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Novel liquid crystalline compounds having an enyne unit

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Novel liquid crystalline compounds having an enyne unit

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Novel series of liquid crystalline compounds having an enyne unit, 1-(4-alkylphenyl)-4-(*trans*-4-alkylcyclohexyl)-but-3-en-1-yne and 1-(4-alkoxyphenyl)-4-(*trans*-4-alkylcyclohexyl)-but-3-en-1-yne are presented. The synthetic methods, mesomorphic phases, and some physical properties of these series are reported.

1. Introduction

The response time for a twisted nematic liquid crystal display is roughly proportional to the products of the viscosity and the square of the cell thickness (ηd^2) [1]. The product of birefringence and the cell thickness (Δnd) should be fixed at a certain value in order to obtain good cell appearance [2]. Therefore, liquid crystalline compounds with low viscosity and high birefringence are of special interest for twisted nematic liquid crystal displays. It is commonly known that liquid crystalline compounds with a highly conjugated part show high birefringence. Tolane derivatives and some compounds with a pyrimidine ring are known to have such properties [3]. In order to obtain a lower dependence of birefringence on the wavelength, the birefringence value of each component of the mixture should be fixed at 0·10–0·20 [4]. Since, tolane and other highly conjugated compounds have more than a 0·2 birefringence value, it is necessary to design a new structural compound having appropriate birefringence and other properties required for good liquid crystal displays. In order to discover such materials, we focused on some new compounds with a conjugated enyne unit. In this paper we report the synthetic methods, mesomorphic phases and some physical properties of these derivatives.

2. Synthesis

Our first attempt to synthesize the new series represented by the formula $Ar–C{\equiv}C–CH{=}CH–C_6H_{11}–R'$ (**3**) is shown in scheme 1, i.e. addition reaction of lithium acetylide to substituted cyclohexylacetaldehyde followed by dehydration of the secondary but-1-yn-3-ol (**2**). Although **3** was obtained as an isomeric mixture, the *trans*-isomer was easily separated by recrystallization. Since the procedure shown in scheme 1 gave a mixture of the stereoisomers, this method was not convenient. Moreover, our attempt to obtain a 1,4-diphenyl-but-3-en-1-yne derivative **9** according to this route only gave a complex mixture. Next, we tried another synthetic method shown in scheme 2. The starting material, substituted vinyl bromide was obtained by

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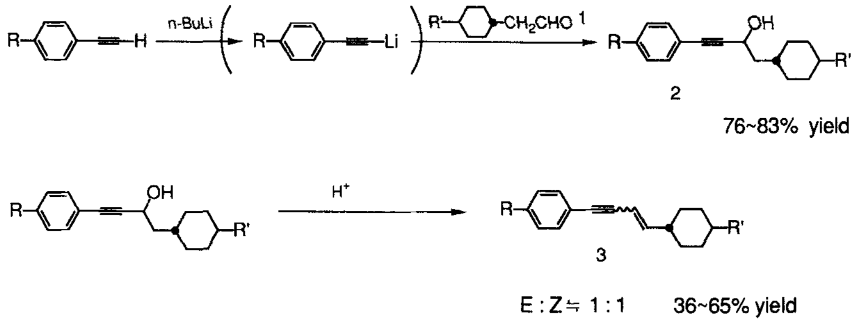
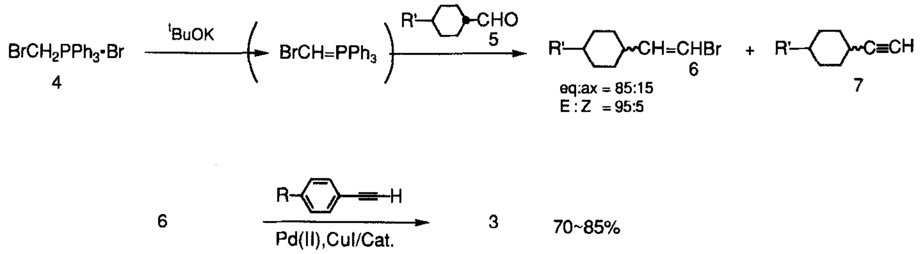
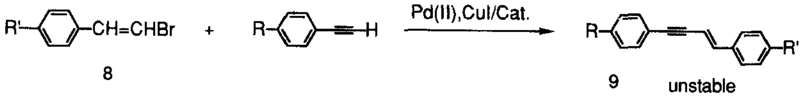
using the Wittig reaction [5] of bromomethylidenetriphenylphosphorane [6] with the substituted cyclohexanecarbaldehyde **5**. This reaction gave the *E*-isomer selectively, but the unfavourable axial isomer of **6** was formed as a by product by epimerization of **5**. Also, 5–15 per cent of dehydrobrominated product **7** was also produced. However, these by products did not participate in the next coupling reaction. Thus, the crude product was employed for the subsequent coupling reaction with ethyne derivatives, mediated by a palladium–copper mixed catalyst in diethylamine [7]. The reaction proceeded stereospecifically and gave the desired product in a moderate yield. Using this method, the diaryl compounds **9** were obtained from the substituted phenylacetylene and the *β*-bromostyrene **8** (see scheme 3). However, since **9** represents a thermally unstable structure, the physical properties of these materials could not be assessed.



