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New disc-shaped mesogens based on pentakis(phenylethynyl)benzene derivatives

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First examples of amphiphilic alkyl pentakis(phenylethynyl)benzene ethers containing functional groups at the terminal position of their alkoxy chains were synthesized by etherification of pentabromophenol with 11-bromoundecan-1-ol and 11-bromoundecanoic acid ethyl ester, respectively, and subsequent palladium catalyzed, fivefold coupling reactions with the substituted phenylacetylene. Two undecanoic acid derivatives with different pentakis(phenylethynyl)phenoxy substituents in the ω-position were prepared by ester cleavage from the corresponding ethyl esters. The thermal behaviours of five penta-alkynes in their pure states, as well as of their charge transfer complexes formed from mixtures with 2,4,7-trinitrofluorenone, were examined.

1. Introduction

Disc-shaped liquid-crystalline compounds were first studied in 1977 [2]. Such so-called discotic mesogens mostly consist of aromatic units as the central cores, substituted with long aliphatic chains which are linked to the central parts by an ether or an ester function [3].

Recently, examples of disc-shaped hydrocarbons, highly unsaturated hexakis(phenylethynyl)arenes [4–7], have been described which exhibit the rarely observed nematic discotic (N_D) phase. As a consequence of their substitution patterns, alkyl pentakis[(4-pentylphenyl)ethynyl]phenyl ethers, having an asymmetric molecular geometry, were found to give an optically biaxial nematic discotic ($N_{D,b}$) phase [8], in contrast to the uniaxial N_D phase of members of the radially symmetric series of hexakis[(4-alkylphenyl)ethynyl]benzenes [4, 5, 7].

Only a few examples of discotic mesogens are known containing just one terminal reactive function, for example, for the synthesis of discotic side group polymers [9–11]. They are based either on fivefold functionalized monohydroxy inositols [9] or the monoacetates of penta-ethers of a hexahydroxytriphenylene [10] and can be obtained in relatively poor chemical yields only. Disc-shaped multiynes with *terminal* polar functional groups have not yet been described.

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† Part 73 of liquid-crystalline compounds; for part 72 see [1].

On the other hand, disc-shaped compounds containing electron donor units can be doped with acceptor molecules to form charge transfer complexes of both the polymeric [12] and low molecular weight [13–16] kind. Using even non-liquid-crystalline disc-shaped electron donor molecules, columnar mesophases may be induced by such doping [12, 13, 16]. Recently, the first binary systems consisting of disc-like electron donor and strong acceptor molecules have been described which exhibit a fourth thermotropic nematic phase, the so-called nematic columnar (N_C) phase [15, 16].

This paper deals with the first representatives of alkyl pentakis(phenylethynyl)-phenyl ethers modified with terminal polar functional groups at the end of their ether chains, their synthesis, their thermal behaviour, and the mesomorphic properties of binary systems obtained after doping with 2,4,7-trinitrofluorenone (TNF).

2. Results and discussion

2.1. *Synthesis*

The synthesis of the new alkynyl-substituted benzene derivatives **1** was carried out starting from commercially available pentabromophenol. Etherification with 11-bromoundecan-1-ol and 11-bromoundecanoic acid ethyl ester [17], respectively, yielded the appropriate alkyl pentabromophenyl ethers containing a hydroxyl or an ethoxycarbonyl function. Palladium catalyzed CC-couplings [4] of these bromo-ethers with phenylacetylene or 4-pentylphenylacetylene yielded the corresponding penta-alkynylbenzene ethers **1a**, **b** and **d**. Neither side reactions caused by the presence of the hydroxyl or the ester substituent, nor any influence of the reaction conditions used on these functional groups could be observed. The pentakis(phenylethynyl)phenoxy-undecanoic acids **1c** and **e** were available by hydrolysis of their parent esters **1b** and **d** (refluxing in ethanol/KOH).

The structures of these new multiynes **1** are given in figure 1. The mesomorphic properties of the pure substances **1** and of their charge transfer complexes with TNF were characterized by polarizing optical microscopy and differential scanning calorimetry (DSC).

