Aggregates of Hexakis(*n*-hexyloxy)triphenylene Self-Assemble in Dodecane Solution: Intercalation of (−)-Menthol 3,5-Dinitrobenzoate Induces Formation of Helical Structures

Justin P. Gallivan[†] and Gary B. Schuster*[‡]

Department of Chemistry, Roger Adams Laboratory, University of Illinois, Urbana, Illinois 61801

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Concentrated dodecane solutions of hexakis(*n*-hexyloxy)triphenylene form columnar aggregates as evidenced by optical spectroscopy. Addition of either ethyl 3,5-dinitrobenzoate, (+)-2′-octyl 3,5-dinitrobenzoate, (−)-2′-butyl 3,5-dinitrobenzoate, or (−)-menthol 3,5-dinitrobenzoate to these solutions results in the formation of charge-transfer complexes as shown by examination of their optical spectra. Investigation of the circular dichroism spectra of the charge-transfer complexes suggests that intercalation of the menthol ester in the columnar aggregate induces a helical twist to the structure.

Introduction

Discotic liquid crystals show promise for application as molecular energy guides, one-dimensional conductors, and nonlinear optical materials.[1,2] In a recent report, concentrated aliphatic hydrocarbon solutions of discogenic materials, particularly hexakis(*n*-pentyloxy)triphenylene (an electron donor) containing an equimolar amount of an electron acceptor, specifically 2,4,7-trinitrofluoren-9-one, are described as forming cylindrical aggregates of alternating donors and acceptors.[2] The D_{3h} symmetry of the hexakis(*n*-alkoxy)triphenylenes suggests aggregation in a hexagonal order where each layer is rotated by 40° with respect to the previous layer, resulting in a column with a helical twist. In solutions containing discogenic columnar aggregates doped with achiral additives, there must be equal populations of right- and left-handed helices (Figure 1). However, intercalation of a chiral substance into the column might induce a preference for helices of one handedness over the other (Figure 2). Although liquid crystals with chiral dopants in the bulk have been carefully studied,[3] and there are reports of achiral dopants in solution,[2,4] we are aware of no reports of achiral discotic molecular aggregates doped with chiral additives in solution. Herein we report a study of chiral dopants that appear to intercalate into stacks of 2,3,6,7,10,11-hexakis(*n*-hexyloxy)triphenylene and induce the formation self-assembling helical superstructures (see Chart 1).

Results

Chiral dopants for hexakis(*n*-hexyloxy)triphenylene (**1**) must simultaneously satisfy several criteria. They must retain a charge-transfer interaction similar to that of 2,4,7-trinitrofluoren-9-one, be soluble in saturated aliphatic hydrocarbon solvents, intercalate into the aggregate without destroying its structure, and induce formation of a helically twisted superstructure. We prepared achiral and chiral dopants and studied their interactions with the (hexyloxy)triphenylene by absorption and circular dichroism spectroscopy.

Absorption Spectra of (Hexyloxy)triphenylene Discogens and Electron Deficient Dopants. The UV–vis absorption spectra of *n*-alkane solutions containing hexakis(*n*-hexyloxy)triphenylene and either ethyl 3,5-dinitrobenzoate (**2**), (+)-2′-octyl 3,5-dinitrobenzoate (**3**), (−)-2′-butyl 3,5-dinitrobenzoate (**4**), or (−)-menthol 3,5-dinitrobenzoate (**5**) (typically, 10^{-3}–10^{-2} M in each component) show charge-transfer bands. The spectrum of the mixture of **1** and **2** is typical; in addition to absorptions due to the locally excited states of each component, it shows a charge-transfer band with a maximum at ca. 423 nm that tails to 565 nm (Figure 3). For comparison, a 1:1 mixture of 2,4,7-trinitrofluoren-9-one and hexakis(*n*-hexyloxy)triphenylene under the same conditions shows a charge-transfer band having a maximum at 470 nm and a tail to 750 nm. The other dinitrobenzoates behave similarly except that the intensity of the charge-transfer band for the menthol ester is lower than the others esters examined, which may signal poorer overlap due its bulkier substituents (Figure 4). Clearly, the dinitrobenzoate esters form complexes with discogen **1**. The association constants for formation of these charge-transfer complexes could not be readily determined since these species are nonstoichiometric and their composition presumably varies with their concentration.[5]

Figure 5 shows the UV–vis absorption spectra for dodecane solutions of **1** at concentrations of 10^{-5}, 10^{-4}, and 10^{-2} M in cuvettes having path lengths of 10, 1 and 0.01 mm, respectively. Neutron scattering experiments[6] reveal that aggregation of **1** does not occur at concentrations of 10^{-5} and 10^{-4} M, and the spectra at these concentrations show ideal Beer's law behavior. In contrast, the 10^{-2} M solution of **1**, a concentration above the aggregation limit according to the neutron scattering

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[†] Undergraduate research participant.

[‡] Current Address: School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332.

