

Liquid Crystal Control of Bimolecular Thermal Reactions. Highly Regioselective Pericyclic Addition of Fumarates to 2,6-Dialkoxyanthracenes in Liquid–Crystalline Media

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Abstract: The ability of liquid crystalline solvent phases to control the stereochemical course of bimolecular thermal reactions of 2,6-dialkoxyanthracenes with a series of fumarates conducted at 130–180 °C has been examined, primarily with respect to the structural compatibility of the solutes with the solvent mesogens. For the case of the model thermal [4 + 2] cycloadditions of 2,6-bis(decyloxy)anthracene to bis(*trans*-4-cyclohexylcyclohexyl) and cholesteryl *trans*-4-cyclohexylcyclohexyl fumarates at 130–150 °C, cholesteryl 2,4-dichlorobenzoate(CDCB) and bis(4-pentyloxyphenyl) *trans*-1,4-cyclohexanedicarboxylate(BPCD) serve well as cholesteric and smectic liquid crystalline solvents and result in the preferential formation of *syn*-isomers with an extremely high level of regioselection (*syn/anti* ≥ 20/1). In contrast, the isotropic solvents with closely related structures give isomer ratios of only ≥ 3/1. Structural similarities between the solutes and the solvent mesogens appear to play a key and influential role in controlling the stereochemical course of the reaction. The temperature dependence for the isomer distribution affords an estimate of the differences of solvation enthalpy and entropy between *syn* and *anti* transition states in the anisotropic media.

There is considerable interest in the properties of anisotropic environments such as crystalline solids,¹ liquid crystals,² micelles,³ monolayers⁴ and host–guest assemblies⁵ which can affect on the chemical behavior of included solute molecules. Thermotropic liquid crystals,^{2,6} for which mesomorphic properties are maintained over a wide temperature range, have high potential as unique reaction solvents, because their rigidity of molecular ordering and fluidity make them suitable for solute diffusion. The potential effect of thermotropic liquid crystals on stereochemical control of a variety of photochemical⁷ and thermal reactions⁸ has been reported subsequent to the pioneering study by Nerbonne and Weiss.⁹ Smectic solvent phases

which possess a high rigidity of ordering have proved to be sufficiently effective to influence the course of uni- and bimolecular photochemical reactions, primarily by controlling the orientation of reactant molecules.¹⁰ The ability of liquid crystal phases to control reactivity is recognized to depend on a number of factors, including the shape of the reactant molecules, flexibility, polarizability, and mesophase type of the medium. The weak anisotropic constraints attributable to liquid crystalline alignments, however, have not been sufficiently strong to effectively control thermochemical reactions, when these are conducted at elevated temperatures, except for a few well documented exceptions.¹¹ Poorly ordered orientation of

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solutes in the transition state might be primarily responsible for the inability of such anisotropic media to regulate thermochemical reactivities. Using this as a hypothesis, we recently reported the promising use of liquid crystal dienophiles which served as stereochemical controllers of uncatalyzed Diels–Alder reactions of 2,6-dialkoxyanthracenes and fumarates.¹² This cycloaddition proceeded with a reasonable level of regioselectivity even at 150 °C. At these conditions, the liquid crystalline fumarates were ordered and aligned during the reaction and, thus, could be utilized as both dienophiles and as anisotropic media. In a preliminary report,¹³ we showed that the molecular ordering inherent in cholesteric liquid crystalline solvent phases was effective enough to regulate such intermolecular pericycloadditions (at 130 °C) with significantly high regioselectivity in favor of *syn*-adducts. This was true for cases where the dienophiles were carefully modified, based on structural similarity to the mesogens.¹⁴

This paper describes the results of an extension of these studies on the ability of liquid crystalline media, including smectic phases, to facilitate the predominant formation of *syn*-isomers (**3**) in the model pericyclic reactions of 2,6-dialkoxyanthracenes (**2**) with a series of fumarates (**1**). The reactions were carried out at 130 to 150 °C. These studies help to clarify the relationship between the effectiveness of the liquid crystal in controlling this type of thermal reaction as well as structural requirements for both reactants and solvent mesogens. The variation in the *syn*(**3**)/*anti*(**4**) isomer ratio was further examined as a function of temperature of the reaction medium of cholesteric and smectic liquid crystals as well as for the closely related isotropic model solvents. This provides information on the effect of the liquid crystalline solvent phase on isomer distribution as this relates to differences in activation parameters between the transition states leading to *syn*(**3**) and *anti*(**4**)-isomers. It is noteworthy that a kinetic treatment of a thermal reaction conducted in liquid crystalline media has been reported by Leigh and Mitchell.¹⁵

Results

Mesomorphic Solvents Employed. Cholesteryl esters, cholesteryl 2,4-dichlorobenzoate (CDCB) and cholesteryl hydrocinnamate (CHC), were obtained commercially, and smectic compounds, bis(4-pentyloxyphenyl)*trans*-1,4-cyclohexanedicarboxylate (BPCD)¹⁶ and *trans*-1,4-cyclohexylenyl bis(4-pentyloxybenzoate) (CBPB),¹⁷ were prepared by standard procedures.¹⁶ The phase-transition temperatures for these derivatives, based on differential thermal analysis, are shown in Figure 1. The mesogenic esters, CDCB and BPCD, have a relatively broad temperature range of cholesteric and smectic mesomorphic states, respectively, at around 150 °C, at which temperature the probe pericycloadditions proceed smoothly. Thus, for the cycloadditions examined at 130 to 180 °C, CDCB and the structurally related CHC served as cholesteric and isotropic solvents. The smectic liquid crystal BPCD was used as an anisotropic (Sm A) solvent for the reactions conducted in the temperature range 150–180 °C, and the structurally similar “inverse ester”, CBPB, served as the isotropic phase solvent for control experiments.

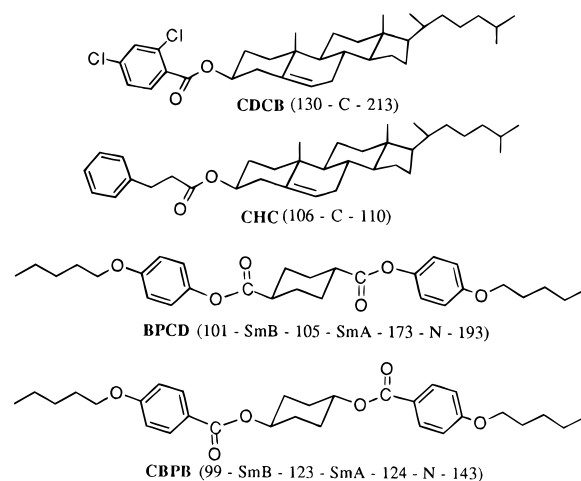


Figure 1. Liquid crystalline range (°C) (C, cholesteric phase; Sm, smectic phase; N, nematic phase).

