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Evidence for random parallel and anti-parallel packing between neighbouring cholesteryl 4-(2-anthryloxy)butyrate (*CAB*) molecules in the cholesteric liquid-crystalline phase

Identification of the four photodimers from *CAB*†

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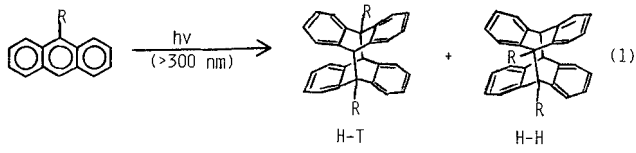
The packing arrangements of cholesteryl 4-(2-anthryloxy)butyrate (*CAB*) have been investigated in its cholesteric liquid-crystalline, neat isotropic, and solution isotropic phases by analysing the distributions of photodimers obtained from each. The four photodimers of *CAB* have been identified unambiguously. Their distribution indicates that neighbouring pairs of *CAB* in the liquid-crystalline phase experience orientations that are parallel and anti-parallel with about equal probability.

1. Introduction

Although the cholesteric phase consists of a twisted nematic-like structure in which a helical arrangement can be detected macroscopically, neighbouring molecules are aligned, on average, in a parallel or anti-parallel orientation. In an attempt to explore the distribution of parallel and anti-parallel pairs in a cholesteric mesophase and to compare it with the packing arrangements experienced by the same molecules in other phases [2], we have synthesized and irradiated cholesteryl 4-(2-anthryloxy)-butyrate (*CAB*) in various environments.

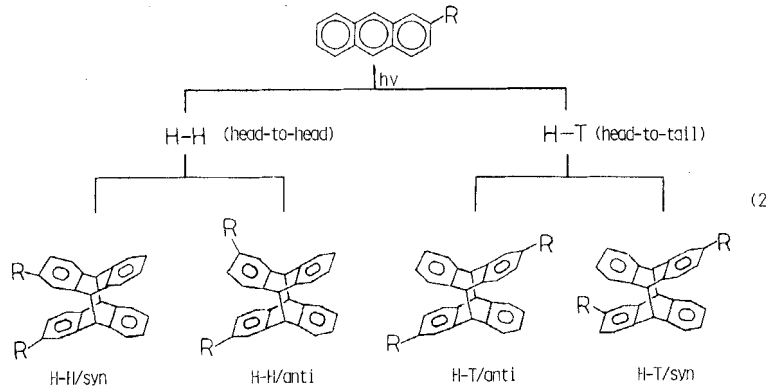
The photodimerization of anthracene and easily accessible 9- or 9,10-substituted anthracenes (equation 1) has been studied extensively in solution and solid phases [3]. The usual course of the reaction is cycloaddition across the 9 and 10 positions [3i], leading to no more than two photodimers.



(1)

The use of *CAB* introduces additional complexities to analyses of the reaction mixtures. Instead of the two possible photodimers from a 9-substituted anthracene, *CAB* allows as many as four, 2 head-to-head (H–H) and 2 head-to-tail (H–T) (equation (2)). However, the two H–H dimers arise from excitation of parallel-aligned *CAB* neighbours and the two H–T dimers derive from anti-parallel alignment. For this reason, the ratio of H–H/H–T should reflect, at least indirectly, the ground state distribution of parallel and anti-parallel pairs of *CAB* molecules. The exact relationship will be scrutinized more carefully in the Results and Discussion Sections.

†See reference [1].



In fact, the four photodimers of a 2-substituted anthracene have not been characterized previously. De Schryver and coworkers [4] examined the intramolecular photodimerizations of a series of polymethylene-bis-2-anthroates that are restrained to form only the H–H/*syn* and H–H/*anti* dimers. They were able to separate and characterize the two photodimers, examining their ratio as a function of polymethylene chain length. Tamaki and coworkers [5] found that irradiation of anthracene-2-sulphonates in water or aqueous solutions containing cyclodextrins produces three separable photodimers. The assignment of two of them as H–H and the third as H–T is based largely upon expected chemical shifts for the isomers.

Here, we describe the synthesis of *CAB*, investigate its various phases, and report the separation, identification, and distribution of its photodimers in each phase. The results indicate that the packing in the non-crystalline phases is rather random with respect to parallel and anti-parallel orientations of neighbouring molecules.

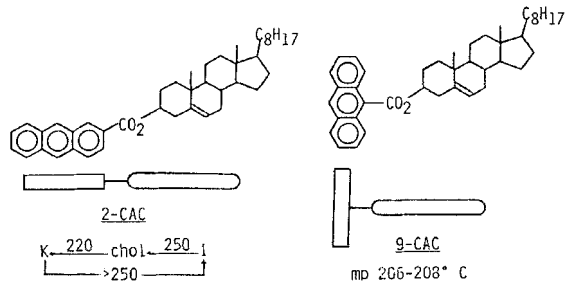
2. Results and discussion

2.1. *Rationale for selection of CAB*

The choice of *CAB* as the target molecule was predicated upon several considerations.

