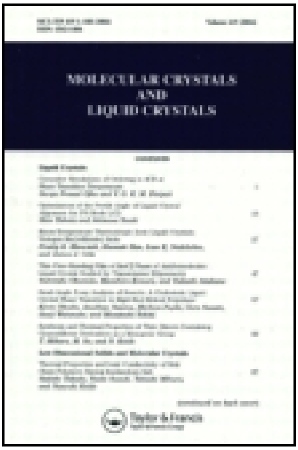

Molecular Crystals and Liquid Crystals

An Homologous Series of Disc-Like Mesogens with Nematic and Columnar Polymorphism

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An Homologous Series of Disc-Like Mesogens with Nematic and Columnar Polymorphism†

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An homologous series of hexa alkoxybenzoates of triphenylene has been prepared with $n = 4$ to $n = 12$. Interphase transitions between solid, mesomorphic and isotropic phases were studied by hot stage microscopy and differential scanning calorimetry. Binary phase diagram studies, optical textures observations and X-ray measurements showed the existence of three different mesomorphic phases: a nematic disc-like phase N_D, a tilted columnar phase D_t and a rectangular disordered columnar phase D_{rd}. Only two different phases were observed in each compound and the following mesophase sequences were found.

$$K - N_D - \mathrm{I}\ (n = 4, 5 \text{ and } 7)$$

$$K - D_t - N_D - \mathrm{I}\quad (n = 6)$$

$$K - D_{rd} - N_D - \mathrm{I}\ (n = 8 \rightarrow 11)$$

This remarkable even-odd effect is discussed and is compared to that observed for classic liquid crystals.

Several hexa alkybenzoates of triphenylene ($n = C_7 - C_{10}$) were also prepared and their mesomorphic properties studied. Only short range N_D were observed.

INTRODUCTION

The existence of one or several columnar phases D has been recently described in some disc-like liquid crystalline series: hexa alkanoates of benzene[1] (HAB), symmetric and dissymetric hexa alkoxytriphenylenes[2-4] (HET), hexa alkanoates of triphenylene[3,5] (HAT), hexa octanoate of rufigallol[6] (HAR), hexa alkanoates of truxene[7] (HATX) and tetra arylpyranylidene pyranes[8] (TAP). We present here the first homologous series of disc-like mesogens where one can

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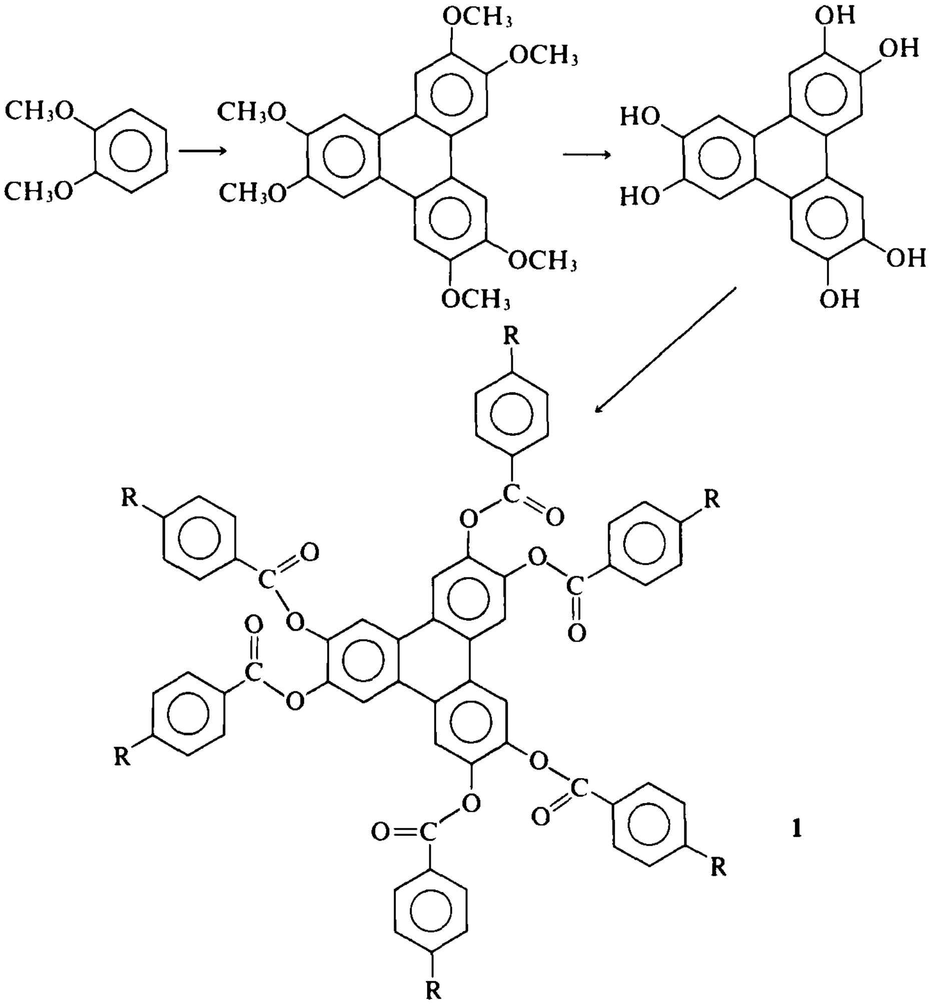
find a N_D nematic phase[9] and several D columnar phases.[10] We have prepared nine members (butoxy to dodecyloxy of the series of hexa *n*-alkoxy and four members of the *n*-alkylbenzoates (heptyl to decyl) of triphenylene (C_nOHBT and C_nHBT respectively) in order to establish both the variation in liquid crystalline properties with increasing terminal alkyl chain length and to provide a comparison of the results obtained with those reported for the hexa alkanoates of triphenylene.

