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Stabilization and induction of discotic mesophases by trifluoroacetic acid

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It is shown that trifluoroacetic acid (TFA) can form 1:1 molar complexes with alkyloxy discotic compounds, thereby enhancing their mesomorphic properties. In particular, when hexa-alkyloxytriphenylenes (THE*n*) (*n* being the number of carbons per side chain) are crystallized from, or mixed with, TFA, complexes are formed which exhibit the $D_{ho}(Col_{ho})$ mesophase, as do the neat THE*n*'s, but with a broader range of thermal stability and a higher degree of order. The mesophases of these complexes are completely miscible with those of the neat compounds. Likewise, 1:1 mixtures of hexa-alkyloxytribenzocyclononene (TBCE*n*) and TFA yield complexes showing enhanced mesomorphic properties for the mesogenic homologues of this series and induced mesomorphism for the lower homologues, which in the neat form are not mesogenic. The mesomorphic properties of these TFA complexes with THE*n* ($n=3-6$) and with TBCE*n* ($n=4-6$) are investigated by means of optical microscopy, differential scanning calorimetry, X-ray diffraction and NMR spectroscopy. It is suggested that the enhancement of the mesomorphic properties is due to formation of oxonium ion complexes.

1. Introduction

The addition of dopants to liquid crystalline phases usually degrades the mesophase structure; the order parameters decrease and the temperature range of the mesophase stability narrows. There are, however, certain dopants that stabilize the mesophase structure and even induce mesomorphism when added to non-mesogenic compounds. The latter effect has been extensively investigated, in particular in discotic liquid crystal systems. The most effective dopants in stabilizing and inducing columnar discotic mesophases are electron acceptors such as 2,4,7-trinitrofluorenone (TNF), 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), 2-(2,4,5,7-tetranitro-9-fluorenylideneaminoxy)propionic acid (TAPA) and even bromine [1–5]. The stabilization of columnar mesophases by these dopants is believed to be due to formation of intercalated charge transfer (CT) complexes whose stability is enhanced by the columnar arrangement. A related effect is that of Lewis acid dopants, of which $AlCl_3$ and $NOBF_4$ have been the most extensively studied examples [6–8]. Although these dopants do not stabilize the mesophase, they interact with the mesogen molecules, forming charge carriers which increase very significantly the electrical conductivity.

A quite different phenomenon of induced mesomorphism is the formation of mesophases by the addition of solvents. The most common examples are the lyomesophases formed from amphiphilic compounds with water [9]. More recently it has been shown that lyotropic mesophases can also be induced by the addition of apolar solvents to discotic compounds [10–13]. The stabilization in this case is attributed to the segregation effect of the apolar aliphatic chains and solvent molecules from the aromatic moieties which prefer a stacked columnar structure with high overlap between the π-orbitals.

In the present work we extend the list of dopants which stabilize and induce discotic mesomorphism to yet another compound, viz. trifluoroacetic acid (CF_3COOH, TFA), which is perhaps a representative of a new family of dopants, i.e. that of Brønsted acids. We show that this dopant when added to discotic mesogens with alkyloxy side chains, such as the series of hexa-alkyloxytriphenylenes (THE*n*) [14–17] and hexa-alkyloxytribenzocyclononenes (TBCE*n*) [18–23] (where *n* is the number of carbons in the alkyloxy side chains) stabilizes their columnar mesophases to a very significant

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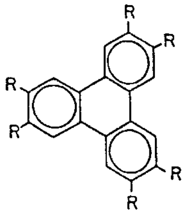
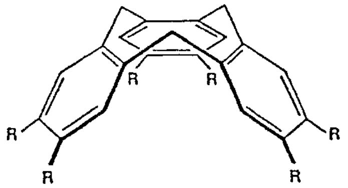
extent and may also induce mesomorphism in the lower homologues which are not mesogenic. It appears that the compounds form 1:1 molar complexes with TFA, and that these constitute the building blocks of the new liquid crystals. Their mesophases are, however, isomorphic with those formed by the mesogenic homologues of the neat compounds.



THE*n*



TBCE*n*

$R = -OC_nH_{2n+1}$

The finding that complexation with TFA stabilizes the mesomorphism of alkyloxy discotic mesogens was completely accidental. For our deuterium NMR studies of the THE*n* mesophases, we used to deuteriate the aromatic core by preparing the intermediate hexahydroxytriphenylene-d_6 from normal hexamethoxytriphenylene by heating under reflux with a $DBr/CH_3COOD/D_2O$ mixture [17, 24]. We then found that the deuteriation can be effected more efficiently by a short heating (a few minutes under reflux at ~90°C) of a solution of isotopically normal THE*n* in TFA-d_1. When the labelled THE*n* compounds were crystallized from the TFA solutions and checked by polarizing microscopy, they exhibited identical mesomorphic textures to those of the mesophases of the neat THE*n*'s, but their clearing points were considerably higher and their melting points much lower.

In the following text we characterize the mesophases formed by the discotic series THE*n* and TBCE*n* doped with TFA, using differential scanning calorimetry (DSC), polarizing optical microscopy, X-ray diffraction and deuterium NMR. We show that the dopant forms a 1:1 adduct with the mesogen molecule and we speculate on its nature.

2. Experimental

The phase transition temperatures and associated transition enthalpies were measured using a Mettler DSC30, with heating/cooling rates of 5 K min^{-1}. The samples were weighed in aluminium capsules, which were pressure sealed before measurement. Polarizing optical microscopic observations were made using a Zeiss Universal microscope equipped with a Mettler FP52 heating stage.