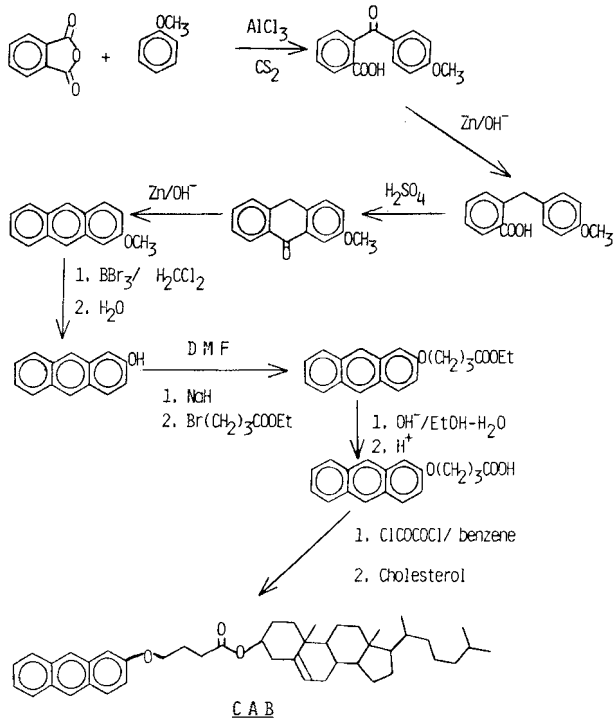
(1) Due to strong deviations from a rod-like shape, cholesteryl 9-anthracenecarboxylate (9-*CAC*) is not mesomorphic [6]. By contrast, 2-*CAC* is both rod-like and forms a cholesteric phase [6].

(2) Steric hindrance between two molecules of 2-*CAC* aligned head-to-head might preclude their photodimerization. Such an example was found in our previous study with 5α-cholestan-3β-yl cinnamate [7]. Thus, a longer space between the anthracenyl and cholesteryl groups was deemed necessary since a primary objective of this work is to relate the head-to-head to head-to-tail ratio of photodimers to the orientations of the constituent molecules in their neat phases.



2.2. *Synthesis of CAB*

The synthesis of *CAB* was accomplished in 8 steps as outlined in Scheme 1. The steps leading to 2-methoxyanthracene were adapted from Iwata and Emoto [8]. This ether, when treated with BBr_3 and then water, afforded 2-hydroxyanthracene that appeared to ketonize slowly even as a dry solid. Thus, it was generated as needed and used immediately with sodium hydride and ethyl 4-bromobutanoate to obtain the stable ester, ethyl 4-(2-anthryloxy)butanoate. Basic hydrolysis of the ester and formation of the acid chloride with oxalyl chloride followed by addition of cholesterol yielded the final product, *CAB*, in 5 per cent overall yield starting from phthalic anhydride and anisole and in 24 per cent yield starting from 2-methoxyanthracene.

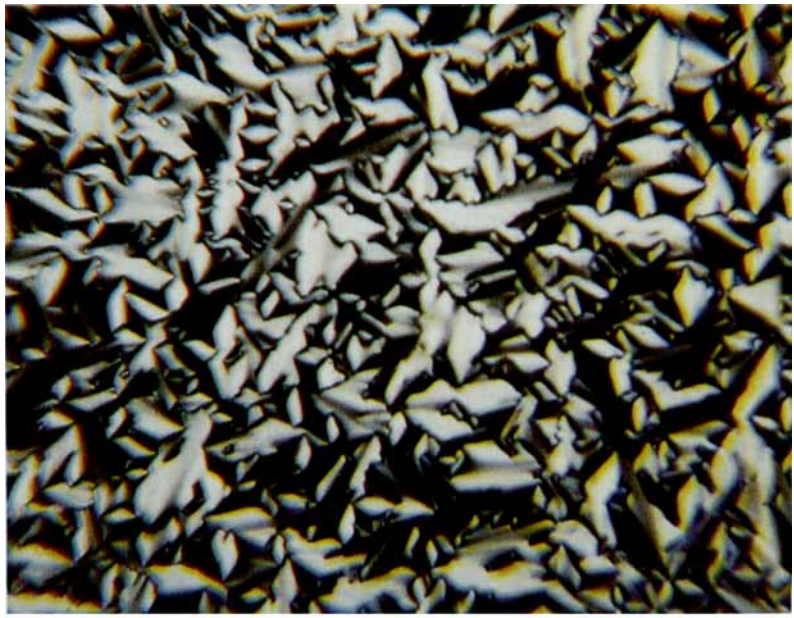


Scheme 1. Synthesis of *CAB*.

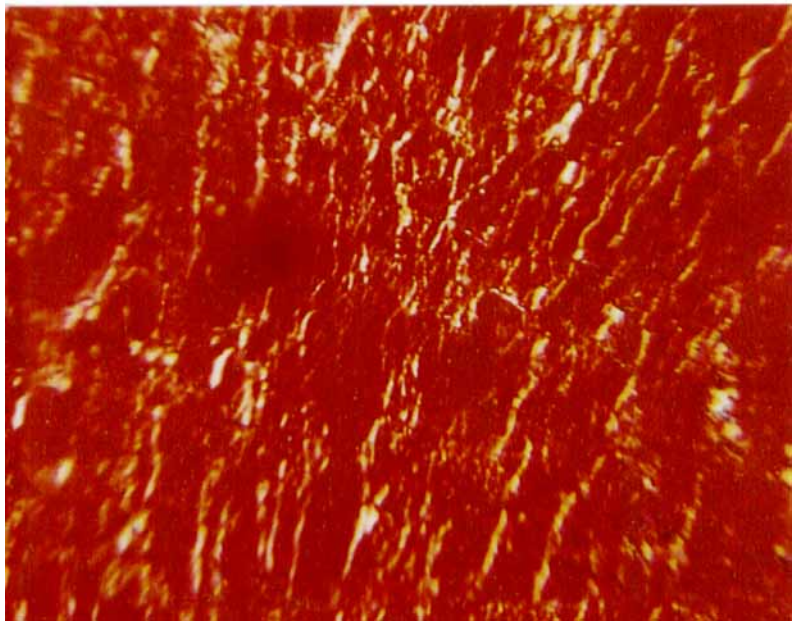
2.3. *Phase characterizations of CAB*

The morphology of the *CAB* phases is based primarily upon optical microscopic observations and miscibility studies. *CAB* melts at 204–206°C upon heating and forms a monotropic mesophase (196–160°C) when cooled. Below 160°C, it solidifies to a solid state which appears identical to the one obtained from solution recrystallization.

