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Synthesis and properties of some novel high birefringence phenylacetylene liquid crystal materials with lateral substituents

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We have synthesized and investigated new 3-ring phenylacetylene liquid crystals with high birefringence values (Δn) to improve the nematic temperature range while retaining a high optical anisotropy. In the case of modifying the terminal ring, the introduction of branched alkoxy chains, fluorine or methyl groups shifted the nematic phase to lower temperatures. In order to minimize the influence of the substituent on Δn , the incorporation of lateral methyl groups was chosen as the most profitable method for obtaining wide and low temperature nematic phases. With these results in mind, we studied the effect of the position of the methyl group on the physical properties. The most effective methyl position for improving the nematic temperature range was on the central ring. From the standpoint of obtaining high Δn values and low viscosity, the central ring was also the best position.

1. Introduction

Liquid crystals (LCs) which exhibit high values of birefringence (Δn) are useful components in liquid crystal mixtures. They are employed in the conventional super twisted nematic (STN) and in high response STN-LCDs with a narrow cell gap as Δn moderators. The value of Δn required is around 0.15–0.18 so that LCs having moderate Δn values are contained in such mixtures. Recently, the remarkable development of multimedia technology has created a strong demand for high performance mobile displays. High Δn liquid crystals are attractive materials for bright reflective displays including PDLCDs [1, 2], cholesterics [3], holographic switching devices [4] and directional reflectors [5, 6]. Besides display applications, these materials are thought to be applicable to laser beam steering [7] and infrared spatial modulators [8].

It is well known that a high Δn value can be achieved by increasing the molecular conjugation length [9]. A considerable number of π -conjugated compounds have been developed as high Δn liquid crystals [10, 13]. However, their Δn values were below 0.4 or they contained a stilbene fragment which, in general, readily undergoes photoisomerization. Fused rings were incorporated into the core in an attempt to obtain higher values

of Δn . 2,6-Disubstituted naphthyl-ethynyl moieties were synthesized and investigated [14]. They exhibited high Δn values of about 0.3, but showed a high temperature nematic phase. 2,6-Naphthynyl-2,5-pyridinyl ethynes exhibited similar properties. Terminal groups which could contribute towards a high value of Δn were also investigated. 2,6-Disubstituted naphthyl homologues containing a terminal cyano-substituent have high Δn values of over 0.4 [15]. Isothiocyanato-substituted biphenyls were synthesized and the terminal group was shown to give a higher Δn than the cyano group [16]. Unfortunately compounds containing these moieties exhibited high melting points and low solubilities.

We have developed durable high Δn liquid crystals based on phenylacetylene and containing molecules highly conjugated along the molecular long axis [17–19]. They exhibited high values of Δn as expected, but were not suitable for practical use because of high transition temperatures and poor solubility.

In this study, we have focused on a 3-ring phenylacetylene (3PA) core which yields materials having high Δn values and wide nematic phases. In order to improve the nematic range temperature while maintaining the desirable optical anisotropy, modified 3PA compounds were investigated. Recently, similar systems of the phenylacetylene compounds having terminal chains of varying length were reported [20, 21], but basic modification of the core is now necessary to establish structure–property

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relationships. Thus, we synthesized 3PA homologues having a modified terminal ring and methyl-substituted core, and investigated the effects of the substituents and their lateral positions on physical properties.

2. Experimental

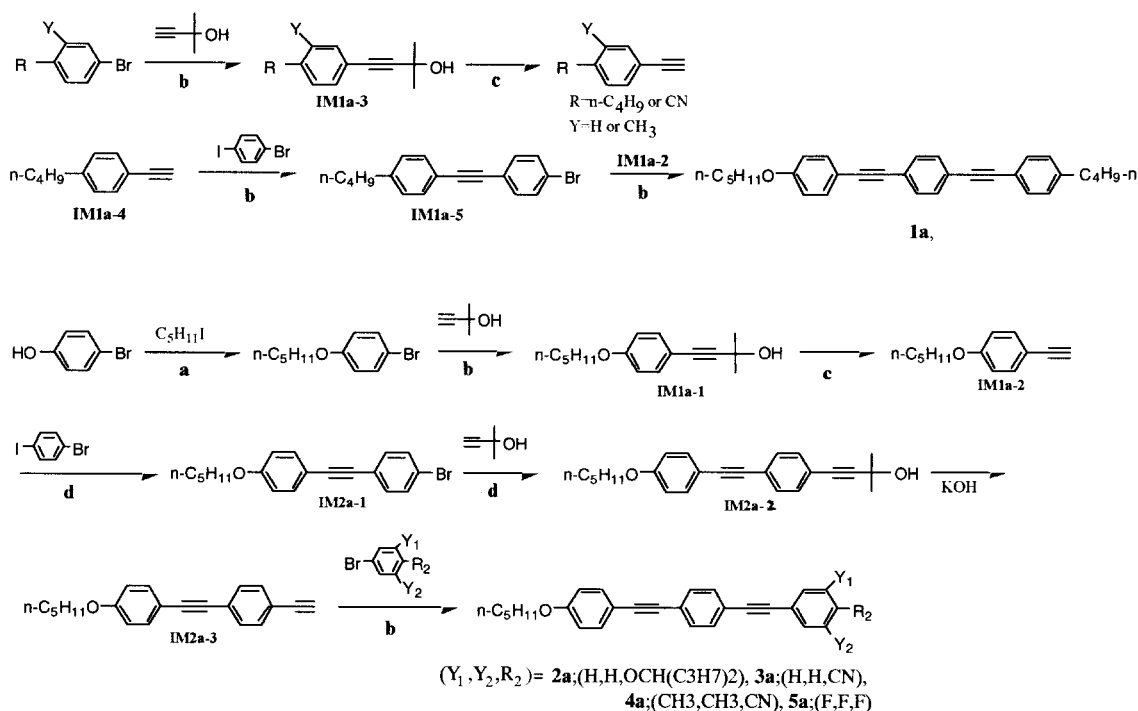
The preparative routes for the 3PA homologues are shown in schemes 1–3. The main synthetic procedures are described in §5. The structures of the final compounds and various synthetic intermediates were characterized by ^1H NMR spectroscopy; all spectra were recorded in CDCl_3 with TMS as internal standard. All ^1H NMR spectra (UNITY 300, Varian 300 MHz) were in accordance with the proposed structures. Mass spectra (SX102, JEOL) were also measured and identified the predicted molecular weights. The purity of each compound was verified by HPLC analysis (ODS A-212 column, Sumika Chemical Analysis Service) and all compounds were greater than 99% pure except for **3b** (94.6%) and **4b** (98.3%).

Transition temperatures and phase sequences were measured using a Mettler FP82 hot stage and control unit in conjunction with an optical microscope (OPTIPHOT2-POL, Nikon) and these were confirmed using differential scanning calorimetry (DSC-200, Seiko Instruments Inc.). Refractive indices were evaluated as extrapolated values from mixtures containing a 10 wt %