RESULTS AND DISCUSSION

a Synthesis

Compounds of this series are prepared according to the scheme below:



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Purification of these compounds was achieved by repeated chromatographies on silica gel with acetone-benzene (5:95) mixtures as the eluting solvent followed by recrystallization from an ethanol-benzene mixture. Purities of the samples were checked by thin layer chromatography and elemental analysis.

b Optical and Thermodynamic Studies

The mesophases of these compounds were observed by means of a polarizing microscope equipped with a heating and cooling stage (Mettler FP 5). Transition temperatures and enthalpies of transition were determined by means of a differential scanning calorimeter (DuPont 990). The results are listed in Table I.

When $R = C_nH_{2n+1}O$—, the two first compounds (n = 4 and 5) have only a N_D nematic phase. This phase is very fluid at high temperature and presented optical textures very similar to those for nematic phases for example, disclination lines with $s = \pm 1/2$ and $s = \pm 1$ were observed[10] (Figure 1). On cooling the isotropic phase of the hexyloxy compound, a nematic-like texture characterized by a typical schlieren texture and shimmering motion was observed. However, on further cooling a D_t columnar mesophase (D for columnar phase and t for tilted) with mosaic areas characteristically oblong in shape (Figure 2) was observed.[10] This is the first such phase observed for disc-like mesogens. The heptyloxy derivative showed only a nematic phase. For the $n = 8$ to $n = 11$ two phases were observed; first at low temperature, a D_{rd} columnar phase (r for rectangular) with a focal conic fan texture (Figure 3) and then at higher temperature a N_D nematic phase. This last, less ordered phase disappeared when $n = 12$ which showed only a more ordered D_{rd} phase. This evolution of the N_D nematic phase range with the alkyl chain length is similar to that observed with rod-like liquid crystals. Elsewhere, the odd-even effect in the

TABLE I
Transition temperatures and enthalpies of fusion of compounds with formula 1

R	K		D_T		D_R		N_D		I	ΔH Kcal/mole
C_4H_9O	·	257	—		—		·	>300	·	
$C_5H_{11}O$	·	224	—		—		·	298	·	4.55
$C_6H_{13}O$	·	186	·	193	—		·	274	·	2.24
$C_7H_{15}O$	·	168	—		—		·	253	·	2.25
$C_8H_{17}O$	·	152	—		·	168	·	244	·	14.58
$C_9H_{19}O$	·	154	—		·	183	·	227	·	3.24
$C_{10}H_{21}O$	·	142	—		·	191	·	212	·	8.30
$C_{11}H_{23}O$	·	145	—		·	179	·	185	·	6.0
$C_{12}H_{25}O$	·	146	—		·	174	—		·	1.46
C_7H_{15}	·	210	—		—		—		·	
C_8H_{17}	·	208	—		—		·	210	·	
C_9H_{19}	·	175	—		·	183	·	192	·	
$C_{10}H_{21}$	·	185	—		·	189	—		·	