Modification of Reactants. The reactants were modified with emphasis on the structural similarities to the mesomorphic solvents CDCB and BPCD, since solutes of a size and shape similar to those of the mesogens would be expected to be rigidly incorporated into an ordered matrix and to show reactivities specific to the solvents. A series of fumarates (**1a–c**) bearing cholesteryl or *trans*-4-cyclohexylcyclohexyl (*trans*-CC) moieties as ester groups were primarily explored as dienophiles. The *trans*-CC moiety represents a partial structure of a cholesterol skeleton with good affinity for CDCB and is stereochemically similar to BPCD. Additional ester moieties including *cis*-CC, straight-chain alkyl, and aryl groups were also examined as seen in **1d–l**. As the enophile counterparts, the 2,6-dialkoxyanthracenes with varying chain length such as 2,6-bis(decyloxy), 2,6-bis(methoxyethoxy), and 2,6-dibutoxy derivatives were used.

Assignment of *syn*- and *anti*-Cycloadducts. When an equimolar mixture of 2,6-dibutoxy- and 2,6-bis(decyloxy)-anthracenes and a series of fumarates was heated in isotropic mesitylene solution at 150 °C (for 48 h), *syn* (**3**), and *anti* (**4**) cycloadducts were obtained in 80–90% yield in a ratio of 2:1. The identities of the *syn*- and *anti*-structures, except for the aryl esters (**1e–h**),^{18, 19} were established on the basis of their NMR signals assignable to the aromatic protons, H^a (H^d) and H^c (H^f), which appeared at δ 6.74–6.90 and δ 7.03–7.20. The assignment was further confirmed by saponification to the *syn*- and *anti*-cycloadduct dicarboxylic acids (R¹ = R² = H) which were readily distinguishable from one another by their NMR spectra.^{18, 19} The *syn*/*anti* ratio was determined by NMR (400M Hz) and/or HPLC (LiCrosorb Si60)-analysis of the product mixture.

Pericycloadditions in Cholesteric Solvent (at 130 °C). A preliminary study showed that CDCB was the anisotropic solvent of choice for the highly regioselective cycloadditions of the fumarates including cholesteryl and *trans*-4-cyclohexylcyclohexyl esters to 2,6-dibutoxy- and 2,6-bis(decyloxy)-anthracenes.¹⁹ Thus, equimolar samples of dienophile (**1**) and diene (**2**) were heated in 30-fold equimolar amounts of the cholesteric CDCB solvent at 130 °C under argon. These concentrations of the solutes (6.67 mol%) were sufficiently low to maintain the mesomorphic reaction phases during the reaction period, as evidenced by differential scanning calorimetric (DSC) analysis and polarizing thermal microscopy of the doped mixtures. Table 1 shows some typical depressions of the DSC-

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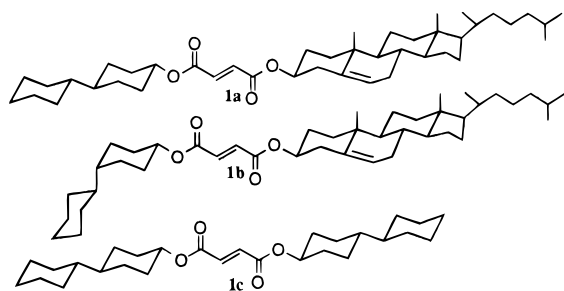
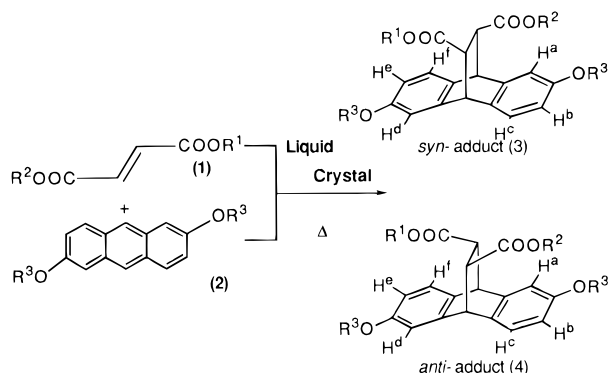


Figure 2. Fumaric acid esters primarily explored as dienophiles.

Scheme 1



detected phase-transition temperatures for reaction mixtures doped with reactants.

Cholesteryl *trans*-4-cyclohexylcyclohexyl (*trans*-CC) (**1a**) and cholesteryl *p*-phenylphenyl fumarates (**1e**) reacted with 2,6-bis(decyloxy)anthracene (**2**) in CDCB solvent at 130 °C to give surprisingly high *syn/anti* ratios of 19:1 and 15.9:1, respectively, while the reactions conducted in the isotropic media such as CHC and mesitylene resulted in significantly lower levels of diastereoselection. As seen in Table 2, the *syn/anti* ratios are highly dependent on the structures of the reactants. The cholesteric reactions with cholesteryl and *trans*-CC fumarates generally proceed with significantly higher stereoselectivities than those in the isotropic media, reflecting the unique effect of the molecular ordering of cholesteric solvent on regioselectivity. Long chain esters such as dioctyl and bis(1-pentylhexyl) fumarates (**1j**, **k**) were not so effective for regiocontrol of the cycloadditions.

Cycloadditions in Smectic Solvent (at 150 °C). The pericyclic reactions of diene and dienophile were conducted at 150 °C in the smectic BPCD solvent and the closely related CBPB, used as isotropic media under analogous conditions as above. In the reaction with 2,6-bis(decyloxy)anthracene in the smectic solvent, cholesteryl (*trans*-4-cyclohexylcyclohexyl) and bis(*trans*-4-cyclohexylcyclohexyl)fumarates (**1a** and **b**) were sufficiently effective dienophiles to allow a high level of diastereoselectivity, with *syn/anti* ratios of 16.9:1 and 15.1:1, respectively. In contrast, the isotropic reactions in CBPB gave *syn/anti* ratios of only $\geq 2.5:1$. Table 3 includes some other examples which favorably reflect the potential effect of smectic solvent phases on regioselective control of thermal cycloadditions.