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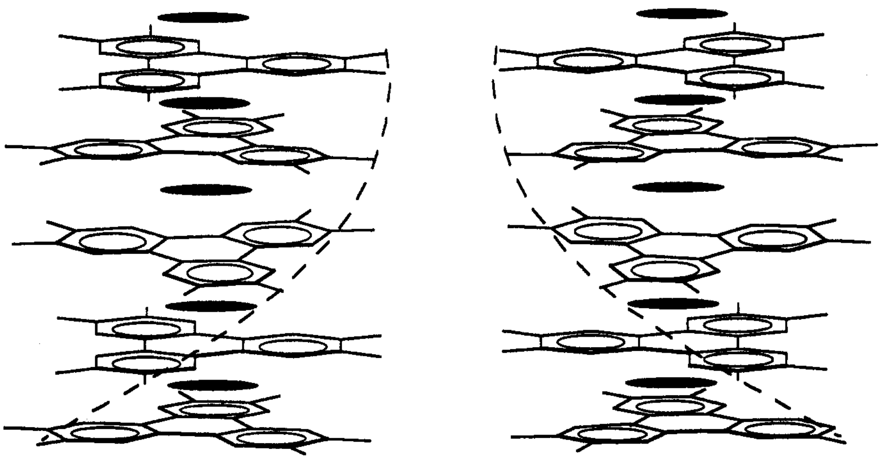


Figure 1. Schematic representation of right- and left-handed helical aggregates formed in alkane solution by doping hexakis(*n*-alkyloxy)triphenylene with an *achiral* electron acceptor (represented by a disk). The alkoxy side chains have been removed for clarity.

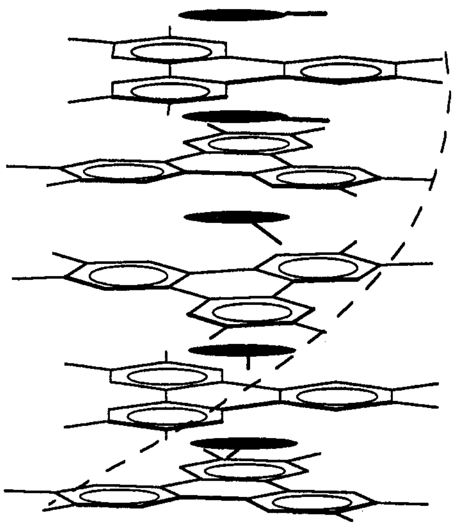
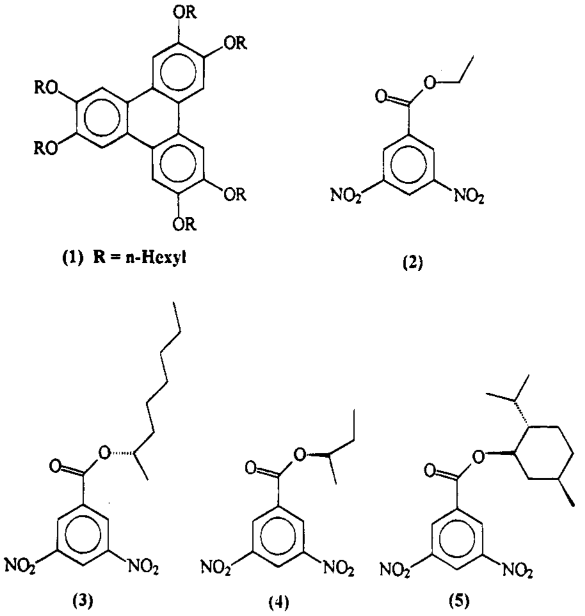


Figure 2. Schematic representation of a right-handed helical aggregates formed in alkane solution by doping hexakis(*n*-alkyloxy)triphenylene with a *chiral* electron acceptor (represented by a disk with a tail).

Chart 1. Aggregating Discogen and Electron Deficient Dopants



results, shows a broadening of the spectrum and an 11% increase in absorption at 278 nm over that expected from Beer's law. Although this change in absorption behavior cannot be unequivocally assigned to an effect of aggregation of **1**, it is an expected consequence, and it is consistent with the neutron scattering experiments.

Markovitsi and co-workers have shown that 2,4,7-trinitrofluoren-9-one forms a charge-transfer complex with 2,3,6,7,10,11-hexakis(*n*-pentyloxy)triphenylene in concentrated *n*-heptane solution as evidenced by a charge-transfer band in the visible region of the spectrum.[2] When the solvent is changed to 1,2-dichloroethane, the intensity of this band is reduced 5-fold. However, in at least one case, the formation constant for a charge-transfer complex of triphenylene and an electron deficient acceptor is the same in dilute dodecane solution as in 1,2-dichloroethane.[7] Consequently, there may be an interaction beyond the formation of 1:1 charge-transfer complexes that accounts for the change in the charge-transfer absorption when the solvent is changed. This effect can be attributed to aggregation of the (pentyloxy)triphenylene. The charge-transfer absorption of the trinitrofluorenone may be more intense with aggregates of the (pentyloxy)triphenylene than it is with the monomer.

Figure 6 shows UV–vis spectra of equimolar mixtures of (hexyloxy)triphenylene and (−)-menthol 3,5-dinitrobenzoate at 10^{-2} M in dodecane and in 1,2-dichloroethane solutions. The dichloroethane solution shows a very low intensity charge-transfer band with an absorbance of 0.002 at 430 nm. In dodecane solution, the intensity of this band is over seven times greater, 0.15 at 430 nm. This observation is consistent with the formation of charge-transfer complexes of the menthol ester with monomers of the (hexyloxy)triphenylene in dichloroethane and with its aggregates in dodecane solution.