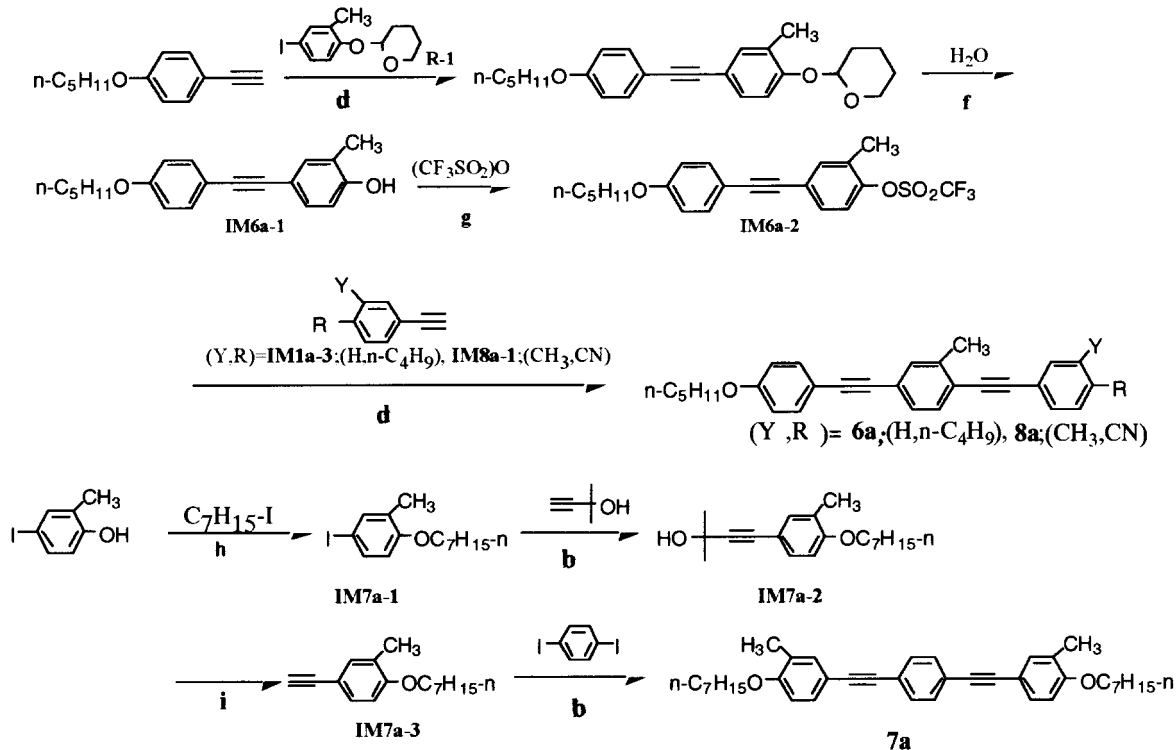
solution of each test compound in MJ931381 (Merck Japan). An Abbe refractometer (2T, Atago) with a sodium lamp (589 nm) was used to measure the refractive indices of the mixtures at 20°C. The birefringence of single compounds was also measured using the hollow prism method [22]. The set-up for the measurement is shown in figure 1. A temperature controlled parallel aligned wedge cell, which was set on a rotational stage equipped with a stepping motor (D80, Suruga Seiki) and encoder system (resolution; 1 arcsec, K1 and CR-16, Canon) was used for the measurement. Each reflection angle of the incident He-Ne laser ($\lambda = 633 \text{ nm}$) light, polarized parallel and perpendicular to the rubbing direction, was measured for the calculation of n_o and n_e .

Order parameters were estimated by measuring polarized IR absorption spectra (FTIR, Magna860, Nicolet). 10 μm thick homogeneously aligned cells were prepared for this measurement; the substrates were CaF_2 plates coated with polyimide (LX-1800, Hitachi Chemicals) and rubbed in one direction. Order parameters were calculated from the dichroic ratio of the acetylene $\text{C}\equiv\text{C}$ stretching absorption peak at around 2220 cm^{-1} , according to the equation $S = (D - 1)/(D + 2)$, where D is the dichroic ratio and S is the order parameter [23].

The viscosity was also estimated as extrapolated values from the same mixture used for the Δn evaluation using a microviscometer (AMV-200, DMA48 for the measurement of density, Anton Parr KG) at 20°C.



Scheme 1. a K_2CO_3 /2-butanone b $\text{PdCl}_2(\text{PPh}_3)_2/\text{PPh}_3/\text{CuI}$ /triethylamine c NaOH /Toluene d $\text{PdCl}_2(\text{PPh}_3)_2/\text{CuI}$ /triethylamine e toluene/ KOH .



Scheme 2. f *p*-toluenesulphonic acid g pyridine/4-pyrrolidin-1-yl pyridine h Na_2CO_3 /methyl ethyl ketone i NaOH/Toluene.

3. Results and discussion

3.1. Terminal substituted series

3.1.1. Mesogenic properties

Phase sequences, transition temperatures and associated enthalpies for compounds **1a–5a** are listed in table 1. Compound **1a**, which has linear terminal alkoxy and alkyl groups, exhibited a high temperature nematic phase

with a midpoint of 200°C . In order to reduce this temperature, we modified the core and/or the terminal chains of the compound. The introduction of a branched terminal alkoxy chain (**2a**), or lateral methyl (**4a**) or fluorine (**5a**) substituents was effective in lowering the liquid crystal temperatures. In particular, lateral methyl and fluorine substituents dramatically decreased the

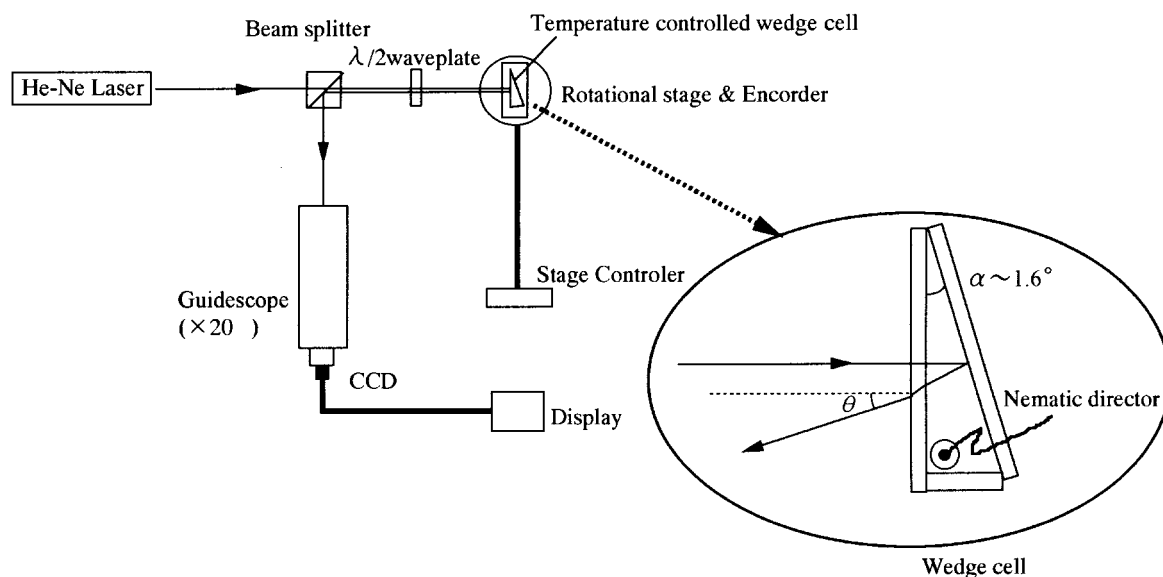
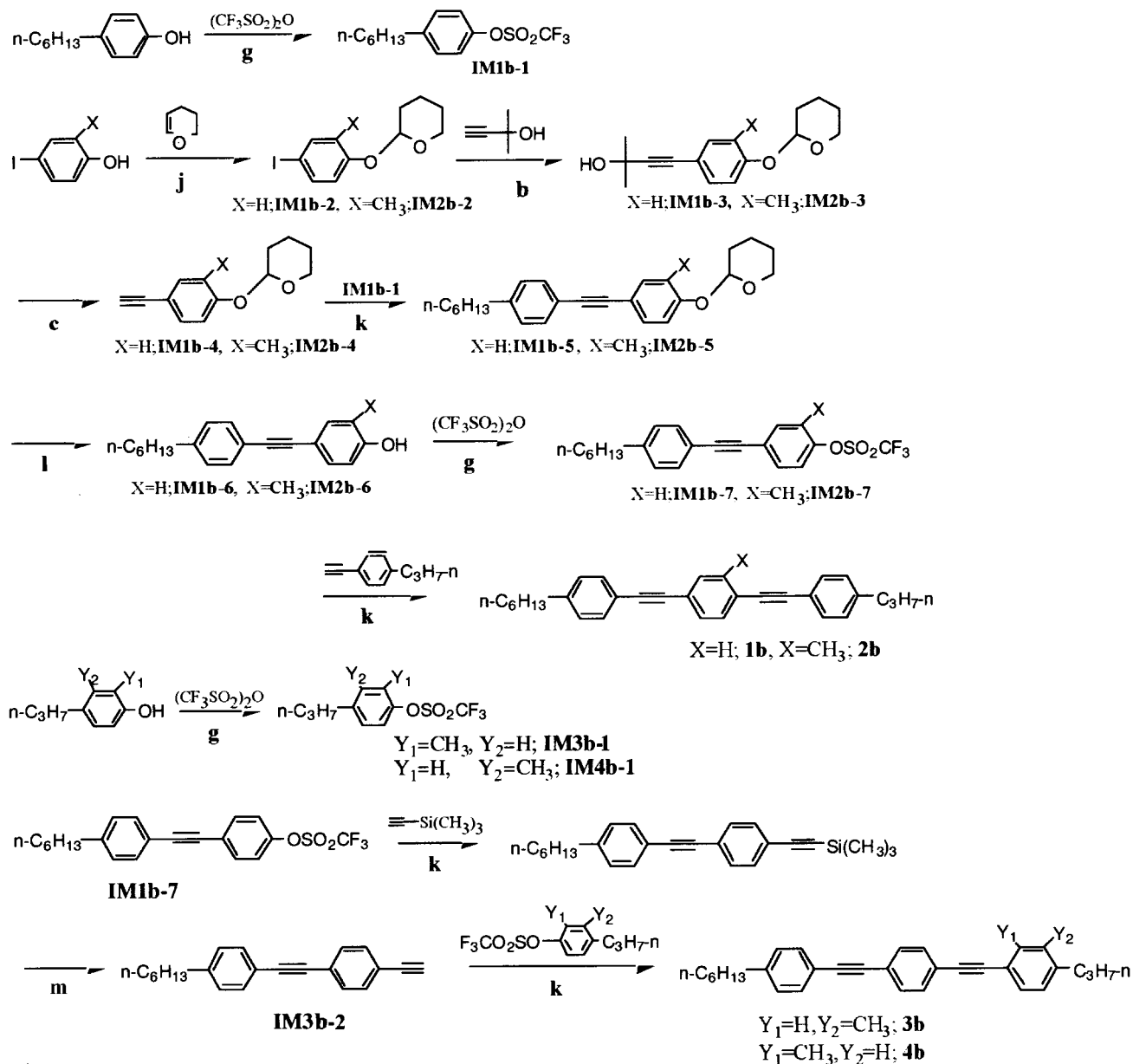