Scheme 1.



Scheme 2.



Scheme 3.

3. Mesomorphic properties

General. The structures of the compounds were confirmed by ^{1}H NMR spectroscopy using a JEOL EX-90 and GC mass spectroscopy using a SHIMADZU GCMS-QP1000A at 70 eV. Transition temperatures were measured using a Rigaku DSC-8230 differential scanning calorimeter and by polarization microscopy using a Mettler FP 52 hot stage to control the temperature of the samples. Bulk viscosities of these compounds were measured using a TOKIMEC ELD-R rotational viscometer, and the birefringence of the samples was measured using an ATAGO 4T and 2T Abbe refractometer.

Tables 1 and 2 show transition temperatures and transition enthalpies of the enyne derivatives. The series with an alkylphenyl moiety has a nematic temperature range (ΔT) from $-18{\cdot}7$ to $61{\cdot}0$ K and an enthalpy of fusion (ΔH) from 7·10 to 18·83 kJ mol^{-1} (see table 1). The alkoxyphenyl derivatives have a nematic temperature range (ΔT) from 37·8 to 82·0 K and an enthalpy of fusion (ΔH) from 11·86 to 22·42 kJ mol^{-1} (see table 2). Each derivative shows a very wide nematic temperature range compared with other compounds containing two rings.

4. Physical properties of mixtures

We prepared two mixtures **A-1** and **A-2**, with the components and properties shown in table 3. The basic physical properties of these mixtures and two reference mixtures **B** and **C**, were examined. References **B** and **C** are well known to have low viscosity [3 (b), 8]. The birefringence value of the enyne mixture was higher than **B** and lower than **C**. The dependence of the viscosity of the enyne derivatives on the reduced temperature is shown in figure 1. All mixtures have low viscosity from 5 to 12 mPa s around their clearing point. Especially, **A-2** shows the lowest viscosity at a reduced temperature. Figure 2 shows the wavelength dependence of the birefringence. In comparison with the reference mixtures, the enyne mixtures show an appropriate birefringence required to make practical mixtures for LC displays. Figure 3 illustrates the dependence of the birefringence on the reduced temperature. **A-1** and **A-2** behaved quite similarly. As we would expect, the highest birefringence mixture of tolane **C** showed a large dependence of birefringence on wavelength, and the lowest Δn mixture **B** showed a slight dependence and **A-1** and **A-2** showed a moderate dependence. Finally, the dependence of birefringence on wavelength was determined for mixtures **D** and **E** (see figure 4). These two mixtures were controlled to have the same clearing point, and birefringence at 470 nm. Mixture **D** contains 35 per cent of the enyne derivative, while mixture **E** was composed of tolane derivatives **C** and a low birefringence cyclohexylcyclohexane derivative. As shown in this graph, mixture **D** has a lower wavelength dependence of birefringence. These results proved that enyne derivatives are good materials to solve one of the problems with display quality arising from a large dependence of birefringence on wavelength.

