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Liquid crystalline esters of (*E*)-3-phenoxyacrylic acid

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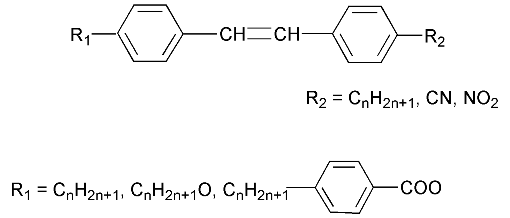
The novel esters of (*E*)-3-phenoxyacrylic acid have been prepared and their mesomorphic properties have been investigated by means of polarised light microscopy, differential scanning calorimetry and X-ray diffraction measurements. The influence of molecular structure on mesophase formation has been studied.

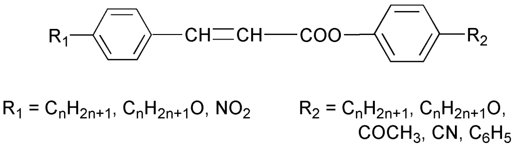
The ethylene linking group is a very useful structural unit connecting one part of a rigid core with another in calamitic mesogene molecules. This fully conjugative group enhances the longitudinal polarisability and extends the molecular length maintaining linearity of the molecule. Typical examples of mesogene with ethylene linking groups are stilbenes[1,2]



$R_2 = C_nH_{2n+1}$, CN, NO_2

$R_1 = C_nH_{2n+1}$, $C_nH_{2n+1}O$, C_nH_{2n+1}–C_6H_4–COO

and substituted 3-phenylacrylic (cinnamic) acid phenyl esters[3,4,5] with the following general formula.



$R_1 = C_nH_{2n+1}$, $C_nH_{2n+1}O$, NO_2 $R_2 = C_nH_{2n+1}$, $C_nH_{2n+1}O$, $COCH_3$, CN, C_6H_5

The most frequently used ways of introducing an ethylene linking group are Wittig[6] olefinations (in stilbene synthesis) or the Perkin reaction and Knoevenagel condensation[7] in the case of phenylacrylic acid derivatives.

In contrast to cinnamic acid derivatives there are only a few examples of 3-phenoxyacrylic esters in the literature.[8,9,10] One of them—the methyl ester of (*E*)-3-(4-methoxyphenoxy)acrylic acid has been identified as a metabolite of the fungus *Poronia Punctata*,[11] but there have been no examples of liquid crystalline substances in this group so far.

Lately we have developed a convenient method for the synthesis of phenyl esters of 3-phenoxyacrylic acid (**3**).[12] It concerns the nucleophilic addition of phenols to a reactive triple bond of substituted phenyl propynoates in the presence of dimethylaminopyridine (DMAP) Scheme 1. The reaction occurs at ambient temperature affording exclusively *E* isomers.

Preliminary microscopic observations revealed that one of them (X = Y = C_6H_5CN) generated a nematic phase.

We report here the mesogenic properties of several other phenoxyacrylic acid derivatives and discuss the relationship between the molecular structure and liquid crystalline behaviour.

Experimental

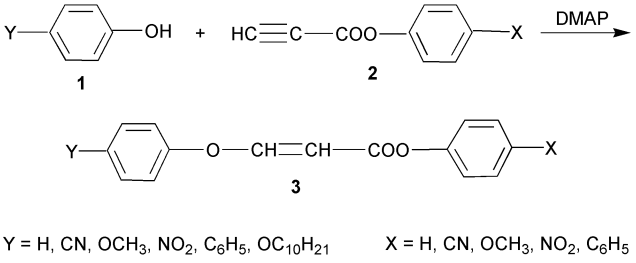
Characterization

The structures of all products (new compounds with the exception of **4a** and **4d**) were confirmed by elemental analysis, IR and ^{1}H NMR spectra. The NMR spectra were obtained on a Varian Gemini 200 MHz spectrometer ($CDCl_3$, TMS as internal standard) and IR on a FTIR Perkin Elmer 2000 spectrometer (CH_2Cl_2).