Temperature Dependence of *syn* to *anti* Ratios. The *syn/anti* adduct ratios were highly temperature dependent between 130 and 180 °C in the cholesteric phase of CDCB and between 140 and 170 °C for the case of the smectic phase of BPCD. The reactions were performed in the isotropic phase of CHC and CBPB. Data relative to the cycloaddition of **1c** to **2** (R = decyl) are summarized in Table 4. For the reactions in the liquid crystal solvents, increasing the reaction temperature caused the

Table 1. Anisotropic Range of Neat and Reactant-Doped Liquid Crystals

	liquid-crystalline range (°C) ^a
CDCB ^b + none	130.0–213.0
CDCB + 6.70 mol% [1a + 2 (R = decyl)]	128.4–206.3
CDCB + 6.70 mol% [1c + 2 (R = decyl)]	126.2–196.4
BPCD ^c + none	101.0–193.1
BPCD + 6.70 mol% [1c + 2 (R = decyl)]	100.2–192.7

^a Measured by differential scanning calorimeter. ^b CDCB: cholesteryl 2,4-dichlorobenzoate. ^c BPCD: bis(*p*-pentylphenoxy) *trans*-1,4-cyclohexanedicarboxylate.

relative isomer yields to shift toward equal values, as would be expected for a homogeneous reaction mechanisms. The product ratios thus obtained were kinetic product ratios and not thermodynamic equilibrium ratios, since no isomerization of either adduct was apparent when pure samples of *syn*- and *anti*-adducts were heated at 130–180 °C for extended periods of time.

Discussion

In liquid crystalline solvents, solute molecules are probably incorporated in an optimum packing arrangement, based on steric and electronic factors. Product distribution would be expected to be regulated considerably when the reactants are designed to be accommodated efficiently in a liquid crystalline matrix, since the reaction should proceed through the pathway in favor of the least disruption of local solvent order at the transition states. Such an effect would be expected to be generally greater in tightly ordered smectic solvents than in cholesterics and nematics.

In this study, the dienophiles were modified primarily based on structural similarities to the mesogenic solvents in such a way that they would be expected to be tightly oriented with their long molecular axes and molecular planes parallel to those of liquid crystalline solvents. The fumarates bearing cholesteryl and *trans*-CC moieties whose shapes are somewhat similar to those of the mesogens and the anthracene derivatives with sufficiently long alkoxy groups would be expected to disturb the solvent order least by rigid incorporation into the liquid crystalline CDCB and BPCD solvent matrixes. This appears to be true as evidenced by the small depressions of the phase-transition temperatures upon addition to the mesomorphic solvents (Table 1).

The results clearly indicate that the observed effects are, as expected, highly dependent on solute structures and that the molecular order in both cholesteric and smectic liquid crystalline solvent phases is capable of efficiently distinguishing between *syn*- and *anti*-transition states, particularly when cholesteryl and *trans*-CC fumarates reacted with 2,6-bis(decyloxy)anthracene which might be structurally compatible with the mesogens. It is noteworthy that extremely high efficiencies of 13–19:1 (at 130 °C in cholesteric CDCB solvent) and 15–17:1 (at 150 °C in smectic BPCD solvent) were attained for the liquid crystalline phases, in contrast to the 2–3:1 ratios observed in the isotropic model solvents with closely related structures. The smectic phase reaction of 2,6-bis(decyloxy)anthracene with bis(*trans*-4-cyclohexylcyclohexyl) fumarate in BPCD gave the highest selectivity of 24:1 at 140 °C. The *trans*-substitution mode of the cyclohexyl moiety is essential for effective control and the reactions of *cis*-CC ester with 2,6-dialkoxyanthracene in either cholesteric or smectic solvent resulted in much lower selectivity (*syn*- to *anti*-ratios of 2–3:1), which is comparable to those observed for isotropic media. Efficiencies of the other esters

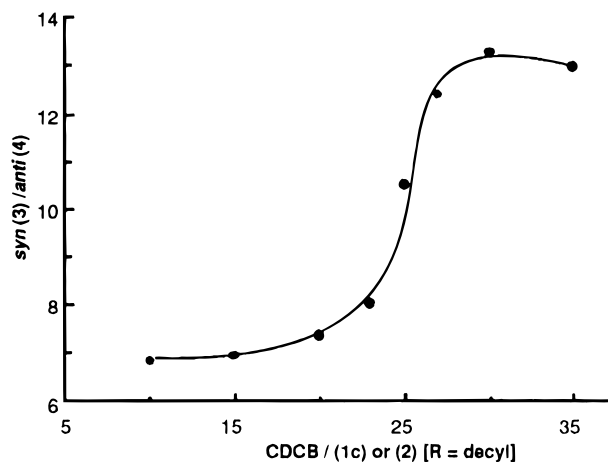


Figure 3. A plot of the *syn* (3)/*anti* (4) ratio as a function of concentrations of the solutes for thermal cycloaddition of **1c** to **2** (R = decyl) in CDCB at 130 °C.

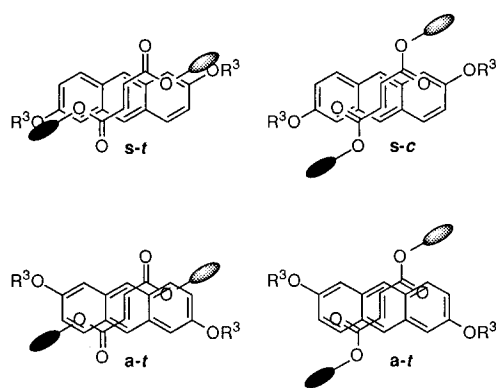


Figure 4. Relative orientation of the solutes.

examined were intermediate between those of *trans*-CC and *cis*-CC moieties.

As seen in Figure 3, the anisotropic rigidity of the local solvent order appears to play an important role in controlling the stereochemical course of the reaction, resulting in a high level of diastereoselection. When less than a 25-fold molar excess of the anisotropic solvent over the reactant diene or dienophile was used, a sharp decrease in diastereoselectivity was observed. This may be the result of either phase separation into solute-rich phases of lower order (probably isotropic) or the formation of a new less ordered mesomorphic phases, which has been extensively discussed by Leigh and co-workers.²⁰

Stereochemical control of bimolecular Diels–Alder reactions are greatly affected by anisotropic solvents, when the structures of reactants are similar to those of the mesogens, which allow them to be firmly accommodated in the liquid crystalline solvent lattice. Thus, the predominant formation of *syn*-adducts can be rationalized by the *syn*-transition states (*s-t* and *s-c*) close to the preferred dipolar orientations as is depicted in Figure 4 in which both diene and dienophile are oriented with their long molecular axes parallel to those of the mesogenic solvent molecules, in spite of relatively small differences in steric shapes between *syn*- and *anti*-orientation.