A thin sample of *CAB*, sandwiched between untreated glass plates, was examined between crossed polarizers at 100× magnification. Under these conditions, cooled isotropic *CAB* formed a single Maltese cross-like pattern at 196°C that was quickly replaced by a fan-shaped texture with focal conics (figure 1 (*a*)). If subjected to a lateral twisting force (i.e. circular motion of one plate with respect to the other), the sample was transformed into an oily streak pattern (figure 1 (*b*)). Although the fan-shaped texture is consistent with either a smectic A [9] or a cholesteric phase [10],



(*a*)



(*b*)

Figure 1. Optical micrographs (× 100) of *CAB* in its cholesteric phase. (*a*) fan-shaped (focal-conic) texture at 185°C. (*b*) oily-streak (Grandjean) texture at 185°C.

the oily streaks are unique to the latter [11]. The cross, fans, and streaks correspond to different states of the cholesteric phase in which, respectively, the *CAB* directors are homeotropically aligned (i.e. perpendicular to the glass plates), the axes of the helices formed by the twist of the directors are perpendicular to the light observation path, and the axes of the helices are parallel to the light observation path [12].

Miscibility studies [13] of *CAB* with known cholesteric liquid crystals also demonstrated the nature of its mesophase. Thus, cholesteryl cinnamate, cholesteryl nonanoate, or cholesteryl propanoate could be mixed with *CAB* in all ranges of compositions while retaining the disturbed oily streak optical pattern characteristic of a cholesteric phase. Addition of small amounts of a non-mesogenic molecule [6], 2-methoxyanthracene or 2-dodecyloxyanthracene, were sufficient to destroy the mesophase of *CAB*.

2.4. *Photodimerization of CAB*

The photodimerization of anthracene and its derivatives has been studied in considerable detail [2*a*, 4, 14]. Reaction emanates from the singlet state of the anthracenyl group [15]. Especially in viscous media, the short lifetime of the singlet states ($\tau \sim 5$–15 ns [16]) precludes significant motion between the moment of excitation and intramolecular cycloaddition. Thus, only concentrated solutions are capable of leading to efficient reaction. Excimer emission, although detectable from solid anthracenes, is negligible in solution [4, 17].

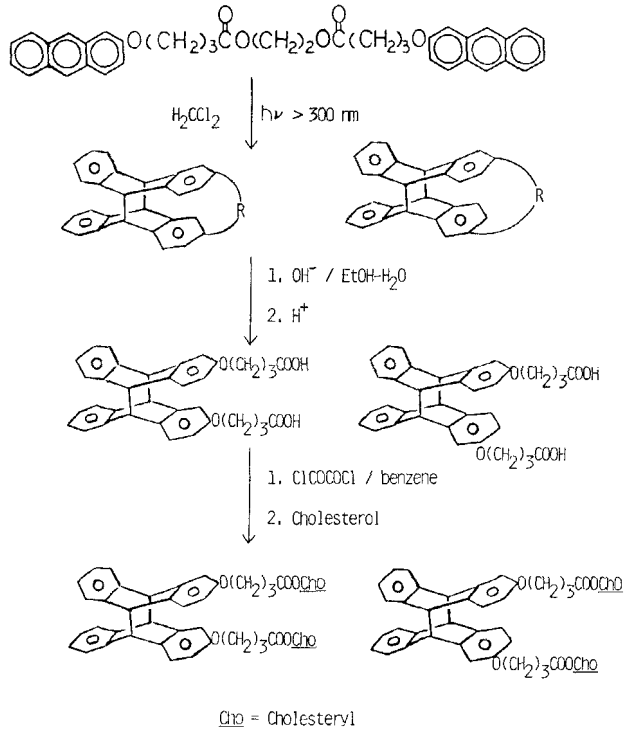
In the absence of oxygen, preparative irradiations (> 300 nm) of *c.* 10^{-2} M *CAB* in benzene at 39°C, in *n*-hexadecane at 190–210°C, or in methylene chloride at 28°C led to similar mixtures of photoproducts. A typical chromatogram of a reaction mixture is shown in figure 2(*a*). Others differed in the relative intensities of product peaks, but not in their number.

In addition to that from unreacted *CAB* (retention time ~ 3 min), three other peaks could be detected. They were separated by a laborious hplc procedure on an analytical silica gel column and marked *DHTA*, *DHTS*, and *D4HH* (see figure 2(*c*)–(*e*)).

