Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

First carbazole-based lamellar liquid crystal system

Eva Perea; Francisco López-Calahorra; Dolores Velasco

To cite this Article Perea, Eva , López-Calahorra, Francisco and Velasco, Dolores(2002) 'First carbazole-based lamellar liquid crystal system', Liquid Crystals, 29: 3, 421 — 428

To link to this Article: DOI: 10.1080/02678290110113531

URL: http://dx.doi.org/10.1080/02678290110113531

LIQUID CRYSTALS, 2002, VOL. 29, NO. 3, 421–428
Taylor & Francis
Taylor & Francis Group

First carbazole-based lamellar liquid crystal system

EVA PEREA, FRANCISCO LÓPEZ-CALAHORRA
and DOLORES VELASCO*
Departament de Química Orgànica, Universitat de Barcelona,
Martí i Franqués 1-11, 08028 Barcelona, Spain

(*Received 6 July 2001; in final form 3 October 2001; accepted 4 October 2001*)

The synthesis and characterization of seven polysubstituted 9-arylcarbazole derivatives is described. The influence of the number of chains peripherally bonded to the core, as well as the length of the chains, on the mesophase behaviour of the synthesized systems has been studied. The nature of the linking group between the core and the peripheral chains has also been considered. One of these compounds displays liquid crystalline behaviour, as confirmed by optical polarizing microscopy, differential scanning calorimetry and X-ray diffraction, being the first carbazole-based lamellar liquid crystal system reported in the literature.

1. Introduction

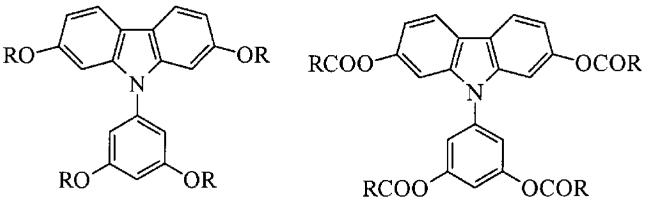
Since the material properties of carbazole were discovered [1], this system and its polymeric analogue poly(*N*-vinylcarbazole) (PVK) have been extensively studied [2]. Due to the photoconductivity of poly(*N*-vinylcarbazole), the study of the photoconductive properties of carbazole and its derivatives is of considerable interest [3]. In addition, when carbazole is substituted in an appropriate way, it can also exhibit non-linear optical behaviour [4]. Thus, the photorefractive properties of carbazole derivatives are also being investigated [5]. For these reasons, carbazole has been used as a functional building block in the fabrication of organic photoconductors, NLO, and photorefractive materials [5]. Carbazole derivatives with liquid crystal behaviour are interesting for the provision of materials which combine the properties of carbazole with those related to the anisotropic ordering of mesophases. However there are few examples of liquid crystalline carbazoles [6]. In our research group, calamitic liquid crystal carbazole derivatives have been obtained [7] and at the present we are studying the modification of the carbazole system in order to obtain columnar liquid crystal phases [8]. Discotic molecules with appropriate chemical structures can exhibit columnar ordered mesophases, which can give transient photoconduction [9]. Typical representatives of this class of materials are the symmetrically substituted hexaalkoxytriphenylene derivatives.

To our knowledge, no examples of discotic liquid crystal systems with a carbazole unit as the central part of the aromatic core have been reported. Recently a hexaalkoxytriphenylene unit covalently attached to one carbazole molecule as a pendant group has been reported to display hexagonal columnar liquid crystalline behaviour but only when doped with trinitrofluorenone [10]. Here we report new carbazole derivatives in which the carbazole group forms part of the aromatic core of the molecule, see figure 1.

2. Experimental

2.1. *Analytical techniques*

Melting points (not corrected) were determined using Büchi apparatus. Analytical thin layer chromatography (TLC) was carried out on pre-coated silica gel (230–400 mesh) containing a fluorescent indicator (UV 254 nm). All substances were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy with a Varian-Gemini XL-200



1a: R=C_6H_{13}
1b: R=$C_{12}H_{25}$
1c: R=$C_{18}H_{37}$
1d: R=$C_{22}H_{45}$

2a: R=$C_{10}H_{21}$
2b: R=$C_{17}H_{35}$
2c: R=$C_{21}H_{43}$

Figure 1. Structures of the 9-arylcarbazole derivatives.

---

*Author for correspondence; e-mail: dvelasco@qo.ub.es

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2002 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290110113531

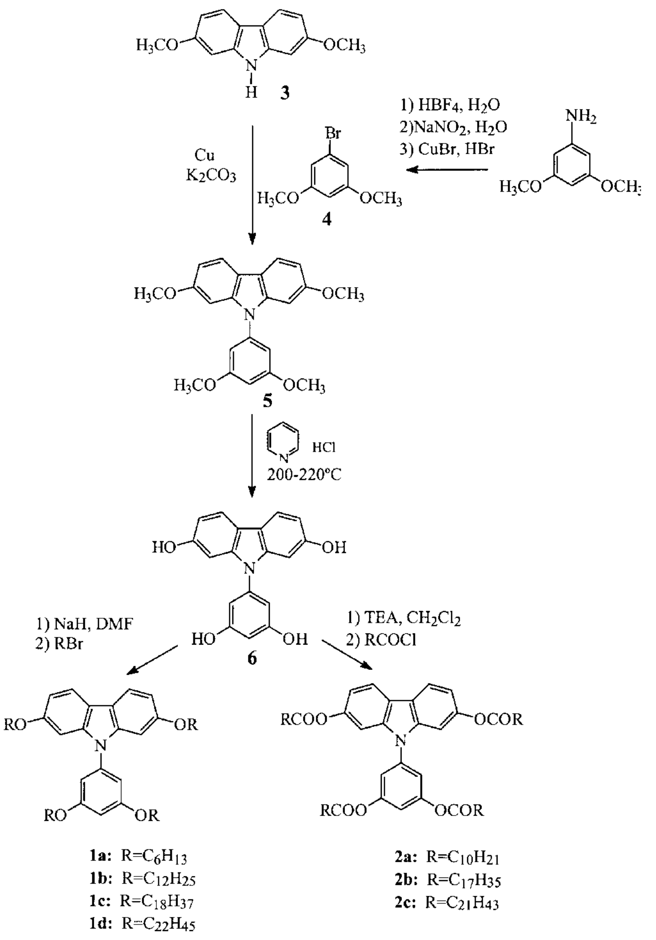
(200 MHz) or a Varian-Unity 300 (300 MHz) spectrometer, and by IR spectroscopy with a Perkin Elmer 1330 Infrared Spectrophotometer. Mass spectra were recorded on a Hewlett-Packard 5890 mass spectrometer using the chemical ionization technique. MALDI mass spectra were obtained on a Voyager DE RP (Perseptive Biosystems, Framingnam, USA) time-of-flight (TOF) mass spectrometer equipped with nitrogen laser (337 nm, 3 ns pulse), using 2,5-dihydroxybenzoic acid (DHB) in THF as the matrix.