X-ray diffraction patterns were recorded on imaging plates (Fuji) using a Searle camera equipped with Franks optics affixed to an Elliot GX6 rotating anode generator operating at 1·2 kW and producing Cu radiation with a 200 μ focus. The samples were held in 1·5 mm quartz or Li-glass X-ray capillaries inside a copper oven, the temperature of which was under triac control, monitored with an Fe-constantan thermocouple. Calcite powder, used as a calibrating material, coated the outside of the capillary wall. The thin finger of the oven, containing the capillary, was inserted between the pole faces of a 0·7 T rare earth-based permanent magnet. In all cases, the long axis of the capillary, the X-ray beam and the direction of the magnetic field were mutually perpendicular. The imaging plates were scanned with a He-Ne laser (Spectra Physics) in conjunction with a home made reader based on an Optronics (Chelmsford, MA) densitometer and interfaced to an Apollo DS3500 workstation (Hewlett-Packard). Images were also processed on a Power Macintosh personal computer using the public domain NIH Image program (written by Wayne Rasband at the US National Institutes of Health and available from the Internet by anonymous ftp from zippy.nimh.nih.gov).

The deuterium NMR measurements were performed at 46·07 MHz with a high power Bruker CXP300 spectrometer using a BVT1000 variable temperature unit. The spectra were recorded by the quadrupole echo sequence with a delay between the two $\pi/2$ pulses of 15 μs. The $\pi/2$ pulses were 2·5 μs long.

The THE*n* and TBCE*n* compounds were prepared as described in references [17] and [18], respectively.

3. Results and discussion

3.1. *The hexa-alkyloxytriphenylene (THEn) series*

The mesomorphic properties of the THE*n* series have been extensively studied by calorimetric, X-ray and NMR techniques [14–17]. The homologues with $n=3$ to 11 are mesomorphic and show the phase sequence

$$Cr \rightarrow Col_{ho} \rightarrow I$$

where Cr is a crystalline phase, Col$_{ho}$ is an ordered hexagonal columnar phase (D$_{ho}$) and I is the isotropic liquid [25]. When the THE*n* compounds are crystallized from TFA and examined while in sealed containers, they exhibit the same phase sequence as the neat compounds, but with quite different transition temperatures. In table 1 we compare the phase transition temperatures (and enthalpies) of the neat THE*n*'s (obtained by crystallization from ethanol) for $n=3$ to 6, with those of the corresponding TFA adducts. It may be seen that in all cases the temperature stability range of the mesophase is considerably wider in the adduct (by 30 to 37°C) as compared to the neat THE*n*'s. An elementary combustion analysis of the THE8–TFA adduct obtained by crystallization from TFA, showed that it consists of a

Table 1. Transition temperatures (in °C) and in brackets transition enthalpies (in kJ mol^{-1}) for neat THE*n* and for the 1:1 THE*n*: TFA molar complexes.

Compound	Cr		Col$_{\text{ho}}$		I
THE3 neat	●	118·2 (46·6)	●	179·2 (20·5)	●
THE3 complex	●	53·2 (9·4)	●	155·2 (9·2)	●
THE4 neat	●	89·5 (26·2)	●	145·5 (23·0)	●
THE4 complex	●	53·1 (45·6)	●	144·0 (11·1)	●
THE5 neat	●	67·3 (29·8)	●	122·7 (8·7)	●
THE5 complex	●	48·9 (37·4)	●	136·5 (9·0)	●
THE6 neat	●	68·0 (39·6)	●	99·9 (5·4)	●
THE6 complex	●	55·2 (39·6)	●	124·6 (7·6)	●

1:1 molar ratio of THE8:TFA. A thermal gravimetric analysis of the THE6–TFA adduct showed a loss of one TFA molecule on heating from room temperature to 140°C, with 90% of the loss reached at 90°C. The decomposition of the THE6–TFA complex is also clearly observed by polarizing microscopy. For example when a sample is placed under a microscope cover glass without sealing and examined on heating, it will melt at 55·2°C and become isotropic at 124·6°C (see table 1). If the sample is now kept at ∼110°C, in the mesophase region, one observes the appearance of an isotropic liquid at the periphery of the sample due to the decomposition of the adduct; the TFA evaporates leaving behind neat THE6, whose clearing temperature is 99·9°C. This outer region gradually grows inward until the whole sample becomes isotropic and the field of view turns completely dark. When the sample is cooled to below 99·9°C, it fully converts to the mesophase. On the other hand, when such a THE6–TFA sample is sealed (for example with epoxy glue at the boundary of the cover glass), no decomposition is observed and the transition temperatures for the 1:1 complex can be reproduced over many heating/cooling cycles. Moreover, when neat THE*n* is mixed at a 1:1 molar ratio with TFA and kept in a sealed vial, it exhibits the same phase transition temperatures as those for a sample obtained by crystallization from TFA (table 1). On heating in an open vial, the complex slowly decomposes yielding neat THE*n* as judged by the phase transition temperatures. Mixing with TFA again yields the modified phase sequence. The complexation–decomposition cycle is completely reversible and can be repeated time and again. Also, when the complex is dissolved in ethanol and the solution recrystallized, neat THE*n* is obtained. We therefore conclude that the THE*n* homologues form well defined, stoichiometric 1:1 complexes with TFA. The complexation also leads to changes in the optical spectrum of the THE*n* compounds as may be judged from the appearance of colours. For example on heating a THE6 solution in TFA it turns green. Likewise, when a 1:1 THE6:TFA mixture is heated to the mesophase region, it becomes dark green. The colour becomes faint however on solidification.

The mesophases of these complexes, when studied by polarizing microscopy, exhibit textures identical to those of the neat compounds and are typical of hexagonal columnar phases. Examples of such polarizing microscopic textures for neat THE6 and its complex are shown in figure 1. Contact preparations of the neat compounds and the corresponding TFA complexes show complete miscibility. A phase diagram for the binary system TFA–THE6, constructed from DSC measurements on gravimetrically prepared mixtures, is shown in figure 2. It shows a gradual change in the melting and clearing temperatures from neat THE6 up to a 1:1 ratio of THE6:TFA. At higher fractions of TFA, the transition temperatures remain fairly constant up to a THE6:TFA ratio of about 1:2, beyond which the mesophase stability range gradually decreases. In the binary phase region of figure 2 the transition enthalpies are fairly constant at 30 to 40 kJ mol^{-1} for the melting and 5 to 8 kJ mol^{-1} for the clearing process.