5. Conclusion

As described above, introduction of a conjugated enyne linkage into the framework of mesogenic molecules has been provided. The new materials have low viscosity and an appropriate birefringence. Thus, a major improvement in mixtures for highly twisted nematic device applications can be achieved.

6. Experimental

6.1. *Preparation of 1-(4-pentylphenyl)-4-(4-*trans*-pentylcyclohexyl)-but-1-yn-3-ol* (**2**, R=R′=C_5H_{11})

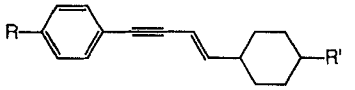
A hexane solution of *n*-butyl lithium (7·4 ml, 1·6 mol l^{-1}) was added dropwise to a tetrahydrofuran (15 ml) solution of 4-pentylphenylacetylene (2·0 g, 11·6 mmol) and stirred for 10 min. The reaction mixture was warmed to room temperature and stirred for 30 min. Then, a THF (10 ml) solution of 4-*trans*-pentylcyclohexylacetaldehyde (**1**, R'=C_5H_{11}, 2·3 g, 11·7 mmol) was added dropwise to the solution during

Table 1. Nematic properties of 1-(4-alkylphenyl)-4-(*trans*-4-alkylcyclohexyl)-but-3-en-1-yne (**3a**–**3l**).

Number	*R*	*R'*	T_m/°C	T_c/°C	Δ*H*/kJ mol^{-1}	Δ*T*†/K
3a	CH_3	C_2H_5	58·4	39·7	18·83	− 18·7
3b	C_2H_5	C_2H_5	19·7	44·0	16·28	23·3
3c	C_2H_5	C_3H_7	31·3	82·4	10·09	60·0
3d	C_2H_5	C_5H_{11}	20·7	81·7	—	61·0
3e	C_3H_7	C_2H_5	27·8	56·2	7·10	28·4
3f	C_3H_7	C_3H_7	51·6	93·8	14·87	42·2
3g	C_3H_7	C_5H_{11}	31·7	92·2	9·68	60·5
3h	C_4H_9	C_2H_5	21·0	45·5	8·75	24·5
3i	C_4H_9	C_3H_7	33·6	84·5	10·73	50·9
3j	C_5H_{11}	C_2H_5	31·1	55·0	9·18	23·9
3k	C_5H_{11}	C_3H_7	47·5	90·7	18·38	43·2
3l	C_5H_{11}	C_5H_{11}	36·5	79·0	—	42·5

† $\Delta T = T_c - T_m$; A negative sign indicates monotropy.

Table 2. Nematic properties of 1-(4-alkoxyphenyl)-4-(*trans*-4-alkylcyclohexyl)-but-3-en-1-yne (**3m**–**3x**).

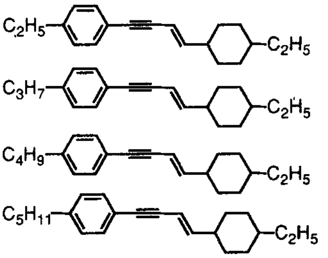


Number	*R*	*R'*	T_m/°C	T_c/°C	Δ*H*/kJ mol^{-1}	Δ*T*†/K
3m	OCH_3	C_2H_5	29·3	80·9	17·17	51·6
3n	OCH_3	C_3H_7	45·9	113·3	15·83	67·4
3o	OCH_3	C_5H_{11}	35·3	117·3	18·88	82·0
3p	OC_2H_5	C_2H_5	62·3	104·2	21·07	41·9
3q	OC_2H_5	C_3H_7	79·8	135·8	—	56·0
3r	OC_2H_5	C_5H_{11}	68·9	126·9	20·38	58·0
3s	OC_3H_7	C_2H_5	60·9	98·7	14·85	37·8
3t	OC_3H_7	C_3H_7	72·1	127·2	22·42	55·1
3u	OC_3H_7	C_5H_{11}	57·9	118·9	14·76	61·0
3v	OC_4H_9	C_2H_5	55·5	98·5	11·86	43·0
3w	OC_4H_9	C_3H_7	63·9	126·1	20·10	62·2
3x	OC_4H_9	C_5H_{11}	60·4	126·8	20·87	66·4