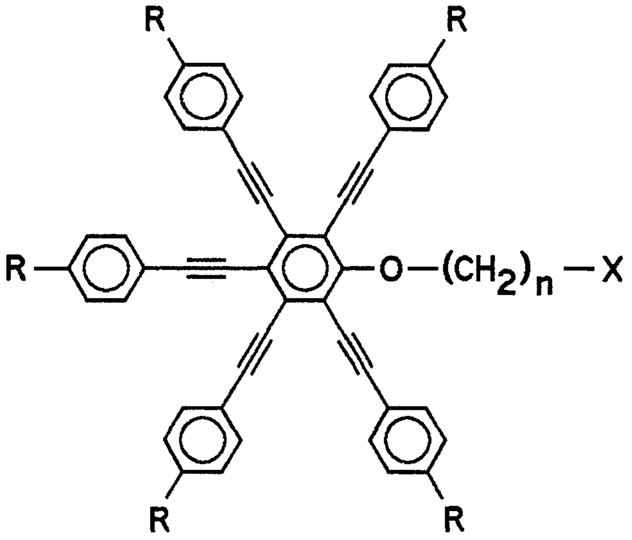
2.2. *Phase behaviour of the pure pentakis(phenylethynyl)benzene derivatives* 1

Depending on the substituents attached to the external sphere of the rigid core (pentyl or hydrogen), a different thermal behaviour of the pentakis(phenyl-ethynyl)benzene derivatives **1** is observed. Compounds **1a–c** containing C_5 alkyl chains in the *para*-position of the outer phenyl substituents exhibit the rare, but, for multialkynyl arenes, well-established [4–8] nematic discotic (N_D) phase giving Schlieren textures and typical thermal fluctuations on cooling from the isotropic melts (for phase transition data, see table 1). Although the temperature range is not very large, the N_D phases of all three compounds **1a–c** are enantiotropic. In agreement with other multi(phenylethynyl)arenes exhibiting N_D phases [4–8], the enthalpy values of 0·2 to 0·3 kJ mol^{-1} obtained by DSC measurements for the N_D–I phase transitions are significantly small. Depending on the terminal functional group on the alkyloxy chain linked to the central benzene unit, the following order for the transition temperatures has been found:

$$C \rightarrow N_D \quad \mathrm{COOEt} < \mathrm{OH} < \mathrm{COOH},$$

$$N_D \rightarrow I \quad \mathrm{COOEt} < \mathrm{OH} \approx \mathrm{COOH}.$$

This tendency may be due in part to the decrease in chain length from the ethoxycarbonyl to the carboxyl group. As expected, the homologues **1d** and **e** without pentyl substituents do not exhibit any mesophase. The same result was obtained with comparable non-liquid-crystalline alkyl pentakis(phenylethynyl)phenyl ethers [16].



1	*n*	X	R
a	11	OH	C_5H_{11}
b	10	COOEt	C_5H_{11}
c	10	COOH	C_5H_{11}
d	10	COOEt	H
e	10	COOH	H

Figure 1. The structures of the pentakis(phenylethynyl)benzene derivatives **1a–e**.

Table 1. Phase transition data for the pure pentaynes **1**. Transition temperatures (°C) were determined by polarizing optical microscopy and DSC on heating at $1°C\,min^{-1}$ and $5°C\,min^{-1}$, respectively, transition enthalpies (kJ/mol) are given in brackets.

Pentayne	Cr†		N_D		I
1a	●	66·4/67·0 (25·8)	●	94·4/94·2 (0·2)	●
1b	●	56·6/57·9 (51·6)	●	69·0/69·2 (0·3)	●
1c	●	83·2/84·0 (43·5)	●	91·2/90·9 (0·2)	●
1d	●	90·2/88·8 (46·9)‡	—		●
1e	●	140·4/139·5 (51·7)‡	—		●

† For the pentaynes **1a**, **d** and **e** polymorphism in the solid state was observed. The transition data are for the highest melting modification.

‡ Enthalpy values were obtained by integration of the broad unresolved peaks.