The X-ray diffraction of the neat THE*n* series was investigated many years ago by Levelut [15, 16] who established the structure of the mesophase as ordered hexagonal columnar of the type, Col$_{\text{ho}}$. We have repeated the X-ray measurements on neat THE6 and extended the study to two more samples with THE6:TFA ratios of 1:1 and 1:2. The results of these measurements are summarized in table 2. For neat THE6, only the innermost reflection, from the {10} planes of the two-dimensional hexagonal lattice, was observed with a *d*-spacing of 19·4 Å, corresponding to an hexagonal lattice parameter $a = 22{\cdot}4$ Å. In addition two broad rings were observed at 4·74 Å, due to scattering from the aliphatic chains, and at 3·68 Å, due to the intracolumnar stacking of the molecules. The 1:1 and 1:2 mixtures with TFA gave very similar diffraction patterns with essentially the same lattice parameters, but they also exhibited rings at, respectively, 7·2 and 7·0 Å, identified as being due to reflections from the {21} planes of the hexagonal lattice. This assignment is based on measurements of magnetically aligned samples. It is shown below that, as for the mesophases of neat THE*n*, those of the 1:1 complexes with TFA also become aligned when cooled from the isotropic liquid within a magnetic field, with the director (columnar axes) perpendicular to the magnetic field. As indicated in §2, in our X-ray camera the sample was placed in a horizontal magnetic field (∼0·7 T), perpendicular to the incident X-ray beam. Upon cooling from the liquid, a planar arrangement of domains was obtained with the columnar axes randomly distributed in a plane which included the vertical axis and the beam direction. The resulting diffraction patterns still showed

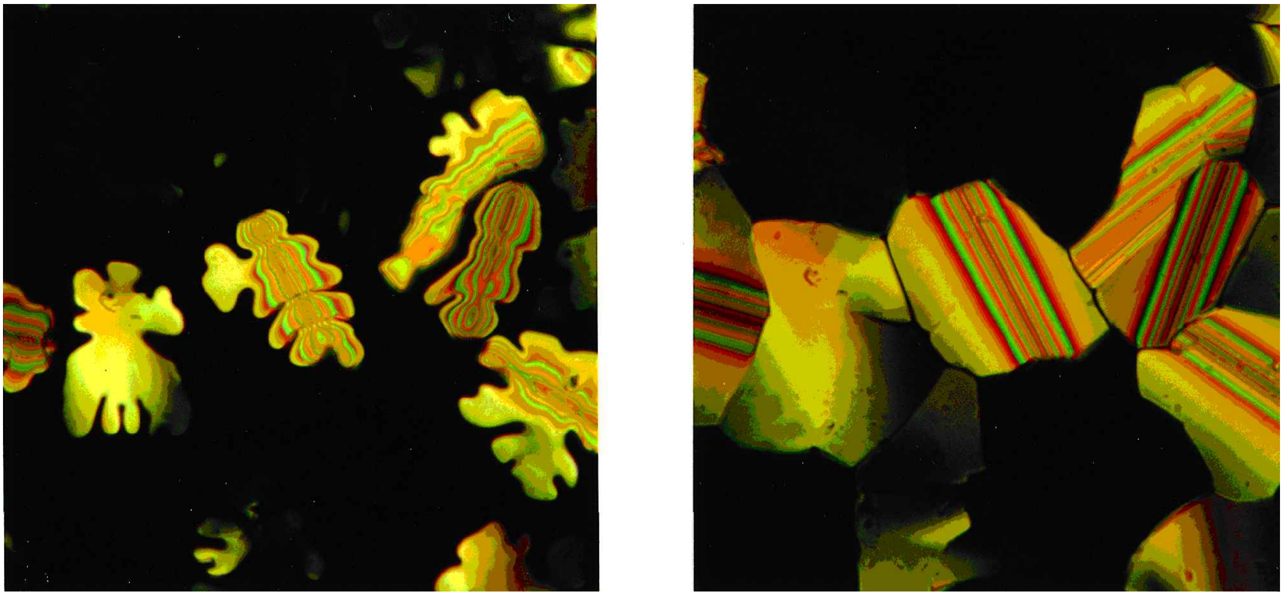


Figure 1. Polarizing optical microscopic pictures of neat THE6 (left at 97°C) and of a 1:1 THE6:TFA complex (right at 120°C) in the mesophase region (× 200).

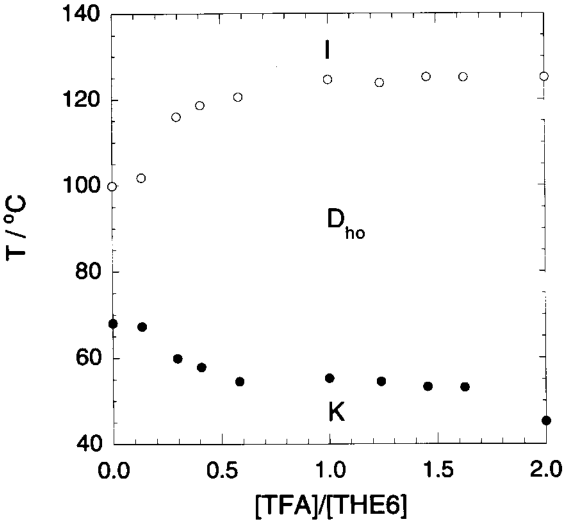


Figure 2. Melting (solid circles) and clearing (open circles) temperatures for the TFA/THE6 mixtures as a function of their molar ratio.

a complete diffuse ring due to scattering from the alkyloxy chains, but the {10} and {21} reflections appeared as arcs with maximum intensity along the equator, while the intercolumnar stacking reflection exhibited arcs with intensity maxima along the meridian. The appearance of the higher order {21} reflection may indicate enhanced ordering of the mesophase of the THE6–TFA complex with respect to that of the neat THE6.