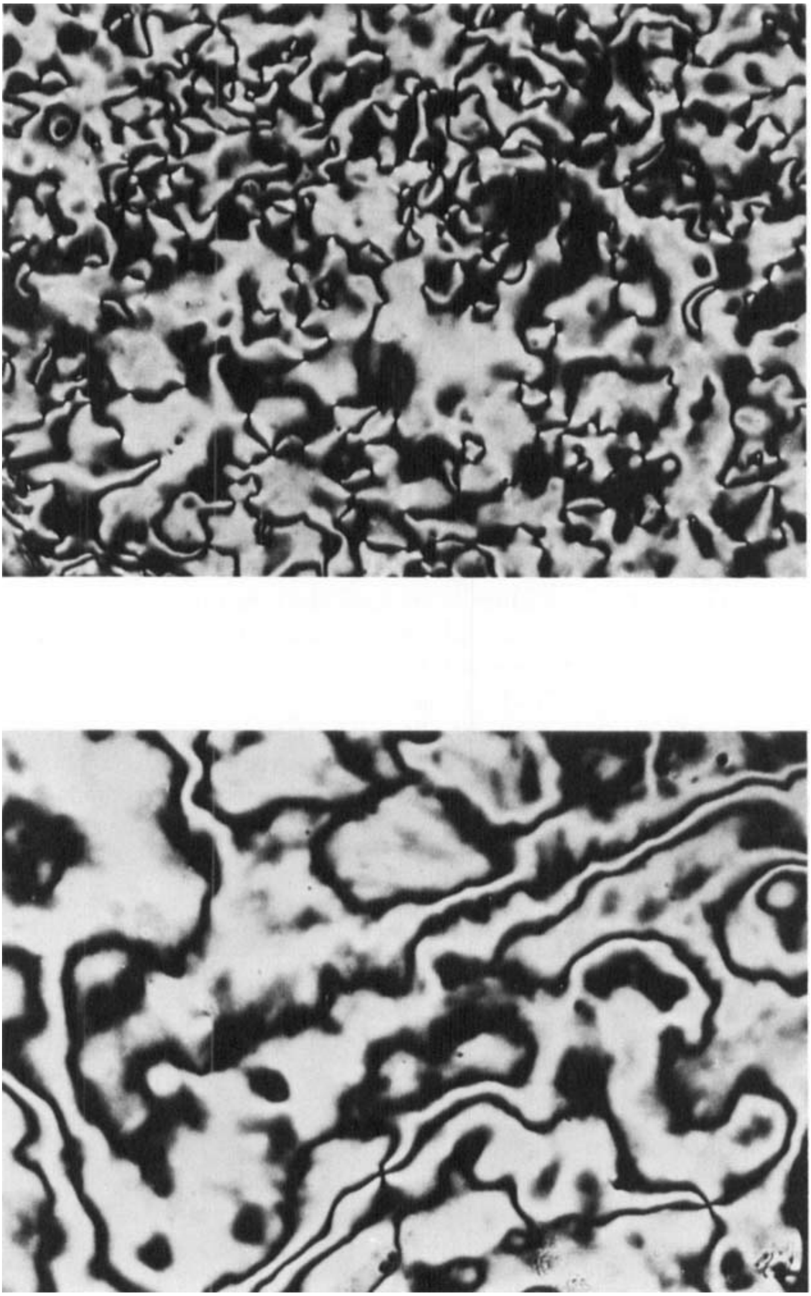


FIGURE 1a, 1b Schlieren texture of nematic phase N_D.

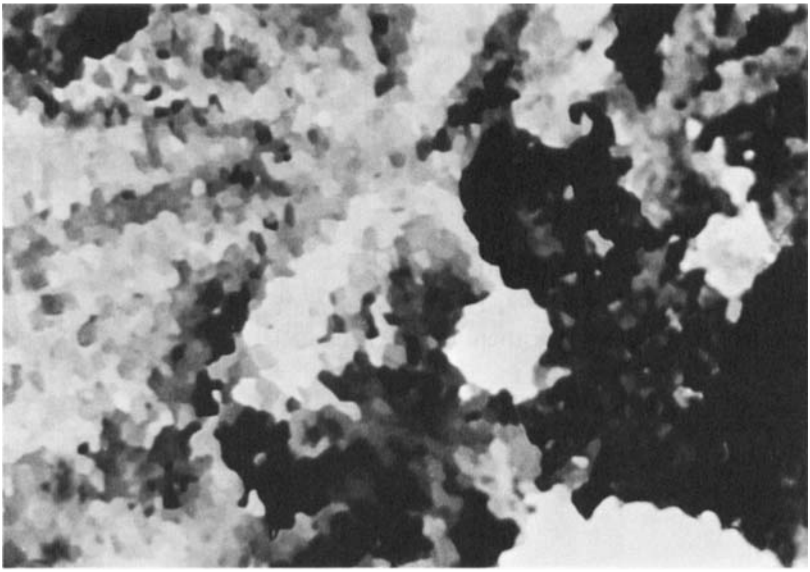


FIGURE 2 Mosaic texture of D_r columnar phase.