Molecular orbital calculations were carried out on empirical structures using the semiempirical AM1 hamiltonian of the MOPAC 93 Program [11] on a Silicon Indigo 2 computer with full optimization of all bond lengths, band angles and torsion angles. The SCF convergence was set to 10^{-8} for calculations of the geometries (PRECISE option in MOPAC). The eigenvector following (EF) method of convergence was used.

All compounds were analysed by optical microscopy with a Mettler FP 82 hot stage controlled by a Mettler FP 80 processor which was used together with a Leitz Ortholux II Pol-BK microscope. Thermal analyses were performed using a Perkin Elmer DSC 7 differential scanning calorimeter at heating rates between 2 and 9 K min^{-1}. X-ray diffractograms were monitored with an Image Plate system with Kiesig geometry.

2.2. *Synthesis*

The synthesis of the new carbazole derivatives is illustrated in the scheme.



Scheme. Synthesis of compounds **1a–d** and **2a–c**.

2.2.1. *2,7-Dimethoxycarbazole (**3**)*

This compound was prepared using the methodology described in the literature [7, 12].

2.2.2. *5-Bromo-1,3-dimethoxybenzene (**4**)*

A mixture of 100 mg (0.653 mmol) of 3,5-dimethoxyaniline and 2.84 ml of HBF_4 in 10 ml of water was stirred at 0°C. 54 mg (0.783 mmol) of $NaNO_2$ in 1.6 ml of water were added and the mixture was stirred at 0°C for 15 min. The solid obtained was filtered and washed first with water and then with Et_2O. Meanwhile, 94 mg (0.653 mmol) of CuBr dissolved in 4 ml of HBr and 10 ml of water were heated at 100°C. The solid obtained in the previous step was added to this solution, and the mixture was stirred at 100°C for 20 min. The cooled mixture was extracted with CH_2Cl_2; the organic layer obtained was dried with $MgSO_4$ and evaporated. The product was purified by flash chromatography with a mixture of hexane/ethyl acetate (8/2) on silica gel; yield 128 mg of **4** (55%). TLC (SiO_2, hexane/ethyl acetate (8/2), UV): $R_f = 0.42$. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 3.77$ (s, OCH_3, 6H), 6.39 (d, CH^2, $J = 2.2$ Hz, 1H), 6.67 (d, $J = 2.2$ Hz, $CH^{4,6}$, 2H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 56.23$ (OCH_3), 99.62 (C^2H), 111.75 (C^4H, C^6H), 126.38 (C^5), 164.63 (C^1–O, C^3–O) ppm.

2.2.3. *2,7-Dimethoxy-9-(3,5-dimethoxyphenyl)carbazole (**5**)* [13]

A mixture of 200 mg (0.880 mmol) of compound **3**, 380 mg (1.749 mmol) of compound **4**, 8 mg of copper bronze and 147 mg (0.535 mmol) K_2CO_3 was stirred at 200–220°C for 12 h. The cooled mixture was extracted with acetone, and the organic layer dried with $MgSO_4$ and evaporated. The product was purified by flash chromatography with a mixture of hexane/ethyl acetate (8/2) on silica gel; yield 205 mg of **5** (32%), m.p. 136–139°C. TLC (SiO_2, hexane/AcOEt (8/2), UV): $R_f = 0.36$. IR (KBr): $\nu_{max} = 3060$ (arC–H st), 1605 (arC–C st), 1250 (arC–O–C st as) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 3.82$ (s, OCH_3, 6H), 3.92 (s, OCH_3, 3H), 6.73 (d, $CH^{1,8}$, 2H), 6.83 (dd, $CH^{3,6}$, $J_{3,4} = 8.6$ Hz, $J_{3,1} = 2.2$ Hz, 2H), 7.13 (d, $CH^{2',6'}$ or $CH^{3',5'}$, $J = 8.8$ Hz, 2H), 7.41 (d, $CH^{2',6'}$ or $CH^{3',5'}$, $J = 9.2$ Hz, 2H), 7.88 (d, $CH^{4,5}$, $J = 8.6$ Hz, 2H) ppm. MS (CI): $m/z = 333$ (M, 4%), 334 (M + 1, 100%).

2.2.4. *2,7-Dihydroxy-9-(3,5-dihydroxyphenyl)carbazole (6)*

A mixture of 150 mg (0.41 mmol) of compound **5** and 917 mg (7.93 mmol) or pyridine hydrochloride was stirred at 200–220°C for 5 h. Ethyl acetate was added to the cooled mixture, and the organic layer obtained was washed with water, dried with $MgSO_4$ and evaporated; yield 125 mg of **6** (98%). TLC (SiO_2, AcOEt, UV): $R_f=0.50$. ^1H NMR (200 MHz, CD_3OD): $\delta=6.25$ (d, $CH^{4'}$, $J=2.2$ Hz, 1H), 6.36 (d, $CH^{2',6'}$, $J=2.2$ Hz, 2H), 6.61 (dd, $CH^{3,6}$, $J_1=8.4$ Hz and $J_2=1.8$ Hz, 2H), 6.71 (d, $CH^{1,8}$, $J=1.8$ Hz, 2H), 7.65 (d, $CH^{4,5}$, $J=8.4$ Hz, 2H) ppm. MS (CI): $m/z=307$ (M, 70%), 308 (M+ 1, 18%), 325 (M+ 18, 10%), 342 (M+ 35, 3%).