Figure 1. Optical set-up for refractive index measurements.



Scheme 3. j *p*-toluenesulphonic acid/chloroform k PdCl₂(PPh₃)₂/triethylamine/DMF l *p*-toluenesulphonic acid/methanol m Na₂CO₃/ethylacetate/ethanol.

Table 1. Transition temperatures and associated enthalpies for the 3PA homologues. Parentheses denote a monotropic transition: Cr = crystal, SmX = unassigned smectic phase, SmA = smectic A phase, N = nematic phase, I = isotropic.

Compound	R ₂	Y ₁	Y ₂	Transition temperatures (°C) and enthalpies (in square brackets, kJ mol ⁻¹)						
				Cr	SmX		SmA	N	I	
1a	C ₄ H ₉	H	H	•			162[19.4]	•	234[1.4]	•
2a	OCH(C ₃ H ₇) ₂	H	H	•	143[32.5]	(• 119[16.3])				•
3a	CN	H	H	•			199[18.8]	•	297[1.5]	•
4a	CN	CH ₃	CH ₃	•			149[37.6]	•	160[0.5]	•
5a	F	F	F	•	129[18.8]	(• 101[3.3])	•	168[2.4]	•	179[0.54]

clearing (T_{NI}) and melting points. Similar effects of lateral fluoro and alkyl substituents have been reported [24], suggesting that these groups are capable of disrupting the intermolecular crystalline packing as well as increasing the breadth of the molecules. The enthalpies associated with the nematic–isotropic transitions were smaller than those seen for compounds without lateral substituents, indicating a lower degree of interaction between the molecules in the mesophases.

The effects of these modifications on the phase sequences differed. Compound **2a**, containing a branched alkoxy group, did not exhibit nematic phase while fluoro substitution induced smectic behaviour but also retained the nematic phase. The incorporation of lateral methyl groups did not change the phase sequence.

3.1.2. Physical properties

The optical properties, the calculated anisotropic polarizabilities ($\Delta\alpha$) and the viscosities are listed in table 2. Most of the compounds exhibited high Δn values of over 0.4. The compounds containing nitrile groups showed very high Δn values of 0.5–0.6. Fluoro substituents, branched alkoxy chains and methyl groups decreased Δn compared with that of the analogous non-laterally substituted compound even though the $\Delta\alpha$ values were similar.

In order to study the effects of the substituents on the properties of the compounds, the temperature dependence of Δn and order parameters of the pure compounds were measured (see figures 2 and 3 respectively). The dependence of Δn on chemical structure was the same as seen for Δn estimated by extrapolation from mixtures with a host nematic.

The order parameters of the non-substituted compounds (**1a** and **3a**) were almost the same, but introducing methyl and fluoro groups resulted in decreased values. The calculated value of $\Delta\alpha$ for **3a** was the largest of all the compounds. Substituents decreased $\Delta\alpha$ because the lateral groups increased the polarizability perpendicular to the long axis of the molecule. It is well known

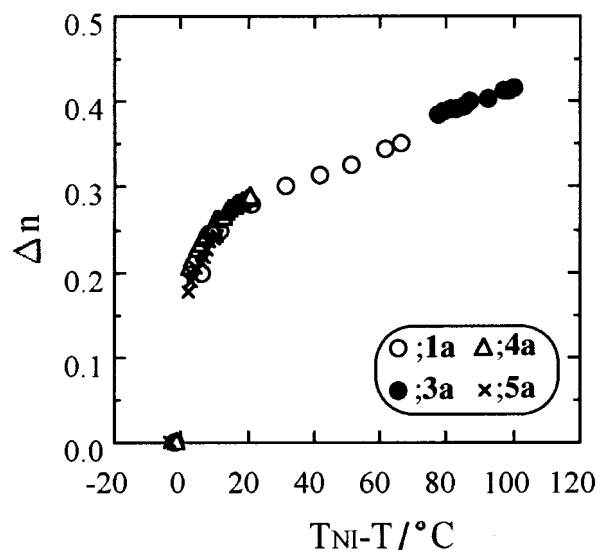


Figure 2. The effect of substituent on birefringence.

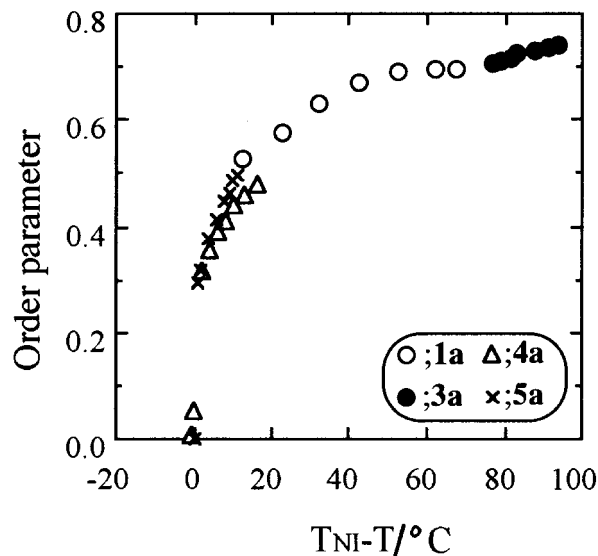


Figure 3. The effect of substituent on the order parameter.

Table 2. Optical properties and viscosities of the 3PA homologues

Compound	n_o^a	n_e^a	Δn^a	$\alpha^b/\text{A.U.}$	$\Delta\alpha^c/\text{A.U.}$	$\eta^a/\text{mPa s}$
1a	1.519	1.966	0.448	359	525	—
2a	1.532	1.888	0.356	397	562	—
3a	1.513	2.114	0.601	342	558	—
4a	1.542	2.012	0.470	362	555	1050
5a	1.511	1.922	0.410	508	328	84

^a Optical properties (at 20°C and $\lambda = 589\text{ nm}$) and viscosity (at 20°C) were extrapolated values of the mixture [liquid crystal (10 wt %) and MJ931381 (90 wt %)].

^b Average polarizability calculated by MOPAC93.

^c $\Delta\alpha = \alpha_x - (\alpha_y + \alpha_z)/2$; α_x = polarizability along the molecular long axis; α_y, α_z = polarizability along the molecular short axis.

that Δn is determined largely by $\Delta\alpha$ and the order parameter, such that incorporating substituents decreases Δn because of the reduction in $\Delta\alpha$ and the order parameter. In the case of Δn estimated by extrapolation from mixtures, the lowering of T_{NI} also caused the decrease in the order parameter at the temperature at which Δn was estimated.