2.3. *Phase behaviour of the charge transfer complexes obtained by doping the penta-alkynes* **1** *with 2,4,7-trinitrofluorenone (TNF)*

The donor–acceptor complexes obtained by mixing equimolar amounts of the penta-alkynylbenzenes **1** and 2,4,7-trinitrofluorenone (TNF) show a quite different thermal behaviour from the pure substances **1** (see table 2). The CT complexes of the disc-shaped molecules **1a–c** containing five pentyl substituents exhibit enantiotropic hexagonal columnar (D_{ho}) phases easily identified by their typical textures. Such induction of D_{ho} phases in nematic discotic substances has already been observed for hexakis[(alkylphenyl)ethynyl]benzene compounds [13]. However, investigations involving contact preparations of TNF with the pure multiynes **1a–c**, as well as with binary 1 : 1 mixtures of compounds **1a–c** and TNF showed that the maximum clearing points and therefore the maximum of stabilities, mostly found for equimolar compositions of disc-shaped multiynes and TNF [16], are shifted to higher concentrations of trinitrofluorenone. This may be due to an additional interaction of the polar terminal substituents of compounds **1a–c** with acceptor molecules and consequently an insertion of a further amount of TNF into the lateral sphere of the hexagonally ordered columns.

Figure 2 shows the schematic phase diagram for the binary system of **1c** and TNF. It is of interest to notice that the equimolar mixture of **1c** and TNF exhibits a pronounced biphasic region (D_h/N) which is changed to D_h/I upon further heating. The phase diagrams of the binary systems obtained by doping **1a** or **b** with TNF are similar to that for **1c**, but 1 : 1 mixtures of **1a** or **b** and TNF exhibit only a biphasic area D_h/I.

The non-liquid-crystalline pentayne ethers **1d** and **e** exhibit induced enantiotropic nematic mesophases by charge transfer interactions in mixtures (contact method) with 2,4,7-trinitrofluorenone. For both systems, the maxima in the clearing temperatures were observed for an equimolar composition. Although the nature of these nematic mesophases cannot yet be identified precisely by polarizing optical microscopy, the

Table 2. Phase transition data for the equimolar charge transfer complexes of the pentaynes 1 with 2,4,7-trinitrofluorenone (TNF). Transition temperatures (°C) were determined by polarizing optical microscopy and DSC; transition enthalpies (kJ/mol) are given in parenthesis.

CT complex of	C		D_{ho}		N_C		I	Maximum of clearing temperature†
1a	—		●	110/±5‡ (4·7)	—		●	126
1b	—		●	88/±11‡ (3·4)	—		●	109
1c	●	49 (39·6)	●	70/±9‡ (1·4)	—		●	110
1d	●	104 (43·9)	—		●	124 (1·0)	●	124
1e	●	120 (27·7)	—		●	145 (1·1)	●	148

† Determined from contact preparations of TNF with pure multiynes **1**, as well as with binary 1 : 1 mixtures of the compounds **1** with TNF.

‡ Phase transitions proceed via pronounced biphasic temperature ranges.

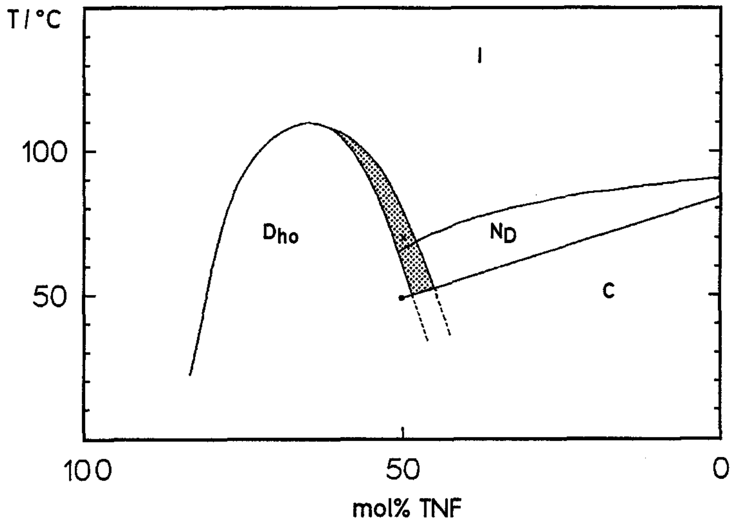


Figure 2. A simplified phase diagram of the binary system 11-{pentakis[(4-pentylphenyl)ethynyl]phenoxy}undecanoic acid, **1c**, and 2,4,7-trinitrofluorenone. The most pronounced biphasic regions are marked in grey.