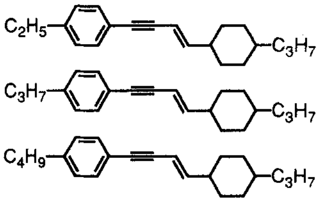
† $\Delta T = T_c - T_m$.

Table 3. Physical properties of the mixtures of enyne derivatives.

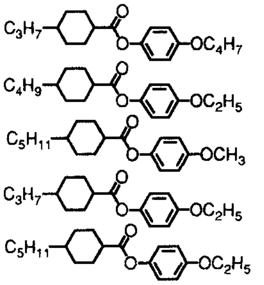
A-1



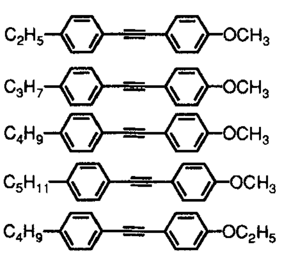
A-2



B



C



	A-1	A-2	B	C
NI/°C	50·3	86·6	74·6	55·3
η/mPa s$_{25°C}$	22·4	19·4	17·9	16·8
$\Delta n_{589\,\mathrm{nm},\,25°C}$	0·165	0·198	0·087	0·266

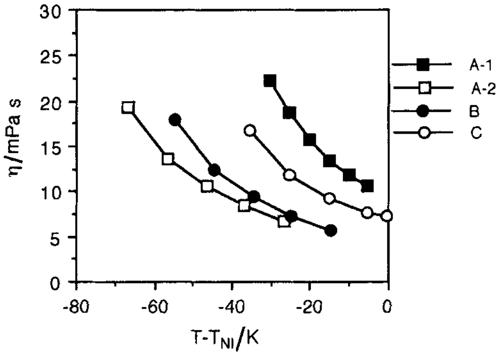


Figure 1. Dependence of viscosity on reduced temperature.

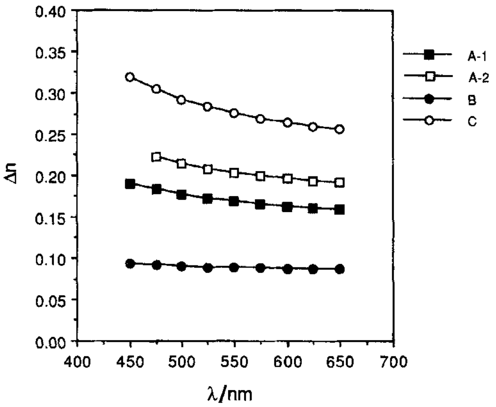


Figure 2. Dependence on birefringence on wavelength at 25°C.

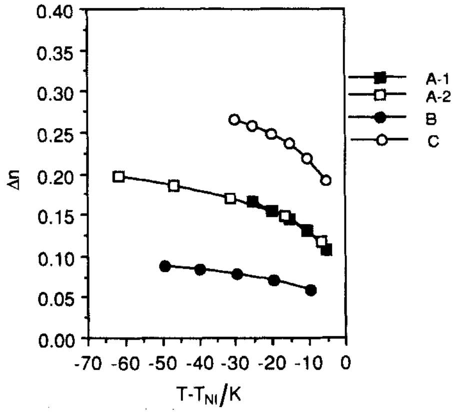


Figure 3. Dependence of birefringence on the reduced temperature.

