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D. Goldmann; S. Mahlstedt; D. Janietz

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Mesomorphic donor–acceptor twin molecules with covalently linked sheet-like pentaalkyne and nitrofluorenone sub-units

by D. GOLDMANN, S. MAHLSTEDT, D. JANIETZ*
Universität Potsdam, Fachbereich Chemie und Institut für Dünnschichttechnologie
und Mikrosensorik, Kantstr. 55, D-14513 Teltow, Germany

P. BUSCH, C. SCHMIDT, A. STRACKE and J. H. WENDORFF
Institut für Physikalische Chemie und Wissenschaftliches Zentrum für
Materialwissenschaften, Philipps-Universität, Hans-Meerwein-Str.,
D-35032 Marburg, Germany

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Charge-transfer (CT) twin mesogens are presented which consist of sheet-like pentayne donor moieties with different peripheral substituents chemically linked with nitro substituted fluorenone sub-units via flexible alkyl spacers. A novel plastic rectangular columnar (Col_{rp}) phase is reported for the laterally unsubstituted member of the pentayne based CT twins. The phase is characterized by a three-dimensional crystal-like correlation of ordered columns in a rectangular lattice, while the molecular sub-units are still able to perform relaxation motions.

The attachment of peripheral substituents to the pentayne moieties results in a distortion of the three-dimensional positional order and the five-fold alkyl substituted homologues exhibit a rectangular columnar ordered (Col_{ro}) mesophase. The rectangular lattice symmetries originate from the chemical linkage of the flat donor and acceptor parts of the molecules placed in an alternating manner within neighbouring columns, and the regular intracolumnar periodicity is enhanced by charge-transfer interactions within the columns.

A further structural modification consists of the incorporation of an asymmetric carbon into the spacer sequence resulting in pentayne based CT-twin mesogens displaying a nematic columnar mesophase with a helical twisting of the columns (N^*_{col}). Dielectric investigations reveal an unusual dynamic behaviour of the donor–acceptor pentaynes. The glass relaxation process is characterized by the occurrence of two relaxation modes, both following a WLF behaviour, a feature which has not previously been reported to our knowledge for columnar phase-forming disc-like liquid crystal materials.

1. Introduction

Specific non-covalent interactions between two different individual molecules may lead to anisometric aggregates of the complementary components at a molecular level, and it has become apparent that a control of thermotropic liquid crystalline structures can be achieved by such attractive intermolecular interactions arising, for example, from hydrogen bonds or charge-transfer situations. It is, for instance, well established that electron-rich disc-like systems such as triphenylene ethers or radial multi-alkynylbenzene derivatives form charge-transfer complexes with flat but non-liquid crystalline electron acceptors such as 2,4,7-trinitrofluoren-9-one (TNF) [1]. The CT interactions of the two different individual molecules incorporating either a donor or acceptor function may cause the stabilization as well as the induction of columnar mesophases [1–3]. Except for a few cases [2, 4], the columnar phases formed by binary mixtures are of the hexagonal or the nematic columnar type.

For example, the doping of non-mesomorphic triphenylene derivatives with an electron acceptor may give rise to the induction of hexagonal columnar ordered (Col_{ho}) phases [1, 2, 5]. Donor acceptor interactions of hexagonal columnar phase forming hexa-alkoxy-triphenylenes with TNF cause a broadening of the temperature range of the already existing mesophase [1, 2] and thus a phase stabilization. Hexa-alkynylbenzene derivatives exhibiting a nematic discotic (N_D) phase as pure compounds [6, 7] form charge-transfer induced hexagonal columnar ordered (Col_{ho}) mesophases [1], whereas binary mixtures of non-liquid crystalline pentakis(phenylethynyl)benzene ethers and TNF have been found to exhibit nematic-columnar (N_{col}) as well as Col_{ho} liquid crystalline structures [8–10].

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*Author for correspondence.

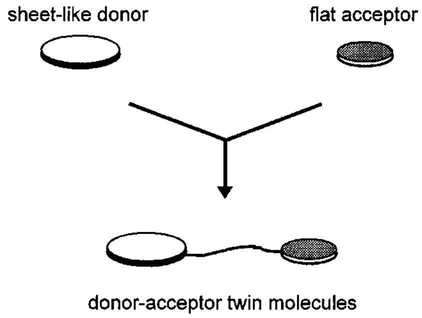

Figure 1. Charge-transfer twin mesogens formed through covalent linkage of flat donor and acceptor sub-units.

The effects described so far are not limited to individual acceptor and donor molecules; they also occur in systems incorporating both the donor and acceptor functions into a single molecule. This approach involves the chemical linkage of a flat anisometric moiety acting as an electron donor with a functional acceptor sub-unit via a flexible alkyl spacer (figure 1) [3]. Such charge-transfer twin molecules incorporating planar electron-rich triphenylene groups separated from an acceptor moiety by a flexible spacer segment have recently been reported [11].

This paper is concerned with the donor–acceptor twin mesogens **3** and **4** (see figure 2), consistent with the general structure type presented in figure 1. Sheet-shaped penta-alkynes and nitro substituted fluorenone derivatives are covalently linked. We expected that the attachment of an intramolecular acceptor function to the periphery of the anisometric pentayne core—i.e. the combination of different structural elements within one molecule—would offer a broader scope for the control and the richness of columnar structures than that displayed between two different disc-like donor and acceptor molecules. We will, in particular, focus on the synthesis, the mesomorphic properties and the unusual structural and dynamic properties of compounds **3** and **4**.