Circular Dichroism Spectra of Hexakis(*n*-hexyloxy)triphenylene and Dinitrobenzoate Dopants. Although there is spectroscopic evidence for aggregation of hexakis(*n*-hexyloxy)triphenylene in the presence of the dinitrobenzoate esters, the question remains whether these assemblies are helical. Circular dichroism spec-

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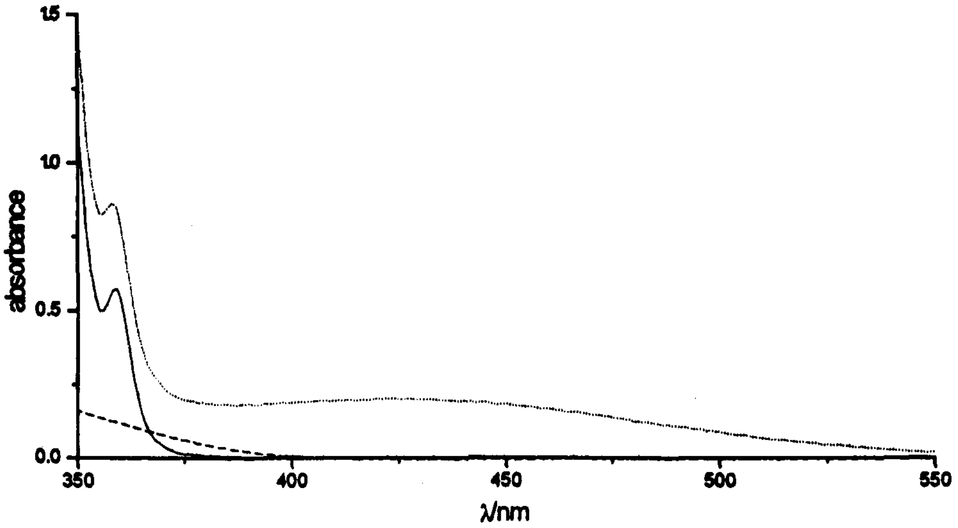

Figure 3. UV–vis absorption spectra of ethyl 3,5-dinitrobenzoate (— —), hexakis(*n*-hexyloxy)triphenylene (—), and an equimolar mixture of ethyl 3,5-dinitrobenzoate and hexakis(*n*-hexyloxy)triphenylene (- -); 10^{-3} M in hexane, 1 cm path length.

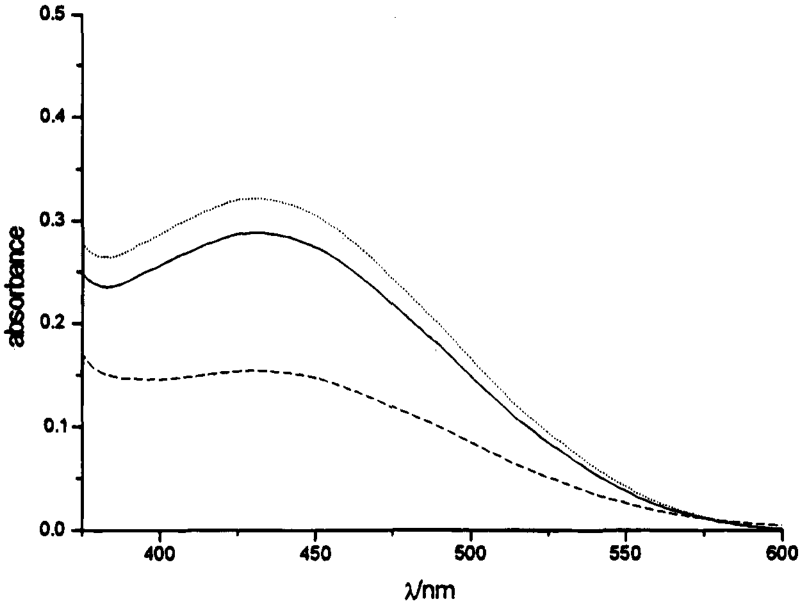

Figure 4. UV–vis absorption spectra of equimolar mixtures of **1** and (−)-menthol 3,5-dinitrobenzoate (— —), **1** and (−)-2′-butyl 3,5-dinitrobenzoate (—), and **1** and (+)-2′-octyl 3,5-dinitrobenzoate (- -); 10^{-2} M in dodecane, 1 mm path length.

troscopy was used to examine the structure of the aggregates and address this issue.[8]

The circular dichroism spectra of dodecane solutions (10^{-2} M) of **3**–**5** were compared with the CD spectra of equimolar mixtures of the esters and hexakis(*n*-hexyloxy)triphenylene. Solutions of the dinitrobenzoate esters alone show no detectable circular dichroism above 420 nm, but the 1:1 mixtures of the esters and hexakis(*n*-hexyloxy)triphenylene show low intensity CD bands from 400 nm to 575 nm (Figure 7). Although the CD spectra are weak, the observation that the (−)-menthol and (−)-butyl ester solutions have signs opposite that of the (+)-octyl ester solution is an additional indication that there is an interaction between the chiral electron acceptors and hexakis(*n*-hexyloxy)triphenylene. However, these results do not necessarily confirm the formation of helical aggregates. The observed CD bands could be due to perturbation of the electronic transition by the chiral ester and not to a preferential helical twist direction of the aggregate.