Table 2. X-ray diffraction spacings (*d*) and average lattice parameters (*a*) for the $\mathrm{Col_{ho}}$ mesophase in neat THE6 and in the 1:1 and 1:2 molar mixtures with TFA.

THE6: TFA	Miller indices {*h k*}	*d*/Å	*a*/Å
1:0 (86°C)[c]	{10}	19·4 4·7[a] 3·7[b]	22·4
(1:1) (65°C)[c]	{10} {21}	19·3 7·2 4·47[a] 3·56[b]	22·1
(1:2) (62°C)[c]	{10} {21}	19·3 7·0 4·46[a] 3·52[b]	21·8

[a] Diffuse ring due to the aliphatic chains.
[b] Broad ring due to stacking periodocity.
[c] Temperature of measurements.

We have also carried out deuterium NMR measurements on neat THE6 and its complex involving various isotopically labelled species. In the left column of figure 3 are shown deuterium NMR spectra of neat THE6-d_6 labelled in the unsubstituted aromatic sites. At room temperature, a rigid spectrum is observed corresponding to a quadrupole coupling constant of $\frac{4}{3}\nu_Q = e^2qQ/h = 190\,\mathrm{kHz}$ and $\eta = 0{\cdot}07$, where $2\nu_Q$ is the overall width of the spectrum. On melting to the $\mathrm{Col_{ho}}$ phase, a typical uniaxial spectrum is obtained with about half the overall width of that observed for the solid. It corresponds to molecules rapidly reorienting about their symmetry axes with an additional small reduction of the average quadrupole coupling constant due to the orientational order

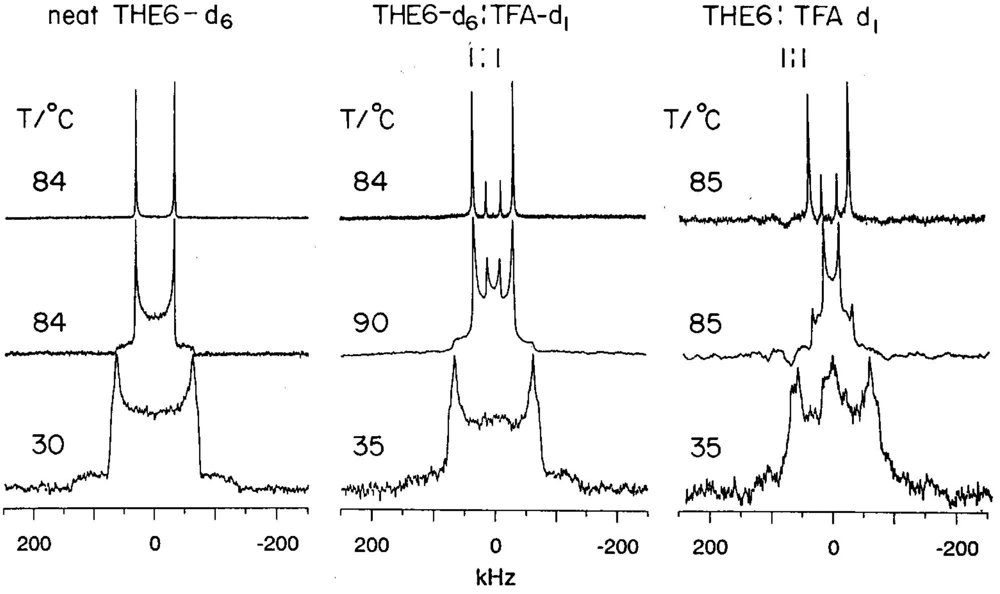


Figure 3. Deuterium NMR spectra of THE6 and of its 1:1 complex with TFA. Left column: Neat THE6-d$_6$. Middle column: 1:1 complex of THE6-d$_6$ and TFA-d$_1$. Right column: 1:1 complex prepared from isotopically normal THE6 and TFA-d$_1$. In all columns the bottom spectrum is of the solid, the middle spectrum is of the non-aligned mesophase obtained by heating the solid, and the top spectrum is of the aligned mesophase obtained by cooling the liquid within the magnetic field.

parameter being smaller than unity [17]. As indicated above, when the sample is heated to the isotropic phase and recooled to the mesophase within the magnetic field of the NMR spectrometer, it becomes aligned with the director perpendicular to the magnetic field. Its deuterium NMR spectrum then consists of a sharp doublet with a splitting identical to that of the perpendicular features of the powder spectrum in the unaligned sample (at the same temperature). This doublet splitting, $\langle \nu_Q \rangle$ is plotted in figure 4 as a function of the temperature. From the ratio of $\langle \nu_Q \rangle$ in the mesophase to that of ν_Q in the solid, the orientational order parameter, S_{zz}, for THE6 can be derived

$$S_{zz}=\left\langle \frac{1}{2}(3\cos^2\theta-1)\right\rangle$$
$$=\langle \nu_Q\rangle\langle \nu_Q\rangle \Big/ \left(-\frac{1}{2}\nu_Q\right)\left(-\frac{1}{2}\nu_Q\right)$$

where z is the symmetry axis of the triphenylene moiety, θ is the angle between this axis and the director, the $-1/2$ coefficient reflects the averaging due to the fast planar reorientation and it is understood that $\langle \nu_Q \rangle$ is negative. It may be seen (see scale on the right of figure 4) that within the mesophase region, S_{zz} decreases from 0·95 at the melting point to 0·87 at the clearing temperature.