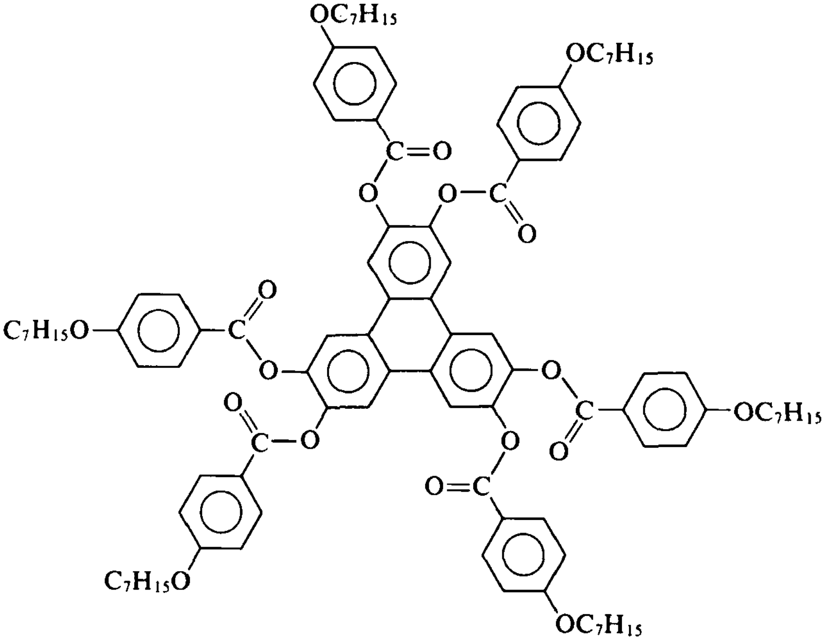
FIGURE 3 Focal conic fan texture of D_r columnar phase.

clearing temperatures for disc-like liquid crystals has also been observed (Figure 4). In contrast, in the series of hexa alkanoates of triphenylene[3,5] the less ordered D_{hd} (*h* for hexagonal and *d* for disordered) appears at the expense of the more ordered D_{rd} columnar phase with increasing alkyl chain length. Also, no odd-even effect is observed in this case.

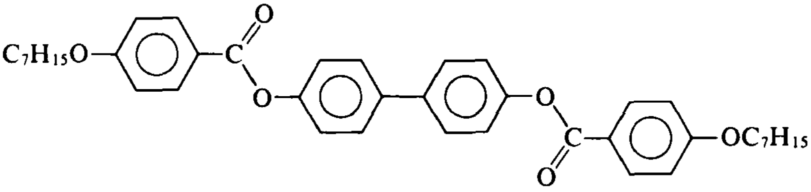
When $R = C_nH_{2n+1}$, The N_D nematic phase was observed only when $n = 8$ and 9, and the nematic range was short.

c Binary phase diagram studies

The N_D nematic phase is not miscible with a nematic phase, not even with that of a "monomer", biphenyl bis-heptyloxybenzoate[11] (BHB) K 150 S_C 201 *N* 316 *I*