The absorption spectrum of the hexakis(*n*-hexyloxy)triphenylene donor shows an increase in intensity at 278 nm in concentrated solutions that is attributed to aggregation. An induced CD spectrum in this region would provide additional evidence for helicity of the aggregate. The CD spectra of a 10^{-2} M dodecane solution of (−)-2′-butyl 3,5-dinitrobenzoate and (+)-2′-octyl 3,5-dinitrobenzoate display relatively broad, weak bands in this spectral region that are unaffected by addition of an equimolar amount of the (hexyloxy)triphenylene to the solution. These experiments were performed on thin solution (0.01 mm path length) samples so that the high concentrations ($\approx 10^{-2}$ M) needed for aggregation could be maintained while keeping the optical density low enough to give meaningful results.[9]

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[8] The entire CD spectrum could not be obtained at once because of the large variations in optical density.

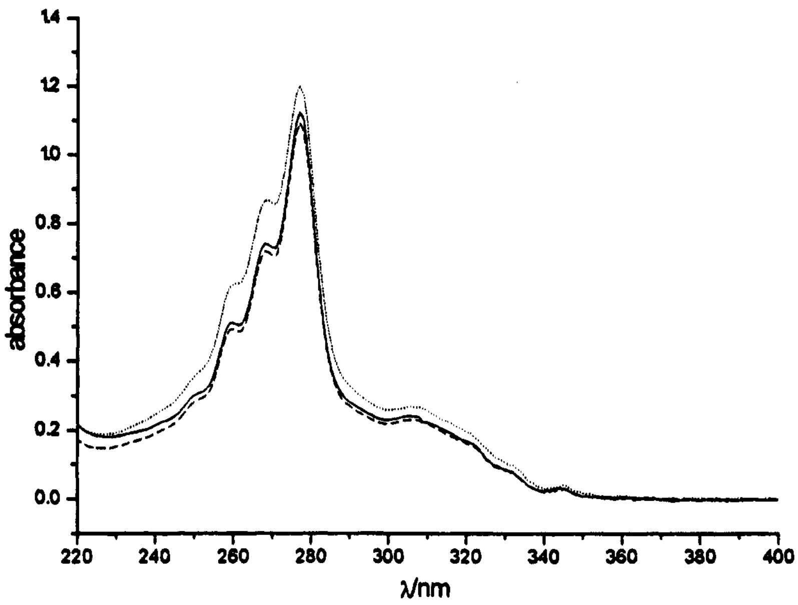

Figure 5. UV–vis absorption spectra of hexakis(*n*-hexyloxy)triphenylene: 10^{-5} M, 10 mm path length (– –), 10^{-4} M, 1 mm path length (—), and 10^{-2} M, 0.01 mm path length (- -); dodecane solvent. Note the increase in absorbance for the concentrated solution at 278 nm.

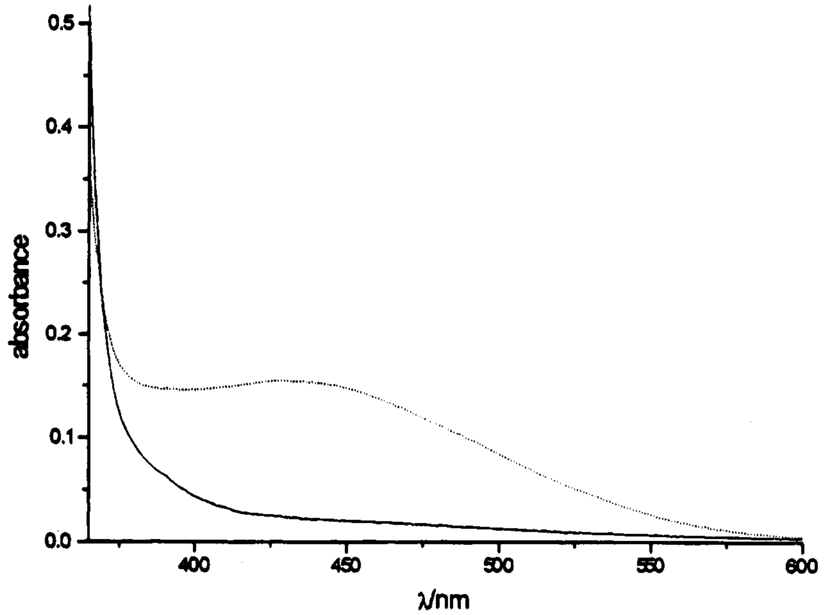

Figure 6. UV–vis absorption spectra of equimolar mixtures of (−)-menthol 3,5-dinitrobenzoate and hexakis(*n*-hexyloxy)-triphenylene at 10^{-2} M in 1,2-dichloroethane (—) and dodecane (- -); 1 mm path length. Absorbance at 430 nm is seven times greater in dodecane than in 1,2-dichloroethane.