2.2.5. *Compounds **1a–d**: general procedure*

2.77 mmol of NaH, 60% dispersion in mineral oil, were suspended in 8 ml of dry DMF; 0.35 mmol of compound **6** were added slowly and the mixture obtained was stirred at room temperature for 15 min. 1.56 mmol of the appropriate 1-bromoalkane dissolved in dried DMF were added and the mixture was stirred at 60°C for 8 h; it was then cooled to 0°C and 20 ml water added. The mixture was extracted with CH_2Cl_2; the organic layer was washed with water, dried with $MgSO_4$ and evaporated. The product was purified by flash chromatography.

*2,7-Dihexyloxy-9-(3,5-dihexyloxyphenyl)carbazole (**1a**)*: Yield 69%, TLC (SiO_2, hexane/AcOEt (8/2), UV): $R_f=0.58$, m.p. 78–80°C. IR (KBr): $\nu_{max}=3080$ (arC−H st), 2941–2871 (alC−H st), 1207 (arC−O−C st as) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): $\delta=0.92$ (t, CH_3, 12H), 1.32 (m, CH_2, 24H), 1.81 (m, $OCH_2\underline{CH_2}$, 8H), 4.01 (t, 4 OCH_2, 8H), 6.57 (d, H4′, $J=2.2$ Hz, 1H), 6.63 (d, $CH^{2',6'}$, $J=2.2$ Hz, 2H), 6.88 (m, $CH^{1,8}$ and $CH^{3,6}$, 4H), 7.82 (d, $CH^{4,5}$, $J=8.3$ Hz, 2H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=14.08$ (CH_3), 22.65, 25.75, 29.3, 31.66 (CH_2), 68.34 (CH_2−O), 68.44 (CH_2−O), 95.26 ($C^{4'}H$), 101.3 ($C^{2'}H$, C6′H), 105.50 (C^1H, C^8H), 108.45 (C^3H, C^6H), 117.6 (C^{4a}, C^{4b}), 119.9 (C^4H, C^5H), 141.1 and 142.8 (C^{8a} and C^{9a}; $C^{1'}$), 157.62 (ArC−O), 161.08 (arC−O) ppm. MS-FAB (+)-NBA: 643.6 (M, 100%), 644.8 (M+ 1, 94%). Elemental analysis: calc. for $C_{42}H_{61}NO_4$ C 78.34, H 9.55, N 2.18; found C 78.39, H 9.53, N 2.17%.

*2,7-Didodecyloxy-9-(3,5-didodecyloxyphenyl)carbazole (**1b**)*: Yield 70%, TLC (SiO_2, $CHCl_3$, UV): $R_f=0.75$, m.p. 68°C. ^1H NMR (200 MHz, $CDCl_3$): $\delta=0.87$ (t, CH_3, $J=6.1$ Hz, 12H), 1.26 (m, CH_2, 80H), 1.79 (m, $OCH_2\underline{CH_2}$, 8H), 3.97 (t, OCH_2, $J=5.8$ Hz, 8H), 6.55 (d, $CH^{4'}$, $J=2.2$ Hz, 1H), 6.64 (d, $CH^{2',6'}$, $J=2.2$ Hz, 2H), 6.86 (m, $CH^{1,8}$ and $CH^{3,6}$, 4H), 7.88 (d, $CH^{4,5}$, $J=8.3$ Hz, 2H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=14.63$ (CH_3), 23.20–32.42 (CH_2), 68.96 (CH_2−O), 71.39 (CH_2−O), 90.60 ($C^{4'}H$), 101.7 ($C^{2'}H$, $C^{6'}H$), 106.23 (C^1H, C^8H), 109.21 (C^3H, C^6H), 117.98 (C^{4a}, C^{4b}), 120.82 (C^4H, C^5H), 141.3 and 142.2 (C1′; C^{8a} and C^{9a}), 158.31 (arC−O), 161.93 (arC−O ppm. MS-FAB (+): $m/z=980$ (M, 100%), 981 (M+ 1, 67%). Elemental analysis: calc. for $C_{66}H_{109}NO_4$ C 80.84, H 11.20, N 1.43; found C 80.80, H 11.23, N 1.42%.

*2,7-Dioctadecyloxy-9-(3,5-dioctadecyloxyphenyl)carbazole (**1c**)*: Yield 73%, m.p. 74–76°C, TLC (SiO_2, hexane/AcOEt (8/2), UV): $R_f=0.95$. IR (KBr): $\nu_{max}=2919$–2851 (alC−H st), 1470 (−CH_2− δ), 1198 (arC−O−C st as), 720 (−CH_2− γ) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): $\delta=0.87$ (t, CH_3, $J=6$ Hz, 12H), 1.25 (m, CH_2, 120H), 1.79 (m, $OCH_2\underline{CH_2}$, 8H), 3.96 (t, OCH_2, $J=6$ Hz, 8H), 6.54 (s, $CH^{4'}$, 1H), 6.63 (s, $CH^{2',6'}$, 2H), 6.86 (m, $CH^{1,8}$ i $CH^{3,6}$, 4H), 7.85 (d, $CH^{4,5}$, $J=8.4$ Hz, 2H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=14.03$ (CH_3), 22.6, 26.0, 29.1–29.6, 31.8 (CH_2), 68.3 (CH_2−O), 68.45 (CH_2−O), 95.3 (arCH), 100.9 (arCH), 105.52 (C^1H, C^8H), 108.5 (C^3H, C^6H), 117.5 (C^{4a} and C^{4b}), 119.8 (C^4H and C^5H), 139.12 i 142.2 (C1′; C^{8a} and C^{9a}), 157.68 (arC−O), 161.13 (arC−O) ppm. MS-MALDI-TOF (+): 1316.20 (M). Elemental analysis: calc. for $C_{90}H_{157}NO_4$ C 82.06, H 12.01, N 106; found C 82.11, H 11.97, N 106%.