Thermal studies were made by differential scanning calorimetry. DSC measurements were carried out at the rate 5 °C min^{-1} using a Perkin Elmer 7 calorimeter. The textures of the mesophases were studied using a polarizing microscope BIOLAR PI equipped with a hot stage. X-Ray measurements were performed using a PHILIPS X'Pert diffractometer as well as a Guinier symmetrical focusing transmission photographic camera. In the case of the diffractometer, copper radiation filtered by nickel absorption filter was applied, while the Guinier camera worked with cobalt radiation. Diffractometer smectic phase measurements were carried out using the reflecting method from a flat sample aligned by glass substrate. The chosen temperature was maintained within ±0.1 °C.

Synthesis

The esters of propynoic acid (**2**, X = CN, NO_2, C_6H_4CN) were synthesised from the appropriate phenols and a twofold excess of propynoic acid in the presence of DCC and DMAP according to literature procedures.[12] 4-Decyloxy-4′-hydroxybiphenyl (mp 151 °C) and 4-butoxy-4′-hydroxybiphenyl (mp 172 °C) were obtained according to ref. 13 and 4-decyloxyphenol (mp 74 °C) according to ref. 12. Other chemicals used were analytical grade commercial products (Aldrich).



Scheme 1

The procedure for preparation of (*E*)-3-phenoxyacrylic acid phenyl esters (**3**) is exemplified by the reaction of 4-cyanophenyl propynoate with 4-decyloxy-4′-hydroxybiphenyl.

(*E*)-3-(4′-Decyloxybiphenyl-4-yl)oxyacrylic acid 4-cyanophenyl ester (3c)

Equimolar amounts of 4-decyloxy-4′-hydroxybiphenyl and 4-cyanophenyl propynoate (0.001 mol) were dissolved in 20 cm^3 of dry methylene chloride and ~0.0001 mol of DMAP was added. After 24 h the solvent was evaporated and products **3c** (the main product) and **4c** (the product of transesterification) were separated by flash chromatography (silica gel, chloroform) with yields of 55% for **3c** and ~8% **4c**.

3c: IR ν/cm^{-1} 2232, 1733; ^{1}H NMR δ (ppm) 0.89 (t, 3H, J = 7.2 Hz), 1.18–1.43 (m, 14H), 1.77–1.84 (m, 2H), 4.00 (t, 2H, J = 6.4 Hz), 5.42 (d, 1H, J = 12.1 Hz), 6.95–.72 (m, 12H), 8.32 (d, 1H, J = 12.1 Hz). Elemental analysis,calculated: C 77.24%, H 7.09%, N 2.81%; found: C 77.15%, H 7.20%, N 2.92%.

4c: IR ν, cm^{-1} 1727; ^{1}H NMR δ (pm) 0.89 (t, 6H, J = 6.0 Hz), 1.18–1.46 (m, 28H), 1.77–1.84 (m ,4H), 3.99 (t, 2H J = 6.2 Hz), 4.01 (t, 2H, J = 6.2 Hz), 5.59 (d, 1H, J = 12.2 Hz), 6.94–7.59 (m, 16H), 8.03 (d, 1H, J = 12.2 Hz). Elemental analysis, calculated: C 80.07%, H 8.58%; found: C 80.19%, H 8.48%.

The average yields for compounds **3a–h** were 50–60%; the products of transesterification (**4a–d**) were isolated with the yields 5–10%. Only compounds **4a** and **4d** have been described earlier.[12] The spectral data and elemental analysis for the new compounds are listed below.

3a: IR ν/cm^{-1} 2232, 1731; ^{1}H NMR δ (ppm) 0.88 (t, 3H, J = 6.6 Hz), 1.15–1.53 (m, 14H), 1.70–1.82 (m, 2H), 3.94 (t, 2H, J = 6.4 Hz), 5.89 (d, 1H, J = 12.0 Hz), 6.86–7.74 (m, 8H), 7.94 (d, 1H, J = 12.0 Hz). Elemental analysis, calculated: C 74.08%, H 7.41%, N 3.32%; found: C 74.20%, H 7.33%, N 3.41%.