In contrast to the effect of adding (−)-2′-butyl or (+)-2′-octyl esters to (hexyloxy)triphenylene, addition of the (−)-menthol-3,5-dinitrobenzoate gives a new peak in the CD spectrum at 278 nm that is not present in the spectrum of the menthol ester alone, Figure 8. It should be noted that the menthol ester does not absorb in this region at these concentrations (OD < 0.01) and that this effect is at the same wavelength (278 nm) that shows the increased intensity in the absorption spectrum of 1 at high concentrations (aggregating conditions). In addition, the CD spectrum of a 1:1 mixture of menthol ester and hexakis(*n*-hexyloxy)triphenylene at 10^{-2} M in 1,2-dichloroethane (a solvent that does not favor aggregation of 1) shows no circular dichroism between 250 and 300 nm. Evidently, aggregation of 1 is necessary for this effect to be seen in the CD spectrum.

Discussion

The three basic requirements for formation of a self-assembling helical superstructure by doping hexakis(*n*-hexyloxy)triphenylene with an electron-accepting compound are: interaction, aggregation, and twist propagation. The first requirement is relatively easy to satisfy: a dopant must be designed to interact with the discotic molecule. The UV–vis absorption spectrum of the ethyl 3,5-dinitrobenzoate and hexakis(*n*-hexyloxy)-triphenylene shows the appearance of a new absorption band outside of the absorption regions of either the ester

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(9) Unless otherwise noted, the remaining CD spectra were taken in a 0.01 mm path length quartz cell.

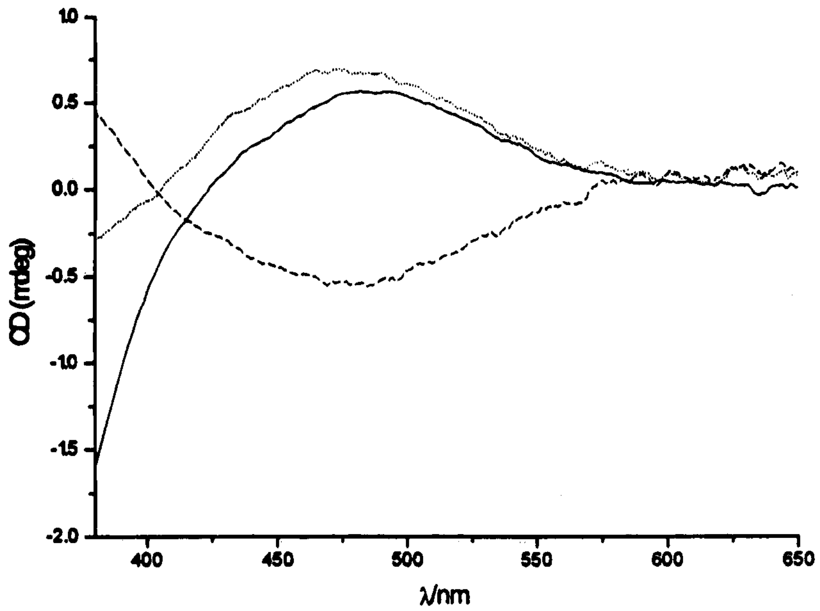

Figure 7. CD spectra of equimolar mixtures of **1** and (+)-2′-octyl 3,5-dinitrobenzoate (— —), **1** and (−)-menthol 3,5-dinitrobenzoate (—) and **1** and (−)-2′-butyl 3,5-dinitrobenzoate (- -); 10^{-2} M in dodecane, 1 mm path length.

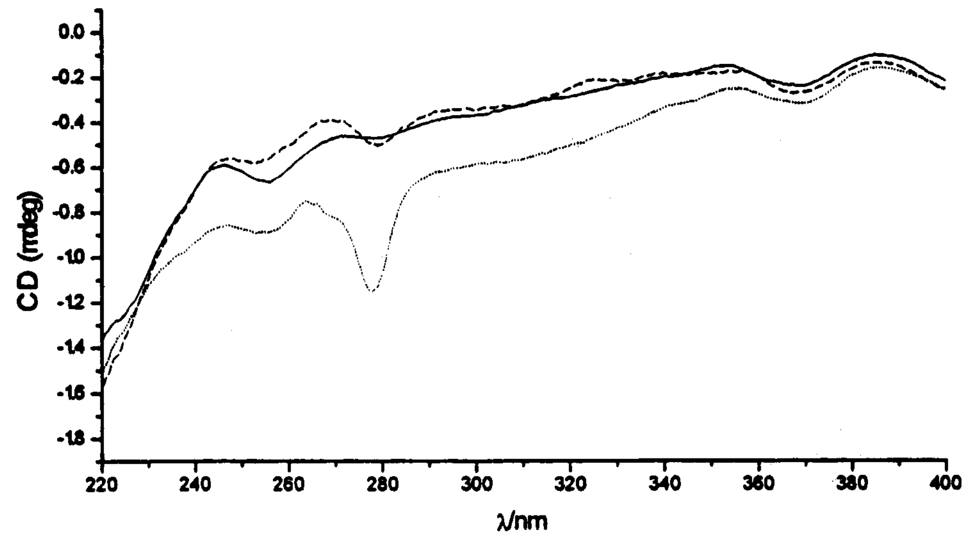

Figure 8. CD spectra of (−)-menthol 3,5-dinitrobenzoate,10^{-4} M, 1 mm cell (—), a mixture of 1^{-4} M (−)-menthol 3,5-dinitrobenzoate and 10^{-2} M **1**, 0.01 mm cell, (— —), and an equimolar mixture of (−)-menthol 3,5-dinitrobenzoate and **1**, 10^{-2} M, 0.01 mm cell (- -). Note the increase in CD for the concentrated mixture at 278 nm.

or the triphenylene. This is evidence of the first requirement, interaction. This charge transfer band was also observed with (−)-2′-butyl 3,5-dinitrobenzoate, (+)-2′-octyl 3,5-dinitrobenzoate and (−)-menthol 3,5-dinitrobenzoate as dopants.