Evidence of the dimeric nature of the products was first obtained from U.V. absorption spectroscopy. The spectrum of *CAB* (figure 3(*a*)) displays the diagnostic vibronic progression of the anthracenyl ^1L_a transition [18]. By comparison, the three isolated product fractions have very similar absorption spectra that are much more consistent with a disturbed, isolated phenyl chromophore: the first absorption maxima occur ~ 270 nm. If photodimerization had occurred across the 1,2, 1,4, or 5,8 positions of the anthracenyl group of *CAB* [14(a), 19], a naphthyl-like absorption would have obtained for the photoproducts. Figures 3(*b*)–(*d*) are clearly inconsistent with the presence of such a chromophore: for example, 2-methoxynaphthalene exhibits absorption maxima to 327 nm (ε 2100) [20].

Authentic H–H/*syn* and H–H/*anti* photodimers (equation 2) were synthesized as shown in Scheme 2. For steric reasons [21], irradiation of a dilute (*c.* 10^{-4} M) solution of 1,2-di(4-(2-anthryloxy)butanoyloxy)ethane (*DBE*) in dichloromethane can yield only the *syn* and *anti* H–H intramolecular photodimers. The dimers were hydrolyzed as a mixture, converted to their diacid dichlorides, and then esterified with an excess of cholesterol. Both *D4HH* and the resulting product mixture (*DHH*) exhibit the same hplc retention times (figures 2(*b*) and (*c*)). Furthermore, the U.V. absorption spectrum of *DHH* (figure 3(*e*)) is very similar to those in figures 3(*b*)–(*d*). On this basis, *D4HH* is assigned (and confirmed by N.M.R. spectroscopy; *vide infra*) to be a mixture of H–H/*syn* and H–H/*anti* dimers.

Proton magnetic resonance spectroscopy of the photodimers and the authentic *DHH* mixture confirmed that they are the species shown in equation (2). In the low field region of the spectra, none of the dimers retained the 9,10 peaks from the



Scheme 2. Synthesis of *DHH*.

anthracenyl group in *CAB* (8·2–8·3 ppm). They did, however, display peaks of the 5,6-double bond (5·4 ppm) in the cholesteryl group (as well as the other aliphatic proton signals). The latter observation eliminates the possibility of an intramolecular addition [7] between the double bond of cholesteryl and the 9,10-positions of anthracenyl. A summary of the assignments of the protons in *CAB* and its H–H photodimers is given in table 1.

Figure 4 presents the low field portions of the 500 MHz N.M.R. spectra of *DHH* and the *CAB* photodimers. It clearly demonstrates that *D4HH* and *DHH* consist of two different mixtures of *syn* and *anti* H–H dimers. This requires that *DHTS* and *DHTA* be the two H–T dimers.

To distinguish the *syn* from *anti* in the H–H and H–T pairs, we rely upon the molecular symmetry of the meso protons, H_d and H_e, of the dimers (4·40–4·45 ppm). Vicinal meso protons in the *syn* dimers are symmetry equivalent and, therefore, do not lead to detectable coupling; the two pairs of meso protons should give rise to two singlets of equal intensity. Vicinal meso protons in the *anti* dimers are symmetry inequivalent and should lead to detectable coupling; the two vicinal pairs of each dimer, taken as a system, are equivalent so that only one *AB* pattern is expected.

On this basis *DHTS* is clearly the H–T/*syn* dimer and *DHTA* is clearly the *anti*. Careful inspection of the meso patterns from *DHH* and *D4HH* allows them to be interpreted as superimposing pairs of singlets and *AB* patterns (see designations on the spectra). The *syn*/*anti* proportions from each mixture calculated in this way are confirmed by examining the 6·5 ppm signals due to the H_a protons: the *syn* doublet

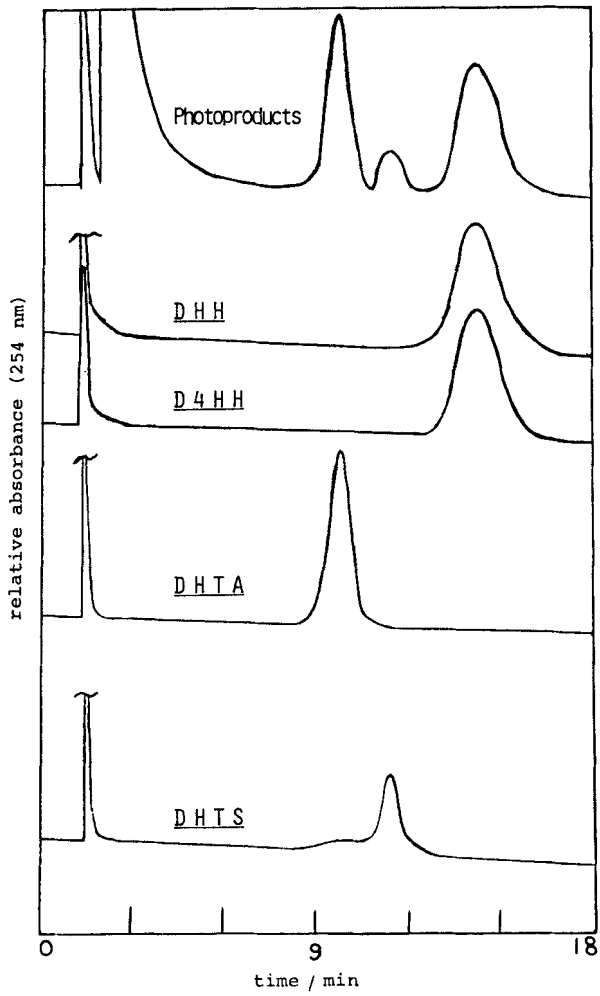


Figure 2. HPLC chromatograms of *CAB* and its photodimers. The peak at *c.* 3 min. is *CAB*. Waters Radial Pak silica column with 2·5 mL/min eluent (80/20 (v/v) hexane/chloroform) flow rate.

appears farther downfield than the *anti*. Both analyses indicate *syn/anti* ratios of *c.* 1/4 and 1/1 in *DHH* and *D4HH*, respectively.

