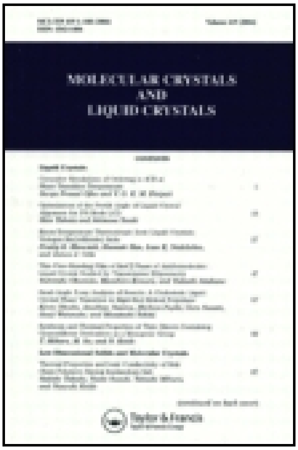

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Polysubstituted N-Arylcarbazoles as Discotic Molecules

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Polysubstituted *N*-Arylcarbazoles as Discotic Molecules

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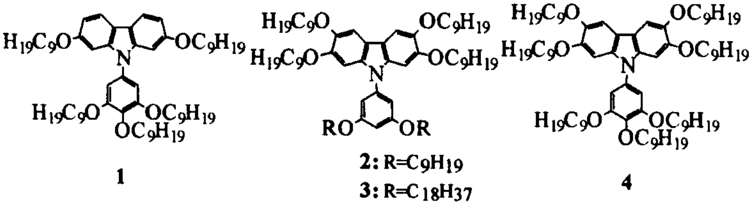
The mesophase behaviour of 9-phenylcarbazole derivatives with five, six and seven alkyl chains attached to the aromatic core is described. The compound with seven alkyl chains displays liquid crystalline behaviour at room temparature, while those with five and six nine-carbon alkyl chains present a columnar liquid crystal phase at room temperature when doped with TNF, as confirmed by optical polarizing microscopy, differential scanning calorimetry and X-ray diffraction.

Keywords: polysubstituted N-arylcarbazoles; discotic molecules; columnar liquid crystal phase

INTRODUCTION

Since the material properties of the carbazole were discovered [1] this system and its polymer poly(N-vinylcarbazole) (PVK) has been studied extensively [2]. Due to the high photoconductivity of the poly(*N*-vinylcarbazole), carbazole [3] and its derivatives are of considerable interest. In addition, when carbazole is substituted appropriately, it can also exhibit non-linear optical behaviour [4] and photorefractive properties [5]. The preparation of carbazole derivatives with liquid crystal order is interesting to develop materials which combine the properties of carbazole with those properties related with the anisotropic ordering of mesophases. However there are few examples of liquid crystalline carbazoles [6]. Discotic molecules which form columnar ordered mesophases can give transient photoconduction [7]. Representatives of this class of materials are triphenylene derivatives symmetrically substituted with six aliphatic ethers. We are interested in carbazole systems in which the core of the molecule is the 9-phenylcarbazole. Here we report the mesophase behaviour of 9-arylcarbazole derivatives with five, six and seven alkyl chains surrounding the core, and the effect of doping with 2,4,7-trinitrofluorenone (TNF) on their liquid crystalline behaviour (figure 1).



1

2: R=C_9H_{19}
3: R=$C_{18}H_{37}$

4

FIGURE 1 9-arylcarbazole derivatives synthesised

N-arylcarbazoles show a discotic core which resembles that of hexasubstituted triphenylene derivatives, systems with a six-fold symmetry which form columnar liquid crystal phases. *N*-arylcarbazoles do not show a six-fold symmetry but, although many discotic mesogens have a high symmetry, disc-like molecules with lower symmetry have been found to form columnar phases [8]. 9-Phenylcarbazole is not a flat molecule, as it is concluded from the value of the dihedral angle between the carbazole and the phenyl system ($\theta_{C_{9a}N_9C_{1'}C_{2'}}$), which is found to be 45° from AM1 semiempirical calculations (figure 2).

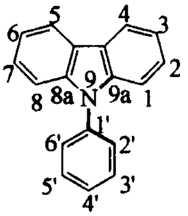


FIGURE 2 Dihedral angle between the carbazole unit and the phenyl substituent.

EXPERIMENTAL

Analytical techniques

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 analysis was performed using a Perkin Elmer DSC 7 differential scanning calorimeter at heating rates between 2 and 9 K/min. X-ray diffractograms were monitored with an Image Plate system with Kiesig geometry. Molecular orbital calculations were carried out on empirical structures using the semiempirical AM1 hamiltonian of the MOPAC 93 Program [9] on a Silicon Indigo 2 computer with full optimization of all bond lengths, 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.

