CH_3 in alkoxy) and 0.88 (t, 3, $J = 6.4$, CH_3); ^{13}C NMR δ 163.80, 162.20, 145.01, 132.48, 128.61, 118.27, 111.65, 83.48, 78.87, 74.35, 72.60, 68.16, 36.00, 31.63, 31.57, 31.09, 30.73, 28.81, 22.63, 22.55, 19.08, 14.05 and 13.74.

5.8. *1-(p-Hexylphenyl)-4-trimethylsilyl-1,3-butadiyne (**9**)*

To a stirred solution of the protected diacetylene **5** (3.92 g, 20.1 mmol) in Et_2O (20 ml) under N_2 at 0°C was added dropwise within 20 min, a 1.5M solution of MeLi/LiPr in Et_2O (16 ml, 24 mmol), this mixture was stirred at r.t. for 3 h. GC analysis of an aliquot showed about equal amounts of the desired diacetylene **7** ($t_R = 0.83$) and starting material **5** ($t_R = 5.38$). Therefore, the reaction mixture was cooled to 0°C, an additional aliquot of 1.5M MeLi/LiBr in hexane (5 ml, 7.5 mmol) added dropwise, the mixture stirred for 1.5 h and then hydrolysed with H_2O. The layers were separated, the aqueous layer extracted with Et_2O (25 ml), the Et_2O extract combined with the original Et_2O layer, dried, filtered and the filtrate distilled under N_2 to remove the Et_2O to yield a dark oil. This material and the iodide **4** (3.7 g, 12.8 mmol) were dissolved in Et_3N (40 ml). This solution was degassed, the reagents $(PPh_3)_2PdCl_2$ (0.12 g, 0.16 mmol) and CuI (0.038 g, 0.19 mmol) added and this mixture stirred at r.t. for 16 h in the dark. The

insoluble solids were removed by filtration and washed thoroughly with H_2O, and Et_2O. The Et_2O was removed from the filtrate *in vacuo* and the remaining liquid extracted with Et_2O (3 × 50 ml). The organic layer was dried, filtered and the filtrate concentrated *in vacuo* to give the crude product. This material was chromatographed through 75 g silica gel that had been slurry packed with a 1% solution of Et_3N in hexane. A gradient elution from 100% hexane to 10% Et_2O/hexane produced 3.49 g (96.4%) of the diacetylene **9** as a yellow oil: ^{1}H NMR δ 7.41 (d, 2, J = 8.2, ArH *ortho* to C), 7.13 (d, 2, J = 8.3, ArH *ortho* to CH_2), 2.60 (t, 2, J = 7.6, α-CH_2), 1.65–1.52 (m, 2, β-CH_2), 1.36–1.29 (m, 6, 3CH_2), 0.89 (t, 3, J = 6.4, CH_3) and 0.24 (s, 9, 3Me). Due to the ease with which deprotection of this compound to the unstable terminal diacetylene **10** occurred, this material was used immediately to prepare the diacetylene **12**.

5.9. *1-(p-Hexylphenyl)-1,3-butadiyne (**10**) and 2-Chloro-5-(4-p-hexylphenylbuta-1-3-diynyl) pyrimidine (**12**)*

A mixture of the diacetylene **9** (3.49 g, 12.4 mmol) and K_2CO_3 (1.5 g) in MeOH (100 ml) was stirred at r.t. for 30 min, diluted with H_2O and the MeOH removed *in vacuo*. The remaining liquid was extracted with CH_2Cl_2 (3 × 50 ml), the organic layer dried and filtered and the filtrate concentrated *in vacuo* to give 2.8 g of the crude product **10**. This material was treated immediately with the iodopyrimidine **11** as described earlier to give 2.11 g (63.0%) of the pyrimidinyldiacetylene **12** as a colourless solid.