*2,7-Didocosyloxy-9-(3,5-didocosyloxyphenyl)carbazole (**1d**)*: Yield 65%, TLC (SiO_2, hexane/CH_2Cl_2 (9/1), UV): $R_f=0.55$, m.p. 83–85°C. IR (KBr): $\nu_{max}=2919$–2852 (alC−H st), 1607 (arC−C st), 1468 (−CH_2− δ), 1189 (arC−O−C st as), 722 (−CH_2− γ) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): $\delta=0.87$ (t, CH_3, $J=6$ Hz, 12H), 1.25 (m, CH_2, 152H), 1.78 (m, $OCH_2\underline{CH_2}$, 8H), 3.96 (t, OCH_2, $J=6.2$ Hz, 8H), 6.56 (d, $CH^{4'}$, $J=2.2$ Hz, 1H), 6.61 (d, $CH^{2',6'}$, $J=2.2$ Hz, 2H), 6.86 (m, $CH^{1,8}$, $CH^{3,6}$, 4H), 7.82 (d, $CH^{4,5}$, $J=9.2$ Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=14.1$ (CH_3), 22.7, 26.1, 29.2–29.67, 30.9, 31.9 (CH_2), 68.3 (CH_2−O), 68.45 (CH_2−O), 95.4 (arCH), 101.1 (arCH), 105.5 (C^1H, C^8H), 109.0 (C^3H, C^6H), 116.0 (C^{4a}, C^{4b}), 120.3 (C^4H, C^5H), 138.9 and 142.3 (C1′; C^{8a} and C^{9a}), 157.8 (arC−O), 161.3 (arC−O) ppm. MS-MALDI-TOF: 1540.35 (M). Elemental analysis: calc. for $C_{106}H_{189}NO_4$ C 82.58, H 12.36, N 0.91; found C 82.64, H 12.31, N 0.91%.

2.2.6. *Compounds **2a–c**: general procedure*

0.645 mmol of compound **6** and 2.39 mmol of triethylamine were dissolved in CH_2Cl_2 under an inert atmosphere. The mixture obtained was stirred at room temperature for 20 min and was then cooled to 0°C. 2.838 mmol of the appropriate alkanoyl chloride dissolved in dried CH_2Cl_2 were added dropwise and the mixture was stirred at room temperature for 12 h. CH_2Cl_2 was added and the solution was washed with aqueous $NaHCO_3$ and water. The organic layer was dried and evaporated, and the product purified by flash chromatography.

*2,7-Didecylcarbonyloxy-9-(3,5-didecylcarbonyloxyphenyl)carbazole (**2a**)*: Yield 61%, TLC (SiO_2, hexane/CH_2Cl_2 (1/1), UV): $R_f = 0.35$, m.p. 51–54°C. IR (KBr): $\nu_{max} = 3080$–3040 (arC–H st), 2852 (alC–C st), 1758 (C=O st), 1609 (arC–C st), 1468 (–CH_2– δ), 1208, 1133 (arC–O–C st as), 724 (–CH_2– γ) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 0.88$ (t, CH_3, $J = 6.6$ Hz, 12H), 1.27 (m, CH_2, 56H), 1.75 (m, $OCOCH_2\underline{CH_2}$, 8H), 2.57 (t, $OCOCH_2$, $J = 7.6$ Hz, 8H), 7.02 (dd, $CH^{3,6}$, $J_{3,4} = 8.1$ Hz and $J_{3,1} = 2.2$ Hz, 2H), 7.06 (d, $CH^{4'}$, $J_{4'2'} = 2.1$ Hz, 1H), 7.14 (d, $CH^{2'6'}$ or $CH^{1,8}$, $J = 2.2$ Hz, 2H), 7.17 (d, $CH^{2'6'}$ or $CH^{1,8}$, $J = 2.2$ Hz, 2H), 8.03 (d, $CH^{4,5}$, $J_{4,3} = 8.2$ Hz, 2H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 14.1$ (CH_3), 22.7, 25.0, 29.1–29.6, 31.9 (CH_2), 34.4 (CH_2–CO), 34.5 (CH_2–CO), 103.3 (arCH), 114.8 (arCH), 115.5 (arCH), 117.6 (C^3H, C^6H), 120.6 (C^4H, C^5H), 121.6 (C^{4a}, C^{4b}), 138.2 ($C^{1'}$), 141.8 (C^{8a}, C^{9a}), 149.5 (arC–O), 152.1 (arC–O), 171.3 (C=O), 173.5 (C=O) ppm. MS-MALDI-TOF: 981 (M+1), 1003 (M+Na). Elemental analysis: calc. for $C_{62}H_{93}NO_8$ C 75.96, H 9.56, N 1.43; found C 75.88, H 9.59, N 1.44%.

*2,7-Diheptadecylcarbonyloxy-9-(3,5-diheptadecylcarbonyloxyphenyl)carbazole (**2b**)*: Yield 65%, TLC (SiO_2, CH_2Cl_2/hexane (8/2), UV): $R_f = 0.52$, m.p. 75–76°C. IR (KBr): $\nu_{max} = 2919$–2852 (alC–H st), 1756 (C=O st), 1613 (arC–C st), 1470 (–CH_2– δ), 1271, 1164 (arC–O–C st as), 720 (–CH_2– γ) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 0.88$ (t, CH_3, $J = 7$ Hz, 12H), 1.26 (m, CH_2, 112H), 1.75 (m, $OCOCH_2\underline{CH_2}$, 8H), 2.57 (t, $OCOCH_2$, $J = 7.4$ Hz, 8H), 6.99 (dd, $CH^{3,6}$, $J_{3,4} = 8.6$ Hz and $J_{3,1} = 2.2$ Hz, 2H), 7.06 (d, $CH^{4'}$, $J_{4'2'} = 1.8$ Hz, 1H), 7.14 (d, $CH^{2'6'}$ or $CH^{1,8}$, $J = 1.8$ Hz, 2H), 7.17 (d, $CH^{2'6'}$ or $CH^{1,8}$, $J = 2.2$ Hz, 2H), 8.03 (d, $CH^{4,5}$, $J_{4,3} = 8.8$ Hz, 2H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 14.1$ (CH_3), 22.7, 24.8, 29.1–29.6, 31.9 (CH_2), 34.3 (CH_2–CO), 34.4 (CH_2–CO), 103.3 (arCH), 114.6 (arCH), 115.6 (arCH), 117.7 (C^3H, C^6H), 120.4 (C^4H, C^5H), 121.6 (C^{4a}, C^{4b}), 138.2 ($C^{1'}$), 141.8 (C^{8a}, C^{9a}), 149.5 (arC–O), 152.1 (arC–O), 171.4 (C=O), 173.7 (C=O) ppm. MS-MALDI-TOF: 1372.1 (M), 1394.81 (M+Na). Elemental analysis: calc. for $C_{90}H_{149}NO_8$ C 78.72, H 10.94, N 1.02; found C 78.67, H 10.97, N 1.02%.