Experimental part

Compound **1** was synthesised as described elsewhere [10]. Compounds with six alkyl chains **2** and **3** and with seven alkyl chains **4** were obtained by a copper catalysed coupling reaction of the compounds 2,3,6,7-tetranonyloxycarbazole and the corresponding 5-bromopolyalkyloxybenzene following the same methodology developed for compound **1** [10].

RESULTS AND DISCUSSION

Table 1 collects the thermal behaviour of the carbazole derivatives **2**, **3** and **4**, together with that obtained for carbazole derivative **1** [10]. Only the compound 2,3,6,7-tetranonyloxy-9-(3,4,5-trinonyloxyphenyl)-carbazole **4** showed a liquid crystalline phase. The thermal behaviour of this compound displays on heating a crystal/liquid crystal transition at -3°C with an associated enthalpy of 1.7 J/g and an isotropic melting at 31°C with an associated enthalpy of 7.9 J/g. On examination by optical microscopy with polarized light this compound shows at room temperature a fluid texture easily sheared.

The X-ray diffraction pattern obtained for the compound **4** at room temperature (figure 3) shows two small-angle maxima. The split of the lowest angle diffraction peak into a doublet is typical for rectangular lattices, where the peaks can be indexed as (200) and (110) [11]. For compound 4, considering a rectangular lattice and indexing the first peak as (200) and the second as (110), the constant lattices would be of a=53. 6 Å and b=24.8 Å (table 2).

TABLE 1 Thermal behaviour of compounds 1-4.

COMPOUND	Cr		Cr$_2$		Col		I
1	•	17 (29.3)	•		-	33 (30.3)	•
2	•	13 (1.3)	•		-	49 (32.8)	•
3	•	35 (35.3)	•		-	48 (52.4)	•
4	•		-	-3 (1.7)	•	31 (7.9)	•

[a] Transition phase temperatures (°C) and enthalpies (J/g) in brackets.

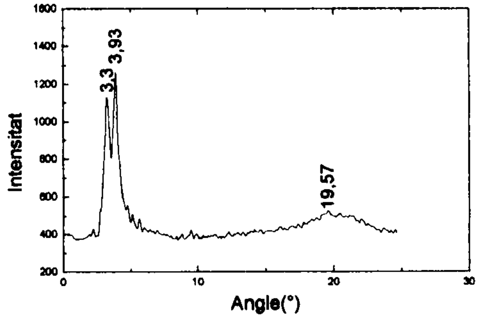


FIGURE 3 X-ray diffractogram obtained for compound 4 at room temperature.

TABLE 2 X ray data for the Col$_r$ mesophase of compound 4 at room temperature.

angle(°)	d (obs) (Å)	Miller indexes hkl
3.3	26.8	(200)
3.9	22.5	(110)
19.6	4.5	

The geometry of compound **4** was calculated by MOPAC 93 [9] using the AM1 method, and a value of 48.9° was obtained for the dihedral angle between the carbazole and the aryl substituent (figure 1). We have to take into consideration that this value corresponds to the molecules in gas state. Due to the low symmetry of this kind of molecule there is not an unique molecular diameter as in a disc-shape molecule. Instead of comparing the intercolumnar distance obtained by X-ray diffraction with the molecular diameter, we took into consideration the maximum distance between the external extremes of the total elongated alkyl chains attached to the aromatic core. Figure 4 shows all the distances calculated by Cerius2 from the optimized AM1 geometry. The maximal value was of 32.8 Å for the flat molecule and of 33.2 Å for that with a dihedral angle of 48.9°. The intercolumnar distance obtained by X-ray diffraction is lower than the maximum distance calculated, which implies a penetration of the alkyl chains into the aliphatic region of the neighbouring columns or a degree of orientational disorder for the alkyl chains. It has been experimentally determined for amphiphilic molecules that the experimental molecular distances are a 65-70% of the value calculated for the molecule with total elongated chains [12]. The intercolumnar distances found by X-ray diffraction for the mesophase formed by compound **4** (22.5 Å, 26.8 Å) represent the 68-81% of the molecular diameter calculated for the molecule with total elongated chains and a dihedral angle of 48.9°.