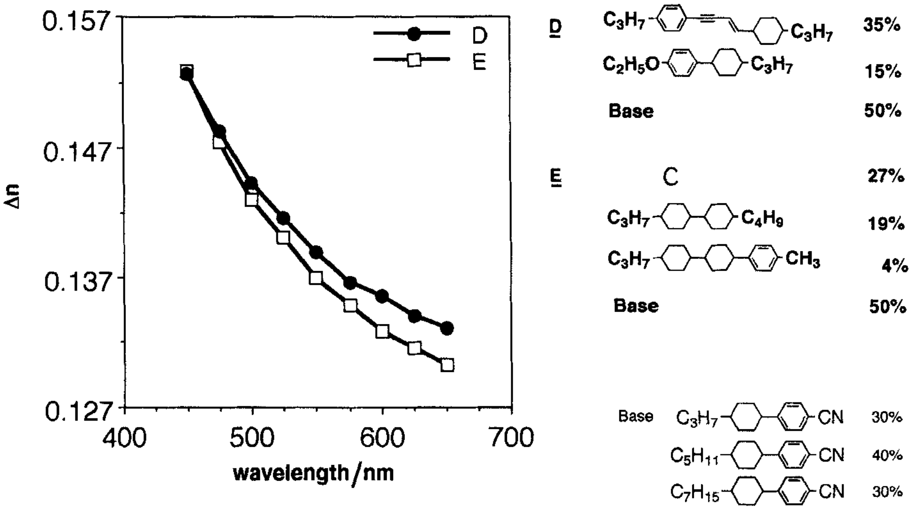


Figure 4. Dependence of birefringence on wavelength of mixture **D** and **E**.

15 min at 0°C and stirred at room temperature for 2 h. The reaction mixture was quenched with dilute HCl, shaken with toluene (10 ml × 3), and the extract washed with water (5 ml × 3). The organic layer was dried over magnesium sulphate and concentrated under reduced pressure. The residual yellow oil was purified by column chromatography (silica gel, heptane : ethyl acetate = 6 : 1), followed by recrystallization to give white crystals (3·3 g, 9·0 mmol, 78 per cent). ^{1}H NMR ($CDCl_3$) δ; 7·34 (2 H, d, $J = 8{\cdot}1$ Hz), 7·10 (2 H, d, $J = 8{\cdot}1$ Hz), 4·63 (1 H, br), 2·59 (2 H, brt, $J = 6{\cdot}3$ Hz), 1·80–0·81 (30 H, m). MS; 368(M^+), 172, 214, 199.

6.2. *Preparation of 1-(4-pentylphenyl)-4-(4-*trans*-pentylcyclohexyl)but-3-en-1-yne* (**3l**)

A toluene (80 ml) solution of **2**, $R = R' = C_5H_{11}$ (2·0 g, 5·45 mmol) and *p*-toluenesulphonic acid (20 mg, 0·1 mmol) was heated under reflux for 8 h. The toluene solution was cooled to room temperature, and shaken with water (10 ml). The organic layer was dried over magnesium sulphate and concentrated under reduced pressure. The resulting brown oil was purified by column chromatography (silica gel, heptane) followed by recrystallization from ethanol giving the *E*-isomer as white crystals (350 mg, 1 mmol, 18 per cent). ^{1}H NMR ($CDCl_3$) δ; 7·31 (2 H, d, $J = 8{\cdot}1$ Hz), 7·10 (2 H, d, $J = 8{\cdot}1$ Hz), 6·18 (1 H, dd, $J = 6{\cdot}7$, 16·1 Hz), 5·63 (1 H, d, $J = 16{\cdot}1$ Hz), 2·59 (2 H, brt, $J = 6{\cdot}6$ Hz), 1·83–0·81 (30 H, m). MS; 350 (M^+), 171.