2. Results and discussion

2.1. *Synthesis*

The synthesis of the donor–acceptor twin molecules **3** was performed by esterification of pentakis(arylethynyl)-benzenes **1** [10, 12] carrying a terminal hydroxy

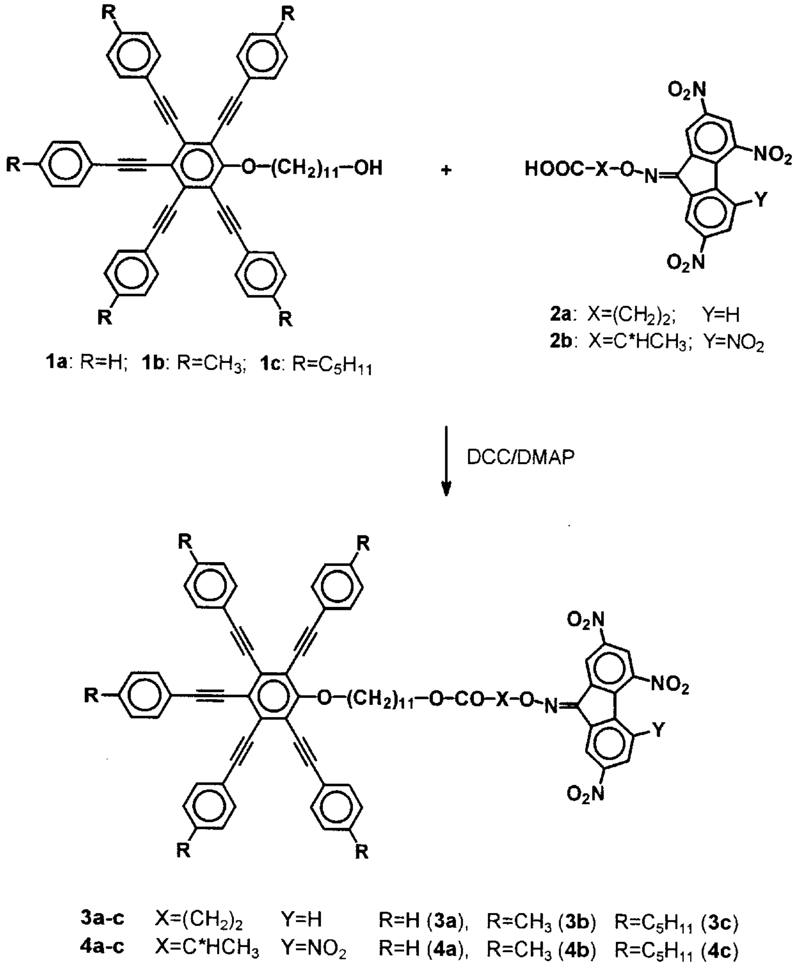

Figure 2. Synthesis of the twin molecules **3** and **4** with flat penta-alkyne donor sub-units and nitrofluorenone based acceptors coupled to each other chemically via a flexible spacer.

substituent with 3-(2,4,7-trinitro-9-fluorenylideneamino-oxy)propionic acid **2a** in the presence of *N*,*N*′-dicyclohexylcarbodiimide (DCC) and catalytical amounts of 4-dimethylaminopyridine (DMAP) [13].

Different substituents were attached to the periphery of the pentayne part of the compounds **3** to influence the size of the molecules and thus the efficiency of the expected donor acceptor interactions, while the structure of the TNF-based acceptor sub-units and the spacer length were kept constant. The appropriate reactions of the hydroxy terminated pentaynes **1** with (−)-2-(2,4,5,7-tetranitro-9-fluorenylideneamino-oxy)propionic acid [(−)-TAPA] **2b**, yielding the twin molecules **4**, were performed to incorporate a centre of chirality as an additional intramolecular functionality into the spacer sequence. Structural proof for the twin molecules **3** and **4** is based on spectroscopic data. Full details are given in the experimental section.

2.2. *Structure formation by the CT-twin molecules 3*

Preliminary investigations have shown that the CT-twin molecules **3a** and **3c** exhibit an enantiotropic liquid crystalline phase characterized by a fan-shaped texture [13]. The laterally unsubstituted pentayne **3a** forms, in addition, an enantiotropic nematic columnar (N_{col}) mesophase at elevated temperatures, and optical microscopy gives evidence for a monotropic nematic phase in the case of the five-fold pentyl substituted member **3c** upon cooling from the isotropic melt. The transition of the donor–acceptor twin **3b** to the isotropic state is accompanied by decomposition of the compound and only non-specific optical textures were observed. The low temperature phases of the CT mesogens **3** can be quenched into a glassy state, the glass transition temperatures decreasing with increasing size of the penta-alkyne sub-units (table 1).

The observed fan-like textures possibly indicate the existence of a higher ordered columnar structure for the low temperature phases of the twin mesogens **3** [13]. X-ray investigations were performed to determine the types of these mesophases. The X-ray diffraction patterns confirm a columnar structure for the donor–acceptor twins **3a–c**. The scattering diagram of the laterally unsubstituted penta-alkyne mesogen **3a** is presented in figure 3. It displays two sharp reflections in the small angle region that can be indexed as (1 0 0) and (1 1 0) reflections on the basis of a rectangular lattice with $a = b$. The amorphous halo in the wide angle region is superimposed by an intense (0 0 1) and a weak (1 0 1) reflection. The (0 0 1) reflection indicates a periodical intracolumnar stacking of the flat donor and acceptor molecular units. The (1 0 1) reflection, on the other hand, points to the correlation between the two-dimensional aspects of the rectangular lattice and the one-dimensional lattice along the columnar direction.