C7OHBT



BHB

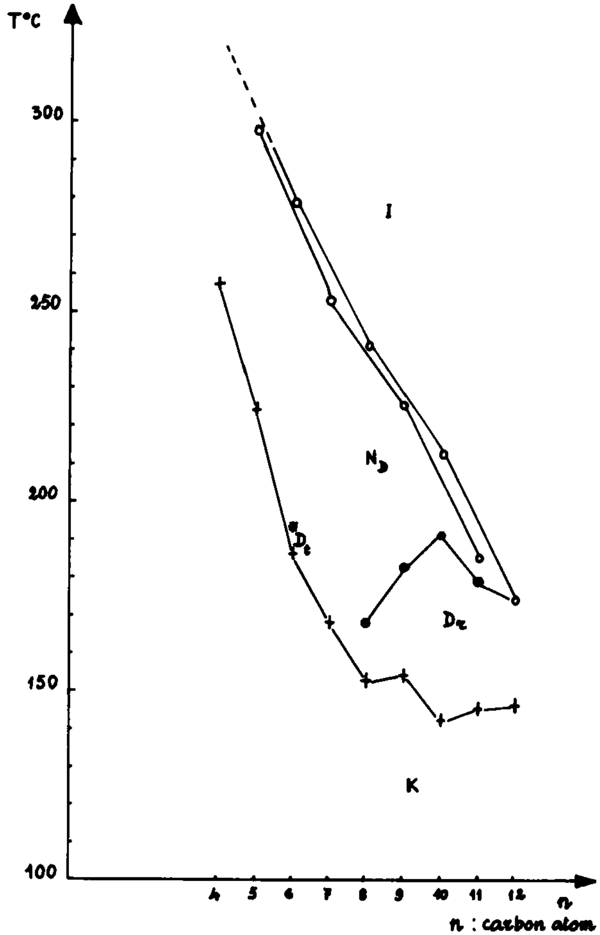


FIGURE 4 Plot of transition temperatures against n, the number of carbon atom in the alkoxy chain of C_nOHBT.

Indeed, with a 75/25 mixture by weight of C_7OHBT and BHB the mesophases disappeared and we obtained directly the transition *K* 155 *I*. However a 50/50 mixture by weight of C_7OHBT and chiral (+) or (−) hexa-3-methyl nonanoate of triphenylene[12] showed an interesting "cholesteric" twist of the N_D nematic phase. A structure is proposed for this "new cholesteric phase."[12]

The two phases N_D and D_{rd} of C_8OHBT were miscible with those of $C_{10}OHBT$ (Figure 5).

d X-ray studies

The X-ray diffraction pattern of a powder sample of the N_D nematic phase is very similar to that for the isotropic liquid phase of $C_{11}OHBT$ or other disc-

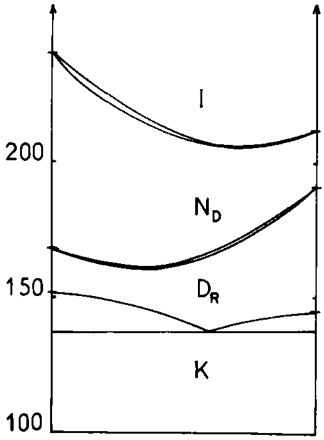


FIGURE 5 Diagram of isobaric state for the mixture of C_8OHBT (on left) with $C_{10}OHBT$ (on right).

like mesogenic compounds. These patterns are very similar to those for a non-oriented nematic phase. Nevertheless, a striking difference lies in the relative intensity of the two rings: the inner one is of a higher intensity in the N_D nematic phase while the outer ring is more intense for nematic phases[13] containing rod-like molecules (Figure 6).

The powder pattern of a non-orientated sample of the D_{rd} columnar phase of $C_{11}OHBT$ is similar to those for the D_{rd} phase of HAT derivatives.[14] This phase likely consists of columns of molecules in a rectangular two dimensional lattice (space group Pgg); the lattice parameters are: $a = 51.8$ Å, $b = 32.6$ Å[13] (Figure 7).

In the tilted columnar phase D_t of the C_6OHBT, the lattice parameters are: $a = 30.7$ Å. $b = 28.4$ Å; it is a quasi square lattice[13] (Figure 8).

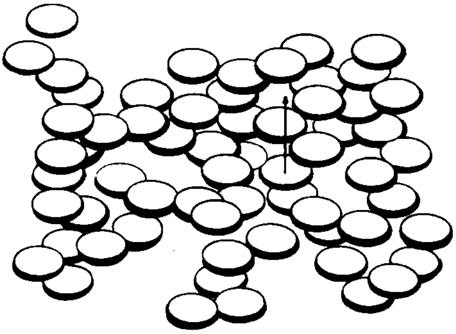


FIGURE 6 Structure of a N_D nematic phase.

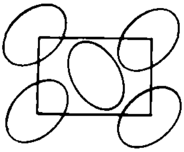


FIGURE 7 Structure of a D_{rd} columnar phase.

CONCLUSION

We have observed the first N_D nematic phase in these hexa alkoxy or alkylbenzoates of triphenylene. They are probably the first example of a pure simple component model of the carbonaceous mesophase. The tilted columnar phase D_t is the fifth identified mesophase found in disc-like mesogens: D_{ho}[15], D_{hd}[14], D_{rd}[14], D_t and N_D (o for ordered). Considering all our results with triphenylene derivatives,[3,5,9,10,13-15] we propose the following sequence for these phases with respect to temperature:

$$K\ D_t\ D_{rd}\ D_{ho}\ D_{hd}\ N_D\ I$$

Previously, we have shown a phenomenon very similar to a re-entrant nematic phase in some truxene derivatives[7] and the existence of a twisted nematic phase N_D^*.[12] These results show clearly the analogy between these new condensed states of matter and classical liquid crystals.