3b: IR ν/cm^{-1} 2232, 1731; ^{1}H NMR δ (ppm) 5.39 (d, 1H, J = 12.0 Hz), 7.22–7.76 (m, 12H), 7.99 (d, 1H, J = 12.0 Hz). Elemental analysis, calculated: C 75.40%, H 3.85%, N 7.65%; found: C 75.28%, H 7.73%, N 7.68%.

3d: IR ν/cm^{-1} 2232, 1732; ^{1}H NMR δ (ppm) 0.99 (t, 3H, J = 7.2 Hz), 1.42–1.57 (m, 2H), 1.79–1.89 (m, 2H), 4.01 (t, 2H, J = 6.4 Hz), 5.74 (d, 1H, J = 12.0 Hz), 6.95–7.72 (m, 12H), 8.03 (d, 1H, J = 12.0 Hz). Elemental analysis, calculated: C 75.53%, H 5.61%, N 3.39%; found: C 75.60%, H 5.54%, N 3.45%.

3e: IR ν/cm^{-1} 1732, 1525, 1348; ^{1}H NMR δ (ppm) 0.89 (t, 3H, J = 6.8 Hz), 1.16–1.51 (m, 14H), 1.74–1.88 (m, 2H), 3.99 (t, 2H, J = 6.4 Hz), 5.95 (d, 1H, J = 12.2 Hz), 6.94–7.60 (m, 10H), 8.01 (d, 1H, J = 12.2 Hz), 8.26–8.36 (m, 2H). Elemental analysis, calculated: C 71.93%, H 6.82%, N 2.71%; found: C 71.85%, H 6,76%, N 2.63%.

3f: IR ν/cm^{-1} 2232, 1732, 1527, 1348; ^{1}H NMR δ (ppm) 5.92 (d, 1H, J = 12.2 Hz), 7.25–7.56 (m, 10H), 8.02 (d, 1H, J = 12.2 Hz), 8.27–8.35 (m, 2H). Elemental analysis, calculated: C 68.39%, H 3.65%, N 7.25%; found: C 68.45%, H 3.72%, N 7.33%.

3g: IR ν/cm^{-1} 2232, 1733; ^{1}H NMR δ (ppm) 0.88 (t, 3H, J = 6.8 Hz), 1.06–1.45 (m, 14H), 1.72–1.85 (m, 2H), 3.94 (t ,2H, J = 6.4 Hz), 5.65 (d, 1H, J = 12.2 Hz), 6.88–7.70 (m, 12H), 7.95 (d, 1H, J = 12.2 Hz). Elemental analysis, calculated: C 77.24%, H 7.09%, N 2.81%; found: C 77.20%, H 7.16%, N 2.77%.

3h: IR ν/cm^{-1} 2231, 1730; ^{1}H NMR δ (ppm) 0.89 (t, 3H, J = 7,0 Hz), 1.21–1.47 (m, 14H), 1.74–1.88 (m, 2H), 4.00 (t, 2H, J = 6.4 Hz), 5.78 (d, 1H, J = 12.2 Hz), 6.95–7.71 (m, 16H), 8.04 (d, 1H, J = 12.2 Hz). Elemental analysis, calculated: C 79.55%, H 6.85%, N 2.44%; found: C 79.65%, H 6.76%, N 2.48%.

4b: IR ν/cm^{-1} 1728; ^{1}H NMR δ (ppm) 0.99 (t, 6H, J = 6.0 Hz), 1.42–1.61 (m, 4H), 1.70–1.87 (m ,4H), 4.00 (t, 2H J = 6.4 Hz), 4.01 (t, 2H J = 6.4 Hz), 5.78 (d, 1H, J = 12.0 Hz), 6.99–7.51 (m, 16H), 8.03 (d, 1H, J = 12.0 Hz). Elemental analysis, calculated: C 78.33%, H 6.76%; found: C 78.27%, H 6.68%.