These scattering characteristics give evidence of a three-dimensional crystal-like positional order. Yet, keeping in mind the observation of a glass transition by DSC and of an amorphous halo that can be attributed to a liquid-like ordering of the flexible spacer, we are forced to the conclusion that the low temperature phase of compound **3a** is, in fact, not crystalline. The features observed here, however, are close to the ones recently reported for triphenylene derivatives [14, 15] and attributed to a plastic hexagonal columnar (Col_{hp}) phase. This phase is characterized by a three-dimensional correlation of the columns, while the molecules within the columns are able to rotate. We thus conclude that the CT-twin **3a** displays a plastic rectangular columnar

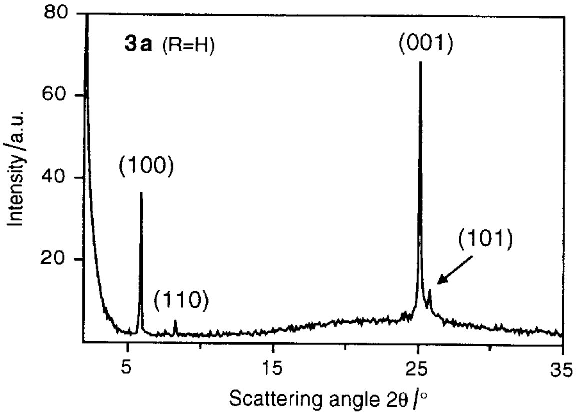

Figure 3. Wide angle X-ray diffractogram obtained for the plastic rectangular columnar (Col_{rp}) phase of the pentayne twin molecule **3a**.

Table 1. Phase transition temperatures (°C) for the donor–acceptor pentaynes **3a–c** as determined by differential scanning calorimetry; transition enthalpies (kJ mol^{-1}) are given in parentheses; transitions observed on cooling **3c** are in square brackets. T_g = glass transition temperature; Col_r = rectangular columnar; N_{col} = nematic columnar; I = isotropic.

Compound	T_g		Col_r		N_{col}		I
3a	•	59·7	•	124·5 (1·5)	•	134·0(0·8)	•
3b	•	34·5	•	224·6 (dec.)			•
3c	•	– 14·9	•	67·4 (2·4)	—		•
			•	[50][a]	•	[59][a]	•

[a] Observed on cooling by polarizing microscopy.

(Col_{rp}) phase with a three-dimensional structure of ordered columns in a rectangular lattice and with a local internal mobility of the molecules or molecular sub-units. The mobility may result from the liquid-like ordering of the spacer and, in addition, probably from rotational movements of the pentayne donor and acceptor groups within the columns. NMR investigations on deuteriated samples would be helpful for a deeper insight into the character of the motions of the molecular sub-units.

The X-ray investigations reveal that the twin compounds **3b** and **3c** exhibit a columnar mesophase with a rectangular lattice symmetry ($a=b$) and a periodical intracolumnar structure. However, whereas in the case of compound **3b** the (1 0 1) reflection is still visible as a shoulder on the high angle side of the (0 0 1) reflection in the wide angle region, it disappears completely for the pentayne twin **3c**, indicating the disappearance of three-dimensional positional order. Distortions probably arise from the peripheral pentyl substituents of the pentayne sub-units due to an interdigitation of the alkyl side chains into neighbouring columns. The lattice parameters of the donor–acceptor mesogens **3** are summarized in table 2.

Figure 4 illustrates the structural model for the rectangular columnar phase of the CT-twin compounds **3**. The donor and acceptor moieties of the molecules are arranged in an alternating manner in neighbouring columns. The chemical linkage of the donor and acceptor sub-units facilitates the formation of such a two-dimensional rectangular lattice, whereas the intracolumnar periodicity results from non-covalent charge-transfer interactions within the columns. These special features give rise to a three-dimensional order, at least in the case of compound **3a**, which is the first example of a mesogen that exhibits a plastic rectangular columnar (Col_{rp}) phase.

Table 2. Lattice constants a and c for the rectangular columnar phases of the pentayne twin molecules **3**.

Compound	a/Å	c/Å
3a	14·8	3·5
3b	15·9	3·6
3c	17·2	4·1

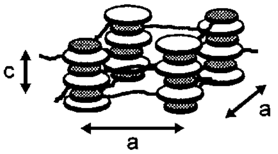

Figure 4. Structural model proposed for the rectangular columnar mesophases of the non-chiral pentayne donor–acceptor twin mesogens **3**.

2.3. *Structure formation by the chiral donor–acceptor pentaynes* **4**

The twin compounds **4** were prepared in order to elucidate the influence of an additional intramolecular chiral functionality on the structure of pentayne based donor–acceptor mesogens. It is apparent from calorimetric and optical investigations that an enantiotropic mesophase exists for each chiral CT-twin **4a**–**c**. The transition temperatures are given in table 3. The first transition corresponds to a glass transition as in the case of the compounds **3**; the second corresponds to the clearing temperature as observed by polarizing microscopy. Within the mesophase range the CT-twin molecules **4** exhibit a strain texture typical for a chiral nematic phase with, however, an unusually high viscosity.

Compared with those for the non-chiral analogues **3**, the X-ray diagrams of the donor–acceptor compounds **4** show a broadening of the reflections in the small angle region as well as at larger scattering angles. Figure 5 displays, as an example, the WAXS diffractogram of compound **4b**. The diffraction pattern can be attributed to a columnar arrangement with only positional short range order of the columns [2, 8].

Taking all these findings into account it seems most reasonable to assume that the pentayne donor–acceptor mesogens **4** exhibit a nematic columnar liquid crystalline structure with a helical twisting of the columns. The corresponding structural model of the chiral nematic

Table 3. Phase transition temperatures of the chiral twin mesogens **4**. T_g = glass transition temperature; T_i = clearing temperature.