phase transition enthalpies summarized in table 2 are quite similar to those found for charge transfer induced nematic columnar (N_C) phases formed from multiethynylbenzene compounds [16 a], suggesting also the occurrence of N_C phases in binary systems derived from **1d** and **1e**.

3. Experimental

The two pentabromophenyl ethers used as starting materials for the synthesis of the compounds **1** were prepared from pentabromophenol. To a suspension of 900 mg (36 mmol) of sodium hydride in 30 ml of absolute DMF, a solution of 14·6 g (30 mmol) of pentabromophenol in 60 ml of absolute DMF was added dropwise with stirring at ambient temperature. After subsequent stirring at room temperature for 4 h, a solution of 30 mmol of 11-bromoundecan-1-ol or 11-bromoundecanoic acid ethyl ester in 60 ml of absolute DMF was added. The solution was stirred for 10 h keeping the temperature constant at 100°C. After standing overnight, the reaction mixture was poured into 300 ml water, and the precipitate was filtered off, washed several times with water and dried *in vacuo*. After recrystallization, the two ethers were obtained as colourless crystals.

11-(Pentabromophenoxy)undecan-1-ol, $C_{17}H_{23}Br_5O_2$ (MW 658·9), mp 94°C (recrystallized from acetone), 68 per cent yield.

11-(Pentabromophenoxy)undecanoic acid ethyl ester, $C_{19}H_{25}Br_5O_3$ (MW 701·0), mp 41°C (recrystallized from ethanol), 62 per cent yield.

To prepare the pentakis(phenylethynyl)benzene derivatives **1a**, **b**, and **d**, 5 mmol of the appropriate pentabromophenyl ether, 50 mmol of 5-pentylphenylacetylene [18] or phenylacetylene, 250 mg of bis(triphenylphosphine)palladium(II) chloride, 250 mg of copper(I) iodide and 500 mg of triphenylphosphine in 50 ml of degassed triethylamine were stirred for 15 hours at 100°C under nitrogen. After cooling to room temperature, the reaction mixture was poured into 180 ml of 5 M hydrochloric acid. Extraction with dichloromethane, drying of the organic solution with sodium sulphate and evaporation of the solvent gave the crude products **1a**, **b** or **d**. The compounds **1a** and **b** were purified by flash chromatography using Kieselgel 60, 230–400 mesh (E. Merck, Darmstadt, Germany):

1a two chromatograms with light petroleumether/ethyl acetate (10:2) as eluent; three recrystallizations from ethanol.

1b one chromatogram with the same eluent system as for **1a** (10:1); one chromatogram with the same eluent system (10:2); two recrystallizations from propan-2-ol.

Compound **1d** was purified by three recrystallizations from ethanol. The carboxylic acids **1c** and **e** were prepared by boiling a mixture of the corresponding ethyl esters **1b** or **d** (3·7 mmol), 1·9 g (34 mmol) of potassium hydroxide and 150 ml of ethanol for 7 h. After cooling to room temperature the precipitated crude products were collected by filtration and dried. Purification was carried out by two flash chromatograms using light petroleumether/ethyl acetate (10:4) as eluent and then two recrystallizations from ethanol.

Phase transition data for compounds **1** are collected in table 1.

11-{Pentakis[(4-pentylphenyl)ethynyl]phenoxy}undecan-1-ol (**1a**, $C_{82}H_{98}O_2$, MW 1115·7): yield 52·0 per cent.

11-{Pentakis[(4-pentylphenyl)ethynyl]phenoxy}undecanoic acid ethyl ester (**1b**, $C_{84}H_{100}O_3$, MW 1157·7): yield 44·3 per cent.

11-{Pentakis[(4-pentylphenyl)ethynyl]phenoxy}undecanoic acid (**1c**, $C_{82}H_{96}O_3$, MW 1129·7): yield 60·7 per cent.