6.3. *Typical procedure for the preparation of 1-(4-alkylcyclohexyl)-2-bromoethene* (**6**)

Potassium tert-butoxide (2·7 mol) was added to a suspension of bromomethyltriphenylphosphonium bromide (2·8 mol) in heptane (3·0 l). The reaction mixture was stirred for 30 min at ambient temperature. A heptane (500 ml) solution of 4-alkylcyclohexanecarbaldehyde (2·2 mol) was added dropwise to the mixture during 1 h. The reaction temperature was kept below 30°C, and after 1 h at room temperature, the mixture was filtered. The filtrate was concentrated, and the resultant yellow oil was distilled under reduced pressure. The yield of **6** was 50–65 per cent. 1-(4-Ethylcyclohexyl)-2-bromoethene; b.p. 121–129°C/22 mmHg, MS; 216, 218 (M^+), 81, 95, 67. 1-(4-Propylcyclohexyl)-2-bromoethene; b.p. 121–125°C/12 mmHg, MS; 230, 232 (M^+), 95, 81, 67. 1-(4-Butylcyclohexyl)-2-bromoethene; b.p. 113–123°C/6 mmHg, MS; 244, 246 (M^+), 81, 95, 41. 1-(4-Pentylcyclohexyl)-2-bromoethene; b.p. 112–121°C/2 mmHg, MS; 256, 258 (M^+), 81, 67, 41.

6.4. *Typical procedure for the synthesis of enyne derivatives* (**3**) *via the catalytic coupling method*

Dichlorobistriphenylphosphinepalladium (14 mmol) and copper (I) iodide (7 mmol) were placed in a three necked round bottomed flask fitted with a dropping funnel and three way stopcock, dried under reduced pressure. Under an argon atmosphere, diethylamine (1500 ml) and **6** (0·8 mol) were added and the mixture stirred for 30 min at room temperature. The diethylamine (200 ml) solution of the 4-alkylphenylacetylene (0·8 mol) was added dropwise to the reaction mixture during 2 h and stirring was continued for 2 h. The reaction mixture was quenched with dilute HCl and shaken with toluene (500 ml × 3). The organic layer was dried over magnesium sulphate and concentrated under reduced pressure. The catalyst was removed by chromatography on a short column of silica gel, the resulting brown oil was crystallized from ethanol. The crystals obtained were purified by distillation and recrystallization from ethanol. The transition temperatures of each derivatives are given in tables 1 and 2. NMR data are listed.

3a; ^{1}H NMR ($CDCl_3$) δ; 7·31 (2 H, d, *J* = 8·2 Hz), 7·09 (2 H, d, *J* = 8·2 Hz), 6·19 (1 H, dd, *J* = 6·6, 15·9 Hz), 5·63 (1 H, d, *J* = 15·9 Hz), 2·33 (3 H, s), 1·84–0·81 (15 H, m).

3b; ^{1}H NMR ($CDCl_3$) δ; 7·31 (2 H, d, *J* = 8·2 Hz), 7·11 (2 H, d, *J* = 8·2 Hz), 6·19 (1 H, dd, *J* = 6·7, 16·1 Hz), 5·63 (1 H, d, *J* = 16·1 Hz), 2·62 (2 H, q, *J* = 7·7 Hz), 1·80–0·80 (15 H, m).

3c; ^{1}H NMR ($CDCl_3$) δ; 7·34 (2 H, d, *J* = 8·2 Hz), 7·11 (2 H, d, *J* = 8·2 Hz), 6·19 (1 H, dd, *J* = 6·7, 16·1 Hz), 5·64 (1 H, d, *J* = 16·1 Hz), 2·63 (2 H, q, *J* = 7·7 Hz), 1·84–0·80 (20 H, m).

3d; ^{1}H NMR ($CDCl_3$) δ; 7·33 (2 H, d, *J* = 8·3 Hz), 7·10 (2 H, d, *J* = 8·3 Hz), 6·19 (1 H, dd, *J* = 6·8, 16·1 Hz), 5·64 (1 H, d, *J* = 16·1 Hz), 2·63 (2 H, q, *J* = 7·6 Hz), 1·83–0·81 (24 H, m).

3e; ^{1}H NMR ($CDCl_3$) δ; 7·32 (2 H, d, *J* = 8·1 Hz), 7·09 (2 H, d, *J* = 8·1 Hz), 6·19 (1 H, dd, *J* = 6·8, 16·1 Hz), 5·64 (1 H, d, *J* = 16·1 Hz), 2·57 (2 H, brt), 1·83–0·80 (20 H, m).