Compound	T_g/°C	T_i/°C
4a	59·1	94·7
4b	74·0	195·0
4c	10·8	76·5

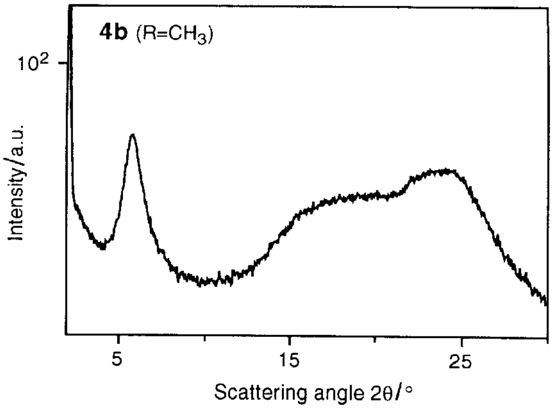

Figure 5. WAXS diffractogram of the chiral twin compound **4b**.

columnar ($\mathrm{N}^{*}_{\mathrm{col}}$) phase is presented schematically in figure 6.

It seems obvious that the structure formation of the twin mesogens **3** and **4** is effected not only by the intermolecular CT interactions, but also by the chemical nature of the spacer connecting the pentayne donor and acceptor molecular parts. The thermal properties of binary mixtures of the hydroxy substituted penta-alkynes **1** (used for the synthesis of compounds **3** and **4**) with electron acceptors illustrate the role of this kind of chemical linkage very distinctly. The peripherally unsubstituted pentayne **1a** shows no liquid crystalline properties as a pure compound [12], but the penta-alkyne **1b** incorporating five methyl groups and the five-fold pentyl substituted homologue **1c** [10] exhibit an enantiotropic nematic-discotic ($\mathrm{N_D}$) mesophase.

The phase behaviour of equimolar mixtures of the hydroxy terminated pentakis(arylethynyl)benzene derivatives **1** with 2,4,7-trinitro-9-fluorenone (TNF)—which are comparable to the twin mesogens **3** and **4** with respect to the molar ratio of donor to acceptor—strongly depends on the substituents attached to the periphery of the penta-alkyne donor. The equimolar mixture of the laterally unsubstituted penta-alkynyl alcohol **1a** and TNF exhibits a CT-induced nematic columnar ($\mathrm{N_{col}}$) mesophase [12], whereas in the case of the five-fold pentyl substituted pentayne **1c**, the donor–acceptor interaction with TNF leads to the induction of a hexagonal columnar ordered ($\mathrm{Col_{ho}}$) phase [10]. The pentayne **1b** incorporating five methyl groups does not show mesophase induction in mixtures with TNF. The equimolar mixture **1b**/TNF exhibits an $\mathrm{N_D}$ phase, however, with a broader temperature range than the pure compound **1b**. On the other hand, **1b** is the only member within the series of compounds **1** that is found to exhibit an induced chiral nematic ($\mathrm{N^{*}_{D}}$) phase using (−)-TAPA as a chiral dopant. This only holds, however, up to a dopant concentration of approximately 35 mol % and not for an equimolar composition. This behaviour is similar to that reported by Praefcke *et al.* for hexadecyl pentayne ethers with different peripheral substituents doped with (−)-TAPA [16]. It is thus apparent that the chemical linkage [3] of the flat pentayne donor with nitrofluorenone based acceptor sub-units gives rise to liquid crystalline structures of the CT twins **3** and **4** which differ significantly from the ones obtained by simply mixing the two components.

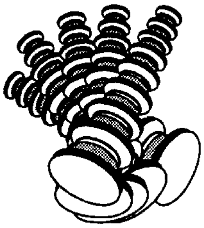

Figure 6. Structural model of the $\mathrm{N}^{*}_{\mathrm{col}}$ phase of the twin compounds **4** incorporating a centre of chirality.

2.4. *Dielectric investigations*

Dielectric relaxation spectroscopy was used to study the freezing-in process of the donor–acceptor molecules **3** and **4** and to characterize the dynamic behaviour within the liquid crystalline phases as a function of the internal order. The twin molecules investigated here show in general two relaxation processes. A thermally activated relaxation process is observed for all compounds at low temperatures (<0°C), and this obeys the Arrhenius law (β-relaxation, figure 7). A further relaxation process was found for compounds **3c** and **4a–c**, this taking place at temperatures above the static glass transition. The process does not show a linear dependence of the relaxation frequency on the inverse of the temperature in the activation diagram (figure 8).

Activation energies in the range of 30–40 kJ mol^{-1} were found for the β-relaxation in all cases. Obviously, these values show no significant dependence on the peripheral substituents of the pentayne groups. This fact and the low values of the activation energies indicate that this relaxation is caused by local rotational or flip motions of the ester group within the spacer [17]. Such a type of motion should not be affected by structural

Table 4. Phase transition temperatures (°C) of the pure pentaynes **1** and of selected binary mixtures with electron acceptors; data from DSC, 2nd heating at 5 K min^{-1}; transition enthalpies (kJ mol^{-1}) in parentheses. $\mathrm{N_D}$ = nematic discotic; $\mathrm{N_{col}}$ = nematic columnar; $\mathrm{Col_{ho}}$ = hexagonal columnar ordered.