Results and discussion

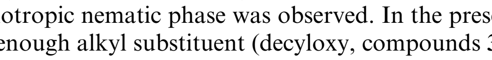
4-Cyanophenol, 4-alkoxyphenol and their 4,4′-biphenyl disubstituted analogues were selected to carry out the addition (Scheme 1). Cyano- and alkoxy- substituents, common in mesogenic compounds, possess quite different properties: a cyano group promotes nematic properties, whereas long alkyl substituents favour smectic order.

The phenyl propynoates (**2**, X = NO_2, CN, C_6H_4CN) were obtained in the reaction of an appropriate phenol with propynoic acid in the presence of DCC (1,3-dicyclohexylcarbodiimide) and DMAP.

The substituents **X** were of electron-withdrawing character since the nucleophilic addition of phenols (Scheme 1) proceeded with better yield in the case of cyano or nitro substituted esters of propynoic acid because of the more polar character of the triple bond in the presence of an electron-acceptor group.

According to the procedure described above a new family of substituted phenyl esters of (*E*)-3-phenoxyacrylic acid (compounds **3a–h**, Table 1) was obtained; most of which had liquid crystalline properties.

However, it turned out that the Michael type addition was accompanied by transesterification leading to the formation of small amounts of "symmetrical' esters of type **4** as by-products (compounds **4a–d**, Table 1). Both of them could be separated using column chromatography.



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The phase transitions temperatures and enthalpies of the synthesised compounds are collected in Table 1. Liquid crystalline properties were observed in the presence of at least one biphenyl moiety linked *via* an esther or ether bond. Two biphenyl moieties cause further stabilisation of the mesophase.

In the case of small polar terminal groups (cyano, nitro) or relatively short (C_4H_9O) alkoxy substituents the enantiotropic or monotropic nematic phase was observed. In the presence of a long enough alkyl substituent (decyloxy, compounds **3c,e,g,h** and **4c**) the esters were shown to be in a smectic A phase (fan shaped texture). The X-ray patterns of magnetically oriented samples confirmed the presence of the smectic A phase: two equatorial diffuse arcs and sharp reflections along the vertical line. In addition the interlayer distances in the case of compounds **3c,e,g,h** and **4c** did not appear to depend on temperature (Fig. 1 and 2). The enthalpy changes observed for SmA–I transitions (Table 1) are within the characteristic range of values compiled by Demus *et al.*.[14]

The interlayer distances from X-ray measurements are given in Table 2.

As can be seen from Table 2 the interlayer distances in the case of the smectic phases of compounds **3c,e,g,h** differ from the lengths of the molecules. The layer spacing (d) is approximately 1.2–1.3 times the actual molecular length (l) calculated (semiempirical AM1, Hyper-Chem) in its fully extended conformation for the compounds containing both a decyloxy and cyano or nitro group. This indicates the presence of an interdigitated bilayered smectic structure of A_d type, which occurs in the case of molecules consisting of lipophilic alkyl chains and two phenyl rings with a polar substituent (*e.g.* 4-octyloxycyanobiphenyl).[15]