The viscosities of these series were slightly higher than for the 3-ring phenylcyclohexyl compounds [25]. The effect of the substituents on the viscosity was almost the same as for conventional liquid crystals; specifically, lower viscosity is observed with fluoro groups and higher viscosities with nitrile substituents.

3.2. Effect of lateral substituent position of the methyl groups on physical properties

As the introduction of methyl groups was effective in lowering the nematic temperature range but with only a small decrease in Δn , we synthesized, therefore, a variety of 3-ring phenylacetylene compounds with lateral methyl groups. The effects of the position and number of substituents on the physical properties were investigated in order to establish the optimum structural modification for these homologues.

3.2.1. Thermal properties

The phase sequences, transition temperatures and associated enthalpies are listed in table 3. A comparison

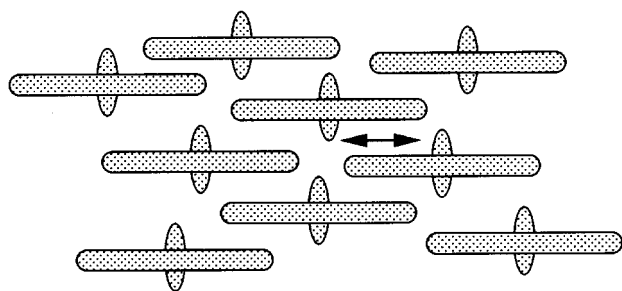
of the transition temperatures for **1b–4b**, reveals that the most effective substitution position for lowering the nematic temperature range was the central ring. The behaviour of T_{NI} and the melting point (T_m) were different: T_m increased in the order **2b** (substituted central ring) < **3b** (substituted terminal ring) < **4b** (substituted terminal ring) < **1b** (non-substituted), whereas T_{NI} increased in the order **4b** < **2b** < **3b** < **1b**. In the case of the alkyl-alkoxy compounds (**6a–8a**), similar trends were observed.

Molecular theories of the nematic phase have been extensively studied and T_{NI} is decided by some very delicate balance between repulsive and attractive forces [26]. The substitution position A (see figure 4) decreased the interaction area of the mesogenic cores to the greatest extent because the substituent is in the centre of the core, and hence the melting point was the lowest of the group. Substitution at position C retains a larger interaction area between the molecules than for substitution at position A, and therefore the melting point decrease was not so large. Substitution at position A increased the distance between molecules but the molecular shape was almost symmetrical and so they behaved like linear molecules. As a result, T_{NI} was not low compared with positions B and C. Substitution at position C destroyed the symmetry of the molecular shape. The interaction area of the mesogenic cores was larger than for compounds substituted in positions A or B, and therefore

Table 3. The effects of the position of a methyl group on physical properties. Parentheses denote a monotropic transition: Cr = crystal, SmX = unassigned smectic phase, N = nematic phase, I = isotropic.

Compound	Transition temperatures (°C) and associated enthalpies (in square brackets, kJ mol ⁻¹)					
	Cr		N	I		
1b		•	147[18.6]	•	209[1.2]	•
2b		•	57[14.4]	•	169[1.3]	•
3b		•	67[13.5]	•	176[1.0]	•
4b		•	85[30.9]	•	143[0.9]	•
6a		•	83[16.4]	•	201[1.4]	•
7a		•	146[54.8]	•	162[1.8]	•
8a		•	106[39.0]	•	191[0.7]	•

Substituted position; A type



Substituted position; C type

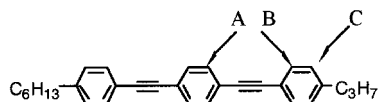
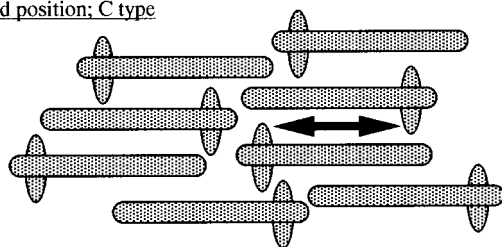


Figure 4. Schematic representation of the substituted 3PA compounds.

the melting point of this compound was the highest. On the other hand, the excluded volume presumably increased because of the wedge-like molecular shape. As a result T_{NI} was lowered by the greatest amount. The large excluded volume may also result in the lowering of the order parameter.

The temperature dependence of the order parameter of **1b–4b** and **6a–8a** are shown in figure 5. The order parameter of **4b** was lower than those of **2b** or **3b**, supporting the suggestion that the excluded volume effect is important. In the case of the alkoxy (**6a**) and cyano (**8a**) substituents, similar thermal properties were observed.

Compound **7a**, which has two methyl substituents, one in each terminal ring, exhibited almost the same values of the order parameter as the non-substituted compound. This is not inconsistent with the excluded volume model. In the case of **7a**, we consider that symmetrical substitution kept the order parameter higher because the symmetrical molecular shape behaved as a simple rod-like molecule containing no substituent.

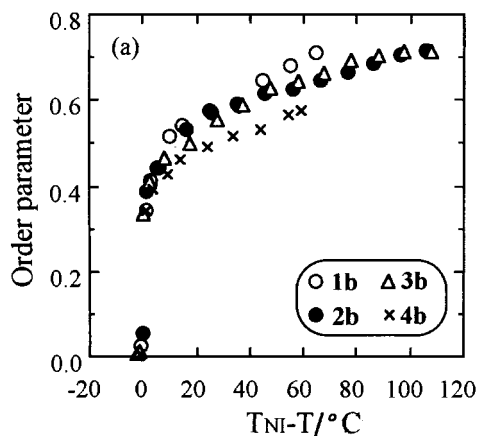
3.2.2. Birefringence and viscosity

The birefringence and viscosities of these compounds are listed in table 4; the temperature dependence of Δn , measured for the pure compound, is also shown in figure 6. Δn slightly decreased on introducing methyl

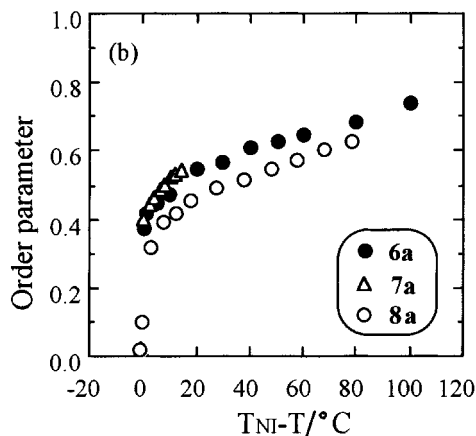
Table 4. Physical properties of methyl substituted 3PA homologues.

Compound	n_o^a	n_e^a	Δn^a	$\eta^a/\text{mPa s}$
1b	1.515	1.947	0.432	84
2b	1.524	1.944	0.419	119
3b	1.527	1.914	0.388	195
4b	1.528	1.932	0.404	104
6a	1.522	1.954	0.432	156
7a	1.514	1.876	0.362	—
8a	1.537	2.027	0.490	1157

^a Optical properties (at 20°C and $\lambda = 589 \text{ nm}$) and viscosity (at 20°C) were extrapolated values of the mixture [liquid crystal (10 wt %) and MJ931381 (90 wt %)].



(a)



(b)

Figure 5. The effect of the position of the methyl group on the order parameter: (a) alkyl type, (b) alkoxy type.

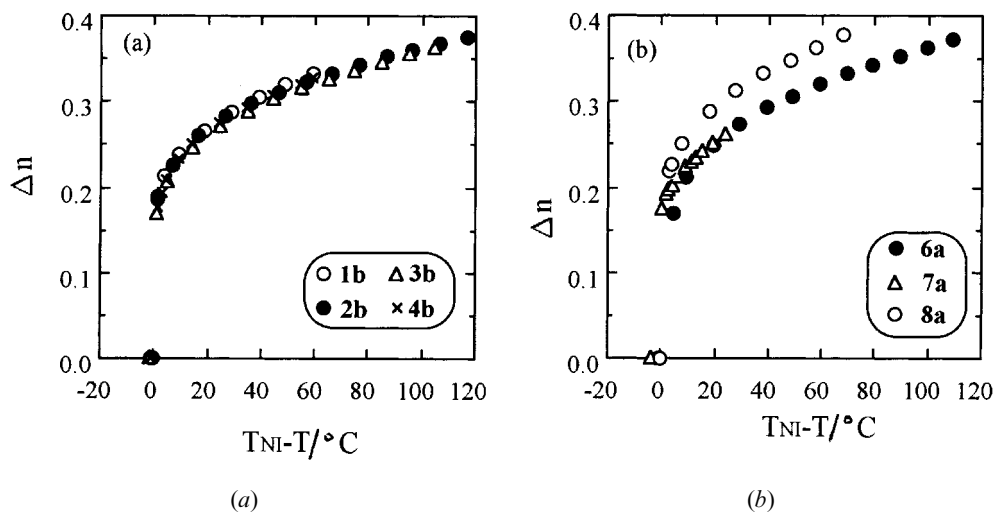


Figure 6. The effect of the position of the methyl group on birefringence: (a) alkyl type, (b) alkoxy type.

groups. However, no differences between them because of the substituent position were observed. In the case of Δn estimated by extrapolation from the mixture with a nematic host, substituent position A (**2b** or **6a**) exhibited the highest values for the methyl substituted homologues. The viscosities of these were also the lowest. From these view points, position A was the most useful substituent position in the case of these 3-ring phenylacetylene homologues.