EXPERIMENTAL

Infrared spectra were recorded using a Perkin Elmer 225 spectrophotometer and NMR spectra with a Bruker 270 MHz.

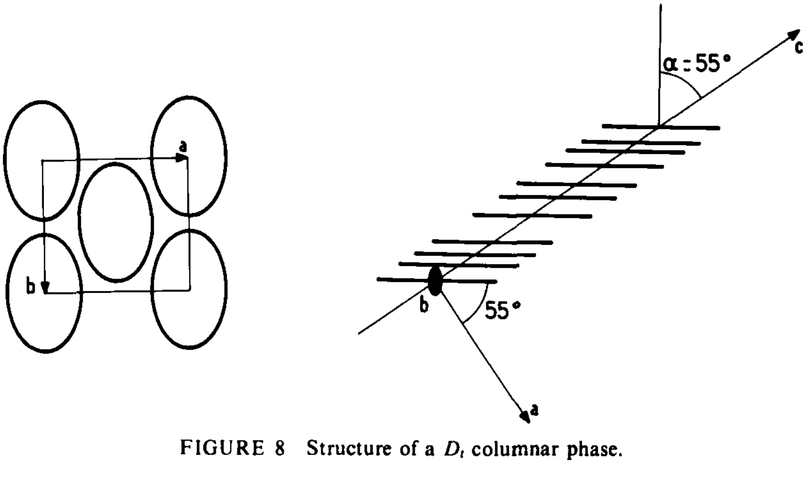


FIGURE 8 Structure of a D_t columnar phase.

MATERIALS

p-alkoxybenzoic acids were prepared by alkylating *p*-hydroxybenzoic acid with an alkyl bromide following the method of Gray *et al.*[16] and *p*-alkoxybenzoyl chlorides by refluxing the corresponding acid with an excess of $SOCl_2$. The latter was then removed by means of a vacuum evaporator and the crude acid chloride used without purification. *p*-alkylbenzoyl chlorides were prepared by the Friedel-Crafts acylation of an alkylbenzene with oxalyl chloride following the method of Reynolds *et al.*;[17] 2,3,6,7,10,11-hexamethoxytriphenylene by treating veratrole[1] with *p*-chloranil in sulfuric acid following the method of Musgrave *et al.*;[18] and 2,3,6,7,10,11-hexahydroxytriphenylene by heating the corresponding hexamethoxy derivative with pyridinium chlorhydrate.

All the 2,3,6,7,10,11 hexa alkoxy or alkylbenzoates of triphenylene were prepared following the same general procedure. The preparation of the undecyloxy derivative is given as a typical procedure.

2,3,6,7,10,11-hexa(p-undecyloxyl)benzoate of triphenylene Undecyloxybenzoyl chloride (620 mg, 2 mmoles) was added to a solution of 2,3,6,7,10,11-hexahydroxytriphenylene (100 mg, ~0.3 mmoles) in anhydrous pyridine (4 ml). This mixture was stirred magnetically at room temperature for 3 days and then poured onto a stirred mixture of crushed ice and concentrated hydrochloric acid. The organic product was extracted into benzene and the benzene solution washed with water, dried (anhydrous sodium sulfate), filtered and then filtrate evaporated to dryness. The residue was chromatographed on silica gel and the product eluted with a benzene-acetone (95:5) mixture. This material was recrystallized from an ethanol-benzene mixture. Yield 250 mg Ir (Nujol) v: 1730 cm^{-1} (COO stretching) 850 cm^{-1} (parasubstitution) and Pmr ($CDCl_3$) δ: 0.89 ($t = 3 \times 6$, 6CH_3 of $C_{11}H_{23}$), 1.284–1.767 (m = 18 × 6, 6 nine CH_2), 3.892 ($t = 2 \times 6$, 6CH_2O) 6.65–7.89 (6 two $d = 4$ aromatic), 8.305 ($s = 6$, 6H triphenylene).

Anal. calcd. for $C_{126}H_{168}O_{18}$: C 76.83; H 8.54; O 14.63
found : C 76.73; H 8.76; O 14.51

Acknowledgments

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