3f; ^{1}H NMR ($CDCl_3$) δ; 7·32 (2 H, d, *J* = 8·2 Hz), 7·09 (2 H, d, *J* = 8·2 Hz), 6·19 (1 H, dd, *J* = 6·8, 16·1 Hz), 5·64 (1 H, d, *J* = 16·1 Hz), 2·57 (2 H, brt), 1·83–0·80 (22 H, m).

3g; ^{1}H NMR ($CDCl_3$) δ; 7·33 (2 H, d, *J* = 8·2 Hz), 7·09 (2 H, d, *J* = 8·2 Hz), 6·18 (1 H, dd, *J* = 6·7, 16·4 Hz), 5·64 (1 H, d, *J* = 16·4 Hz), 2·57 (2 H, brt), 1·83–0·84 (26 H, m).

3h; ^{1}H NMR ($CDCl_3$) δ; 7·33 (2 H, d, *J* = 8·2 Hz), 7·09 (2 H, d, *J* = 8·2 Hz), 6·19 (1 H, dd, *J* = 6·7, 15·9 Hz), 5·63 (1 H, d, *J* = 15·9 Hz), 2·59 (2 H, brt), 2·10–0·80 (22 H, m).

3i; ^{1}H NMR ($CDCl_3$) δ; 7·33 (2 H, d, *J* = 8·4 Hz), 7·09 (2 H, d, *J* = 8·4 Hz), 6·18 (1 H, dd, *J* = 6·8, 16·1 Hz), 5·63 (1 H, d, *J* = 16·1 Hz), 2·59 (2 H, brt), 2·10–0·80 (24 H, m).

3j; ^{1}H NMR ($CDCl_3$) δ; 7·33 (2 H, d, *J* = 8·5 Hz), 7·09 (2 H, d, *J* = 8·5 Hz), 6·18 (1 H, dd, *J* = 6·7, 16·1 Hz), 5·63 (1 H, d, *J* = 16·1 Hz), 2·58 (2 H, brt), 2·10–0·80 (24 H, m).

3k; ^{1}H NMR ($CDCl_3$) δ; 7·36 (2 H, d, *J* = 8·2 Hz), 7·12 (2 H, d, *J* = 8·2 Hz), 6·22 (1 H, dd, *J* = 6·6, 15·8 Hz), 5·67 (1 H, d, *J* = 15·8 Hz), 2·57 (2 H, brt), 1·87–0·84 (26 H, m).

3l; ^{1}H NMR ($CDCl_3$) δ; 7·31 (2 H, d, *J* = 8·1 Hz), 7·10 (2 H, d, *J* = 8·1 Hz), 6·18 (1 H, dd, *J* = 6·7, 16·1 Hz), 5·63 (1 H, d, *J* = 16·1 Hz), 2·59 (2 H, brt), 1·83–0·81 (30 H, m).

3m; ^{1}H NMR ($CDCl_3$) δ; 7·35 (2 H, d, *J* = 9·0 Hz), 7·82 (2 H, d, *J* = 9·0 Hz), 6·17 (1 H, dd, *J* = 6·6, 15·8 Hz), 5·62 (1 H, d, *J* = 15·8 Hz), 3·80 (3 H, s), 1·83–0·84 (21 H, m).

3n; ^{1}H NMR ($CDCl_3$) δ; 7·37 (2 H, d, *J* = 9·0 Hz), 6·82 (2 H, d, *J* = 9·0 Hz), 6·18 (1 H, dd, *J* = 6·5, 16·2 Hz), 5·63 (1 H, d, *J* = 16·2 Hz), 3·81 (3 H, s), 1·83–0·84 (17 H, m).

3o; ^{1}H NMR ($CDCl_3$) δ; 7·35 (2 H, d, *J* = 8·8 Hz), 6·82 (2 H, d, *J* = 8·8 Hz), 6·17 (1 H, dd, *J* = 6·6, 16·1 Hz), 5·63 (1 H, d, *J* = 16·1 Hz), 3·80 (3 H, s), 2·10–0·80 (21 H, m).