4. Conclusions

We have synthesized and evaluated the properties of substituted 3-ring phenylacetylene homologues. In the investigation of modifying the terminal ring, it was found that a methyl substituent was effective in lowering the nematic temperature while keeping a high Δn value compared with a fluorine group or introducing a branched terminal chain. With these results, we studied the effect of the position of the methyl substituent on the physical properties. The most effective methyl substituent position for improving the nematic range was the central ring. Based on the estimated values of Δn , and the measured order parameters and viscosities, the best substituent position was also on the central ring.

These results led us to investigate the 3PA homologues with different types of substituent on the central ring, with results that have been reported elsewhere [27]. We obtained useful components and nematic mixture of high Δn , 0.40 (at 589 nm, 20°C), with a nematic phase from 2 to 171°C by using mainly this series.

5. Synthesis

5.1. 1-[(4-Pentyloxyphenyl)ethynyl]-4-[(4-butylphenyl)ethynyl]benzene, **1a**

A solution of *p*-bromophenol (91 g) and K_2CO_3 (104.7 g) in 2-butanone (182 g) was degassed with nitrogen.

n-Pentyl iodide (125 g) was added to the mixture which was then stirred at 80°C for 10 h. The product was filtered off, washed with water and 5% aqueous NaOH and dried magnesium sulphate. It was concentrated to give *p*-bromo-*n*-pentoxybenzene; yield 115.96 g (83.9%).

A solution of *p*-bromo-*n*-pentoxybenzene (41.0 g), dichlorobis(triphenylphosphine)palladium (II) ($PdCl_2-(PPh_3)_2$, 1.02 g), CuI (0.41 g), triphenylphosphine (PPh_3 , 0.82 g) and triethylamine (68.3 g) in ethyl acetate (164 g) was degassed with nitrogen. 3-Methyl-1-butyne-3-ol (21.3 g) was added to the mixture which was then stirred at 60–65°C for 8 h. The product was filtered off and washed with ethyl acetate. The filtrate was concentrated and purified by column chromatography (silica gel, *n*-hexane/ethyl acetate, 5/1) to give **IM1a-1**; yield 21.0 g (95.2%).

A solution of **IM1a-1** (21.0 g) and NaOH (1.0 g) in toluene (84.0 g) was degassed with nitrogen and stirred at 90–95°C for 4 h. The product was concentrated and purified by column chromatography (silica gel, *n*-hexane with 0.1% triethylamine) to give **IM1a-2**; yield 14.03 g (70.5%).

A solution of *p*-bromobutylbenzene (25 g), $PdCl_2-(PPh_3)_2$ (1.00 g), CuI (0.50 g), PPh_3 (1.00 g) and triethylamine (47.4 g) in ethyl acetate (47.4 g) was degassed with nitrogen. 3-Methyl-1-butyne-3-ol (14.8 g) was added and the mixture stirred at 52–53°C for 7 h. The product was filtered off and washed with ethyl acetate. The filtrate was concentrated and purified by column chromatography (silica gel, acetonitrile/ethyl acetate, 10/1) to give **IM1a-3**; yield 25.4 g (72.0%).

A solution of **IM1a-3** (18.2 g) and NaOH (0.72 g) in toluene (72.8 g) was degassed with nitrogen and stirred at 90–95°C for 5 h. The product was condensed and purified by column chromatography (silica gel, *n*-hexane) to give **IM1a-4**; yield 13.00 g (93.8%).

A solution of *p*-bromophenyliodide (5.09 g), PdCl₂(PPh₃)₂ (0.20 g), CuI (0.10 g), PPh₃ (0.20 g) and triethylamine (4.86 g) in ethyl acetate (20.4 g) was degassed with nitrogen. A solution of **IM1a-4** (1.90 g) in ethyl acetate (1.90 g) was added to the mixture at 55°C and stirred at 55–60°C for 4 h. The product was filtered off and washed with ethyl acetate. The filtrate was concentrated and purified by column chromatography (silica gel, *n*-hexane) to give **IM1a-5**; yield 21.0 g (73.6%).

A solution of **IM1a-5** (2.90 g), PdCl₂(PPh₃)₂ (0.12 g), CuI (0.06 g), PPh₃ (0.12 g) and triethylamine (3.75 g) in ethyl acetate (14.5 g) was degassed with nitrogen. A solution of **IM1a-2** (2.09 g) in ethyl acetate (2.1 g) was added to this mixture at 55°C, which was then stirred at 55–60°C for 2.5 h. The product was concentrated and washed with *n*-hexane. The dry cake was purified by column chromatography (silica gel, *n*-hexane/chloroform, 3/1) to give **1a**; yield 3.45 g (88.1%). ¹H NMR (δ): 0.91 (t, 6H, *J* = 7.8 Hz), 1.26–1.51 (m, 6H), 1.51–1.70 (m, 2H), 1.71–1.89 (m, 2H), 2.63 (t, 2H, *J* = 7.8 Hz), 3.98 (t, 2H, *J* = 7.8 Hz), 6.83–6.91 (m, 2H), 7.10–7.21 (m, 2H), 7.38–7.55 (m, 8H). IR (CaF₂ cell) ν_{\max} : 2958, 2932, 2872, 2208, 1602, 1515, 1469, 1386, 1279, 1243 cm⁻¹. MS *m/z* 420 (M⁺).

5.2. 1-[(4-Pentyloxyphenyl)ethynyl]-4-{[4-(1-propylbutoxy)phenyl]ethynyl}benzene, **2a**

A solution of *p*-bromophenyliodide (36.4 g), PdCl₂(PPh₃)₂ (1.01 g), CuI (0.40 g) and triethylamine (43.3 g) in toluene (36.4 g) was degassed with nitrogen. **IM1a-2** (20.2 g) was added to the mixture at 50°C and stirring continued for 1 h. The product was filtered, concentrated and purified by recrystallization in ethanol to give **IM2a-1**; yield 34.7 g (92.8%).

A solution of **IM2a-1** (34.7 g), PdCl₂(PPh₃)₂ (1.74 g), CuI (0.69 g), PPh₃ (1.74 g) and triethylamine (51.1 g) in toluene (51.1 g) was degassed. 3-Methyl-1-butyne-3-ol (17 g) was added to the mixture at 60°C which was stirred for 4 h. The product was filtered off and washed with toluene. The filtrate was concentrated, purified by column chromatography (silica gel, toluene) and washed with *n*-hexane to give **IM2a-2**; yield 33 g (87.8%).

A solution of **IM2a-2** (29.3 g) and KOH in toluene was degassed and stirred at 90°C for 2 h. The product was purified by column chromatography (silica gel, *n*-hexane) to give **IM2a-3**; yield 17.94 g (69.9%).

A mixture of **IM2a-3** (2.88 g), PdCl₂(PPh₃)₂ (0.14 g), CuI (0.06 g), PPh₃ (0.14 g) and triethylamine (14.6 g) in toluene (14.6 g) was degassed with nitrogen. 4-Bromo-1,1-dipropyl-methoxybenzene was added to the mixture at 50°C which was stirred for 6 h at 75°C. The product was filtered off, concentrated and purified by column chromatography (silica gel, *n*-hexane with 0.1% triethylamine) to give **2a**; yield 2.44 g (50.7%). ¹H NMR (δ):

0.89–1.00 (m, 9H), 1.30–1.51 (m, 8H), 1.51–1.72 (m, 4H), 1.72–1.87 (m, 2H), 3.97 (t, 2H, *J* = 6.3 Hz), 4.22–4.33 (m, 1H), 6.80–6.91 (m, 4H), 7.39–7.50 (m, 8H). IR (CaF₂ cell) ν_{\max} : 3069, 3040, 2959, 2934, 2872, 2526, 2212, 1888, 1603, 1565, 1515, 1498, 1467, 1380, 1303, 1281, 1240 cm⁻¹. MS *m/z* 478 (M⁺).