*2,7-Didocosylcarbonyloxy-9-(3,5-didocosilcarb onyloxyphenyl)carbazole (**2c**)*: Yield 46%, TLC (SiO_2, hexane/CH_2Cl_2 (1/1), UV): $R_f = 0.40$, m.p. 88–90°C. IR (KBr): $\nu_{max} = 3090$–3040 (arC–H st), 2917–2850 (alC–H st), 1756 (C=O st), 1611 (arC–C st), 1468 (–CH_2– δ), 1162 (arC–O–C st as), 720 (–CH_2– γ) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 0.88$ (t, CH_3, $J = 6.3$ Hz, 12H), 1.05–1.50 (m, CH_2, 144H), 1.74 (m, $OCOCH_2\underline{CH_2}$, 8H), 2.57 (t, $OCOCH_2$, $J = 7.5$ Hz, 8H), 7.01 (dd, $CH^{3,6}$, $J_{3,4} = 8.2$ Hz and $J_{3,1} = 2.0$ Hz, 2H), 7.06 (d, $CH^{4'}$, $J_{4'2'} = 2.0$ Hz, 1H), 7.14 (d, $CH^{2'6'}$ or $CH^{1,8}$, $J = 1.8$ Hz, 2H), 7.17 (d, $CH^{2'6'}$ or $CH^{1,8}$, $J = 2.2$ Hz, 2H), 8.03 (d, $CH^{4,5}$, $J_{4,3} = 8.2$ Hz, 2H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 14.1$ (CH_3), 22.6, 24.7, 29.0–29.6, 31.9 (CH_2), 34.3 (CH_2–CO), 34.4 (CH_2–CO), 103.2 (arCH), 114.8 (arCH), 115.0 (arCH), 117.6 (C^3H, C^6H), 120.6 (C^4H, C^5H), 120.9 (C^{4a}, C^{4b}), 138.0 ($C^{1'}$), 141.4 (C^{8a}, C^{9a}), 149.4 (arC–O), 152.0 (arC–O), 171.4 (C=O), 172.6 (C=O) ppm. MS-MALDI-TOF: 1619.58 (M+Na). Elemental analysis: calc. for $C_{106}H_{181}NO_8$ C 79.69, H 11.42, N 0.88; found C 79.63, H 11.46, N 0.88%.

3. Results and discussion

In this paper we report the synthesis and mesophase behaviour of a series of carbazole derivatives with 9-phenylcarbazole as the central core. *N*-phenylcarbazoles have a core which resembles that of triphenylene derivatives. Hexasubstituted triphenylene derivatives with a six-fold symmetry have been extensively studied and form columnar liquid crystal phases. *N*-arylcarbazoles do not have six-fold symmetry, and although many known discotic mesogens have a high symmetry, disc-like molecules with lower symmetry have been also found to form columnar phases [14]. We have studied the influence of the number of chains peripherally attached to the core, as well as the length of the chains, on the mesophase behaviour. A series of four chain compounds **1a–d**, with an ether linkage between the aromatic core and the alkyl chains of different lengths (6, 12, 18 and 22 carbon atoms) were prepared (figure 1). It is well known that the nature of the linking group between the core and the chains also has a great influence on the thermal behaviour of discotic molecules [15]. Compounds **2a–c**, with four alkyl chains of different lengths (10, 17 and 21 carbon atoms), but with an ester linking group have also been synthesized (figure 1) and characterized.

The thermal behaviour of the carbazole derivatives **1a–d** and **2a–c** was investigated by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The values of the transition temperatures and the associated enthalpies for the second heating cycle of each compound are listed in table 1. Compounds with esters as the linking group between the aromatic core and the alkyl chains (**2a–c**) displayed lower isotropic melting points than their analogous alkoxy compounds (**1b–d**), with the exception of those compounds with the longest alkyl chains, **1d**, and **2c**, which had similar melting points.

All compounds with ester linking groups (compounds **2a–c**) showed a crystal–crystal transition with associated enthalpy changes from 34.2 to 48.9 J g^{-1}, while only two of the four compounds with ether linking groups displayed such a transition. On heating, compound **2a** displays a crystal–crystal phase transition at

Table 1. Transition temperatures (°C) and associated enthalpy changes (J g^{-1}, in brackets) for compounds **1a–d** and **2a–c**.

Compound	*n*	Cr		Cr_2		M^a		I
1a	6	•		—		—	77 (63.7)	•
1b	12	•		—		—	60 (63.1)	•
1c	18	•	40 (3.9)	•	63 (66.3)	•	71 (15.8)	•
1d	22	•	65 (89.8)	•		—	85 (118.5)	•
2a	10	•	18 (48.9)	•		—	28 (11.6)	•
2b	17	•	49 (42.3)	•		—	59 (68)	•
2c	21	•	84 (34.2)	•		—	90 (70.3)	•

[a] M refers to a lamellar mesophase.