5.10. *2-Chloro-5-(hept-1-ynyl)pyrimidine (**14**)*

To a degassed solution of the bromide **11** (X = Br) (6.1 g, 31 mmol) and 1-heptyne (3.6 g, 38.1 mmol) in Et_3N (90 ml) were added CuI (0.03 g, 0.16 mmol) and $(PPh_3)_2PdCl_2$ (0.21 g, 0.30 mmol); this mixture was stirred at r.t. under N_2 for 16 h. The insoluble solids were removed by filtration, washed thoroughly with H_2O and Et_2O and the Et_2O removed from the filtrate *in vacuo*. The remaining liquid was extracted with Et_2O (2 × 100 ml). The organic layer was dried and filtered and the filtrate concentrated *in vacuo* to give the crude product. This material was chromatographed through 100 g silica gel using a gradient elution from 1:1 CH_2Cl_2/hexane to CH_2Cl_2 to give 6.64 g of the desired product as a light brown oil. However, a ^{1}H NMR spectrum of this material showed the presence of a minor impurity with δ = 8.6. This was removed by distillation at 120–12°/1 torr to give 4.77 g (73.1%) of the chloropyrimidinyl acetylene **14** as a colourless liquid: TLC (CH_2Cl_2) R_f = 0.28; IR (film) 2966, 2929, 2862, 2230, 1579, 1524, 1402 and 1165 cm^{-1}; ^{1}H NMR δ 8.60 (s, 2, pyrim H), 2.45 (t, 2, J = 7.0, α-CH_2), 1.75–1.60 (m, 2, β-CH_2), 1.50–1.34 (m, 4, 2CH_2) and 0.93 (t, 3, J = 7.0, CH_3); ^{13}C NMR δ 160.6, 158.5, 118.9, 99.5, 72.6, 30.9, 27.8, 22.0, 19.3 and 13.8.

5.11. *5-(Hept-1-ynyl)-2-methoxypyrimidine (**16**)*

To a stirred solution of the chloropyrimidine **14** (2.41 g, 11.6 mmol) in THF (11 ml) at − 78° under N_2, was added a solution of 0.5M NaOMe in MeOH (24 ml, 12 mmol). The solidified reaction mixture was allowed to warm to r.t., stirred for 3 h, diluted with H_2O and the MeOH removed *in vacuo*. The remaining liquid was extracted with Et_2O (3 × 50 ml) and the organic layer dried, filtered and concentrated *in vacuo* to give the crude product. The material was chromatographed through 40 g silica gel using CH_2Cl_2, to give 2.05 g (86.5%) of the methoxypyrimidine **16** as a colourless liquid: TLC (CH_2Cl_2) R_f = 0.25; IR (film) 2964, 2940, 2868, 2229, 1597, 1542, 1476 and 1416 cm^{-1}, ^{1}H NMR δ 8.51 (s, 2, pyrim H), 4.01 (s, 3, OMe), 2.41 (t, 2, J = 7.0, α-CH_2), 1.70–1.55 (m, 2, β-CH_2), 1.45–1.30 (m, 4, 2CH_2) and 0.92 (t, 3, J = 6.9, Me); ^{13}C NMR δ 163.5, 161.1, 113.5, 95.4, 73.6, 55.0, 31.0, 28.1, 22.1, 19.3 and 13.9.

5.12. *2-Chloro-5-heptylpyrimidine (**22**)*

A mixture of the methoxypyrimidine **16** (2.05 g, 10.0 mmol) and 10% Pd/C (0.25 g) in MeOH (30 ml) was stirred for 16 h, filtered and the filtrate concentrated *in vacuo* to give the crude alkylpyrimidine **19**. This material could be purified to a yellow liquid by chromatography through silica gel (60–100 mesh) using CH_2Cl_2: IR (film) 2964, 2922, 2856, 1603, 1566, 1476, 1416 and 1332 cm^{-1}; ^{1}H NMR δ 8.34 (s, 2, pyrim H), 3.99 (s, 3, OMe), 2.53 (t, 2, J = 7.6, α-CH_2), 1.70–1.50 (m, 2, β-CH_2) 1.40–1.20 (m, 8, 4CH_2) and 0.88 (t, 3, J = 6.4, CH_3); ^{13}C NMR δ 164.23, 158.66, 128.34, 54.56, 31.60, 30.81, 29.23, 28.86, 28.79, 22.48 and 13.93.