5.3. 1-[(4-Pentyloxyphenyl)ethynyl]-4-[(4-cyanophenyl)ethynyl]benzene, **3a**

A solution of **IM2a-3** (3.46 g), PdCl₂(PPh₃)₂ (0.17 g), CuI (0.07 g), PPh₃ (0.17 g) and triethylamine (14.6 g) in toluene (14.6 g) was degassed with nitrogen. A solution of 4-bromobenzonitrile (3.28 g) in toluene was added to the mixture which was stirred at 50°C for 3 h. The product was filtered off after adding THF (100 ml) and washed with toluene. The filtrate was concentrated and washed by stirring with toluene and ethanol. It was purified by column chromatography (silica gel, chloroform) and recrystallized from toluene to give **3a**; yield 2.78 g (59.1%). ¹H NMR (δ): 0.94 (t, 3H, *J* = 7.2 Hz), 1.30–1.52 (m, 4H), 1.72–1.87 (m, 2H), 3.97 (t, 2H, *J* = 6.6 Hz), 6.85–6.93 (m, 2H), 7.41–7.53 (m, 6H), 7.55–7.69 (m, 4H). IR (CaF₂ cell) ν_{\max} : 2959, 2224, 2204, 1593, 1515, 1469, 1281, 1244 cm⁻¹. MS *m/z* 389 (M⁺).

5.4. 1-[(4-Pentyloxyphenyl)ethynyl]-4-[(3,5-dimethyl-4-cyanophenyl)ethynyl]benzene, **4a**

A solution of **IM2a-3** (3.46 g), PdCl₂(PPh₃)₂ (0.17 g), CuI (0.07 g), PPh₃ (0.17 g) and triethylamine (14.6 g) in toluene (14.6 g) was degassed with nitrogen. A solution of 4-bromo-2,6-dimethylbenzonitrile (3.03 g) in toluene was added and the mixture stirred at 50°C for 3 h. The product was filtered off, concentrated and washed by stirring with *n*-hexane. It was purified by column chromatography (silica gel, *n*-hexane/chloroform, 2/1) to give **4a**; yield 3.24 g (64.6%). ¹H NMR (δ): 0.94 (3H, t), 1.42 (4H, m), 1.80 (2H, m), 2.53 (6H, s), 3.97 (2H, t), 6.85–6.90 (2H, m), 7.27 (2H, d), 7.43–7.58 (6H, m). IR (CaF₂ cell) ν_{\max} : 2933, 2871, 2216, 2204, 1604, 1566, 1514, 1469, 1383, 1282, 1246 cm⁻¹. MS *m/z* 417 (M⁺).

5.5. 1-[(4-Pentyloxyphenyl)ethynyl]-4-[(3,4,5-trifluorophenyl)ethynyl]benzene, **5a**

A solution of **IM2a-3** (3.46 g), PdCl₂(PPh₃)₂ (0.17 g), CuI (0.07 g), PPh₃ (0.17 g) and triethylamine (14.6 g) in toluene (14.6 g) was degassed with nitrogen. A solution of 1-bromo-3,4,5-trifluorobenzene (3.8 g) in toluene was added to the mixture which was then stirred at 50°C for 3 h. The product was filtered off and washed with toluene. The filtrate was concentrated and purified by column chromatography (silica gel, *n*-hexane/chloroform, 4/1) to give **5a**; yield 3.36 g (66.6%). ¹H NMR (δ): 0.94 (t, 3H, *J* = 7.2 Hz), 1.38–1.47 (m, 4H), 1.75–1.89 (m, 2H), 3.97 (t, 2H, *J* = 6.3 Hz), 6.82–6.92 (m, 2H),

7.08–7.20 (m, 2H), 7.41–7.53 (m, 6H). IR (CaF₂ cell) ν_{\max} : 2936, 2873, 2205, 1723, 1606, 1597, 1526, 1473, 1427, 1378, 1281, 1249, 1206 cm⁻¹. MS m/z 4.18 (M⁺).

5.6. 1-[(4-Pentyloxyphenyl)ethynyl]-3-methyl-4-[(4-butylphenyl)ethynyl]benzene, **6a**

A solution of *p*-ethynyl-*n*-pentyloxybenzene (34.4 g), PdCl₂(PPh₃)₂ (1.38 g), triphenylphosphine (1.38 g), CuI (0.69 g) and triethylamine (81.50 g) in ethyl acetate (81.5 g) was degassed with nitrogen. A solution of **R-1** (64.0 g) in ethyl acetate (32.0 g) was added and the mixture stirred at 50–55°C for 2.5 h. The product was filtered off, washed with ethyl acetate and concentrated. THF (194.0 g), water (21.5 g) and *p*-toluenesulphonic acid were added and stirred in; toluene (400 ml) was then added. The product was washed with water, concentrated and purified by column chromatography (silica gel, *n*-hexane/acetic acid, 20/1) to give **IM6a-1**; yield 41.72 g (76.7%).

A solution of **IM6a-1** (14.72 g), 4-pyrrolidin-1-yl pyridine (0.29 g) and pyridine (29.4 g) in toluene (73.6 g) was degassed with nitrogen. A solution of anhydrous trifluoromethanesulfonic acid (21.16 g) in toluene (42.3 g) was added and the mixture stirred at 0°C. The organic material was extracted into toluene, and concentration after washing twice with water. The residue was purified by column chromatography (silica gel, *n*-hexane/acetic acid, 20/1) to give **IM6a-2**; yield 18.8 g (87.8%).

A solution of **IM6a-2** (4.26 g), PdCl₂(PPh₃)₂ (0.17 g) and triethylamine (10.12 g) in DMF (10.1 g) was degassed with nitrogen. A solution of **IM1a-3** (4.74 g) in DMF (13.6 g) was added to the mixture which was then stirred at 62°C for 16 h. Water and toluene were added at room temperature and the organic material was extracted into the organic solvent. It was concentrated after washing 3 times with water. The residue was purified by column chromatography (silica gel, *n*-hexane/acetic acid, 20/1) and recrystallization from *n*-hexane to give **6a**; yield 2 g (45.8%). ¹H NMR (δ): 0.93 (3H, t), 1.29–1.43 (6H, m), 1.47–1.66 (2H, m), 1.79 (2H, m), 2.49 (3H, s), 2.62 (2H, t), 3.96 (2H, t), 6.86 (2H, d), 7.16 (2H, d), 7.25–7.46 (7H, m). IR (CaF₂ cell) ν_{\max} : 3028, 2958, 2931, 2871, 2201, 1596, 1511, 1469, 1387, 1282, 1244 cm⁻¹. MS m/z 434 (M⁺).

5.7. 1,4-Phenylene bis[3-methyl-4-(heptyloxy)ethynylbenzene], **7a**

A solution of 4-hydroxy-3-methyl-iodo benzene (14.04 g) and Na₂CO₃ (7.95 g) in 2-butanone (28.1 g) was degassed with nitrogen and heated at 80°C. A solution of *n*-heptyliodide (11.31 g) in 2-butanone (11.3 g) was added and the mixture stirred for 5.5 h at 80–85°C. K₂CO₃ (6.91 g) was added and stirring continued for 10 h. The product was filtered off, washed with ethyl acetate (30 ml) and concentrated. Toluene (50 g) and 5%

aqueous solution of NaOH (50 g) were added and the product was extracted into the organic solvent. It was concentrated and purified by column chromatography (silica gel, *n*-hexane) to give **IM7a-1**; yield 11.58 g (68.5%).

A solution of **IM7a-1** (11.5 g), PdCl₂(PPh₃)₂ (0.23 g), PPh₃ (0.23 g), CuI (0.12 g) and triethylamine (14.00 g) in ethyl acetate (46.0 g) was degassed with nitrogen and heated to 56°C. A solution of 3-methyl-1-butyne-3-ol (4.37 g) in ethyl acetate (4.4 g) was added and the mixture stirred for 1.5 h at 56–60°C. The product was filtered off, washed with ethyl acetate and concentrated; it was purified by column chromatography (silica gel, *n*-hexane/ethylacetate 5/1) to give **IM7a-2**; yield 8.25 g (82.1%).