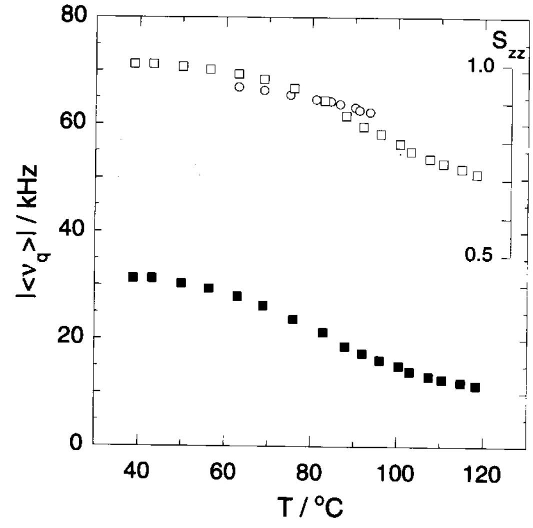


Figure 4. The average quadrupole splitting, $\langle \nu_Q \rangle$, of the various deuterons in neat THE6-d$_6$ (open circles) and in a 1:1 THE6-d$_6$:TFA-d$_1$ complex (open and solid squares, respectively) in the mesophase region. $\langle \nu_Q \rangle$ corresponds to the full splitting of the perpendicular features in the powder spectrum of the non-aligned sample or to the doublet splitting in the aligned sample. The scale on the right refers to the orientational order parameter of THE6-d$_6$ calculated as the ratio $2|\langle \nu_Q \rangle|/\nu_Q$.

In the second column of figure 3 the deuterium spectra of a 1:1 THE6-d$_6$:TFA-d$_1$ complex are displayed. The bottom trace corresponds to the solid phase; the middle trace, to the unaligned mesophase obtained on heating the solid, and the top trace, to the aligned mesophase obtained on cooling the isotropic liquid within the magnetic field. The spectra clearly consist of two subspectra due to THE6-d$_6$ and TFA-d$_1$. In the mesophase region, the two components can easily be identified from their relative intensities by two axially symmetric powder patterns in the non-aligned sample, and by the two sharp doublets in the aligned state. To confirm the assignment, we also recorded similar spectra for a 1:1 mixture of (normal) THE6 and TFA-d$_1$ (right column in figure 3). The noisy spectrum at the bottom must be ascribed to CF$_3$COOD in the solid complex. On heating, it gives a narrow axially symmetric powder spectrum due to TFA-d$_1$ in the mesophase, but at the set temperature of 85°C, within a few minutes deuterium exchange is sufficient to produce a discernible signal from THE6-d. By the time the sample is heated to the isotropic liquid and recooled to the mesophase (just a few minutes), deuterium exchange is complete, as may be seen in the top trace. Plots of the average quadrupolar splittings for the THE6-d$_6$ and TFA-d$_1$ in the 1:1 mixture are included in figure 4. It may be seen that S_{zz} for THE6 in the 1:1 mixture becomes essentially unity at the low temperature end of the mesophase stability range and reduces sigmoidally to ~0·7 at the clearing temperature. An interpretation of the TFA-d$_1$ spectrum in terms of an order parameter is not possible because its structure and mode of motion in the complex are not known.

The NMR spectra of THE6-d$_6$/TFA-d$_1$ mixtures with molar ratios smaller or larger than 1:1 (up to THE6:TFA of 1:2·3) in the mesophase region are similar to those shown in figure 3. There is no doubling of the spectrum due, for example, to neat and complex species. In the ratio range 1:0 to 1:2, the $\langle \nu_Q \rangle$ values are quite similar for all mixtures, but at higher ratios, both the THE6-d$_6$ and TFA-d$_1$ splittings decrease considerably upon addition of TFA. These results indicate that whatever the nature of the THE6–TFA complex, there is fast exchange in the mesophase between the complex and free THE6 on the NMR time scale.

To learn about the dynamics of the molecules in the mesophases of the neat and complexed THE*n*, we performed T_1 relaxation time measurements of the deuterons using the inversion recovery method. Such measurements were reported earlier for neat THE6 [26]. The results for the perpendicular features of the spectra in neat THE6-d$_6$ and in a 1:1 mixture of THE6-d$_6$:TFA-d$_1$ are shown in figure 5. Those for TFA-d$_1$ in the solid phase of the 1:1 complex were obtained for a freshly prepared sample before heating to the mesophase (as in the middle column of figure 3), i.e. before deuterium exchange took place. The results for both samples show a clear discontinuity at the solid to mesophase transition, with T_1 dropping from ~1 s in the solid state to ~10 ms in the mesophase. Within the mesophase, the temperature dependence of T_1 exhibits a minimum of about 5·8 ms for TFA-d$_1$ and somewhat lower minima (of 4·1 ms) for THE6-d$_6$ in both the neat and complex samples. As for the analysis of the $\langle \nu_Q \rangle$ values the situation for TFA-d$_1$ is complicated because of the lack of structural information. The results (a minimum and levelling off at low temperatures) suggest two types of motion (for example, reorientation and chemical exchange between complexation sites), but there are too few data to speculate further.

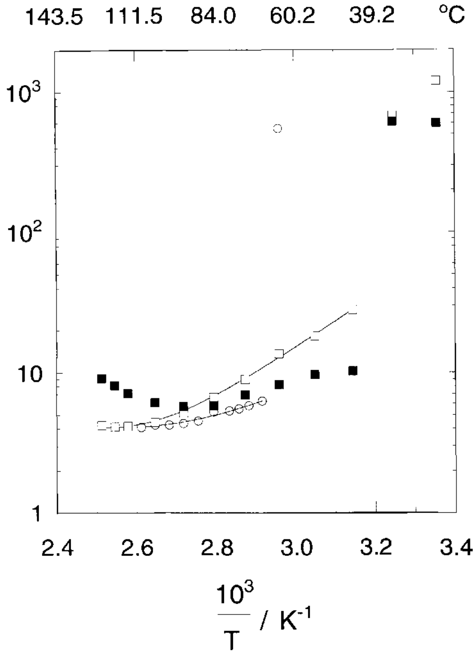


Figure 5. Deuterium T_1 relaxation times for the THE6-d$_6$ and TFA-d$_1$ deuterons in neat THE6-d$_6$ and in a 1:1 THE6-d$_6$:TFA-d$_1$ complex as a function of the inverse absolute temperature in the mesophase and solid regions. Symbols as in figure 4. The solid lines are calculated using parameters given in the text.