2.5. *Thermal stability of photodimers*

It is known that head-to-head photodimers of 9-substituted anthracenes are unstable to heat even at room temperature [14 (*a*)]. To determine whether the *CAB* photodimers are stable under the conditions of their formation, they were heated for various periods in eicosane. Analyses were performed by U.V. absorption (i.e., following the increase in ^1L_a absorption intensity from newly reformed *CAB*) or by hplc (i.e. following the decrease in size of dimer peaks relative to an internal standard). Both the H–H and H–T dimers exhibit half-lives of *c.* 40 min. and rate constants $\sim 0{\cdot}014\,\text{min}^{-1}$ at 174°C. The rate of decomposition of *DHTA* doubled when the temperature was raised from 172° to 184°C. Thus, we extrapolate the half-life of the

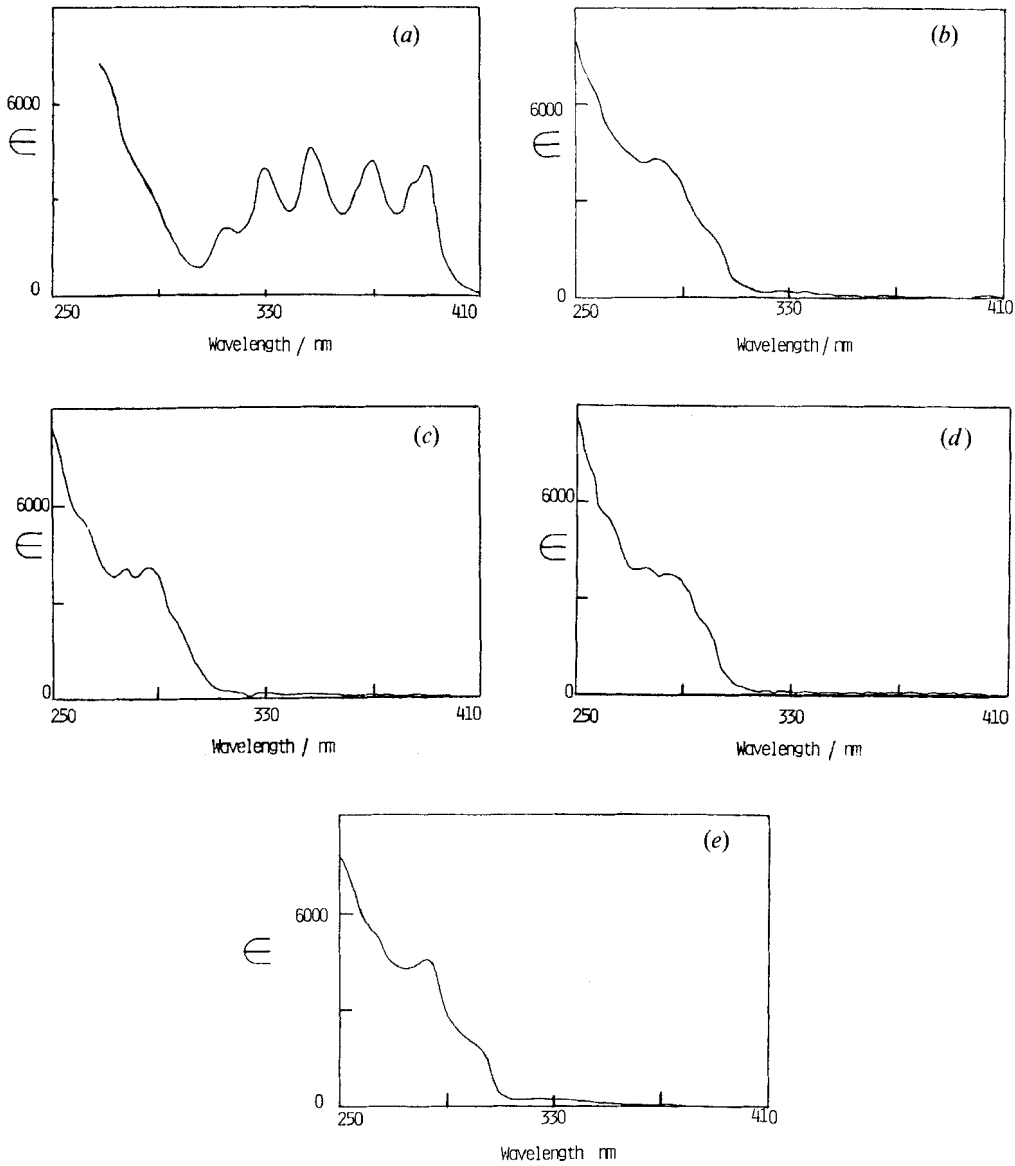
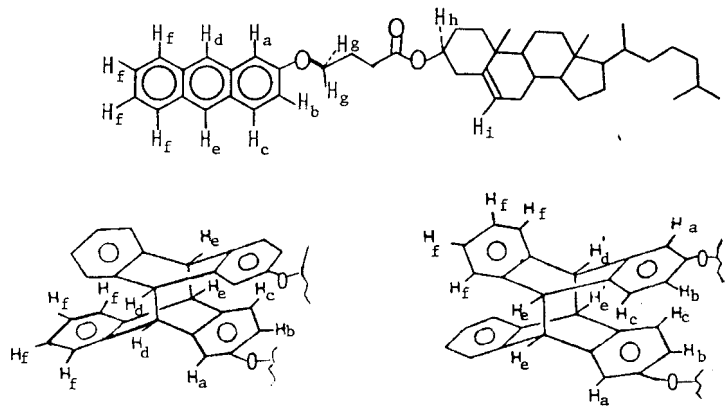