With evidence for interaction, the next step is to show aggregation of the donor and acceptor. Neutron scattering experiments reveal that hexakis(*n*-alkyloxy)triphenylenes self-assemble into columnar aggregates in alkane solution at concentrations above 10^{-3} M.[6] UV−vis absorption spectra of hexakis(*n*-hexyloxy)triphenylene solutions confirm this spectroscopically. At low concentrations (10^{-4} M and below), the solutions show ideal Beer's law behavior. However, at 10^{-2} M the spectrum broadens and the intensity at λ_{max} (278 nm) increases relative to the prediction of Beer's Law. In conjunction with the neutron scattering experiments,[6] this represents spectroscopic evidence for aggregation of the donor compound. The question remains whether a dopant can be intercalated into the aggregate without breaking it apart.

In dodecane solution, the charge transfer band of an equimolar mixture of hexakis(*n*-hexyloxy)triphenylene and (−)-menthol 3,5-dinitrobenzoate at 10^{-2} M is seven times more intense than the same mixture in 1,2-dichloroethane. An explanation that this increase in intensity is due to aggregation has been reported and it is consistent with the data.[2] Thus there is evidence for both interaction and aggregation of hexakis(*n*-hexyloxy)triphenylene and these esters.

The final requirement for helix formation is the ability to propagate a twist through the aggregate. Figure 2 illustrates helix formation with a chiral dopant in the hexakis(*n*-hexyloxy)triphenylene stack. A factor that must be considered is whether the hexakis(*n*-hexyloxy)triphenylene will maintain a twist or aggregate randomly. X-ray diffraction studies have shown that

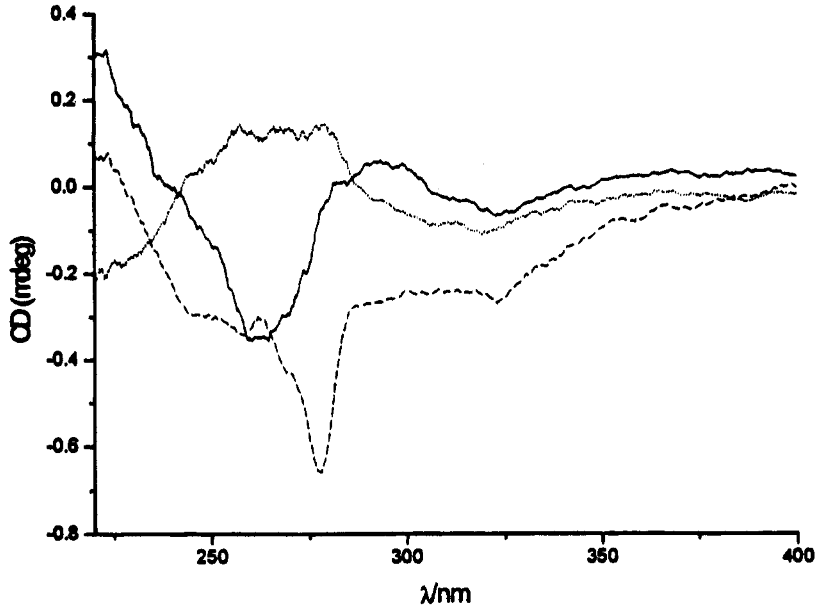

Figure 9. Induced CD spectra obtained by subtracting the CD spectrum of a 10^{-2} M solution of ester in dodecane from the spectrum of an equimolar mixture of the ester and **1** at 10^{-2} M in dodecane (0.01mm path). (−)-Menthol 3,5-dinitrobenzoate (− −), (−)-2′-butyl 3,5-dinitrobenzoate (—), and (+)-2′-octyl 3,5-dinitrobenzoate (- -).

hexathiotriphenylenes exhibit long range helical ordering in a hexagonally ordered discotic phase (D_{ho}) because of interactions of the side chains.[10] It is reasonable to propose that similar steric effects will operate in dissolved aggregates and that a helix may be formed. To confirm helix formation, the CD spectra of equimolar mixtures of hexakis(*n*-hexyloxy)triphenylene and (−)-2′-butyl 3,5-dinitrobenzoate, (+)-2′-octyl 3,5-dinitrobenzoate, and (−)-menthol 3,5-dinitrobenzoate at 10^{-2} M in dodecane were measured. Two main regions of the spectrum were investigated—above and below 350 nm. Above 350 nm, a charge-transfer band is present. The intensity of the charge-transfer band of the menthol ester is only ca. half that of the octyl and butyl esters, indicating poorer overlap in the former than for the latter two.