18°C with an associated enthalpy change of 48.9 J g^{-1} followed by isotropic melting at 28°C with an associated enthalpy change of 11.6 J g^{-1}. Despite the enthalpy value associated with melting, the texture observed by POM and the X-ray diffraction (XRD) pattern obtained for this compound at 24°C, show that the first phase transition observed corresponds to a crystal–crystal and not to a crystal–liquid crystal transition.

Only the compound 2,7-dioctadecyloxy-9-(3,5-dioctadecyloxyphenyl)carbazole, **1c**, was found to exhibit a liquid crystalline phase. Table 1 shows the thermal behaviour of this compound, which displays an enantiotropic liquid crystalline phase between 63 and 71°C. Between these temperatures, the sample shows birefringence and it is easily shared, as observed by POM at 70°C (figure 2).

The XRD pattern obtained for compound **1c** at 70°C (figure 3) shows three small angle maxima with a reciprocal spacing ratio of 1 : 1/2 : 1/13 (table 2) and a diffuse wide angle halo at 4.3 Å. Figure 3 compares the XRD pattern obtained at 70°C with one obtained at room temperature.

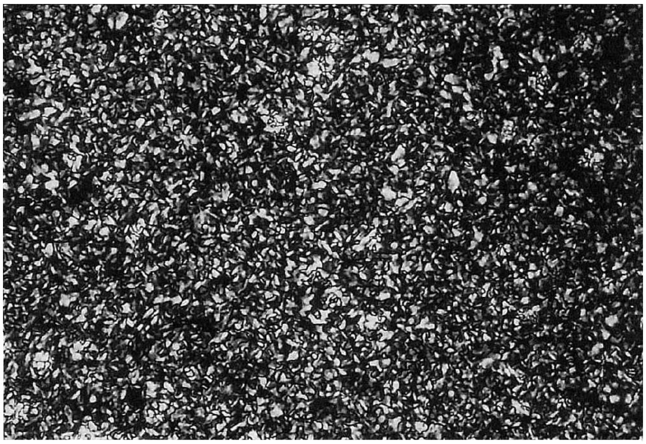


Figure 2. Mesophase texture of compound **1c** at 70°C.

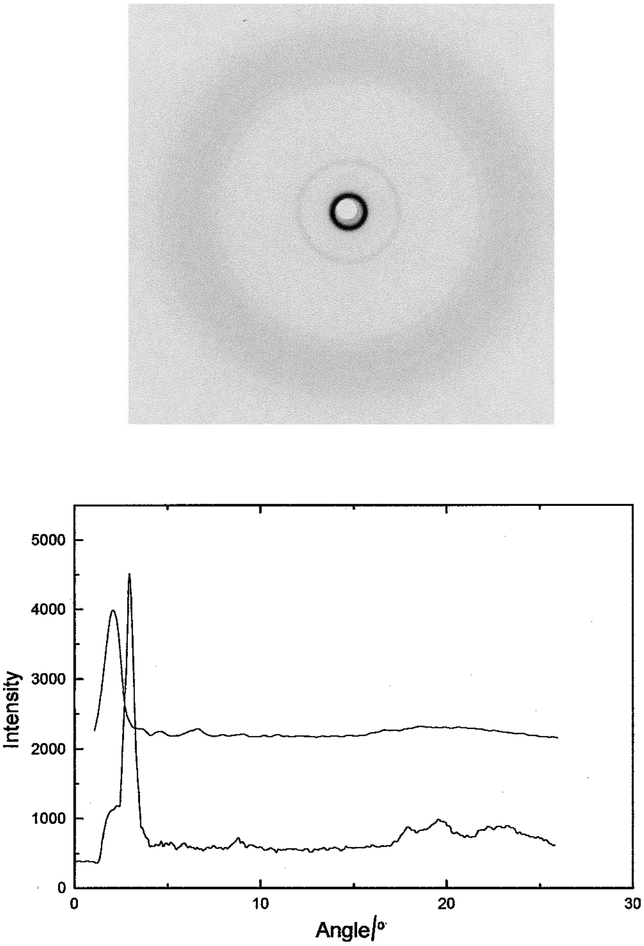


Figure 3. X-ray diffraction patterns obtained for compound **1c** at room temperature (lower trace) and 70°C (upper trace).

Table 2. X-ray data for the lamellar mesophase of compound **1c** at 70°C.

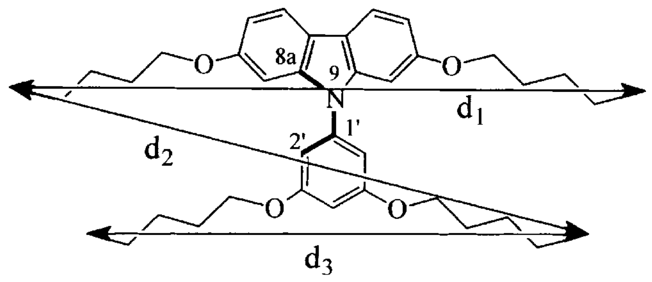
Angle/°	*d* (obs)/Å	Miller indices *h k l*	*d* (calc)/Å
2.11	41.9	(100)	
4.23	20.9	(200)	20.9
6.35	13.9	(300)	13.9
20.52	4.3^a		

[a] Diffuse halo.

From the ratio obtained between the small angle maxima, and considering that the molecule has only four alkyl chains surrounding the aromatic core [16], we suggest that compound **1c** shows a lamellar mesophase. For a lamellar mesophase, the three small angle maxima can be indexed as (0 0 1), (0 0 2) and (0 0 3). The layer spacing can be calculated from the (0 0 1) reflection and for compound **1c** is 41.9 Å.

For lamellar mesophases, the interlayer distance obtained corresponds to the molecular diameter. The geometry of compound **1c** was calculated by MOPAC 93 [11] using the AM1 method, and a value of 43.5° was obtained for the dihedral angle, θ, between the carbazole and the aryl substituent (table 3)). We note that this value corresponds to the molecules in the gas state. Due to the low symmetry of this kind of molecule there is no unique molecular diameter as in a disc-shape molecule. Instead of comparing the interlayer distance obtained by XRD with the molecular diameter, we took into consideration the maximum distance between the ends of the elongated alkyl chains attached to the aromatic core. The maximum value was 55.9 Å for both the flat molecule and that with a dihedral angle of 43.5° (table 3). The interlayer distance obtained by XRD is lower than the maximum distance calculated, which could imply a penetration of the alkyl chains into the aliphatic region of the neighbouring layer (figure 4 or a degree of orientational disorder for the alkyl chains [17]. The interlayer distance found by XRD for the mesophase formed by compound **1c** represents 75% of the largest molecular diameter calculated for the molecule.