Figure 5 shows a semilogarithmic plot of inverse temperature vs the ratio of *syn*- and *anti*-cycloadducts obtained in cholesteric CDCB and isotropic CHC solvents. Similar plots were obtained from the cycloadditions conducted in smectic BPCD and model isotropic solvents (Figure 6). Differences in enthalpy

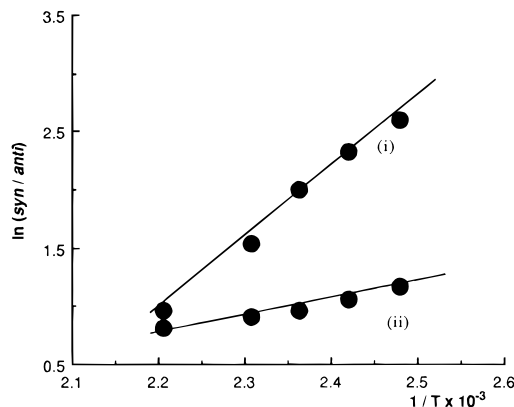


Figure 5. The *syn* to *anti* ratio dependence as a function of temperature, obtained from the reaction of **1c** and **2** (R = decyl) in (i) cholesteric CDCB and (ii) isotropic CHC solvents in the molar ratio of 1:1:30 between 130 and 180 °C.

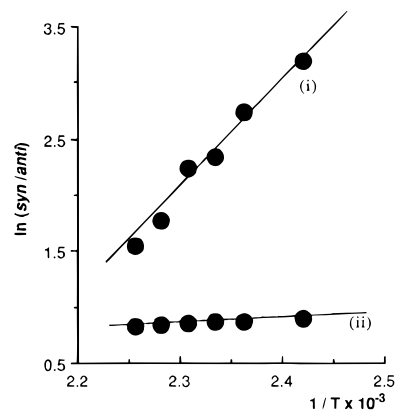


Figure 6. The *syn* to *anti* ratio dependence as a function of temperature, obtained from the reaction of **1c** and **2** (R = decyl) in (i) smectic BPCD and (ii) isotropic CBPB solvents in the molar ratio of 1:1:30 (between 140 and 170 °C).

($\Delta\Delta H^\ddagger_{\text{syn-anti}}$) and entropy ($\Delta\Delta S^\ddagger_{\text{syn-anti}}$), of the transition states leading to *syn* and *anti* cycloadducts are given by the shapes and intercepts of the plots (eq 1).

$$\ln (\text{syn}/\text{anti}) = -\Delta\Delta H^\ddagger_{\text{syn-anti}}/RT + \Delta\Delta S^\ddagger_{\text{syn-anti}}/R \quad (1)$$

As seen in Table 5, the liquid crystalline phases stabilize the *syn*-transition states by 13–19 kcal/mol, relative to the *anti*-reactive complexes. Large negative entropy differences greatly favor the formation of *syn*-adducts and the rather small enthalpy associated with bulk liquid crystalline order in mesophases. The result presented here provide a spectacular example of liquid crystal control, compared to the lower effects reported by Leigh and co-worker¹⁵ for a related case of cycloadditions.

Conclusions

Regioselective control of bimolecular pericyclic reactions conducted in liquid crystalline media depends primarily on structural similarities between the solutes and the mesogenic solvent molecules. Thus, the thermal cycloadditions of anthracenes and fumaric acid derivatives designed on the basis of structural compatibilities with the solvent mesogens proceed in either cholesteric or smectic liquid crystals with an extremely high level of diastereoselection. This study demonstrates the potential of thermotropic liquid crystalline media in controlling stereochemical courses of thermochemical reactions conducted at elevated temperatures. Studies of the temperature dependence of the isomeric *syn*- and *anti*-ratios afford estimates of the

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Table 2. Isomer Ratios from Thermal Cycloadditions of 1 to 2 in Cholesteric (CDCB) and Isotropic Solvents (CHC, Mesitylene)^a

fumarates (1)			anthracenes (2) R ³	syn(3)/anti(4) ratio ^b	
R ¹	R ²			CDCB(c) ^c	CHC(i) ^c (mesitylene)
cholesteryl	<i>trans</i> -CC ^d	(1a)	Dec	19.0	2.8 (1.7)
cholesteryl	<i>trans</i> -CC	(1a)	Bu	7.3	3.2 (1.3)
cholesteryl	<i>cis</i> -CC	(1b)	Dec	4.3	1.8 (1.4)
cholesteryl	<i>cis</i> -CC	(1b)	Bu	4.0	1.6 (1.2)
<i>trans</i> -CC	<i>trans</i> -CC	(1c)	Dec	13.3	3.2 (1.3)
<i>trans</i> -CC	<i>trans</i> -CC	(1c)	Bu	7.3	2.6 (1.3)
<i>trans</i> -CC	<i>trans</i> -CC	(1c)	MeOEt	6.2	2.2 (1.4)
<i>cis</i> -CC	<i>cis</i> -CC	(1d)	Dec	1.0	
cholesteryl	<i>p</i> -Ph-Ph	(1e)	Dec	15.9	2.8 (1.6)
<i>trans</i> -CC	<i>p</i> -Ph-Ph	(1f)	Dec	9.5	2.5 (1.6)
cholesteryl	<i>p</i> -MeO-Ph	(1g)	Dec	8.1	3.3 (1.9)
cholesteryl	<i>p</i> -MeO-Ph	(1g)	Bu	11.5	3.0 (1.9)
<i>trans</i> -CC	<i>p</i> -MeO-Ph	(1h)	Dec	8.1	2.4 (1.7)
<i>trans</i> -CC	<i>p</i> -MeO-Ph	(1h)	Bu	7.3	3.0 (1.5)
cyclohexyl	cyclohexyl	(1i)	Dec	2.3	
octyl	octyl	(1j)	Dec	1.7	
1-pentylhexyl	1-pentylhexyl	(1k)	Dec	2.0	

^a The mixture of 1 and 2 in the solvent (CDCB, CHC, and mesitylene) in a molar ratio of 1:1:30 was heated at 130 °C for 48 h. ^b Determined by ¹H-NMR (400 MHz). ^c CDCB (c): cholesteryl 2,4-dichlorobenzoate (cholesteric); CHC (i): cholesteryl hydrocinnamate (isotropic). ^d CC: 4-cyclohexylcyclohexyl.