11-[Pentakis(phenylethynyl)phenoxy]undecanoic acid ethyl ester (**1d**, $C_{59}H_{50}O_3$, MW 807·1): yield 59·6 per cent.

11-[Pentakis(phenylethynyl)phenoxy]undecanoic acid (**1e**, $C_{57}H_{46}O_3$, MW 779·0): yield 72·8 per cent.

Structural proof for the new penta-alkynes **1** is based on spectroscopic data; a typical example is provided by the data for **1b**:

IR(CCl_4): 2220 (C≡C), 1740 cm^{-1} (C=O).

^{1}H NMR ($CDCl_3$), δ: 7·58–7·48 (m; 10 H, phenyl H), 7·21–7·14 (m; 10 H, phenyl H), 4·35 (t, J = 6·5 Hz; 2 H, O–CH_2), 4·12 (q, J = 7 Hz; 2 H, CO–O–CH_2), 2·63 (t, J = 7·5 Hz; 10 H, phenyl-CH_2), 2·27 (t, J = 7·5 Hz; 2 H, O–CO–CH_2), 1·92 (m; 2 H, CH_2 decyl chain), 1·68–1·52 (m; 4 H and 10 H, CH_2 decyl and pentyl chains, respectively), 1·25 (t, J = 7 Hz; 3 H, CO–O–CH_2–$C\underline{H}_3$), 1·42–1·22 (m; 10 H and 20 H, CH_2 decyl and pentyl chains, respectively), 0·91 ppm (t, J = 7 Hz; 15 H, CH_3).

^{13}C NMR ($CDCl_3$), δ: 173·86 (s; 1 C, C=O), 160·23 (s; 1 C, phenyl C–O), 143·98, 143·87, 143·68 (3s; 5 C, phenyl $\underline{C}$–CH_2), 131·75, 131·63, 131·57, 128·51 (4d; 20 C, phenyl CH), 128·73, 124·05, 120·70, 120·52, 120·47, 120·08 (6s; 10 C, phenyl $\underline{C}$–C≡C), 99·50, 99·34, 97·27 (3s; 2, 2 and 1 C, respectively, inner ethynyl C), 87·07, 86·59, 84·07 (3s; 2, 1 and 2 C, respectively, outer ethynyl C), 74·73 (t; 1 C, O–CH_2), 60·11 (t; 1 C, CO–O–$\underline{C}H_2$), 35·95 (t; 5 C, phenyl-CH_2), 34·38 (t; 1 C, O–CO–$\underline{C}H_2$), 31·45, 30·93, 30·58, 29·57, 29·45, 29·27, 29·16, 26·34, 24·99, 22·52 (10d; 23 C, CH_2 decyl and pentyl chains, respectively), 14·24 (q; 1 C, CH_3), 14·01 ppm (q; 5 C, CH_3).

3.1. *Preparation of the charge transfer complexes*

The CT complexes were prepared by mixing equimolar amounts of the pentakis(phenylethynyl)benzene derivatives **1a–e** with 2,4,7-trinitrofluorenone as electron acceptor in solution in dichloromethane. The formation of the electron donor acceptor complexes was indicated by a colour change to orange, whereas the blue fluorescence of the dissolved compounds **1** disappears. After shaking and allowing the mixture to stand for a few minutes, the solvent was removed *in vacuo*. Phase transition data for the CT complexes are given in table 2.

3.2. *Instrumental*

IR spectra were obtained with a Beckmann IR 3. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Varian Unity 400 and Bruker AM 270, respectively. The thermal behaviour of the pure compounds **1** and of their charge transfer complexes was assessed by polarizing optical microscopy, using a Leitz Laborlux 12 Pol in conjunction with a Mettler FP 82 hot stage, and by differential scanning calorimetry (DSC) using a Mettler TA 3000/DSC 30.

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[17] Obtained by acid-catalyzed azeotropic esterification of 11-bromoundecanoic acid.

[18] Prepared from 1-(4-pentylphenyl)-1-chloroethene via 4-pentylacetophenone, see [6].