Table 3. Calculated maximum distances between the ends of the elongated alkyl chains for compounds **1a–d**.



Compound	Angle $\theta_{8a\,9\,1'2'}$,°	d_1/Å	d_2/Å	d_3/Å
1a	0	25.9	25.3	21.2
1a	43.5	25.9	23.8	21.2
1b	0	40.8	40.0	36.5
1b	43.5	40.8	37.2	36.5
1c	0	55.9	55.0	51.5
1c	43.5	55.9	54.6	51.5
1d	0	66.0	65.3	61.6
1d	43.5	66.0	61.6	61.6

The effect on the mesophase behaviour of doping with a strong electron acceptor was also studied (table 4). Compound **1c** was doped with 2,4,7-trinitrofluorenone (TNF); a charge transfer complex was prepared with a 0.25 mole fraction of TNF. The 3 : 1 molar charge transfer complex was found to be non-mesogenic,

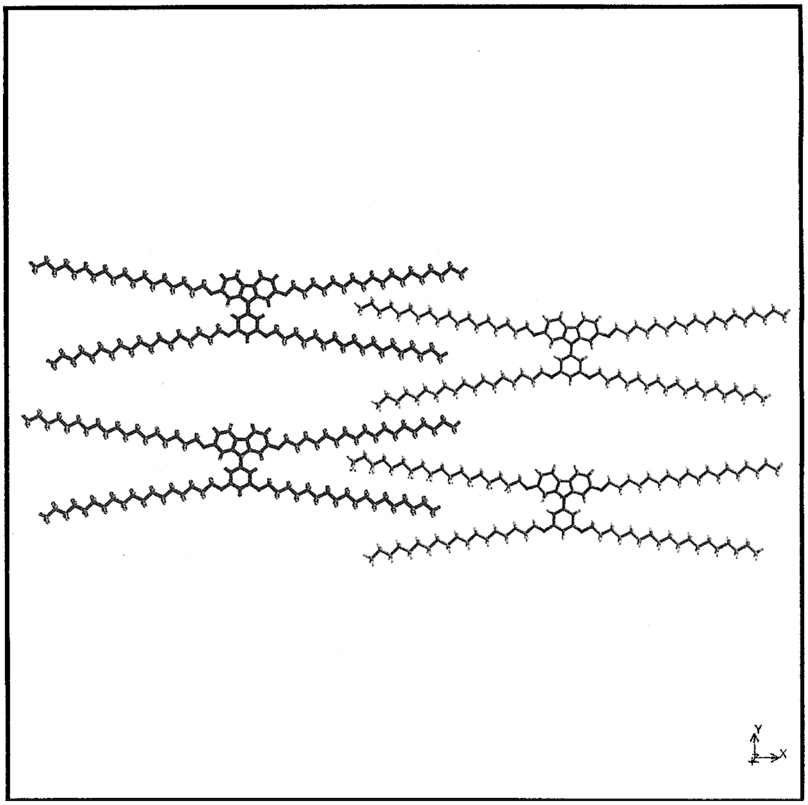


Figure 4. Model of interdigitation of the alkyl chains between neighbouring layers based on a distance between layers of 41.87 Å.

Table 4. Transition temperatures (°C) and enthalpy values ($J\,g^{-1}$, in brackets) of the compound **1c** doped with TNF.

Compound	%TNF	Cr		Cr_2		I
1c	25	•	57 (32.1)	•	71 (86.7)	•
1c	50		phase separation			

displaying on heating a crystal–crystal transition at 57°C with an associated enthalpy change of $32.1\,J\,g^{-1}$, and an isotropic melting at 71°C with an associated enthalpy change of $86.7\,J\,g^{-1}$. The 3:1 molar complex melting point is the same as that of the pure compound **1c**, but it has a much higher associated enthalpy change. On cooling, crystallization was observed at 51°C with an associated enthalpy change of $77.8\,J\,g^{-1}$. When a high mol% of TNF was used (50 mol %), phase separation was observed. The 3:1 charge transfer complex was studied by XRD and the results obtained support those found by DSC and POM.

4. Conclusions

The first system with a carbazole unit as the central part of the aromatic core to display a lamellar phase is reported. When doped with TNF, the liquid crystalline phase is lost. For the tetraalkyl-9-arylcarbazole derivatives studied, the chain length and the nature of the linking group between the aromatic core and the alkyl chains are important factors determining mesophase behaviour, as only dioctadecyloxy-9-(3,5-dioctadecyloxyphenyl)-carbazole displayed a liquid crystal phase. The characterization of a series of new 9-arylcarbazole derivatives with 5, 6 and 7 alkyl chains attached to the aromatic core is in progress.

This work has been financially supported by Comisión Interministerial de Ciencia y Tecnologia (Project PB 96-1491). E.P. gratefully thanks the Comissió Inter-departamental de Recerca i Innovació Tecnològiques (Generalitat de Catalunya) for a doctoral fellowship. The authors gratefully thank Prof. Dr Heino Finkelmann for the use of his laboratory in the Institüt für Makromolekulare Chemie, Albert-Ludwigs-Universität (Freiburg, Germany), and for his advice in the interpretation of the results obtained.

References

[1] Hoegl, H., 1965, *J. phys. Chem.*, **69,** 755.

[2] (*a*) Zhu, Z., and Moore, J. S., 2000, *J. org. Chem.*, **65,** 116; (*b*) Safoula, G., Touihri, S., Bernède, J. C., Jamali, M., Rabiller, C., Molinie, P., and Napo, K., 1999, *Polymer*, **40,** 1999; (*c*) Bouguettaya, M., Vallière, M., and Chevrot, C., 1999, *J. appl. polym. Sci.*, **73,** 1483; (*d*) Isoshima, T., Tsuyuki, M., Wada, T., and Sasabe, H., 1999, *Mol. Cryst. liq. Cryst.*, **327,** 5.