Table 3. Isomer Ratios from Thermal Cycloadditions of 1 to 2 in Smectic (BPCD) and Isotropic Solvents (CBPB)^a

fumarates (1)			anthracenes (2) R ³	syn(3)/anti(4) ^b	
R ¹	R ²			BPCD(s) ^c	CBPB(i) ^d
cholesteryl	<i>trans</i> -CC	(1a)	Dec	16.9	2.2
<i>trans</i> -CC ^e	<i>trans</i> -CC	(1c)	Dec	15.1	1.8
[<i>trans</i> -CC	<i>trans</i> -CC	(1c)	Dec	24.0	2.4] ^f
<i>trans</i> -CC	<i>trans</i> -CC	(1c)	Bu	6.3	1.8
<i>cis</i> -CC	<i>cis</i> -CC	(1d)	Dec	1.0	1.0
<i>cis</i> -CC	<i>cis</i> -CC	(1d)	Bu	1.0	1.0
<i>trans</i> -CC	<i>p</i> -Ph-Ph	(1f)	Dec	7.5	1.8
<i>trans</i> -CC	<i>c</i> -C ₆ H ₁₁ C ₃ H ₆	(1l)	Dec	5.7	1.8

^a The reaction was performed in a molar ratio of 1:2:BPCD or CBPB of 1:1:30 at 150 °C for 48 h. ^b Determined by ¹H-NMR (400 MHz). ^c BPCD (s): bis(*p*-pentyloxyphenyl) *trans*-1,4-cyclohexanedicarboxylate. ^d CBPB (i): *trans*-1,4-cyclohexylene bis(*p*-pentyloxybenzoate). ^e CC: 4-cyclohexylcyclohexyl. ^f Performed at 140 °C.

differences of the solvation enthalpy and entropy of the transition complexes leading to *syn*- and *anti*-cycloadducts in the liquid crystalline solvents. Clearly, more studies will be required in order to develop a complete understanding of the nature of liquid crystal control of thermochemical reactions.²¹

Experimental Section

General Methods. Melting points and phase-transition temperatures were determined on a Yanaco micro melting point apparatus equipped with a polarizing microscope and/or RICO-differential scanning calorimeter (DSC) and are corrected. ¹H NMR spectra were recorded on JNX-GX400(400 MHz) in CDCl₃ with TMS as an internal standard. High resolution mass spectra (HRMS) were determined on a JEOL JMS-DX303HF high resolution mass spectrometer. Thermochemical reactions were carried out in an insulated silicon oil bath which was regulated at constant temperature ±1.0 °C by mercury thermoregulator and transistor relay.

Cholesteryl 2,4-dichlorobenzoate (CDCB) and cholesteryl hydrocinnamate (CHC) were purchased from Aldrich and Tokyo Kasei and were purified by recrystallization from hexane and CH₂Cl₂.

Bis(4-pentyloxyphenyl) *trans*-1,4-Cyclohexanedicarboxylate (BPCD). To a solution of *trans*-1,4-cyclohexanedicarbonyl chloride (5.1 g, 30 mmol) in THF (150 mL) were added 4-pentyloxyphenol (10.8 g, 60 mmol), triethylamine (6.1 g, 60 mmol), and 4-dimethylaminopyridine (1.1 g, 9 mmol), and the mixture was stirred at 50 °C for 8 h. Evaporation of the solvent followed by chromatography on silica gel (CH₂Cl₂–hexane = 8:1) gave the smectogen as colorless crystals (12.8 g, 89%), which exhibited smectic temperature range of 101 → SmB → 105 → SmA → 173 → N → 193 °C as determined by

(21) Dondoni, A.; Medici, A.; Colonna, S.; Gottarelli, G.; Samori, B. *Mol. Cryst. Liq. Cryst.* **1979**, 55, 47.

Table 4. Isomer Ratios from Thermal Cycloaddition of Bis(*trans*-4-cyclohexylcyclohexyl) Fumarate (1c) to 2,6-Bis(decyloxy)anthracene (2) in Cholesteric, Smectic and Isotropic Solvents as a Function of Temperature^a

reaction temp (°C)	syn(3)/anti(4) ^b solvent (phase)			
	CDCB(c) ^c	CHC(i) ^d	BPCD(s) ^e	CBPB(i) ^f
130	13.3	3.2		
140	10.1	2.8	24.0	2.4
150	7.4	2.5	15.1	2.4
160	4.6	2.4	9.3	2.3
170			4.7	2.3
180	2.6	2.2		

^a The mixture of 1c and 2 in the solvent in a molar ratio of 1:1:30 was heated for 48 h. ^b Determined by ¹H-NMR (400 MHz). ^c CDCB (c): cholesteryl 2,4-dichlorobenzoate (cholesteric). ^d CHC (i): cholesteryl hydrocinnamate (isotropic). ^e BPCD (s): bis(*p*-pentyloxyphenyl) *trans*-1,4-cyclohexanedicarboxylate. ^f CBPB (i): *trans*-1,4-cyclohexylene bis(*p*-pentyloxybenzoate).

DSC: ¹H NMR δ 6.97 (4H, ddd, *J* = 9.2, 2.2, 3.3 Hz), 6.86 (4H, ddd, *J* = 9.2, 2.2, 3.3 Hz), 3.92 (4H, t, *J* = 6.6 Hz), 2.50–2.63 (2H, m), 2.17–2.35 (4H, m), 1.71–1.84 (4H, m), 1.55–1.70 (4H, m), 1.26–1.50 (8H, m), 0.93 (6H, t, *J* = 6.9 Hz); HRMS (FAB) Calcd for C₃₀H₄₀O₆: 496.2825. Found: 496.2811. Anal. Calcd for C₃₀H₄₀O₆: C, 72.55; H, 8.12. Found: C, 72.53; H, 8.10.