Compound/mixture	Phase transitions				
1a	Cr	117·8 (29·9)			I
1b	Cr	171·6 (43·9)	$\mathrm{N_D}$	226·6 (0·5)	I
1c	Cr	67·0 (25·8)	$\mathrm{N_D}$	94·2 (0·2)	I
1a/TNF (1 : 1)	Cr	131·0 (30·0)	$\mathrm{N_{col}}$	158·0 (1·1)	I
1b/TNF (1 : 1)	Cr	119·9 (7·1)	$\mathrm{N_D}$	219·3 (0·1)	I
1c/TNF (1 : 1)	Cr	—	$\mathrm{Col_{ho}}$	110·0 (4·7)	I
1b/TAPA (85 : 15)	Cr	169·9 (29·1)	$\mathrm{N^{*}_{D}}$	213·6 (0·3)	I

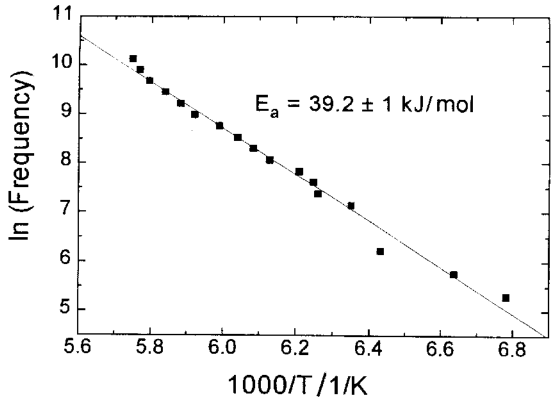

Figure 7. Arrhenius diagram for the secondary relaxation of compound **3b**.

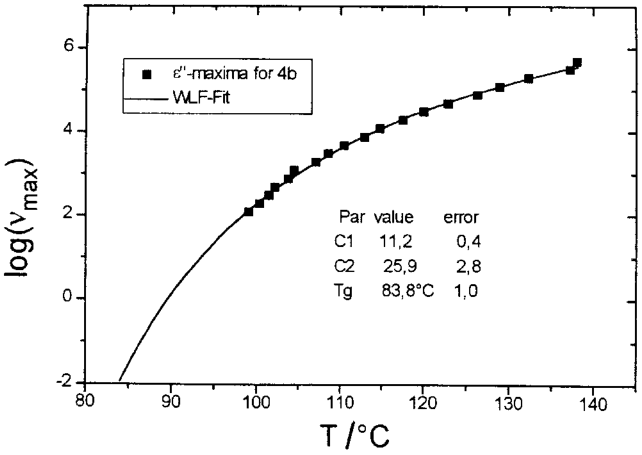

Figure 8. WLF diagram for the α-relaxation of **4b**.

properties of the discotic end groups because of the long spacer segments.

The relaxation process above the static T_g shows a relaxation strength which is about one order of magnitude larger than that of the low temperature relaxation. This relaxation process is related to the glass transition (α-process) and its temperature dependence can be described by the Williams–Landel–Ferry (WLF) equation [18], as is apparent from figure 8,

$$\log\left(\frac{\nu_T}{\nu_{T_g}}\right) = \frac{C_1(T - T_g)}{C_2 + (T - T_g)}. \qquad (1)$$

Using the WLF equation, a static glass transition temperature (taking the temperature at a frequency of 0·01 Hz or a relaxation time of 100 s) can be extrapolated from the dielectric relaxation data and this agrees with the calorimetric value (figure 8). Table 6 shows the fitted WLF parameters for the twins investigated. For an 'ideal' polymer, the WLF parameters are $C_1 = 17{\cdot}4$ and $C_2 = 51{\cdot}6$°C.

It is apparent from table 6 that it is the parameter C_2 in particular which depends strongly on the system investigated. We will now discuss these findings in terms of fragility as proposed by Angell. The fragility parameter m is defined as

$$m = \frac{d(\log \tau)}{d(T/T_g)} \text{ at } T_g. \qquad (2)$$

The limits for a strong glass are $m = 16$ and for a fragile glass $m = 200$ [19]. High values for C_2 lead to a decrease in the slope of the WLF curve, indicating lower fragility. In the case of triphenylene systems, we have observed the behaviour of a strong glass within a highly ordered columnar phase. The glass relaxation process was thermally activated with an activation energy of about 100 kJ mol^{-1} [14]. Figure 9 presents the Angell plots of the twin systems investigated, along with the limits for strong and fragile glasses. It is apparent that compounds **3** and **4** cover the range between strong and fragile glasses. The glass relaxation process is probably related to a freezing-in of rotational processes along the columnar axis. Earlier dielectric investigations in combination with NMR measurements of triphenylene systems lead to these conclusions [20].

Figure 10 shows a surprising result. It displays the relaxation behaviour of compound **4c**, for which we measured a superposition of two relaxation processes in the range of the glass relaxation. This kind of double relaxation was also observed for the compounds **3c**, **4a**

Table 5. Activation energies for the low temperature β-relaxation process of compounds **3** and **4**.

Compound	E_a/kJ mol^{-1}
3a	33
3b	39
3c	37
4a	38
4b	36
4c	30

Table 6. WLF parameters and glass temperatures (dielectric spectroscopy and DSC) for the CT-twin molecules **3c** and **4a**–**c**.

	WLF parameter		Glass transition	
Compound	C_1	C_2/°C	$T_{g,DK}$/°C	$T_{g,DSC}$/°C
3c	13·3	103·9	–20·0	–14·4
4a	8·8	13·4	72·5	59·1
4b	11·2	25·9	83·8	74·4
4c	10·8	54·0	15·8	10·8

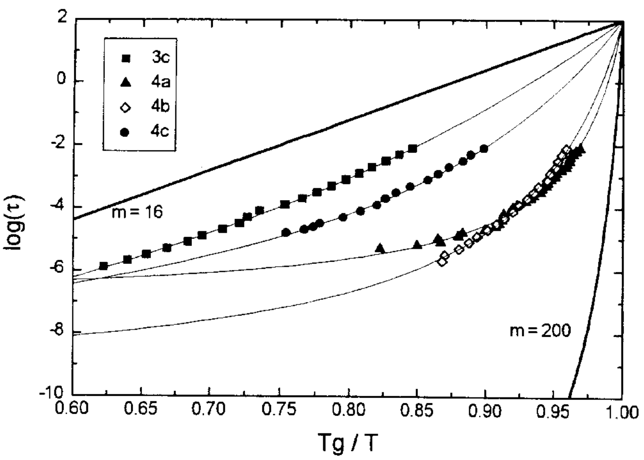

Figure 9. Angell plots for the glass relaxation of the twin compounds **3** and **4**.