For the THE6-d$_6$ deuterons, a more complete analysis was possible. It is natural to assume that the dominant relaxation mechanism for these deuterons involves planar diffusional reorientation, for which the contribution to the relaxation rate for the perpendicular features is given by [27]

$$\frac{1}{T_1}=\frac{(2\pi\nu_Q)^2}{8}\left(\frac{\tau}{1+\omega_0^2\tau^2}+\frac{\tau}{1+4\omega_0^2\tau^2}\right)$$

where τ is the correlation time for the motion and $\omega_0 = 2\pi\nu_0$ is the deuterium Larmor frequency. From this equation, a T_1 minimum of 4·1 ms is calculated, which is exactly the value measured experimentally. Analysis of the whole set of relaxation data in terms of an Arrhenius equation yields for the activation energies of τ, 24·6 and 36·0 kJ mol^{-1} for the neat and the 1:1 complex, respectively, with corresponding pre-exponential factors of $1{\cdot}5 \times 10^{-12}$ and $5{\cdot}0 \times 10^{-12}$ s. Since the data pertain to the near T_1 minimum region, the activation parameters are subject to large errors, but the correlation time at the T_1 minima (∼120°C for both systems), $\tau = 0{\cdot}8/\omega_0 = 2{\cdot}8 \times 10^{-9}$ s, provides a very good estimate for the planar reorientational diffusion process in the mesophases.

3.2. *The hexa-alkyloxytribenzocyclononene (TBCEn) series*

The homologues of this series with $n=6$ to 12 exhibit an hexagonal columnar mesophase which was termed $\mathrm{P_A}$ [18, 22]. The transition temperatures and enthalpies for the neat homologues with $n=4$, 5 (not mesomorphic) and 6 (mesomorphic) are summarized in table 3. We prepared 1:1 molar complexes of these homologues with TFA and studied their mesomorphic properties by DSC, optical microscopy and X-ray diffraction. The samples were prepared gravimetrically and sealed in appropriate containers for the various measurements. For the mesomorphic TBCE6 homologue, we find that the complex exhibits a very much stabilized mesophase with the melting point decreased by about 50°C and the clearing point increased by about 6°C compared with the neat compound (see table 3). The isotropic phases of these complexes are yellow, while the mesophases and solids are pale yellow.

The $n=4$ and 5 homologues are not mesomorphic, yet their 1:1 complexes with TFA are very much so, with mesophases spanning a temperature range of over 80°C. Under the polarizing microscope, they exhibit the same fan-shaped structure as the $\mathrm{P_A}$ phases of the higher homologues (see figure 6). Moreover, the mesophase of the $n=4$ complex is completely miscible with that of the $n=5$ complex and both are miscible with the $\mathrm{P_A}$ mesophase of neat TBCE6, indicating that they are all isomorphic. However, the mesophase of the TBCE4:TFA 1:1 complex is not miscible with the solid phase of TBCE4. A contact preparation of the two species under a polarizing microscope exhibits separate regions for the $\mathrm{P_A}$ mesophase of the 1:1 complex and for the solid phase of neat TBCE4. This provides support for the assumed 1:1 stoichiometry of the TBCE*n*–TFA complexes.

Table 3. Transition temperatures (in °C) and in brackets transition enthalpies (in kJ mol^{-1}) for neat TBCE*n* and for the 1:1 TBCE*n*: TFA molar complexes.

Compound	Cr		$\mathrm{P_A}$		I
TBCE4 neat	•			135·1 (22·4)	•
TBCE4 complex	•	35·9 (16·1)	•	123·2 (19·7)	•
TBCE5 neat	•			103·8 (16·6)	•
TBCE5 complex	•	39·1 (28·5)	•	120·7 (20·2)	•
TBCE6 neat	•	39·8 (16·4)	•	91·8 (13·2)	•
TBCE6 complex	•	− 10 to + 15 (∼6)[a]	•	97·4 (10·6)	•

[a] A very broad and weak transition.

The X-ray structure of the $\mathrm{P_A}$ mesophases of some of the higher homologues in this series ($n=8$, 9, 10) were studied earlier by Poupko *et al.* [22]. The mesophases exhibited two (for $n=8$) or three (for $n=9$, 10) low angle reflections that could be indexed according to a two dimensional hexagonal columnar lattice and an additional broad reflection at $d \sim 4{\cdot}5$ Å, which was ascribed to the intramolecular stacking. We have now extended these measurements to the mesophases of the 1:1 TBCE*n*:TFA complexes with $n=4$, 5 and 6. The results are summarized in table 4. For the $n=6$ complex, only one low angle reflection is observed, while for the mesophases of the $n=5$ and 4 complexes, a larger number of diffraction rings is detectable with the inner three clearly identifiable as the {1 0}, {1 1} and {2 0} reflections from a two dimensional hexagonal lattice. The diffraction pattern also exhibits a diffuse ring at ∼4·4 Å due to scattering from the aliphatic chains. For $n=5$ and 6, it is possible that a sharper reflection, which may be identified with the intracolumnar stacking distance, is superimposed on this diffuse ring. It is thus clear that TFA has an effect on the TBCE*n* series similar to its effect on the THE*n* series, i.e. stabilization of the columnar mesophase. However, in addition we find that it also induces mesomorphism in the non-mesomorphic lower homologues of the series.