3p; ^{1}H NMR ($CDCl_3$) δ; 7·33 (2 H, d, *J* = 9·0 Hz), 6·80 (2 H, d, *J* = 9·0 Hz), 6·17 (1 H, dd, *J* = 6·7, 16·1 Hz), 5·63 (1 H, d, *J* = 16·1 Hz), 4·02 (2 H, q, *J* = 7·3 Hz), 2·05–0·80 (18 H, m).

3q; ^{1}H NMR ($CDCl_3$) δ; 7·34 (2 H, d, *J* = 9·0 Hz), 6·80 (2 H, d, *J* = 9·0 Hz), 6·17 (1 H, dd, $J=7{\cdot}1$, 16·1 Hz), 5·63 (1 H, d, $J=16{\cdot}1$ Hz), 4·02 (2 H, q, $J=7{\cdot}1$ Hz), 2·10–0·80 (20 H, m).

3r; ^{1}H NMR ($CDCl_3$) δ; 7·34 (2 H, d, $J=8{\cdot}8$ Hz), 6·80 (2 H, d, $J=8{\cdot}8$ Hz), 6·16 (1 H, dd, $J=6{\cdot}6$, 15·9 Hz), 5·62 (1 H, d, $J=15{\cdot}9$ Hz), 4·02 (2 H, q, $J=7{\cdot}1$ Hz), 1·83–0·84 (24 H, m).

3s; ^{1}H NMR ($CDCl_3$) δ; 7·34 (2 H, d, $J=9{\cdot}0$ Hz), 6·80 (2 H, d, $J=9{\cdot}0$ Hz), 6·17 (1 H, dd, $J=6{\cdot}7$, 16·1 Hz), 5·63 (1 H, d, $J=16{\cdot}1$ Hz), 3·97 (2 H, brt), 2·10–0·80 (20 H, m).

3t; ^{1}H NMR ($CDCl_3$) δ; 7·36 (2 H, d, $J=9{\cdot}0$ Hz), 6·84 (2 H, d, $J=9{\cdot}0$ Hz), 6·19 (1 H, dd, $J=6{\cdot}8$, 16·3 Hz), 5·64 (1 H, d, $J=16{\cdot}4$ Hz), 3·94 (2 H, brt), 1·94–0·84 (22 H, m).

3u; ^{1}H NMR ($CDCl_3$) δ; 7·34 (2 H, d, $J=9{\cdot}0$ Hz), 6·81 (2 H, d, $J=9{\cdot}0$ Hz), 6·16 (1 H, dd, $J=6{\cdot}8$, 16·1 Hz), 5·63 (1 H, d, $J=16{\cdot}1$ Hz), 3·91 (2 H, brt), 2·10–0·80 (26 H, m).

3v; ^{1}H NMR ($CDCl_3$) δ; 7·34 (2 H, d, $J=9{\cdot}0$ Hz), 6·80 (2 H, d, $J=9{\cdot}0$ Hz), 6·18 (1 H, dd, $J=6{\cdot}7$, 16·4 Hz), 5·63 (1 H, d, $J=16{\cdot}4$ Hz), 3·94 (2 H, brt), 2·10–0·80 (24 H, m).

3w; ^{1}H NMR ($CDCl_3$) δ; 7·33 (2 H, d, $J=9{\cdot}0$ Hz), 6·81 (2 H, d, $J=9{\cdot}0$ Hz), 6·17 (1 H, dd, $J=6{\cdot}8$, 16·1 Hz), 5·63 (1 H, d, $J=16{\cdot}1$ Hz), 3·95 (2 H, brt), 2·20–0·84 (24 H, m).

3x; ^{1}H NMR ($CDCl_3$) δ; 7·34 (2 H, d, $J=9{\cdot}0$ Hz), 6·81 (2 H, d, $J=9{\cdot}0$ Hz), 6·16 (1 H, dd, $J=6{\cdot}8$, 16·1 Hz), 5·63 (1 H, d, $J=16{\cdot}1$ Hz), 3·95 (2 H, brt), 2·19–0·80 (28 H, m).

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