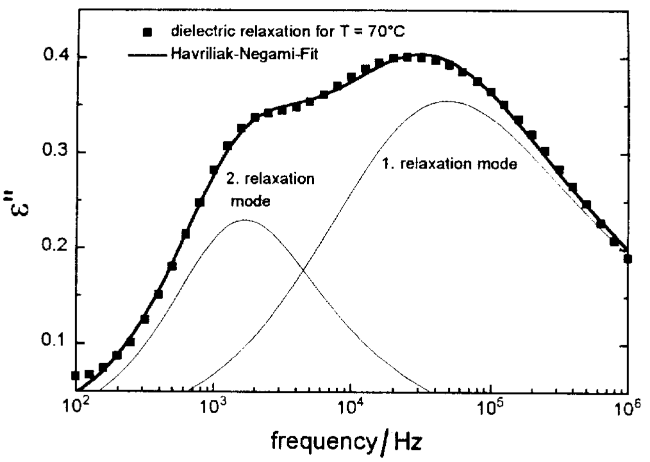

Figure 10. Double relaxation of **4c** above the glass transition at 70°C.

and **4b**, but here the two relaxation modes appeared so close together that a separation was not possible. It is well known that the glass relaxation of discotic materials consists, in general, of a single relaxation process. The occurrence of two relaxation modes above T_g in the region of the glass transition process, however, has frequently been reported for calamitic liquid crystalline and even for amorphous side group polymers, where the thermally activated δ-relaxation is superposed on the glass transition [21–23]. This δ-relaxation is known to arise from a rotational movement of the calamitic side groups around the long axis of the polymer main chain. A narrow distribution of relaxation times is often found for this process [22]. In order to obtain more information on the double relaxation behaviour, we have analysed the relaxation time distribution for the discotic systems.

The dielectric relaxation was characterized using the empirical Havriliak–Negami equation [24]

$$\varepsilon^* = \varepsilon_\infty + \frac{\Delta\varepsilon}{[1 + (\mathrm{i}\omega\tau_0)^{1-\alpha}]^{\beta}} \qquad (3)$$

where ε_∞ is the dielectric permittivity at infinite frequencies. $\Delta\varepsilon$ represents the relaxation strength and the Havriliak–Negami parameters α and β describe the width and symmetry of the corresponding relaxation time distribution.

In order to achieve a separation for the two relaxation processes of **4c**, we used a fitting function that is adapted to the loss factor of the dielectric permittivity, ε'' and which consists of two single Havriliak–Negami functions

$$\varepsilon''(\omega) = \varepsilon''_{\mathrm{HN1}}(\omega) + \varepsilon''_{\mathrm{HN2}}(\omega). \qquad (4)$$

Table 7 shows the fitting parameters obtained for the two relaxation curves at $T = 70$°C.

The second relaxation mode (at lower frequencies and higher temperatures, respectively) can be characterized by a narrow ($\alpha \approx 0$) and relatively symmetric ($\beta = 0{\cdot}7$) distribution of relaxation times, whereas the first relaxation mode shows a less symmetric and relatively broad distribution. This result seems to indicate a superposition of the glass relaxation (mode 1) with a 'δ-like' secondary relaxation process. Nevertheless, the temperature dependence for both processes follows the WLF equation, with similar WLF parameters and the extrapolated static glass transition temperatures are close to the ones obtained by DSC (table 8).

A detailed characterization and analysis of this unusual dynamic behaviour will follow in a further publication. Up to now, we suppose that the appearence of the double relaxation is caused by a slight separation of the rotational movement for the penta-alkyne groups

Table 7. Fitting parameters for the relaxation of **4c** at 70°C.

Parameter	Relaxation mode 1	Relaxation mode 2
τ_{HN}/s	$8{\cdot}55 \times 10^{-6}$	$1{\cdot}28 \times 10^{-4}$
$\Delta\varepsilon$	1·54	0·58
α	0·26	0·04
β	0·45	0·70

Table 8. WLF parameters for the separated relaxation modes of the twin **4c**.

Parameter	Relaxation mode 1	Relaxation mode 2
C_1	11·9	10·8
C_2/°C	42·2	54·0
$T_{g,\mathrm{DK}}$/°C	14	16
$T_{g,\mathrm{DSC}}$/°C	10·8	

on the one hand and the acceptor units on the other, within the frequency domain.

3. Conclusions

The donor–acceptor twin compounds **3** and **4**, based on flat electron-rich penta-alkyne and nitrofluorenone sub-units, are representatives of a novel class of liquid crystals. The structure formation of the twin mesogens **3** and **4** results from a delicate balance between non-covalent intermolecular charge-transfer interactions and the chemical linkage of the pentayne donor with the acceptor sub-units. Mesomorpic rectangular columnar structures as displayed by the compounds **3** have not been reported previously for this kind of combination of different structural elements within one molecule, or for binary mixtures consisting of disc-like donor and acceptor molecules. The novel plastic rectangular columnar (Col_{rp}) phase formed by the pentayne twin **3a** bridges the gap between the crystalline state and ordered columnar liquid crystalline phases. Furthermore, the structure formation of the twins **3** and **4** is effected by the chemical nature of the spacer giving rise to chiral nematic phases for the compounds **4** different from those of the mesogens **3**. It seems obvious that the combination of flat pentayne based donor and acceptor sub-units within one molecule offers novel modes of controlling liquid crystalline structures.