***trans*-1,4-Cyclohexylene Bis(4-pentyloxybenzoate) (CBPB).** A mixture of 4-pentyloxybenzoyl chloride (23 mmol) prepared in situ, *trans*-1,4-cyclohexanediol (1.3 g, 11.3 mmol), and 4-dimethylaminopyridine (0.14 g, 1.1 mmol) in dry pyridine (40 mL) was stirred at 80 °C for 10 h to give the smectogen as colorless crystals (5.3 g, 94%), which

Table 5. Activation Parameters for Diels–Alder Reaction of Bis(*trans*-4-cyclohexylcyclohexyl) Fumarate (**1c**) with 2,6-Bis(decyloxy)anthracene (**2**) in Liquid Crystalline and Isotropic Solvents

medium	phase	$\Delta\Delta S_{\text{syn-anti}}^{\ddagger}$ (eu)	$\Delta\Delta H_{\text{syn-anti}}^{\ddagger}$ (kcal/mol)
CDCB ^a	cholesteric	-26 ± 1	-13 ± 1
CHC ^b	isotropic	-4 ± 1	-3 ± 1
BPCD ^c	smectic	-38 ± 2	-19 ± 1
CBPB ^d	isotropic	-6 ± 1	-3 ± 1

^a CDCB: cholesteryl 2,4-dichlorobenzoate. ^b CHC: cholesteryl hydrocinnamate. ^c BPCD: bis(*p*-pentyloxyphenyl) *trans*-1,4-cyclohexanedicarboxylate. ^d CBPB: *trans*-1,4-cyclohexylene bis(*p*-pentyloxybenzoate).

showed smectic temperature range of 99 → SmB → 123 → SmA → 124 → N → 143 °C as determined by DSC: ¹H NMR δ 7.99 (4H, ddd, J = 8.8, 1.8, 2.9 Hz), 6.92 (4H, ddd, J = 8.8, 1.8, 2.9 Hz), 5.01–5.22 (2H, m), 4.01 (4H, t, J = 6.6 Hz), 2.13–2.15 (4H, m), 1.66–1.86 (8H, m), 1.33–1.48 (8H, m), 0.94 (6H, t, J = 6.9 Hz); HRMS (FAB) Calcd for C₃₀H₄₀O₆: 496.2825. Found: 496.2788. Anal. Calcd for C₃₀H₄₀O₆: C, 72.55; H, 8.12. Found: C, 72.54; H, 8.05.

Fumaric Acid Esters (1). A series of unsymmetrical and symmetrical esters were prepared from the corresponding fumaric acid monoester and fumaryl dichloride, respectively, by standard procedures and typical compounds are given as follows.

Moncholesteryl Fumarate. The mixture of cholesterol (50 g, 129.3 mmol) and sodium hydride (3.1 g) in dioxane (300 mL) was treated with fumaryl chloride (19.8 g, 129.3 mmol) at 80 °C for 10 h. Hydrolysis (H₂O) followed by chromatography on silica gel gave the liquid crystalline monoester as colorless crystals (36.2 g, 57.7%), mp 207 → C → 254 °C (from hexane–CH₂Cl₂): [α]_D²⁵ –19.6° (c 1.0, CHCl₃); ¹H NMR δ 10.5 (1H, br), 6.93 (1H, d, J = 5.8 Hz), 6.83 (1H, d, J = 5.8 Hz), 5.40–5.41 (1H, m), 4.69–4.77 (1H, m), 0.68–2.39 (44H, m). Anal. Calcd for C₃₁H₄₈O₄: C, 76.86; H, 9.92. Found: C, 76.92; H, 10.08.

Mono-*trans*-4-cyclohexylcyclohexyl Fumarate. Analogous treatment fumaryl dichloride with *trans*-4-cyclohexylcyclohexanol (mp 174 °C) which was purely isolated from commercial material by chromatography on silica gel (Kiesel gel 60 (70–230 mesh, Merck)) gave the monoester as colorless crystals (1.62 g, 76.2%): mp 174 °C (from hexane); ¹H NMR δ 8.35 (1H, br), 6.90 (2H, dd, J = 13.2, 12.6 Hz), 4.67–4.82 (1H, m), 2.01–2.05 (2H, m), 1.63–1.81 (7H, m), 1.32–1.41 (2H, m), 1.06–1.25 (7H, m), 0.91–0.99 (2H, m). Anal. Calcd for C₁₆H₂₄O₄: C, 68.55; H, 8.63. Found: C, 68.51; H, 8.70.

Cholesteryl *trans*-4-cyclohexylcyclohexyl Fumarate (1a). Yield: 67.2%; mp 185 → C → 258 °C (from hexane); [α]_D²⁵ –6.24° (c 1.0, CHCl₃); ¹H NMR δ 7.26 (2H, s), 6.81 (2H, s), 5.39 (1H, d, J = 3.7 Hz), 4.69–4.77 (2H, m), 0.68–2.37 (61H, m). Anal. Calcd for C₄₃H₆₈O₄: C, 79.58; H, 10.56. Found: C, 79.81; H, 10.81.

Cholesteryl *cis*-4-cyclohexylcyclohexyl Fumarate (1b). Yield: 58.0%; mp 107 °C (from hexane); [α]_D²⁵ –10.2° (c 1.0, CHCl₃); ¹H NMR δ 6.83 (2H, d, J = 5.1 Hz), 5.40 (1H, d, J = 3.7 Hz), 5.08–5.13 (1H, m), 4.71–4.74 (1H, m), 2.38 (2H, d, J = 7.3 Hz), 0.86–2.03 (60H, m), 0.68 (3H, m). Anal. Calcd for C₄₃H₆₈O₄: C, 79.58; H, 10.56. Found: C, 79.79; H, 10.73.

Bis(*trans*-4-cyclohexylcyclohexyl) Fumarate (1c). Yield: 97.8%; mp 170 °C (from hexane–CH₂Cl₂); ¹H NMR δ 6.81 (2H, s), 4.72–4.77 (2H, m), 2.01–2.05 (2H, m), 1.59–1.80 (14H, m), 0.95–1.35 (22H, m). Anal. Calcd for C₂₈H₄₄O₄: C, 75.62; H, 9.99. Found: C, 75.34; H, 10.13.

Bis(*cis*-4-cyclohexylcyclohexyl) Fumarate (1d). Yield: 92.9%; mp 104 °C (from hexane–CH₂Cl₂); ¹H NMR δ 6.84 (2H, s), 5.09–5.13 (2H, m), 1.90–1.94 (2H, m), 1.50–1.74 (14H, m), 1.31–1.41 (4H, m), 1.08–1.26 (10H, m), 0.95–0.99 (4H, m). Anal. Calcd for C₂₈H₄₄O₄: C, 75.62; H, 9.99. Found: C, 75.35; H, 10.21.