Figure 3. U.V./vis absorption spectra of *CAB* and its photodimers. (*a*) 4·6 × 10^{-5}M *CAB* in hexadecane. (*b*) 2·7 × 10^{-5}M *D4HH* in hexadecane. (*c*) 2·3 × 10^{-4}M *DHTA* in methylene chloride. (*d*) 2·0 × 10^{-4}M *DHTS* in methylene chloride. (*e*) 3·1 × 10^{-5}M *DHH* in hexadecane.

dimers at 207°C, the highest temperature at which *CAB* was irradiated, to be about 10 min. Since irradiations (and, therefore, heating) at this isotropic temperature and near 180°C in the cholesteric phase were continued for very short periods (usually 60 s) to provide only low conversions of *CAB* to photodimers, the thermal decomposition of products is negligible: the photodimer distributions observed are the same as those that are formed.

Table 1. ^{1}H NMR assignments of *CAB* and its head-to-head dimers.



Protons†	Dimer		*CAB*	
	Ppm	Multiplicity‡	Ppm	Multiplicity
Ha	6·3	d, J(HaHb) = 3 Hz	–	
Hb	6·5	d–d, J(HbHa) = 3 Hz	7·10–7·18	
		J(HbHc) = 8 Hz	7·35–7·46	m
Hc	6·74		7·53–8·00	
	6·78	d, J(HcHb) = 8 Hz		
Hf	6·8–6·9	m		
Hd	4·4–4·45	see figure 4	8·2	s
He			8·3	s
Hg	3·9	m	4·17	m
Hh	4·5–4·7	m	4·5–4·7	m
Hi	5·4	d	5·4	d

† in $CDCl_3$/TMS.
‡ d, doublet; d–d, doublet–doublet; s, singlet; m, multiplet.

2.6. *Photodimerization of CAB in various phase*

Photodimers of *CAB* were detected after irradiation of solutions of 'normal' solvents, the neat isotropic phase, and the monotropic cholesteric phase [22]. The solid phase of *CAB* did not yield photodimers after protracted irradiation. The results are summarized in table 2. In all cases, the per cent conversion of *CAB* was kept low (< 20 per cent) to avoid severe disturbance of the phase morphology by products. The most obvious conclusion that can be deduced from table 2 is that H–H and H–T dimerizations in each of the phases (except the solid) occur with about equal probability. In the solid phase, the anthracenyl groups must be locked into positions (based upon intermolecular separations or orientations) that preclude their reaction.

2.7. *Analysis of data*

The H–H/H–T ratios can be expressed by equation (3). Implicit in it is the assumption that *CAB* pairs do not have sufficient time to reorient themselves from

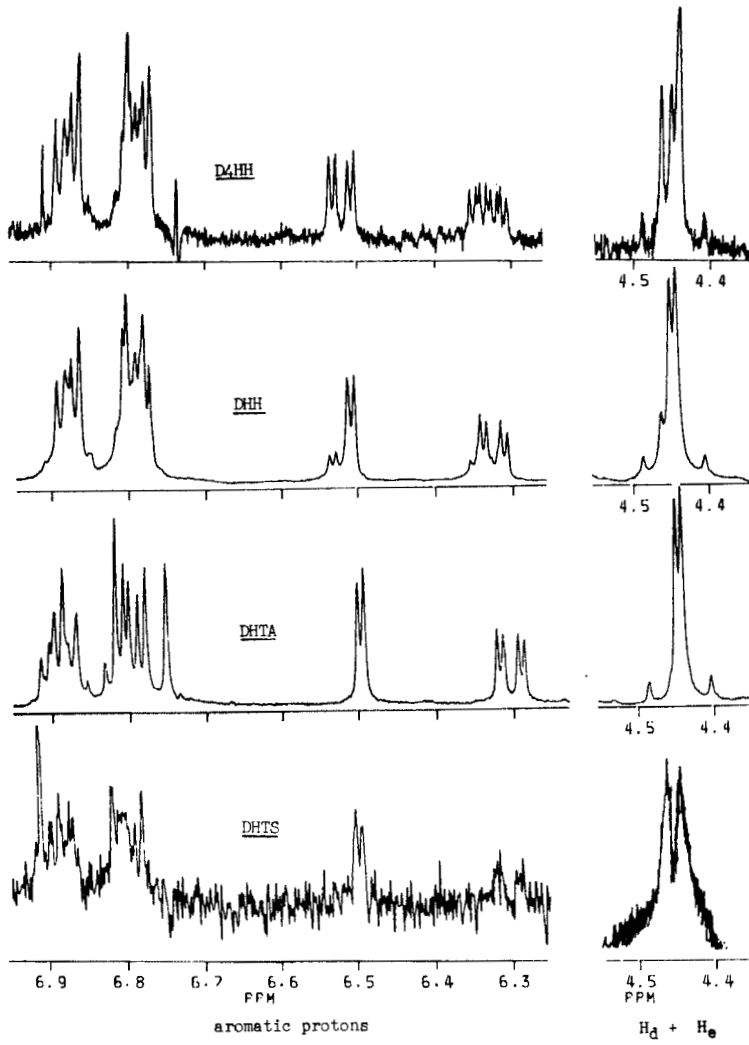


Figure 4. 500 MHz ^{1}H NMR low field absorptions of *CAB* photodimers in $CDCl_3$ (TMS).