4. Experimental

4.1. *Synthesis of the pentayne based donor–acceptor twin compounds **3** and **4***

To prepare the twin mesogens **3**, 0·60 mmol of the appropriate hydroxyundecyl pentakis(phenylethynyl)-phenyl ether **1** [10] and 2·0 mmol of 3-(2,4,7-trinitro-9-fluorenylideneamino-oxy)propionic acid **2a** [11] were dissolved in 8 ml of dry dioxane with heating; 5 ml of absolute dichloromethane were added and the mixture was cooled to 0°C. Under a nitrogen atmosphere a catalytic amount of DMAP dissolved in 0·5 ml of CH_2Cl_2 was added with stirring of the mixture followed by the dropwise addition of 2·0 mmol of DCC in 1·5 ml of CH_2Cl_2. Stirring was continued at room temperature for 70 h. The resulting precipitate was filtered off, washed with CH_2Cl_2 and the combined solutions were evaporated in vacuum. The residual crude products **3** were purified by flash chromatography using Kieselgel 60, 230–400 mesh (E. Merck, Darmstadt); details are given below.

The synthesis of the chiral twins **4** was performed analogously to the above procedure, but using equimolar amounts of the hydroxy-substituted pentaynes **1** and (−)-TAPA **2b**. The commercially available (−)-TAPA was used without further purification.

The phase transition temperatures of the pure compounds **3** and **4** are collected in tables 1 and 3, respectively.

4.1.1. *11-[Pentakis(phenylethynyl)phenoxy]undecyl 3-(2,4,7-trinitro-9-fluorenylideneamino-oxy)-propionate, **3a***

Two flash chromatograms with light petroleum/ethyl acetate (10:3) as eluent; one recrystallization from CH_2Cl_2/ethanol. Yield 61·2%, $C_{73}H_{56}N_4O_{10}$ (M_W 1149·3). IR (KBr): $\nu = 2210$ (C≡C), 1735 (COO), 1530 (NO_2), 1340 (NO_2) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ (ppm) = 1·29–1·47 (m, 12H, CH_2), 1·67 (m, 4H, CH_2), 1·94 (m, 2H, CH_2), 2·90 (t, 2H, CH_2–CO–O, $J = 6·4$ Hz), 4·17 (t, 2H, CH_2–O–CO, $J = 6·4$ Hz), 4·33 (t, 2H, CH_2–O–phenyl, $J = 6·1$ Hz), 4·79 (t, 2H, CH_2–O–N, $J = 6·4$ Hz), 7·44 (m, 15H, phenyl), 7·63 (m, 10H, phenyl), 8·13–9·28 (m, 5H, TNF).

4.1.2. *11-[Pentakis(4-methylphenylethynyl)phenoxy]-undecyl 3-(2,4,7-trinitro-9-fluorenylideneamino-oxy)propionate, **3b***

One flash chromatogram with light petroleum/ethyl acetate (10:5) as eluent; one recrystallization from CH_2Cl_2/ethanol. Yield 56·1%, $C_{78}H_{66}N_4O_{10}$ (M_W 1219·4). IR (KBr): $\nu = 2220$ (C≡C), 1740 (COO), 1530 (NO_2), 1345 (NO_2) cm^{-1}. ^{1}NMR ($CDCl_3$): δ (ppm) = 1·38 (m, 12H, CH_2), 1·68 (m, 4H, CH_2), 1·93 (m, 2H, CH_2), 2·46 (s, 15H, CH_3), 2·90 (t, 2H, CH_2–CO–O, $J = 6·7$ Hz), 4·16 (t, 2H, CH_2–O–CO, $J = 6·4$ Hz), 4·29 (t, 2H, CH_2–O–phenyl, $J = 5·8$ Hz), 4·77 (t, 2H, CH_2–O–N, $J = 6·7$ Hz), 7·23 (m, 10H, phenyl), 7·50 (m, 10H, phenyl), 8·11–9·25 (m, 5H, TNF).

4.1.3. *11-[Pentakis(4-pentylphenylethynyl)phenoxy]-undecyl 3-(2,4,7-trinitro-9-fluorenylideneamino-oxy)propionate,* **3c**

Two flash chromatograms with light petroleum/ethyl acetate (10:1) as eluent. Yield 43·0%, $C_{98}H_{106}N_4O_{10}$ (M_W 1499·9). IR (KBr): $\nu = 2220$ (C≡C), 1750 (COO), 1530 (NO_2), 1340 (NO_2) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ (ppm) = 0·85 (t, 15H, CH_3, $J = 6·6$ Hz), 1·18–1·31 (m, 30H, CH_2, pentyl chains), 1·58 (m, 16H, CH_2, undecyl chain), 1·81 (m, 2H, CH_2, undecyl chain), 2·56 (t, 10H, CH_2, pentyl chains, $J = 7·5$ Hz), 2·78 (t, 2H, CH_2–CO–O, $J = 6·6$ Hz), 4·05 (t, 2H, CH_2–O–CO, $J = 6·3$ Hz), 4·18 (t, 2H, CH_2–O–phenyl, $J = 5·8$ Hz), 4·66 (t, 2H, CH_2–O–N, $J = 6·3$ Hz), 7·12–7·19 (m, 10H, phenyl), 7·37–7·43 (m, 10H, phenyl), 7·99–8·94 (m, 5H, TNF).