For the $n=4$ homologue, three additional sharp rings with *d* spacings between 4 and 4·6 Å were observed (see figure 7). These, we were unable to index in terms of the two dimensional hexagonal lattice derived from the three inner rings. We therefore attempted to interpret them in terms of a three dimensional hexagonal columnar structure with vertical correlations between the columns. Indeed, as shown in table 4, these three extra peaks fit well the {*h k 1*} reflections corresponding to the {*h k 0*} rings of the two dimensional lattice, with a vertical repeat $c=4{\cdot}8$ Å. The absence of a {0 0 1} reflection in this case may be due to an intensity minimum of the molecular form factor at the corresponding scattering angle.

Since the TBCE*n* molecules lack an inversion centre, they possess an electric dipole along their C_3 symmetry axis. It is most likely that in the columns they are stacked with their dipoles parallel to each other, resulting in a net macroscopic dipole. Hexagonal antiferroelectric structures cannot be formed [18], and we must assume that the domains are either ferroelectric with all macroscopic electric dipoles parallel, or their orientations are randomly distributed on the hexagonal lattice. So far no information on the ferroelectric properties of this phase is available. Given the polar nature of the TBCE*n* core and the resolution to which we observed crystalline

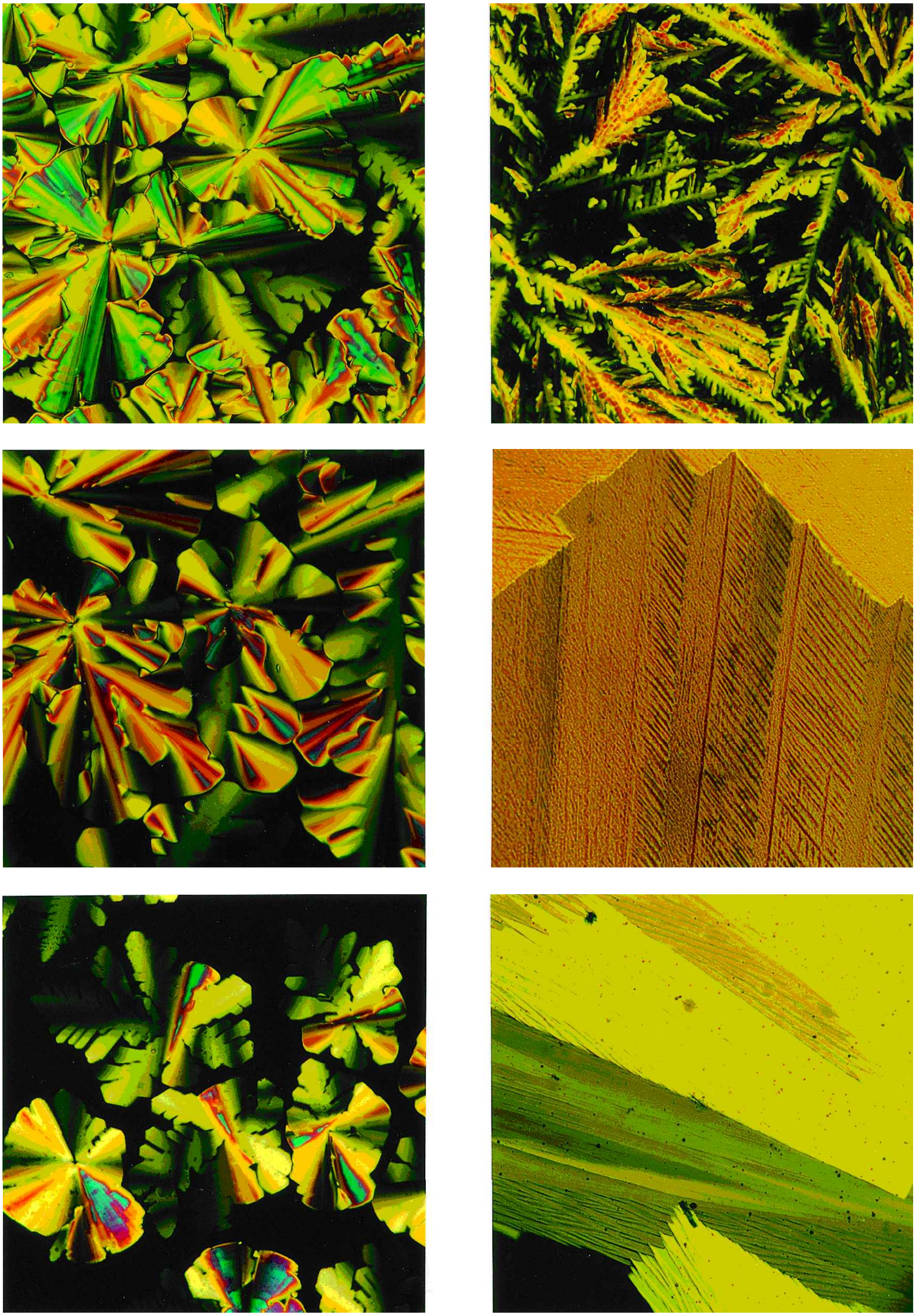


Figure 6. Polarizing optical microscopic pictures of TBCE*n* (right) and 1:1 TBCE*n*:TFA complexes (left) in the phase preceeding the isotropic liquid. Top: $n=6$, 76°C (right) and 92°C (left). Middle: $n=5$, 100°C (right) and 90°C (left). Bottom: $n=4$, 119°C (right) and 115°C (left). Magnification × 100.

Table 4. X-ray diffraction spacings (d) and lattice parameters (a and c)[a] for the hexagonal P_A mesophase in the 1:1 TBCEn:TFA molar complexes for $n=4$, 5 and 6 at 62°C.