More revealing are the CD spectra of the equimolar, 10^{-2} M solutions of the hexakis(*n*-hexyloxy)triphenylene and the chiral esters. There is a clear effect of adding the hexakis(*n*-hexyloxy)triphenylene to the solutions of the chiral esters. There are two features to be noted. All three esters display a broadening of the spectrum and an induced CD in the region in which both the donor and acceptor absorb, but only the menthol ester shows a sharp peak at 278 nm, the maximum of the hexakis(*n*-hexyloxy)triphenylene, a region outside of the absorption range of the dopant at this concentration, Figure 9. This is the same wavelength that showed an increased intensity in the UV spectrum that is attributed to aggregation. However, in 1,2-dichloroethane solutions, an equimolar mixture of hexakis(*n*-hexyloxy)triphenylene and (−)-menthol 3,5-dinitrobenzoate at 10^{-2} M shows no circular dichroism. Therefore, it is reasonable to conclude that the unique CD band in the dodecane solutions containing the menthol ester is due to the formation of aggregates and that these aggregates are chiral since this effect is seen only in solutions of the "bulky" menthol ester, where the weaker absorbance of the charge-transfer band indicates weaker complex formation compared with the "flatter" octyl and butyl esters. This observation suggests that there are two effects operating: a chiral charge-transfer association present in all three ester−hexakis(*n*-hexyloxy)triphenylene solutions and an additional steric effect present only in solutions containing the menthol ester. This special effect of the bulky menthol ester is attributed to perturbation of the order of the alkyl chains in columnar hexakis(*n*-hexyloxy)triphenylene stacks by the menthol substituent. This intercalating dopant causes a twist of the form a helix. Although this effect is small, it is similar in magnitude (0.7 mdeg) to the circular dichroism induced in racemic helical polymers by chiral solvents.[11]

Additional support for this conclusion comes from molecular mechanics calculations. Figure 10 shows structures calculated for the butyl and menthol esters intercalated between two molecules of hexakis(*n*-hexyloxy)triphenylene. The side chain of the butyl ester fits easily between the side chains of hexakis(*n*-hexyloxy)triphenylene, but for the menthol ester, interaction of the isopropyl group in particular forces the side chains of the hexakis(*n*-hexyloxy)triphenylene apart, and as a result, the triphenylene "cores" are twisted with respect to one another where they are not with the butyl ester.

Conclusion

Although further studies are needed to confirm the detailed structures, it is clear from the induced circular dichroism data that doping concentrated dodecane solutions of hexakis(*n*-hexyloxy)triphenylene with (−)-menthol 3,5-dinitrobenzoate generates a helical aggregate.

Experimental Section

UV−vis spectra were recorded on a Cary 1E UV−vis spectrophotometer. Circular dichroism spectra were obtained using a Jobin-Yvon CD-6 spectropolarimeter and a JASCO J-720 spectropolarimeter at the University of Illinois Laboratory for Fluorescence Dynamics. Solvents used for absorption

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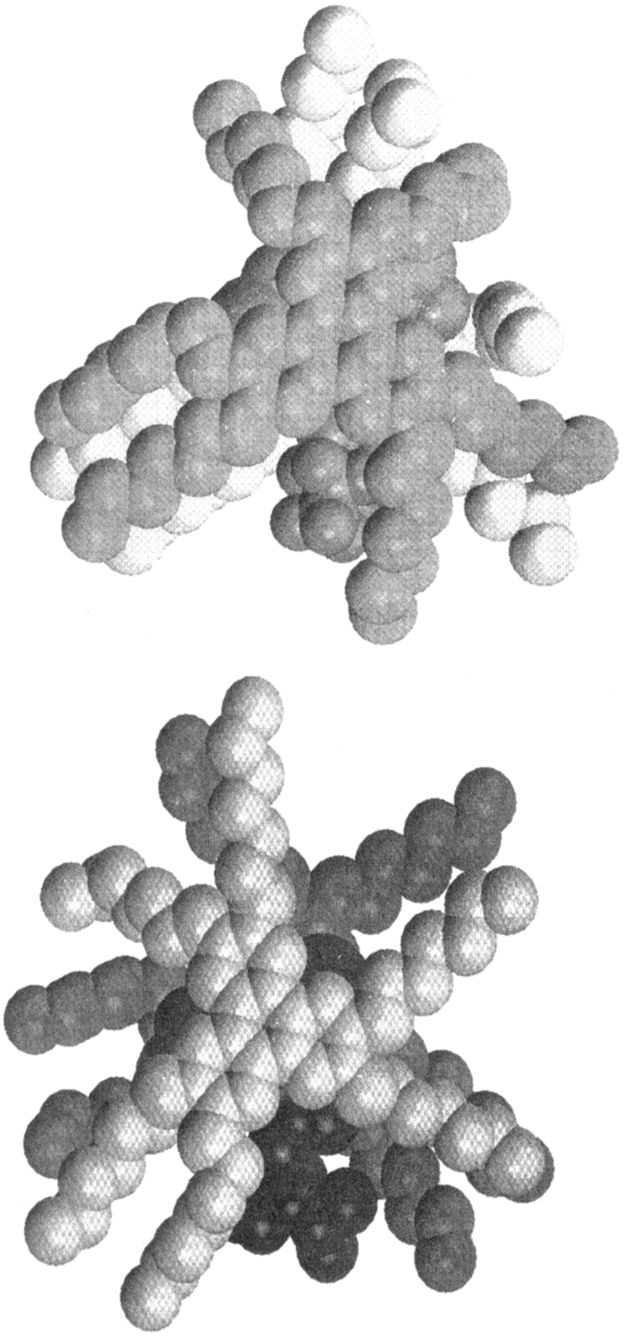