A solution of **IM7a-2** (8.20 g) and NaOH (0.3 g) in toluene (41.0 g) was degassed with nitrogen and stirred for 3 h at 90–95°C. The organic material was concentrated and the product purified by column chromatography (silica gel, *n*-hexane with 0.1% triethylamine) to give **IM7a-3**; yield 5.89 g (89.5%).

A solution of 1,4-diiodobenzene (3.3 g), PdCl₂(PPh₃)₂ (0.10 g), PPh₃ (0.10 g), CuI (0.05 g) and triethylamine (6.07 g) in ethyl acetate (19.8 g) was degassed with nitrogen and heated at 56°C. A solution of **IM7a-3** (5.07 g) in ethyl acetate (5.1 g) was added and the mixture stirred for 4 h at 56–60°C. After filtration, the product was concentrated and purified by column chromatography (silica gel, *n*-hexane/chloroform, 10/1) to give **7a**; yield 4.64 g (86.7%). ¹H NMR (δ): 0.82–0.93 (m, 6H), 1.21–1.52 (m, 16H), 1.71–1.87 (m, 4H), 2.20 (s, 6H), 3.92–4.05 (m, 4H), 6.70–6.81 (m, 2H), 7.27–7.37 (m, 4H), 7.38–7.50 (m, 4H). IR (CaF₂ cell) ν_{\max} : 2928, 2858, 2202, 1719, 1601, 1511, 1495, 1467, 1379, 1289, 1243 cm⁻¹. MS m/z 534 (M⁺), 252.

5.8. 1-[(4-Pentyloxyphenyl)ethynyl]-3-methyl-4-[(3-methyl-4-cyanophenyl)ethynyl]benzene, **8a**

A solution of **IM6a-2** (7.68 g), PdCl₂(PPh₃)₂ (0.71 g) and triethylamine (15.2 g) and ethyl acetate (15.2 g) in DMF (31.3 g) was degassed with nitrogen. A solution of **IM8a-1** (5.3 g) in ethyl acetate (16 g) was added and the mixture stirred at 68°C for 17 h. Ethyl acetate and water were added at room temperature and the organic material was extracted into the organic solvent. It was concentrated after twice washing with water. The residue was purified by column chromatography (silica gel, *n*-hexane/acetic ester, 10/1; *n*-hexane/acetic ester, 20/1) to give **8a**; yield 1.73 g (23.0%). ¹H NMR (δ): 0.94 (3H, t), 1.42 (4H, m), 1.80 (2H, m), 2.49 (3H, s), 2.55 (3H, s), 3.97 (2H, t), 6.87 (2H, d), 7.25–7.59 (8H, m). IR (CaF₂ cell) ν_{\max} : 2934, 2221, 2196, 1724, 1593, 1509, 1471, 1244 cm⁻¹. MS m/z 417 (M⁺).

5.9. 1-[(4-Hexylphenyl)ethynyl]-
4-[(4-propylphenyl)ethynyl]benzene, **1b**

A solution of 4-*n*-hexyl-1-hydroxybenzene (26.74 g), pyridine (53.48 g) and 4-pyrrolidin-1-yl pyridine (0.53 g) in toluene (133.7 g) was degassed with nitrogen. A solution of anhydrous bis-trifluoromethanesulfonic acid (63.5 g) was added to the mixture which was stirred for 1.5 h at 1–2°C and 2 h at room temperature. Water and toluene were added and the organic material was extracted with toluene; it was concentrated after washing with water. The residue was purified by column chromatography (silica gel, *n*-hexane) to give **IM1b-1**; yield 43.6 g (93.0%).

A solution of *p*-iodophenol (100 g) and *p*-toluenesulfonic acid (0.2 g) in chloroform (531 g) was degassed with nitrogen. 3,4-Dihydro-2H-pyran (57.3 g) was added to the mixture which was stirred at 0°C for 5 h. Triethylamine was added and the product was concentrated to give **IM1b-2**; yield 140 g (96.5%).

A solution of **IM1b-2** (140 g), PdCl₂(PPh₃)₂ (1.6 g), CuI (1.7 g) and PPh₃ (0.6 g) in triethylamine (1432 ml) was degassed with nitrogen. 3-Methyl-1-butyne-3-ol (57.3 g) was added to the mixture which was stirred at 70°C for 4 h. The product was filtered off and washed with ethyl acetate at room temperature. The filtrate was concentrated to give **IM1b-3**; yield 127 g (98.0%).

A solution of **IM1b-3** (127 g) and NaOH (18 g) in toluene (636 g) was degassed with nitrogen and then stirred for 12.5 h at 93–96°C. The products were concentrated and purified by column chromatography (silica gel, ethyl acetate/*n*-hexane, 1/4 with 0.1% triethylamine) to give **IM1b-4**; yield 82.7 g (87.4%).

A solution of **IM1b-1** (97 g), PdCl₂(PPh₃)₂ (3.3 g) and triethylamine (80 ml) in DMF (1250 ml) was degassed with nitrogen. A solution of **IM1b-4** (75.9 g) in DMF was added and the mixture stirred at 65°C for 4 h. Diethyl ether (600 ml) and water (500 ml) were added to the mixture and the product was extracted into the organic solvent. It was washed with water, dried and concentrated to give **IM1b-5**; yield 120 g (75.2%).

A solution of **IM1b-5** (120 g) and *p*-toluenesulfonic acid (4.2 g) in methanol (1200 ml) was degassed with nitrogen. It was then stirred for 0.5 h at 0°C and 5 h at room temperature. Triethylamine (50 ml) was added. The products were concentrated and purified by column chromatography (silica gel, ethyl acetate/*n*-hexane, 1/4) to give **IM1b-6**; yield 82.7 g (87.6%).

A solution of **IM1b-6** (30 g), 4-pyrrolidin-1-yl pyridine (4.8 g) and pyridine (172 ml) in dichloromethane (430 ml) was degassed with nitrogen. A solution of anhydrous trifluoromethane sulfonic acid (40 g) in dichloromethane was added and the mixture stirred for 2 h at 0°C. Water and dichloromethane were added at room temperature and the product was extracted into the organic solvent.

It was concentrated after washing twice with water. The residue was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane, 1/8) to give **IM1b-7**; yield 40.7 g (87.4%).

A mixture of **IM1b-7** (4 g), PdCl₂(PPh₃)₂ (0.1 g) and triethylamine (2.7 g) in DMF (39 ml) was degassed with nitrogen. A solution of 1-ethynyl-4-propylbenzene (2.7 g) in DMF was added to the mixture which was stirred at 65°C for 4 h. Water and diethyl ether were added and the product was extracted into the organic solvent. It was washed with water, dried and concentrated. The residue was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane, 1/20 with 0.1% triethylamine) and recrystallized from *n*-hexane to give **1b**; yield 1.99 g (50.6%). ¹H NMR (δ): 0.82–0.98 (m, 6H), 1.25–1.39 (m, 6H), 1.52–1.71 (m, 4H), 2.51–2.64 (m, 4H), 7.11–7.20 (m, 4H), 7.39–7.51 (m, 8H). IR (CaF₂ cell) ν_{max}: 2958, 2928, 2858, 2209, 1722, 1516, 1461 cm⁻¹. MS *m/z* 404 (M⁺).

5.10. 1-[(4-Hexylphenyl)ethynyl]-3-methyl-
4-[(4-propylphenyl)ethynyl]benzene, **2b**

A solution of 4-hydroxy-3-methylidobenzene (35.11 g) and *p*-toluene sulphonic acid (0.11 g) in chloroform (175.6 g) was degassed with nitrogen. 3,4-Dihydro-2H-pyran (18.93 g) was added and the mixture stirred for 2 h at –2–1°C. Triethylamine (1 g) was added at room temperature and the product was concentrated. It was purified by column chromatography (silica gel, *n*-hexane/ethyl acetate, 20/1 with 0.1% triethylamine) to give **IM2b-2**; yield 46.4 g (93.8%).