4.1.4. *11-[Pentakis(phenylethynyl)phenoxy]undecyl 2-(2,4,5,7-tetranitro-9-fluorenylideneamino-oxy)-propionate, **4a***

Two flash chromatograms with light petroleum/ethyl acetate (10:3) as eluent. Yield 42·3%, $C_{73}H_{55}N_5O_{12}$

(M_W 1194·3). IR (KBr): $\nu = 2200$ (C≡C), 1745 (COO), 1530 (NO_2), 1340 (NO_2) cm^{-1}. ^1H NMR ($CDCl_3$): δ (ppm) = 1·26–1·45 (m, 12H, CH_2), 1·68 (m, 4H, CH_2), 1·72 (d, 3H, CH_3, $J = 7·0$ Hz), 1·94 (m, 2H, CH_2), 4·19 (t, 2H, CH_2–O–CO, $J = 6·0$ Hz), 4·34 (t, 2H, CH_2–O–phenyl, $J = 5·9$ Hz), 5·24 (q, 1H, CH, $J = 7·0$ Hz), 7·35–7·43 (m, 15H, phenyl), 7·50–7·61 (m, 10H, phenyl), 8·50 (d, 1H, TAPA, $J = 2·0$ Hz), 8·65 (d, 1H, TAPA, $J = 2·0$ Hz), 8·74 (d, 1H, TAPA, $J = 2·0$ Hz), 9·37 (d, 1H, TAPA, $J = 2·0$ Hz).

4.1.5. *11-[Pentakis(4-methylphenylethynyl)phenoxy]-undecyl 2-(2,4,5,7-tetranitro-9-fluorenylidene-amino-oxy)propionate,* **4b**

One flash chromatogram with light petroleum/ethyl acetate (10:2) as eluent. Yield 63·3%, $C_{78}H_{65}N_5O_{12}$ (M_W 1264·4). IR (KBr): $\nu = 2200$ (C≡C), 1750 (COO), 1535 (NO_2), 1340 (NO_2) cm^{-1}. ^1H NMR ($CDCl_3$): δ (ppm) = 1·26–1·67 (m, 16H, CH_2), 1·71 (d, 3H, CH_3, $J = 7·0$ Hz), 1·90 (m, 2H, CH_2), 2·42 (s, 15H, CH_3), 4·17 (t, 2H, CH_2–O–CO, $J = 6·0$ Hz), 4·30 (t, 2H, CH_2–O–phenyl, $J = 6·0$ Hz), 5·21 (q, 1H, CH, $J = 7·0$ Hz), 7·16–7·23 (m, 10H, phenyl), 7·36–7·49 (m, 10H, phenyl), 8·42 (d, 1H, TAPA, $J = 2·0$ Hz), 8·60 (d, 1H, TAPA, $J = 2·0$ Hz), 8·67 (d, 1H, TAPA, $J = 2·0$ Hz), 9·30 (d, 1H, TAPA, $J = 2·0$ Hz).

4.1.6. *11-[Pentakis(4-pentylphenylethynyl)phenoxy]-undecyl 2-(2,4,5,7-tetranitro-9-fluorenylidene-amino-oxy)propionate,* **4c**

Two flash chromatograms with light petroleum/ethyl acetate (10:1) as eluent. Yield 53·6%, $C_{98}H_{105}N_5O_{12}$ (M_W 1544·9). IR (KBr): $\nu = 2200$ (C≡C), 1755 (COO), 1540 (NO_2), 1340 (NO_2) cm^{-1}. ^1H NMR ($CDCl_3$): δ (ppm) = 0·94 (t, 15H, CH_3, $J = 6·6$ Hz), 1·26–1·60 (m, 16H, CH_2, undecyl chain and 30H, CH_2, pentyl chains), 1·72 (d, 3H, CH_3, $J = 7·0$ Hz), 1·92 (m, 2H, CH_2, undecyl chain), 2·67 (t, 10H, CH_2, pentyl chains, $J = 6·5$ Hz), 4·18 (t, 2H, CH_2–O–CO, $J = 6·0$ Hz), 4·32 (t, 2H, CH_2–O–phenyl, $J = 6·0$ Hz), 5·20 (q, 1H, CH, $J = 7·0$ Hz), 7·17–7·25 (m, 10H, phenyl), 7·34–7·52 (m, 10H, phenyl), 8·37 (d, 1H, TAPA, $J = 2·0$ Hz), 8·52 (d, 1H, TAPA, $J = 2·0$ Hz), 8·69 (d, 1H, TAPA, $J = 2·0$ Hz), 9·31 (d, 1H, TAPA, $J = 2·0$ Hz).

4.2. *Preparation of binary charge-transfer complexes*

Binary mixtures of the hydroxy-substituted penta-alkynylbenzenes **1** and either TNF or (−)-TAPA as the electron acceptors were prepared by dissolving the components separately in dichloromethane, mixing the solutions and evaporating the solvents (see also [16]). Thermal investigations were performed after drying of the residues in vacuum. Molar ratios and phase transition data for the CT complexes are summarized in table 4.

4.3. *Instrumental*

IR spectra were recorded with an M 80 spectrometer (Carl Zeiss Jena); ^1H NMR spectra were obtained using a Bruker AMX 300 spectrometer. Texture observations were made using an Olympus BHS polarizing microscope in conjunction with a Linkam TMH/S 600 hot stage and a Linkam TP 92 control unit. Photo micrographs were obtained with an Olympus OM-4 Ti system camera. Calorimetric investigations were carried out with a Perkin Elmer DSC 7 and a Mettler TA 3000/DSC 30. Wide angle X-ray scattering analyses were performed with a Siemens 5000 diffractometer. The relaxation behaviour was analysed using dielectric relaxation spectroscopy covering a frequency range from 100 Hz to 1 MHz (Hewlett Packard impedance analyser HP 4284A). A nitrogen gas heating system ensured a precision of 0·62 K within a temperature range of 100–470 K. The experimental set-up is described in detail elsewhere [25].

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