The crude product **19** was dissolved in 6N HCl (50 ml), heated under reflux for 1 h, then poured onto ice. This mixture was neutralized with concd NH_4OH and extracted with EtOAc (3 × 50 ml). The organic layer was dried and concentrated *in vacuo* to give the crude pyrimidine. This material was dissolved in $POCl_3$ (14 ml) containing Et_3N (0.70 ml), heated under reflux in anhydrous conditions for 3 h and cooled to r.t. H_2O was added dropwise and this mixture was extracted with CH_2Cl_2 (3 × 50 ml). The organic layer was washed with saturated aqueous $NaCO_3$, dried, filtered and the filtrate concentrated *in vacuo* to give the crude product. This was chromatographed through 50 g silica gel using 1:1 CH_2Cl_2/hexane to give 1.49 g (70.3%, overall) of the chloropyrimidine **22** as a pale yellow liquid: TLC (CH_2Cl_2) R_f = 0.19, IR (film) 3026.0, 2927.3, 2861.5, 1578.2, 1551.8, 1459.7, 1407.1, 1249.1 and 1170.1; ^{1}H NMR δ 8.46 (s, 2, pyrim H), 2.61 (t, 2, J = 7.7, α-CH_2), 1.70–1.55

(m, 2, β-CH_2), 1.33–1.28 (m, 8, 4CH_2) and 0.91–0.85 (m, 3, CH_3); ^{13}C NMR δ 159.21, 156.25, 134.03, 31.54, 30.50, 29.46, 28.81, 22.47 and 13.93.

5.13. *5-(Hept-1-ynyl)-2-hydrazinopyrimidine (**17**)*

A solution of the chloropyrimidine **14** (1.0 g, 4.8 mmol) and $NH_2NH_2.H_2O$ (4.0 ml) in EtOH (8 ml) was heated under reflux under N_2 for 2 h, the EtOH was then removed by vacuum distillation until the residue began to solidify. The remaining mixture was filtered and the solid recrystallized from EtOH/H_2O to give 0.72 g (73.5%) of the hydrazine **17** as a colourless solid: TLC (EtOAc) $R_f = 0.46$; m.p. 82.0–83.0°C; IR (Nujol) 3315, 3277, 3207, 1639, 1600, 1537 and 1281 cm^{-1}; ^{1}H NMR δ 8.32 (s, 2, pyrim H), 7.05 (br s, 1, NH), 3.99 (s, br s, NH_2), 2.40 (t, 2, $J = 7.0$, α-CH_2), 1.64–1.57 (m, 2, β-CH_2), 1.44–1.34 (m, 4, 2CH_2) and 0.93 (t, 3, $J = 7.1$, CH_3); ^{13}C NMR δ 162.16, 160.21, 109.76, 93.68, 74.49, 31.07, 28.30, 22.16, 19.39 and 13.93.