Compound	Miller indices $\{h\,k\,l\}$	d_{meas}/Å	d_{calc}/Å	a/Å	c/Å
TBCE4	{100}	15·2	15·3	17·7	4·8
	{110}	9·0	8·9		
	{200}	7·6	7·7		
	{101}	4·6	4·6		
	{111}	4·2	4·2		
	{201}	4·1	4·1		
		4·4[b]			
TBCE5	{10}	16·5	16·5	19·0	
	{11}	9·5	9·5		
	{20}	8·3	8·3		
		4·5[c]			
TBCE6	{10}	17·2	17·2	19·9	
		4·4[c]			

[a] d_{meas} and d_{calc} are, respectively, the observed and calculated d-spacings, a is the two-dimensional hexagonal lattice parameter and c is the axial lattice parameter.

[b] Diffuse ring due to the aliphatic chains.

[c] Diffuse ring due to the aliphatic chains, possibly superimposed on a reflection due to intracolumnar stacking.

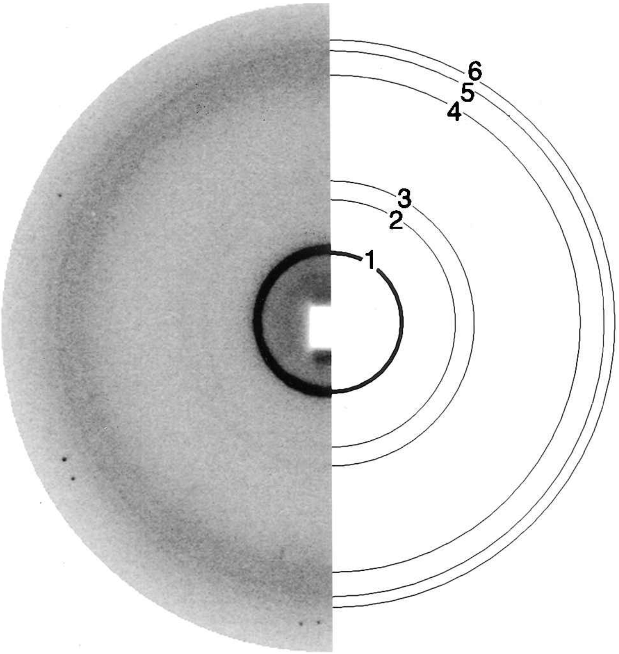


Figure 7. Left side: the X-ray diffraction pattern recorded for the mesophase of the 1:1 TBCE4:TFA complex at 62°C. Right side: a graphical representation of the six sharp rings observed in the diffraction pattern. The rings are numbered 1 to 6, corresponding to the Miller indexes {1 0 0}, {1 1 0}, {2 0 0}, {1 0 1}, {1 1 1} and {2 0 1}, as assigned in table 4.

sampling (~4 Å), a random (up-down) distribution of the electric dipole moment of the column is considered the less likely alternative. From the experimental lattice parameters, it follows that there is just one molecule (column) in a two-dimensional cell [22]. Therefore, for a ferroelectric structure, and recalling the azimuthal disorder of the molecules [22], only the primitive space groups *P*6 and *P*6*mm* are allowed.

The detection of the three dimensional correlations in columnar liquid crystals is unusual although it has been reported before [20]. It indicates a more highly ordered structure, which must however still be considered as a mesophase because of the sequence of miscibilities described above. The mesophase thus occupies a border state with the solid phase; it shows a degree of three dimensional correlation between the centre of mass of the constituent molecules, but their azimuthal orientations are uncorrelated. It is interesting that despite this lack of azimuthal order within the columns, there is a lateral correlation between molecules in neighbouring columns.

4. Summary and conclusion

We have demonstrated that trifluoroacetic acid (TFA) when added to alkyloxy discogenic compounds, such as hexa-alkyloxytriphenylene (THEn) and hexa-alkyloxytribenzocyclononene (TBCEn), stabilizes and even induces the formation of columnar mesophases. The TFA dopant appears to form 1:1 molar complexes with the alkyloxy compounds. The mesophases formed by these complexes are isomorphic with those of the neat discotic compounds or, in the case of induced mesomorphism, with those formed by the mesogenic homologues of the series. The mesophases formed by the TFA complexes differ from those of the neat compounds in two important aspects: their range of thermal stability is wider and they have a higher degree of ordering as manifested by the larger number of X-ray reflections.

It is of interest to speculate about the possible structure of the TFA complexes. A likely mechanism may be the formation of oxonium ions of the type

$$\mathrm{CF_3COOH + A\text{–}O\text{–}B \rightarrow [CF_3COO]^{-}[A\text{–}OH^{+}\text{–}B]}$$

Such complex formation is often found on reacting ether compounds with strong acids [28]. In the mesophase region, the complex will be highly dynamic in the sense that there are fast proton jumps between different oxygen bridges with a concomitant rapid migration of the CF_3COO^- groups. This conclusion is derived from the fact that just a single deuterium signal with an average axially symmetric quadrupole coupling tensor is observed in the mesophase region. Moreover, since the same applies to mixtures with different (from 1:1) ratios of TFA to mesogen, the averaging must involve intermolecular exchange as well. The most likely site for the CF_3COO^- anion would be in the aliphatic chain region close to a bridging oxygen. This would not alter the stacking arrangement, as found experimentally by X-ray diffraction, and would allow for minimum charge separation. It may also account for the observed lateral correlation.

Conclusive identification of the complexes formed would require extensive investigation by various spectroscopic methods such as IR, UV and NMR. Another important extension of the work is to check which other strong Brønsted acids stabilize and induce mesomorphism. Acetic acid did not show an effect, but it might be interesting to try stronger reagents such as methane- or toluene-sulphonic acids. It would also be interesting to extend the study to calamitic liquid crystals. If suitable dopants are found for such systems, the effect may have technical application in that it can be used to widen the range of stability of the mesophases employed in electro-optical and other liquid crystalline devices.

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