Cholesteryl *p*-Phenylphenyl Fumarate (1e). Yield: 70.7%; mp 174 → C → 269 °C (from CCl₄); [α]_D²⁵ –15.3° (c 1.0, CHCl₃); ¹H NMR δ 7.56–7.61 (4H, m), 7.42–7.45 (2H, m), 7.33–7.45 (1H, m), 7.20–7.25 (2H, m), 7.06 (2H, s), 5.41–5.42 (1H, m), 4.75–4.78 (1H, m), 0.68–2.41 (43H, m). Anal. Calcd for C₄₃H₅₆O₄: C, 81.13; H, 8.81. Found: C, 81.02; H, 8.95.

***trans*-4-Cyclohexylcyclohexyl *p*-Phenylphenyl Fumarate (1f).** Yield: 79.5%; mp 171 °C (from hexane–CCl₄); ¹H NMR δ 7.19–7.62 (9H, m), 7.02 (2H, s), 4.79 (1H, m), 2.07 (2H, d, J = 11.4 Hz), 1.56–1.82 (6H, m), 1.35–1.43 (2H, m), 0.92–1.26 (8H, m). Anal. Calcd for C₂₈H₃₂O₄: C, 77.75; H, 7.46. Found: C, 77.88; H, 7.40.

Cholesteryl *p*-Methoxyphenyl Fumarate (1g). Yield: 78.2%; mp 129 → C → 240 °C (from hexane–CCl₄); [α]_D²⁶ –11.3° (c 1.0, CHCl₃); ¹H NMR δ 7.05 (2H, dm, J = 10.3 Hz), 7.02 (2H, s), 6.90 (2H, dm, J = 10.3 Hz), 5.40–5.43 (1H, m), 4.71–4.79 (1H, m), 3.80 (3H, s), 0.68–2.4 (43H, m). Anal. Calcd for C₃₈H₅₄O₅: C, 79.59; H, 9.52. Found: C, 79.83; H, 9.68.

***trans*-4-Cyclohexylcyclohexyl *p*-Methoxyphenyl Fumarate (1h).** Yield: 60.8%; mp 107 °C (from hexane–CCl₄); ¹H NMR δ 7.05 (2H, dd, J = 8.1, 2.2 Hz), 7.014 (1H, s), 7.008 (1H, s), 6.91 (2H, dd, J = 8.1, 2.2 Hz), 4.66–4.82 (1H, m), 3.81 (3H, s), 2.02–2.08 (2H, m), 1.57–1.82 (7H, m), 1.32–1.41 (2H, m), 1.07–1.25 (7H, m), 0.94–1.01 (2H, m). Anal. Calcd for C₂₃H₃₀O₅: C, 71.42; H, 7.76. Found: C, 71.18; H, 7.79.

Dicyclohexyl Fumarate (1i). Yield: 89.5%; mp 37 °C (from hexane); ¹H NMR δ 6.82 (2H, s), 4.72–4.88 (2H, m), 1.24–1.89 (20H, m). Anal. Calcd for C₁₆H₂₄O₄: C, 68.54; H, 8.65. Found: C, 68.33; H, 8.61.

Diocetyl Fumarate (1j). Yield: 75.0%; ¹H NMR δ 6.82 (2H, s), 4.17 (4H, t, J = 6.7 Hz), 0.87–1.76 (30H, m); HRMS (EI) Calcd for C₂₀H₃₆O₄: 340.2614. Found: 340.2610.

Bis(1-pentylhexyl) Fumarate (1k). Yield: 68.3%; ¹H NMR δ 6.72 (2H, s), 4.88–5.03 (2H, m), 0.78–1.79 (44H, m); HRMS (CI) Calcd for C₂₆H₄₈O₄: 424.3552. Found: 424.3548.

***trans*-4-Cyclohexylcyclohexyl (Cyclohexylpropyl) Fumarate (1l).** Yield: 70.8%; mp 55 °C (from EtOH); ¹H NMR δ 6.82 (2H, s), 4.72–4.88 (2H, m), 4.18 (2H, t, J = 3.3 Hz), 2.23–2.28 (2H, m), 1.65–1.82 (14H, m), 1.36–1.42 (2H, m), 1.06–1.25 (13H, m), 0.86–0.99 (4H, m). Anal. Calcd for C₂₅H₄₀O₄: C, 74.22; H, 9.97. Found: C, 73.97; H, 10.12.

2,6-Dialkoxyanthracenes (2). Compounds (**2**) were obtained by alkylation of 2,6-dihydroxyanthracene (mp 297 °C, 78%)¹⁹ prepared by reacting anthraflavic acid with an excess of the corresponding alkyl bromide (8.0 equiv) in the presence of Cs₂CO₃ (3.0 equiv) in boiling acetone for 10 h.

2,6-Dibutoxyanthracene. Yield: 81.0%; mp 202 °C (from CCl₄); ¹H NMR δ 8.15 (2H, s), 7.80 (2H, d, J = 9.9 Hz), 7.14 (2H, d, J = 2.2 Hz), 7.13 (2H, dd, J = 2.2, 9.9 Hz), 4.09 (4H, t, J = 6.6 Hz), 1.84 (4H, tt, J = 6.6, 7.7 Hz), 1.55 (4H, tt, J = 7.3, 7.7 Hz), 1.01 (6H, t, J = 7.3 Hz); HRMS (EI) calcd for C₂₂H₂₆O₂: 322.1933. Found: 322.1915. Anal. Calcd for C₂₂H₂₆O₂: C, 81.95; H, 8.18. Found: C, 82.23; H, 7.90.

2,6-Bis(decyloxy)anthracene. Yield: 75.3%; mp 141 °C (from hexane); ¹H NMR δ 8.16 (2H, s), 7.82 (2H, d, J = 8.8 Hz), 7.15 (2H, d, J = 2.6 Hz), 7.14 (2H, dd, J = 2.6, 8.8 Hz), 4.09 (4H, t, J = 6.6 Hz), 1.87 (4H, tt, J = 6.6, 7.0 Hz), 1.28–1.57 (28H, m), 0.89 (6H, t, J = 7.0 Hz); HRMS (EI) calcd for C₂₂H₂₆O₂: 490.3811. Found: 490.3821. Anal. Calcd for C₂₂H₂₆O₂: C, 83.21; H, 10.27. Found: C, 83.00; H, 10.52.