5.14. *5-Heptyl-2-hydrazinopyrimidine (**20**)*

A mixture of the hydrazine **17** (2.5 g, 12 mmol) and 10% Pd/C (0.50 g) in EtOAc (30 ml) was stirred for 16 h under H_2 (1 atm) atmosphere and then filtered through Celite. The filtrate was concentrated *in vacuo* and the remaining solid recrystallized from EtOAc hexane to give 0.73 g of the desired product as a colourless solid. An additional 0.91 g was obtained by chromatographing the mother liquor through 5 g silica gel using EtOAc to give a total yield of 1.64 (64.8%) of the alkylpyrimidine **20**: TLC (EtOAc) $R_f = 0.20$; m.p. 75.0–78.5°C; IR (Nujol) 3272, 1647, 1608, 1568, 1457, 1273 and 1201 cm^{-1}; ^{1}H NMR δ 8.20 (s, 2, pyrim H), 6.55 (br s, 1, NH), 3.88 (br s, 2, NH_2), 2.46 (t, 2, $J = 7.6$, α-CH_2), 1.59–1.52 (m, 2, β-CH_2), 1.30–1.20 (m, 8, 4CH_2) and 0.88 (t, 3, $J = 6.6$, CH_3), 1.30–1.20 (m, 8, 4CH_2) and 0.88 (t, 3, $J = 6.6$, CH_3); ^{13}C NMR 163.32, 157.73, 125.38, 31.69, 31.15, 29.46, 28.98, 28.96, 22.55 and 14.00.

5.15. *2-Bromo-5-heptylpyrimidine (**23**)*

To a stirred solution of the alkylpyrimidine **20** (0.91 g, 4.4 mmol) in HOAc (20 ml) in a 10°C water bath was added dropwise a solution of Br_2 (0.5 ml, 9.8 mmol) in HOAc (15 ml). The reaction mixture was stirred at r.t. for 10 min; it was then poured cautiously into H_2O (50 ml) and the mixture extracted with Et_2O (2 × 100 ml). The organic extract was washed with saturated aqueous $NaHCO_3$ (5 × 50 ml) followed by saturated aqueous $NaHSO_3$ (2 × 50 ml); it was dried over anhydrous K_2CO_3 and filtered. The filtrate was concentrated *in vacuo* to give the crude product. This material was chromatographed through 60 g alumina (Act II) using CH_2Cl_2. All fractions shown by TLC to contain the product were combined, filtered through 5 g silica gel to remove a $R_f = 0$ spot and the filtrate concentrated *in vacuo* to give 0.35 g (31.2%) of the bromide **23** as an orange liquid: TLC (CH_2Cl_2) $R_f = 0.21$; ^{1}H NMR δ 8.40 (s, 2, pyrim H), 2.58 (t, 2, $J = 7.7$, α-CH_2); 1.80–1.60 (m, 2, β-CH_2) 1.40–1.28 (m, 8, 4CH_2) and 0.88 (t, 3, $J = 6.4$, CH_3) and ^{13}C NMR δ 159.20, 150.35, 134.52, 31.60, 30.52, 29.58, 28.88, 22.53 and 1400.

5.16. *1-(p-Cyanophenyl)-4-trimethylsilyl-1,3-butadiyne (**18**)*

This material was prepared in the same manner as the diacetylene **9** using bis(trimethyl-silyl)-1,3-butadiyne (1.8 g, 9.4 mmol) and the iodide **15** (1.03 g, 4.5 ml). The crude product was chromatographed through 50 g silica gel that was slurry packed with 20% CH_2Cl_2/hexane containing 1% Et_3N to yield 0.73 g of a grey solid. However, ^{1}H NMR showed that this material was a 1 : 1 mixture of the desired product **18** and the deprotected diacetylene **21**. A small amount of the protected material **18**, free of the unprotected diacetylene, was obtained from a smaller scale reaction and used for characterization: TLC (30% CH_2Cl_2/hexane) $R_f = 0.21$, ^{1}H NMR δ 7.59 (2, d, $J = 8.7$, ArH *ortho* to C≡C) 7.52 (2, d, $J = 8.6$, ArH *ortho* to CN) and 0.22 (s, 9, 3Me); ^{13}C NMR δ 133.0, 132.0, 126.3, 118.0, 112.4, 93.6, 86.9, 78.1, 74.3 and − 0.64.