Table 2. Distribution of photodimers from *CAB* in isotropic and liquid-crystalline phases.

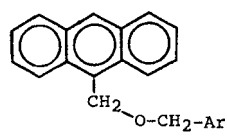
Phase	Temp °C†	Dimers		
		H–T/*ANTI*	H–T/*SYN*	H–H
Isotropic‡	25·5	37	17	46
Cholesteric	184·4	33	12	56
Cholesteric	183·5	33	13	55
Cholesteric	178·0	34	12	54
Neat isotropic	204·4	31	20	50
Neat isotropic	206·7	36	17	47
Solid	25·0	§	§	§

† ±0·5°
‡ 1·47 per cent (by weight) in toluene.
§ None observed after protracted irradiation.

pre-H–H to pre-H–T (or vice versa) arrangements during the very short singlet lifetimes of the anthracenyl groups (< 15 ns [16]). Thus, χ_{H-H} and $1 - \chi_{H-H}$, the mole fraction of pre-H–H and pre-H–T arranged pairs of *CAB* in the ground state [23], are represented by the photodimer distributions within the ordered phases. If Φ_{H-H} and Φ_{H-T}, the quantum efficiencies for H–H and H–T photodimers, are nearly equal, the data in table 2 indicate that $\chi_{H-H} \simeq 0{\cdot}5$: longitudinal orientational pairing in the ground state is non-discrete or non-existent.

Circumstantial evidence for $\Phi_{H-H} \simeq \Phi_{H-T}$ comes from the photodimer distribution obtained in the low viscosity solvent, toluene, where equation (3) should not strictly apply (since reorientations within the singlet lifetime of *CAB* may be substantial). Still, in this system which presumably has no pre-arranged *CAB* pairs, the H–H/H–T ratios remain near unity. This implies that equal fractions of the collisions that provide pre-H–H and pre-H–T arrangements can lead to photodimers. If Φ_{H-T} were greater than Φ_{H-H}, H–H/H–T in toluene should have been $\ll 1$.

Even more compelling evidence for $\Phi_{H-H} \simeq \Phi_{H-T}$ is found from studies conducted on 9-substituted anthracenes in isotropic solvents. Desvergne, Castellan, and Bouas-Laurent [24] found that (9-anthrylmethyloxymethyl)arenes (*AMA*) produce H–H and H–T photodimers (equation 1) with nearly equal efficiency in methylcyclohexane at room temperature. The 2-alkoxy 'substituent' of *CAB* is similarly small near anthracene and large when far from it. Thus, appropriate conformational twists should allow two *CAB* molecules to collide in a head-to-head orientation with minimal steric impediment. Also, the solvent polarities in table 2 should favor photodimer ratios near unity: the photodimer ratios from 9-methylanthracene vary from one in cyclohexane to 1·5 in diethyl ether [25(a)]. However, 9-hydroxymethylanthracene, whose small substituent is capable of forming strong intermolecular hydrogen bonds with another solute or with a polar solvent molecule, exhibits photodimer ratios that vary from > 15 in cyclohexane to 1·2 in diethyl ether [25(b)].



AMA

Ar = phenyl
Ar = 2-naphthyl
Ar = 9-phenanthryl
Ar = 1-pyrenyl

$$\frac{\text{H–H}}{\text{H–T}} = \frac{\chi_{H-H}\Phi_{H-H}}{(1 - \chi_{H-H})\Phi_{H-T}}. \tag{3}$$

The conclusion reached from the above arguments views *CAB* as a somewhat rigid, rod-like molecule in which the director is approximately parallel to the long axes of both the cholesteryl and anthracenyl groups. An alternative explanation of the lack of phase specificity in the photodimerizations is that *CAB* is not rod-shaped in its ordered phases. Due to the fluxional nature of the 4-oxybutyryl spacer group, the anthracenyl and cholesteryl groups can adopt very different orientations with respect to one another, and certainly must explore many conformations in the isotropic phase of neat *CAB*.

There is sparce, but consistent, data to support extended conformations as most probable for cholesteric molecules in their neat phases. For instance, Burks and Engelman found from neutron scattering studies that the preferred conformation of

(partially deuterated) cholesteryl myristate is extended in its crystalline, smectic, cholesteric, *and* isotropic phases [26]. X-ray diffraction studies on cholesteryl myristate confirm the extended nature of the molecules in the ordered phases. They also suggest that the smectic and cholesteric phases pack locally in a fashion that is similar to the solid (i.e. with neighbouring cholesteryl groups next to one another and extended chains interdigitated) [27]. In a more germane study, Sisido *et al.* [28] used circularly polarized fluorescence to ascertain that the most probable conformations of cholesteryl ω-arylalkanoates in their cholesteric phases have the aryl groups projected at the end of all-trans polymethylene chains [28]. These studies, when taken in total, indicate a shape for the preferred conformation of *CAB* that is fully extended and rod-like.

There is, in principle, a more ordered model for *CAB* packing that is compatible with non-specific dimer formation. If cholesteryl units pack together (as in the case of cholesteryl myristate), the anthracenyl groups may be interdigitated as in a bilayer. However, an anthracenyl group is only slightly smaller in size than a cholesteryl moiety and is of comparable thickness. Thus, spatial considerations disfavour such an arrangement for *CAB*.