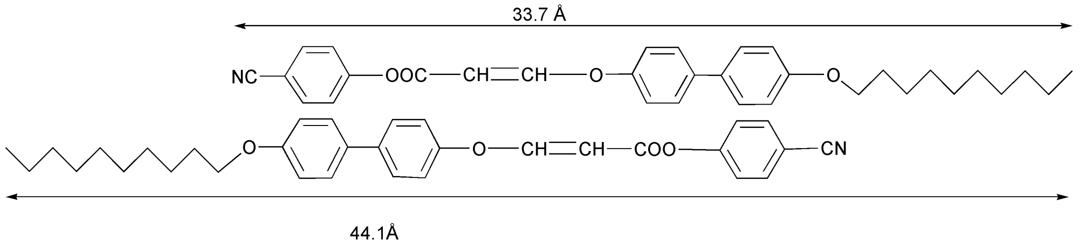
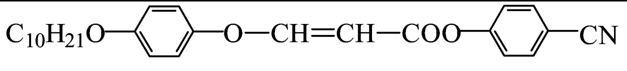
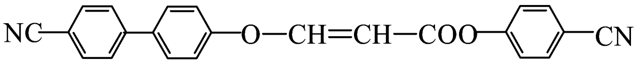
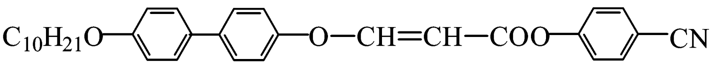
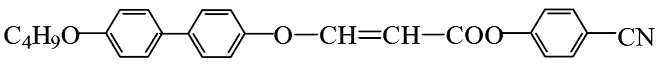
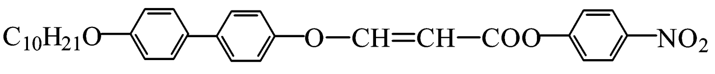
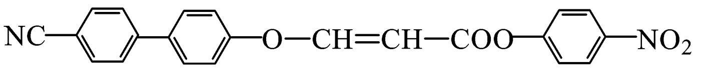
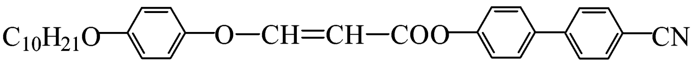
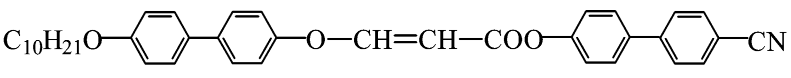
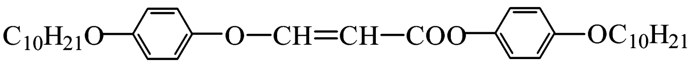
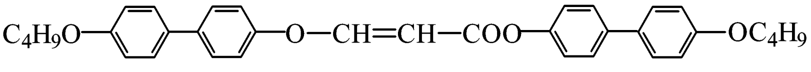
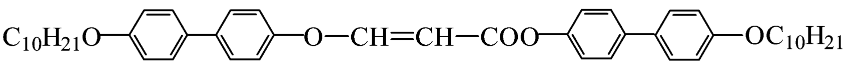
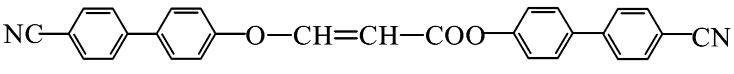


Table 1 Phase transition temperatures (°C) and enthalpies (kJ mol^{-1}, in square brackets) for substituted phenyl esters of (*E*)-3-phenoxyacrylic acid

No	Chemical formula	Phase transitions
3a		Cr 73 I
3b		Cr 240 I
3c		Cr 85.4 [38.8] SmA 89.6 [4.9] I
3d		Cr 137.1 I; (I 90.6 [8.3] N 86.6 [28.8] Cr)
3e		Cr 95.6 [36.5] SmA 130.1 [3.8] I
3f		Cr 158 I; (I 154 [9.4] N 82 [30.2] Cr)
3g		Cr 90.9 [35.3] SmA 118.0 [4.1] I
3h		Cr 106.7 [33.1] SmA 187.0 [4.5] I
4a		Cr 48 I[12]
4b		Cr 187.5 I
4c		Cr 151.4 [26.6] SmA 160.2 [6.0] I
4d		Cr 212 N 270 I[12]

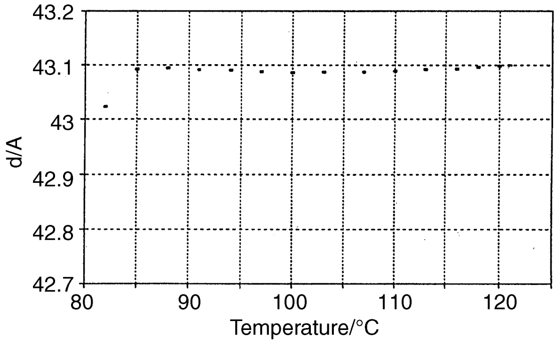


Fig. 1 Temperature dependence of layer spacing for compound **3g**.