5.17. *1-(p-Cyanophenyl)-1,3-butadiyne (**21**)*

The crude mixture of **18** and **21** (0.40 g) was completely deprotected by stirring a MeOH (20 ml) solution of this with K_2CO_3 (0.10 g) at r.t. for 30 min. This mixture was poured into H_2O, the MeOH removed *in vacuo* and the remaining liquid extracted with CH_2Cl_2 (2 × 25 ml). The organic layer was dried, filtered and the filtrate concentrated *in vacuo* to give 0.36 g (35.7%) of the crude diacetylene **21** as shown by ^{1}H NMR δ 7.6 (ArH) and 2.6 (C≡CH).

5.18. *Attempted synthesis of the diacetylene **3** from compound **21***

To a stirred solution of the crude diacetylene **21** and the chloride **22** (0.34 g, 1.6 mmol) in Et_3N (10 ml) was added CuI (0.01 g, 0.05 mmol) and $(PPh_3)_2PdCl_2$ (0.03 g, 0.04 mol). This mixture was heated under reflux for 16 h and filtered; the insoluble material washed thoroughly with Et_2O and H_2O, the filtrate concentrated *in vacuo* and the remaining liquid extracted with Et_2O (3 × 25 ml). The organic layer was dried, filtered and the filtrate concentrated *in vacuo* to give a liquid. This material was chromatographed through 40 g silica gel using hexane to give 0.33 g (97.1% recovery) of the starting chloride **22** as shown by ^{1}H NMR. None of the desired diacetylene **3** could be isolated. This was also true when the diacetylene **21** was treated with the bromide **23**.

5.19. *5-Heptyl-2-(3-hydroxy-3,3-dimethylprop-1-ynyl)-pyrimidine (**27**)*

A mixture of the chloropyrimidine **22** (0.50 g, 2.4 mmol), the alcohol **25** (0.30 g, 3.6 mmol), CuI (0.01 g, 0.05 mmol) and $(PPh_3)_2PdCl_2$ (0.05 g, 0.07 mmol) in Et_3N (5 ml) was heated under reflux under N_2 for 16 h. The insoluble materials were removed by filtration, washed thoroughly with Et_2O and H_2O, and the Et_2O removed from the filtrate *in vacuo*. The remaining liquid was extracted with Et_2O (2 × 50 ml); the organic layer was separated, dried, filtered and the filtrate concentrated *in vacuo*. Chromatography of this material through 30 g silica gel using a 30% EtOAc/hexane solution gave 0.12 g (24.0%) of the starting chloropyrimidine **22** followed by 0.35 g (57.3%) of the desired pyrimidine **27** as a brown solid: TLC (30% EtOAc/hexane) $R_f = 0.10$; IR (Nujol) 3309, 2256, 1591, 1552, 1427 and 1177 cm^{-1}; ^1H NMR δ 8.54 (s, 2, pyrim H), 3.59 (s, 1, OH), 2.60 (t, 2, $J = 7.6$, α-CH_2), 1.66 (s, 6, 2Me), 1.65–1.57 (m, 2, β-CH_2), 1.33–1.26 (m, 8, $4CH_2$) and 0.88 (t, 3, $J = 6.6$, Me); ^{13}C NMR δ 156.9, 150.3, 134.3, 92.4, 80.6, 65.0, 31.6, 30.9, 30.5, 30.3, 28.9, 28.8, 22.5 and 14.0.

A larger scale reaction (16.0 mmol) gave a 73.1% yield of the pyrimidine **27** when additional amounts of the reagents **25** (3.1 ml), $(Ph_3P)_2PdCl_2$ (0.10 g) and CuI (0.015 g) were added after a 16 h reflux, with refluxing continued for another 24 h.

5.20. *2-Ethynyl-5-heptylpyrimidine (**29**)*

To a solution of the acetylene **27** (0.60 g, 4.83 mmol) in toluene (20 ml) was added powdered NaOH (0.20 g, 4.83 mmol); this mixture was heated under reflux for 1 h, cooled to 0°C and filtered. The solvent was removed from the filtrate to give the crude acetylene **29** which was used without purification.