2,6-Bis(methoxyethoxy)anthracene. Yield: 63.4%; mp 195 °C (from hexane); ¹H NMR δ 8.17 (2H, s), 7.83 (2H, d, J = 9.1 Hz), 7.20 (2H, dd, J = 2.2, 9.1 Hz), 7.16 (2H, d, J = 2.2 Hz), 4.26 (4H, dd, J = 4.7, 5.6 Hz), 3.84 (4H, dd, J = 4.7, 5.6 Hz), 3.49 (6H, s); HRMS (EI) calcd for C₂₀H₂₂O₄: 326.1518. Found: 326.1491. Anal. Calcd for C₂₀H₂₂O₄: C, 73.59; H, 6.79. Found: C, 73.32; H, 6.70.

Cycloaddition in Liquid Crystalline Solvents. General Procedure. A degassed mixture of 2,6-dialkoxyanthracene (0.3 mmol) and the fumarate (0.3 mmol) in cholesteric (CDCB) or smectic (CBPB) solvent (9 mmol) was stirred under argon gas at 130 or 150 °C for 48 h, retaining the liquid crystalline phases during the period of reaction. A large portion of the liquid crystalline solvents were removed from the reaction mixture by chromatography on silica gel with CH₂Cl₂–hexane (1:2) as eluent, and the cycloadducts were obtained as a diastereomeric mixture in 60–70% yields.

The *syn/anti*-isomer ratios were obtained on the basis of the resolved peaks of the aromatic protons in the ¹H NMR spectra of the cycloadducts. This ratio was further confirmed by saponification of the cycloadducts with KOH (at 80 °C for 4 h in EtOH) to the

dicarboxylic acids. Diastereoselectivity was further measured using on a LiCrosorb Si60 Column (1.0% ethyl acetate/hexane). Clear-cut separation of *syn*- and *anti*-cycloadducts was performed by careful chromatography on silica gel. Typical cycloadducts are given below.

Bis(*trans*-4-cyclohexylcyclohexyl) 2,6-Bis(decyloxy)-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylates. *syn*-Adduct: mp 125 °C; ^1H NMR δ 7.19 (2H, d, J = 8.1 Hz), 6.76 (2H, d, J = 2.2 Hz), 6.55 (2H, dd, J = 8.1, 2.2 Hz), 4.52–4.61 (2H, m), 4.41–4.58 (2H, m), 3.88 (2H, t, J = 12.5 Hz), 3.86 (2H, t, J = 12.6 Hz), 3.35–3.38 (2H, m), 0.82–2.20 (78H, m). Anal. Calcd for $\text{C}_{62}\text{H}_{94}\text{O}_6$: C, 79.61; H, 10.13, Found: C, 79.39; H, 10.11.

anti-Adduct: mp 121 °C; ^1H NMR δ 7.05 (2H, d, J = 8.1 Hz), 6.89 (2H, d, J = 2.2 Hz), 6.58 (2H, dd, J = 8.1, 2.2 Hz), 4.52–4.61 (2H, m), 4.41–4.58 (2H, m), 3.88 (2H, t, J = 12.5 Hz), 3.86 (2H, t, J = 12.6 Hz), 3.35–3.38 (2H, m), 0.82–2.20 (78H, m). Anal. Calcd for $\text{C}_{62}\text{H}_{94}\text{O}_6$: C, 79.61; H, 10.13, Found: C, 79.37; H, 10.24.

Cholesteryl (*trans*-4-Cyclohexylcyclohexyl) 2,6-Bis(decyloxy)-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylates. *syn*-Adduct: mp 140 °C; ^1H NMR δ 7.19 (2H, d, J = 8.1 Hz), 6.74–6.79 (2H, m), 6.55–6.62 (2H, m), 5.32 (1H, d, J = 5.5 Hz), 4.55–4.60 (2H, m), 4.47–4.53 (2H, m), 3.85–3.88 (2H, m), 3.37–3.41 (2H, m), 0.68–2.36 (101H, m). Anal. Calcd for $\text{C}_{77}\text{H}_{118}\text{O}_6$: C, 81.14; H, 10.44, Found: C, 81.37; H, 10.71.

anti-Adduct: mp 137 °C; ^1H NMR δ 7.03–7.09 (2H, m), 6.90 (2H, J = 1.8 Hz), 6.55–6.62 (2H, m), 5.32 (1H, d, J = 5.5 Hz), 4.55–4.60 (2H, m), 4.47–4.53 (2H, m), 3.85–3.88 (2H, m), 3.37–3.41 (2H, m), 0.68–2.36 (101H, m). Anal. Calcd for $\text{C}_{77}\text{H}_{118}\text{O}_6$: C, 81.14; H, 10.44, Found: C, 81.23; H, 10.54.

2,6-Bis(decyloxy)-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic Acid. *syn*-Adduct: ^1H NMR δ 7.14 (2H, d, J = 8.1 Hz), 6.84 (2H, d, J = 2.2 Hz), 6.60 (2H, dd, J = 2.2, 8.1 Hz), 4.30 (2H, s), 3.88 (4H, t, J = 7.0 Hz), 3.31 (2H, s), 1.72 (4H, t, J = 7.0 Hz), 1.18–1.52 (28H, m), 0.88 (6H, t, J = 7.0 Hz).

anti-Adduct: ^1H NMR δ 7.17 (2H, d, J = 8.0 Hz), 6.84 (2H, d, J = 2.2 Hz), 6.56 (2H, dd, J = 2.2, 8.0 Hz), 4.30 (2H, s), 3.88 (4H, t, J = 7.0 Hz), 3.31 (2H, s), 1.72 (4H, t, J = 7.0 Hz), 1.18–1.52 (28H, m), 0.88 (6H, t, J = 7.0 Hz).

Supporting Information Available: Table 1s of chemical shifts assignable to H^a (H^d), H^b (H^e), and H^c (H^f) protons for all the cycloadducts described here and ^1H NMR spectra of typical *syn*- and *anti*-cycloadducts (**3** and **4**) ($\text{R}^1 = \text{R}^2 = \text{trans-CC}$, $\text{R}^3 = \text{decyl}$) (2 pages). See any current masthead page for ordering information.

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