[3] (*a*) Scott, J. C., Pautmeier, L. Th., and Moerner, W. E., 1992, *J. opt. Soc. Am. B*, **9,** 2059; (*b*) Esen, R., Nakhimowsky, L. A., and Shanks, H. R., 1996, *Mol. Cryst. liq. Cryst.*, **287,** 255; (*c*) Strohriegl, P., and Grazulevicius, J. V., in *Handbook of Organic Conductive Molecules and Polymers*, Vol. 1, edited by H. S. Nalwa (John Wiley), pp. 559–590.

[4] (*a*) Zhang, Y., Wang, L., Wada, T., and Sasabe, H., 1996, *Chem. Commun.*, 559; (*b*) Chang, C., Whang, W., Hsu, C., Ding, Z., Hsu, K., and Lin, S., 1999, *Macromolecules*, **32,** 5637; (*c*) Kimura-Suda, H., Wada, T., Choi, S., Zhang, Y., and Sasabe, H., 1999, *Mol. Cryst. liq. Cryst.*, **327,** 91; (*d*) Dìaz, J. L., Dobarro, A., Villacampa, B., and Velasco, D., 2001, *Chem. Mater.*, **13,** 2528.

[5] (*a*) Zhang, Y., Wada, T., and Sasabe, H., 1998, *J. mater. Chem.*, **8,** 809; (*b*) Zhang, Y., Cui, Y., and Prasad, P. N., 1992, *Phys. Rev. B*, **46,** 9900; (*c*) Zhang, Y., Wada, T., Wang, L., and Sasabe, H., 1997, *Chem. Mater.*, **9,** 2798; (*d*) Zhang, Y., Wang, L., Wada, T., and Sasabe, H., 1996, *Macromol. Chem. Phys.*, **197,** 1877.

[6] (*a*) Lux, M., and Strohriegel, P., 1987, *Makromol. Chem.*, **188,** 811; (*b*) Chapoy, L. L., Biddle, D., Halström, J., Kovacs, K., Brunfeldt, K., Qasim, M. A., and Christensen, T., 1983, *Macromolecules*, **16,** 181; (*c*) Chapoy, L. L., Munck, D. K., Rasmussen, K. H., Diekmann, E. J., Sethi, R. K., and Biddle, D., 1984, *Mol. Cryst. liq. Cryst.*, **105,** 353; (*d*) Kosaka, Y., Kato, T., and Uryu, T., 1994, *J. polym. Sci. A: polym. Chem.*, **32,** 711; (*e*) Kosaka, Y., Kato, T., and Uryu, T., 1994, *Macromolecules*, **27,** 2658; (*f*) Kosaka, Y., and Uryu, T., 1995, *Macromolecules*, **28,** 870; (*g*) Kosaka, Y., and Uryu, T., 1995, *J. polym. Sci. A: polym. Chem.*, **33,** 2221; (*h*) Kosaka, Y., and Uryu, T., 1995, *J. polym. Sci. A: polym. Chem.*, **33,** 2917.

[7] (*a*) Von Arnim, V., Finkelmann, H., Dobarro, A., and Velasco, D., 1996, *Makromol. Chem. Phys.*, **197,** 2729; (*b*) Dobarro, A., Velasco, D., Arnim, V., and Finkelmann, H., 1997, *Makromol. Chem. Phys.*, **198,** 2563.

[8] Perea, E., Lòpez-Calahorra, F., Velasco, D., and Finkelmann, H., 2001, *Mol. Cryst. liq. Cryst.*, **365,** 695.

[9] (*a*) Ochse, A., Kettner, A., Kopitzke, J., Wendorff, J. H., and Bässler, H., 1999, *Phys. Chem. chem. Phys.*, **1,** 1757; (*b*) Chandrasekhar, S., and Prasad, S. K., 1999, *Contemp. Phys.*, **40,** 237.

[10] Manickam, M., Kumar, S., Preece, J. A., and Spencer, N., 2000, *Liq. Cryst.*, **27,** 703.

[11] Stewart, J. J. P., 1993, MOPAC 93.00 Manual, (Fujitsu Limited, Tokyo, Japan).

[12] Hsieh, B. R., and Litt, M. H., 1985, *Macromolecules*, **18,** 1388.

[13] (*a*) Dunlop, H. G., and Tucker, S. H., 1939, *J. chem. Soc.*, 1945; (*b*) Golman, H., and Honeycutt, J. B., 1957, *J. org. Chem.*, **22,** 226; (*c*) Bucharan, C., and Tucker, S. H., 1958, *J. chem. Soc.*, 2750.

[14] (*a*) Itoh, T., Takada, A., Fukuda, T., Miyamoto, T., Yakoh, Y., and Watanabe, J., 1991, *Liq. Cryst.*, **9,** 221; (*b*) Carfanga, C., Iannelli, P., Roviello, A., and

Sirigu, A., 1987, *Liq. Cryst.*, **2,** 611; (*c*) Malthête, J., Collet, A., and Levelut, A. M., 1989, *Liq. Cryst.*, **5,** 123.

[15] (*a*) Zimmermann, H., Billard, J., Gutman, H., Wachsel, E. J., Poupko, R., and Luz, Z., 1992, *Liq. Cryst.*, **12,** 245; (*b*) Werth, M., and Spiess, H. W., 1993, *Makromol. Chem. rapid Commun.*, **14,** 329.

[16] (*a*) Ohta, K., Higashi, R., Ikejima, M., Yamamoto, I., and Kobayashi, N., 1998, *J. mater. Chem.*, **8,** 1979; (*b*) Ohta, K., Yamaguchi, N., and Yamamoto, I., 1998, *J. mater. Chem.*, **8,** 2637.

[17] Magid, L. J., Triolo, R., and Johnson, J. S., 1984, *J. phys. Chem.*, **88,** 5730.