5.21. *4-Cyano-B,B-dibromomostyrene (**28**)*

To a stirred suspension of Zn powder (14.4 g, 0.22 mol) and PPh_3 (63.5 g, 0.24 mol) in CH_2Cl_2 (230 ml) at 0°C was added dropwise a solution of CBr_4 (73.0 g, 0.22 mol) in CH_2Cl_2 (285 ml) within 2 h; this reaction mixture was allowed to warm to r.t. and stirred for 48 h. A solution of the aldehyde **26** (14.4 g, 0.11 mol) in CH_2Cl_2 (40 ml) was added dropwise over 30 min. The reaction mixture was stirred at r.t. for 2 h, then filtered through silica gel which was then washed thoroughly with CH_2Cl_2. The solvent was removed from the filtrate *in vacuo* to give the crude product (34.1 g). This material was purified by chromatography on silica gel using 5% EtOAc/hexane to give 20.1 g (63.7%) of the solid olefin **28**: m.p. 86–88°; IR (Nujol) 2234 (med, CN) and 1600 cm^{-1} (str, Ar); ^1H NMR δ 7.63 (s, 4, ArH) and 7.48 (s, 1, C=CH); ^{13}C NMR δ = 139.57, 135.14, 132.2, 128.91, 111.95 and 93.41.

5.22. *1-(p-Cyanophenyl)-2-bromoacetylene (**30**)*

To a stirred solution of the olefin **28** (4.0 g, 0.14 mol) in toluene (75 ml) was added dropwise a 1.0M solution of *t*-BuOK in THF. The reaction mixture was heated under reflux for 4 h, cooled to r.t., filtered and the filtrate cooled to − 78°C. The resulting yellow precipitate was removed by filtration, washed thoroughly with toluene and dried to give 1.7 g (58.6%) of the alkyne **30**: m.p. 146–147°, IR (Nujol) 2247 (med, CN), 2196 (med, C≡C) and 1601 cm^{-1} (str, Ar); ^1H NMR δ 7.6 (d, 2, $J = 8.1$, ArH *ortho* to C≡C) and 7.5 (d, 2, $J = 8.1$, ArH *ortho* to CN); ^{13}C NMR δ 132.5, 132.0, 127.47, 118.21, 112.06, 78.56 and 55.35.

5.23. *4-[4-(5-Heptyl-2-pyrimidinyl)-1,3-butadiynyl]-benzonitrile (**3**)*

The crude acetylene **29** was dissolved in abs EtOH (30 ml), and CuCl (2 mg) in $BuNH_2$ (2.5 ml) and NH_2OH (0.12 g, 1.7 mmol) were added. This stirred mixture was cooled to 0°C and the bromoacetylene **30** (0.36 g, 1.73 mmol) in abs EtOH (10 ml) added dropwise. Stirring was continued at 0° for 2 h; the mixture was then allowed to warm to r.t., stirred for 17 h and cooled to − 78°C. The insoluble solids were removed by filtration and washed with cold abs EtOH to give 0.14 g (23.9%) of the product. This material was recrystallized from MeOH to give the diacetylene **3**: m.p. 130° (dec); IR (Nujol) 2368 (med, CN), 2234 (med, C≡C) and 1543 cm^{-1} (str, Ar); ^1H NMR δ 8.5 (s, 2, pyrim H), 7.6 (s, 4, ArH), 2.58 (t, 2, $J = 7.5$, α-CH_2), 1.6 (m, 2, β-CH_2) 1.2 (m, 8, $4CH_2$) and 0.85 (t, 3, $J = 6.7$, Me) and ^{13}C NMR δ = 157.17, 149.61, 135.36, 133.24, 132.1, 125.94, 118.07, 112.96, 81.2, 79.89, 77.63, 70.48, 31.63, 30.49, 28.98, 28.9, 22.55 and 14.02.

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