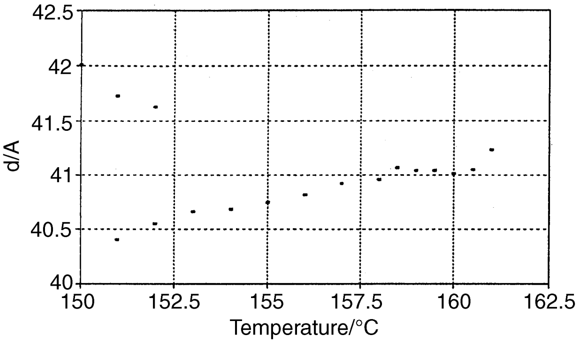
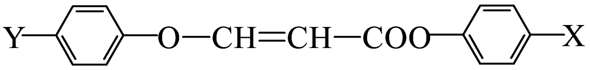
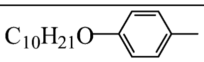
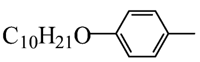
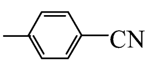
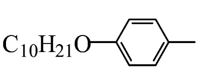
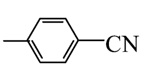
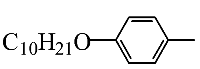
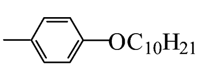


Fig. 2 Temperature dependence of layer spacing for compound **4c**.

Table 2 Interlayer distance and calculated molecular length as a function of the molecular structure



No	Y	X	l/Å	d/Å	d/l
3c		$-CN$	33.7	44.1	1.30
3e		$-NO_2$	32.5	41.0	1.26
3g	$C_{10}H_{21}O-$		34.9	43.1	1.23
3h			38.0	46.0	1.21
4c			49.9	40.9	0.82

If the polar and aliphatic parts of a molecule have length a and b respectively, one finds for many cases approximately $d = a + 2b$. In the case of phenoxyacrylic acid derivatives the polarizable part of the molecule includes rigid cores consisting of three or four phenyl rings connected *via* –O–CH=CH–COO– bonds, and the spacing d is in every case about 10 Å longer than the length of the molecule. The length of the decyloxy chain in its fully extended conformation is about 14 Å, but numerous X-ray studies have shown that in various smectic A phases the lamellar spacings (d) are considerably shorter than the corresponding molecular lengths due to chain deformations. Furthermore the calculated molecular geometry (semiempirical AM1, Hyper-Chem) has shown that phenyl esters of phenoxyacrylic acid are a little bent in shape (Fig. 3).

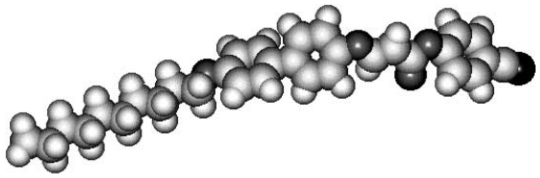


Fig. 3 Model of molecular structure of **3c**.

It is noteworthy, that if the molecule has two nonpolar decyloxy substituents (compound **4c**) the d/l value is in the range typical for the monolayer smectic A phase (taking into account some deformations of the alkyl chains) and is almost stable within the range of the mesophase (Fig. 2). In the case of biphenyl derivatives the calculated angle between the biphenyl fragments is about 120–130° and suggests the possibility of formation of banana-shaped molecules,[16,17] but our observations does not support this hypothesis so far.

Conclusion

A new class of liquid crystalline compounds based on substituted phenoxyacrylic acid phenyl esters was developed. They exhibit nematic and smectic A mesomorphism. The 4-nitrophenyl, 4-cyanophenyl and biphenylyl esters of (*E*)-3-(4′-decyloxybiphenyl-4-yl)oxyacrylic acid form interdigitated bilayered smectic structures of A_d type.

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