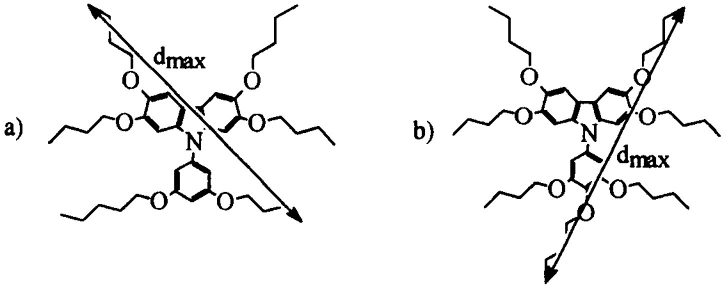


FIGURE 4 Calculated maximum distances between external extremes of the elongated alkyl chains for compounds a) **2** and **3**; b) **4**.

Charge transfer complexes with TNF

Compounds **1** and **2** were non-mesogenic but they showed a liquid crystalline phase when they were doped with 25% molar 2,4,7-trinitrofluorenone (TNF) (Table 3). Both complexes were found to be liquid crystalline at room temperature. On heating, complex **1**/TNF displays an isotropic melting and at 37°C with an associated enthalpy of 20.9 J/g, while complex **2**/TNF melts to the isotropic state at 31°C with an associated enthalpy of 21.2 J/g.

Both charge transfer complexes were studied by X-ray diffraction and the results support those obtained by DSC analysis and polarizing optical microscopy (Figure 5). The complex **1**/TNF shows a single peak at the low-angle region, which can be indexed as (100) (figure 5a). This peak corresponds to a distance of 26 Å. The dihedral angle was estimated for the pentaalkylated 9-arylcarbazole **1** to be 44.1° The molecular diameter of the molecule with elongated chains was calculated as 32.4 Å for the flat molecule and 33.5 Å for the molecule with a dihedral angle of 44.1°.

TABLE 3 Thermal behaviour of **1** and **2** doped with 25% molar of TNF.

COMPOUND	Cr		Cr_2		Col		I
1	●		-	12 (25.8)	●	37 (20.9)	●
2	-		-		●	31 (21.2)	●

The X-ray diffractogram of the 3:1 molar charge transfer complex of compound **2** with TNF (figure 5b) shows four small angle maxima with a reciprocal ratio of $1:1/\sqrt{3}:1/\sqrt{7}:1/\sqrt{9}$ which can be indexed as (100), (110), (210) and (300) (table 4) in an hexagonal lattice with a lattice constant of a=23.0 Å.

The dihedral angle between the carbazole and the aryl in compound **2** was also calculated by AM1 method (MOPAC 93) as 49.4°. The molecular diameter of this molecule (figure 4a) is of 30.9 Å for the flat molecule and of 33.1 Å for the molecule with a dihedral angle of 49.4°. The value obtained by X-ray diffraction for the intercolumnar distance (23.0 Å) is lower than those theoretically calculated. It represents the 69% of the expected value for the molecule with total elongated chains and a dihedral angle of 49.4°.

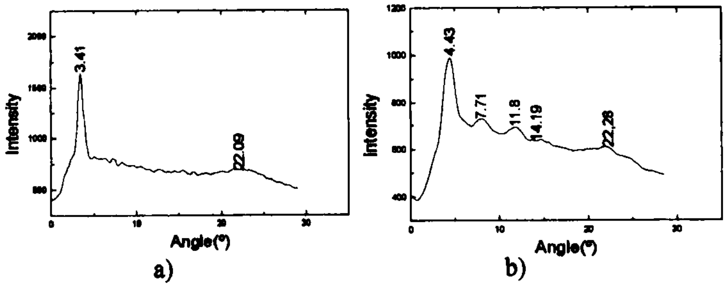


FIGURE 5 X-ray diffractograms at room temperature of a) the 3:1 molar charge transfer complex compound **1**/TNF and b) the 3:1 molar charge transfer complex compound **2**/TNF.

TABLE 4 X-ray data for the Col$_h$ phase of the 3:1 molar charge transfer complex of compound **2** with TNF at room temperature.

Angle (°)	d (obs) (Å)	Miller indexs hkl	d (calc) (Å)
4.4	20.0	(100)	
7.7	11.5	(110)	11.5
11.8	7.5	(210)	7.5
14.2	6.2	(300)	6.7
22.3	4.0	(001)	

CONCLUSIONS

We have synthesised the first systems with a carbazole unit as the main part of the aromatic core which display columnar liquid crystalline behaviour. The 9-arylcarbazole derivative peripherally bonded with seven alkyl chains was found to be liquid crystalline at room temperature, while the derivatives with five and six alkyl chains of nine carbon atoms show a columnar liquid crystal phase when doped with TNF.

Acknowledgements

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