A solution of **IM2b-2** (46.4 g), PdCl₂(PPh₃)₂ (0.46 g), PPh₃ (0.46 g), CuI (0.23 g) and triethylamine (59.0 g) in ethyl acetate (59.0 g) was degassed with nitrogen. 3-Methyl-1-butyne-3-ol (18.42 g) was added and the mixture stirred at 63°C for 6 h. The product was concentrated and purified by column chromatography (silica gel, *n*-hexane/ethyl acetate, 5/1 with 0.1% triethylamine) to give **IM2b-3**; yield 34.92 g (86.4%).

A solution of **IM2b-3** (34.92 g) and NaOH (1.05 g) in toluene (139.7 g) was degassed with nitrogen and stirred for 6.5 h at 95–98°C. The product was concentrated and purified by column chromatography (silica gel, *n*-hexane/ethyl acetate, 20/1 with 0.1% triethylamine) to give **IM2b-4**; yield 25.29 g (91.0%).

A solution of **IM2b-4** (9.31 g), PdCl₂(PPh₃)₂ (0.19 g) and triethylamine (16.76 g) in DMF (46.6 g) was degassed with nitrogen. A solution of **IM1b-1** (23.77 g) in DMF (9.7 g) was added to the mixture which was then stirred at 66–69°C for 4 h. Ethyl acetate (100 ml) and water (100 ml) were added at room temperature and the product was extracted into the organic solvent. It was concentrated after washing three times with water. The

residue was purified by column chromatography (silica gel, *n*-hexane/ethyl acetate, 20/1 with 0.1% triethylamine) to give **IM2b-5**; yield 6.26 g (35.8%).

A solution of **IM2b-5** (6.26 g) and *p*-toluene sulphonic acid (0.13 g) in methanol (25.0 g) was degassed with nitrogen. The mixture was stirred at 20–32°C for 2 h. It was concentrated after adding triethylamine (2 g). The product was purified by column chromatography (silica gel, *n*-hexane/ethyl acetate, 10/1 with 0.1% triethylamine) to give **IM2b-6**; yield 4.67 g (91.4%).

A solution of **IM2b-6** (4.67 g), pyridine (9.3 g) and 4-pyrrolidin-1-yl pyridine (0.09 g) in toluene (28.0 g) was degassed with nitrogen. Anhydrous trifluoromethane sulphonic acid (6.76 g) was added at 2°C. The mixture was stirred for 0.5 h at 2°C and for 2 h at 22–27°C. Water (50 ml) and ethyl acetate (50 ml) were added and the product was extracted into the organic solvent. It was concentrated after washing with water and purified by column chromatography (silica gel, *n*-hexane) to give **IM2b-7**; yield 6.10 g (89.6%).

A solution of **IM2b-7** (6.10 g), PdCl₂(PPh₃)₂ (0.31 g) and triethylamine (4.36 g) in DMF (36.6 g) was degassed with nitrogen and heated at 65°C. 1-Ethynyl-4-*n*-propylbenzene (3.87 g) in DMF (4.0 g) was added to the mixture which was stirred at 64–67°C for 5.5 h. Ethyl acetate (100 ml) was added and the product was concentrated after washing with water (100 ml). It was purified by column chromatography (silica gel, *n*-hexane with 0.1% triethylamine) and recrystallized from ethanol to give **2b**; yield 3.83 g (62.6%). ¹H NMR (δ): 8.01–9.99 (m, 6H), 1.21–1.40 (m, 6H), 1.51–1.71 (m, 4H), 2.49 (s, 3H), 2.53–2.68 (m, 4H), 7.10–7.20 (m, 4H), 7.28–7.36 (m, 1H), 7.36–7.50 (m, 6H). IR (CaF₂ cell) ν_{\max} : 3027, 2958, 2929, 2858, 2205, 1902, 1597, 1513, 1458, 1379, 1261, 1181, 1113 cm⁻¹. MS *m/z* 418 (M⁺).

5.11. 1-[(4-Hexylphenyl)ethynyl]-4-[(2-methyl-4-propylphenyl)ethynyl]benzene, **3b**

A solution of 4-*n*-propyl-3-methylhydroxybenzene (4.54 g), 4-pyrrolidin-1-yl pyridine (0.09 g) and pyridine (9.08 g) in toluene (22.7 g) was degassed with nitrogen. A solution of anhydrous bis(trifluoromethanesulfonic) acid (12.70 g) in toluene (31.7 g) was added at –2°C and the mixture stirred at –2–5°C for 7 h. Toluene and water were added and the product was extracted. It was washed twice with water and purified by column chromatography (silica gel, *n*-hexane/ethylacetate, 20/1) to give **IM3b-1**; yield 7.34 g (81.4%).

A solution of **IM1b-7** (24.63 g), PdCl₂(PPh₃)₂ (0.74 g) and triethylamine (9.10 g) in DMF (246.3 g) was degassed with nitrogen. A solution of trimethylsilylethyne (8.84 g) in DMF (8.8 g) was added and the mixture stirred at 65–68°C for 2.5 h. After washing with ethyl acetate,

n-hexane and water, the product was concentrated. Ethyl acetate (23.3 g), ethanol (93.2 g) and Na₂CO₃ (2.47 g) were added and the mixture stirred at room temperature for 21.5 h. The product was concentrated and purified by column chromatography (silica gel, *n*-hexane with 0.1% triethylamine) to give **IM3b-2**; yield 8.39 g (46.8%).

A solution of **IM3b-2** (2.82 g), PdCl₂(PPh₃)₂ (0.14 g) and triethylamine (1.52 g) in DMF (42.3 g) was degassed with nitrogen. A solution of **IM3b-1** (4.30 g) in DMF (12.9 g) was added to it and the mixture stirred at 60–65°C for 20 h. Ethyl acetate and water were added and the product was extracted into the organic solvent, concentrated and purified by column chromatography (silica gel, *n*-hexane with 0.1% triethylamine) and recrystallization from ethanol to give **3b**; yield 0.68 g (16.0%). ¹H NMR (δ): 0.82–0.98 (m, 6H), 1.23–1.39 (m, 6H), 1.56–1.71 (m, 4H), 2.50 (s, 3H), 2.52–2.68 (m, 4H), 6.95–7.08 (m, 2H), 7.13–7.20 (m, 2H), 7.36–7.52 (m, 7H). IR (CaF₂ cell) ν_{\max} : 3025, 2958, 2929, 2858, 2208, 1902, 1607, 1515, 1459, 1378, 1339, 1304, 1227 cm⁻¹. MS *m/z* 418 (M⁺).

5.12. 1-[(4-Hexylphenyl)ethynyl]-4-[(3-methyl-4-propylphenyl)ethynyl]benzene, **4b**

A solution of 4-*n*-propyl-2-methylhydroxybenzene (3.98 g), 4-pyrrolidin-1-yl pyridine (0.16 g) and pyridine (7.96 g) in toluene was degassed with nitrogen. A solution of anhydrous bis(trifluoromethanesulfonic) acid (16.81 g) in toluene (11.2 g) was added and the mixture stirred for 2.5 h at –2–5°C and 5 h more at 60–65°C. Ethyl acetate and water were added and the product was extracted. It was washed with water and purified by column chromatography (silica gel, *n*-hexane) to give **IM4b-1**; yield 5.91 g (77.8%).

A solution of **IM4b-1** (2.82 g), PdCl₂(PPh₃)₂ (0.22 g) and triethylamine (1.52 g) in DMF (42.3 g) was degassed with nitrogen. A solution of **IM3b-2** (4.30 g) in DMF (8.6 g) was added and the mixture stirred at 60–65°C for 20 h. Ethyl acetate, *n*-hexane and water were added and the product was extracted into the organic solvent and concentrated. It was purified by column chromatography (silica gel, *n*-hexane with 0.1% triethylamine) and recrystallization from ethanol and *n*-hexane to give **4b**; yield 0.32 g (7.2%). ¹H NMR (δ): 0.82–0.95 (m, 3H), 0.95–1.06 (m, 3H), 1.22–1.41 (m, 6H), 1.52–1.72 (m, 4H), 2.30 (s, 3H), 2.51–2.67 (m, 4H), 7.05–7.20 (m, 3H), 7.25–7.39 (m, 2H), 7.40–7.56 (m, 6H). IR (CaF₂ cell) ν_{\max} : 3026, 2958, 2929, 2858, 2210, 1904, 1604, 1516, 1464, 1404, 1379, 1307 cm⁻¹. MS *m/z* (M⁺).

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