Figure 10. Molecular force field calculation of the structure of two hexakis(*n*-hexyloxy)triphenylene molecules intercalating (−)-2′-butyl 3,5-dinitrobenzoate (top) or (−)-menthol 3,5-dinitrobenzoate (bottom). The view in both cases is the same —looking down on the complex. In the case of the (−)-2′-butyl ester, the side chains of hexakis(*n*-hexyloxy)triphenylene can accommodate this group without much disruption. For the menthol ester, however, the side chains are forced out of the way and the triphenylene cores are twisted with respect to one another.

and CD spectroscopy were spectrophotometric grade when available and twice distilled otherwise. NMR spectra were taken on a Varian XL-200 Spectrometer at the University of Illinois Molecular Spectroscopy Laboratory. Elemental Analyses were performed at the University of Illinois Microanalytical Laboratory.

Ethyl 3,5-dinitrobenzoate:[12] mp 93.5 °C; ^{1}H NMR (CDCl$_3$) 200 MHz δ 9.18 (1H, t), 9.12 (2H, t), 4.5 (2H, q), 1.45 (3H, t). Anal. Calcd for $C_9H_8N_2O_6$: C, 45.01; H, 3.36; N, 11.66. Found: C, 45.06; H, 3.38; N, 11.57.

(−)-Menthol 3,5-dinitrobenzoate. Prepared in 89% yield from (−)-menthol (Fisher Chemical Co.). After recrystallization from ethanol: mp 153 °C (lit.[12] 153 °C); $[\alpha]^{25}_D = -3.94°$ (CHCl$_3$); ^{1}H NMR (CDCl$_3$) 200 MHz δ 9.2 (1H, t), 9.15 (2H, t), 5.05 (1H, m), 1.2 (4H, m), 0.92 (1H, m), 0.80 (3H, d). Anal. Calcd for $C_{17}H_{22}N_2O_6$: C, 58.28; H, 6.33; N, 8.00. Found: C, 58.55; H, 6.33; N, 7.93.

(−)-2′-Butyl 3,5-dinitrobenzoate. Prepared in 95% yield from (−)-2-butanol. After 3-fold recrystallization from ethanol: mp 89 °C, $[\alpha]^{25}_D = -1.79°$ (CHCl$_3$); ^{1}H NMR (CDCl$_3$) 200 MHz δ 9.21 (1H, t), 9.16 (2H, t), 5.0 (1H, m), 1.89 (2H, m), 1.41 (3H, d), δ1.0 (3H, t). Anal. Calcd for $C_{11}H_{12}N_2O_6$: C, 49.26; H, 4.51; N, 10.44. Found: C, 49.28; H, 4.52; N, 10.42.

(+)-2′-Octyl 3,5-Dinitrobenzoate.[13] 3,5-Dinitrobenzoic acid (1.0 g, 4.7 mmol), (*S*)-(+)-2-octanol (0.68 g, 5.2 mmol), dicyclohexylcarbodiimide (DCC, 1.07 g, 5.2 mmol), and 4-(dimethylamino)pyridine (DMAP, 64 mg, 0.5 mmol) were stirred in 25 mL of ether at room temperature for 21 h. The mixture was filtered and the filtrate evaporated to give 976 mg of a yellow solid. The solid was dissolved in ether and washed with water twice, 5% acetic acid twice, and three more times with water. The organic layer was dried over MgSO$_4$, and the solvent was evaporated to give 773 mg of pale yellow solid which was recrystallized repeatedly from methanol to give 743 mg (2.3 mmol) of white needles in 49% yield: mp 52.5 °C; $[\alpha]^{25}_D = +1.79°$ (CHCl$_3$); ^{1}H NMR (CDCl$_3$) 200 MHz δ 9.21 (1H, t), 9.16 (2H, t), 5.23 (1H, m), 1.87 (2H, m), 1.41 (11H, m), 0.85 (3H, t). Anal. Calcd for $C_{15}H_{20}N_2O_6$: C, 55.55; H, 6.22; N, 8.64. Found: C, 55.40; H, 6.23; N, 8.92.

2,3,6,7,10,11 Hexakis(*n*-hexyloxy)triphenylene.[14,15] 1,2-Bis(*n*-hexyloxy)benzene (1.5 g, 5.5 mmol) was added to a vigorously stirred solution of ferric chloride (2.7 g, 17 mmol) and H$_2$SO$_4$ (2 drops) in 20 mL of CH$_2$Cl$_2$. After 1 h, the mixture was quenched with 60 mL of methanol. The solvent was removed in vacuum from the yellow solution to give a black solid that was adsorbed onto silica and eluted with 1:1 light petroleum ether:CH$_2$Cl$_2$ to give a yellow solid that was twice recrystallized from ethanol to give 632 mg (0.77 mmol) of hexakis(*n*-hexyloxy)triphenylene in 42% yield.

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