With only one example, it is unwise to generalize our results. Other cholesteric mesogens with appropriate substituents may exhibit specific preferences for head-to-head or head-to-tail pair-wise interactions. Clearly, determination of the pair-wise orientation of other cholesteric molecules and testing of our *CAB* conclusion by an independent experimental method would be very useful.

3. Experimental

3.1. *Instrumentation*

Ultraviolet-visible absorption spectra were recorded on a Perkin-Elmer model 552 spectrophotometer. Temperatures of samples were measured to a precision of $\pm 0{\cdot}5°$ using a calibrated thermistor directly attached to the sample containers (unless otherwise stated). Infrared spectra were recorded on a Perkin-Elmer PE-457 grating spectrophotometer using pressed KBr pellets for solid samples and films between NaCl plates for liquid samples. They were calibrated with a polystyrene film. N.M.R. spectra were obtained on a 90 MHz Fourier Transform Bruker FHX-10 or a Nicolet NT-500 MHz spectrometer (where indicated). For optical microscopy, a Kofler hot-state microscope was used with a plane polarizer above and below the sample stage, from which melting points and transition temperatures were measured, and liquid-crystalline phases were identified. Photographs were recorded using a 35 mm SLR camera connected to the microscope objective through a camera-compatible microscope adapter. High performance liquid chromatography (HPLC) analyses were performed on a Waters Associates liquid chromatograph equipped with a Model 440 constant wavelength (254 nm) absorbance detector and a Waters Associates Rad-Pak B silica column ($10 \times 0{\cdot}8$ cm; $10\,\mu$ particles) in a Waters radial compression module. The eluent was 2/47/51 (v/v/v) ethyl acetate/$CHCl_3$/hexanes or 28/72 (v/v) $CHCl_3$/hexanes. Irradiations were performed with a Hanovia 450 W medium pressure mercury arc (Model 679A36) equipped with a Pyrex filter. Samples were degassed to *c.* 10^{-4} torr by three freeze-pump-thaw cycles and flame-sealed on a mercury-free vacuum line equipped with a mechanical forepump and an oil diffusion pump. Elemental analyses were performed by E+R Microanalysis Laboratory.

3.2. *2-Methoxyanthracene* [8]

A well-stirred mixture of 20 g zinc dust (Baker), 2 mL Fehling I solution, and 120 ml of distilled water were added to a suspension of 8·0 g (36·0 mmol) 2-methoxy-9-anthrone [8] and 200 mL of 10 per cent aqueous NaOH. The mixture was refluxed for 30 min and filtered hot to give a grey solid. The solid was heated on a stream both and swirled vigorously while 120 mL of conc. HCl were added drop-wise over a 40 min. period. A crude, slightly yellow solid was collected on a Büchner funnel, washed with 100 mL water and 50 mL methanol and then recrystallized from benzene twice to give 6·4 g (86 per cent) of plate-like crystals: m.p. 182·5–183·5°C. (lit. [8] m.p. 163–165°C). I.R. (KBr): 1635, 1480, 1465, 1435, 1345, 1220–1175, 1300–1270, 1025, 950, 880, 800, 740 cm^{-1}. ^1H N.M.R. ($CDCl_3$/TMS): δ 8·3 (1 H, s, anthracenyl meso proton), 8·2 (1 H, s, anthracenyl meso proton), 7·75–8·05 (3 H, m, oxyanthracenyl protons), 7·05–7·50 (4 H, m, oxyanthracenyl protons), 3·95 (3 H, s, $ArOCH_3$). U.V. (benzene): λ_{max} 277 (ε 9500), 315 (ε 2300), 329 (ε 4100), 347 (ε 4700), 370 (ε 4400), 390 nm (ε 4300); [lit. [8] λ_{max} 314 (ε 2400), 329 (ε 4670), 346·5 (ε 4680), 368·5 (ε 3980), 388·5 nm (ε 3890)].

3.3. *2-Hydroxyanthracene*

A solution of 2·0 g (9·6 mmol) of 2-methoxyanthracene and 25 mL methylene chloride was stirred and chilled at −70°C (acetone/dry-ice bath) under a dry atmosphere. A solution of 60 mL of methylene chloride and 11 mL of 1 N boron tribromide in methylene chloride (Aldrich) was added slowly through a compensating addition funnel. The mixture was then allowed to warm slowly to ambient temperature under a dry atmosphere. After 24 h, 20 mL of water were added and the mixture was extracted with anhydrous ethyl ether (4 × 25 mL). A brown solid, 1·7 g (92 per cent), decomp. *c.* 200°C (lit. [29] decomp. 200°C), was obtained after ether evaporation and drying under vacuum for 16 h. The product was immediately used for the synthesis of ethyl 4-(2-anthryloxy)butanoate. I.R. (KBr): 3540–3460, 3460–3100 (–OH), 1630, 1480, 1460, 1410, 1380, 1320, 1280–1270, 1200–1170, 950, 880, 800, 735 cm^{-1}. ^1H N.M.R. (CD_3COCD_3/TMS): δ 8·3, 8·44, 8·8; 8·13–7·8; 7·15–7·52 (ArH).

3.4. *Ethyl 4-(2-anthryloxy)butanoate*

A 30 mL solution of dimethylformamide containing 1·01 g (5·3 mmol) of 2-hydroxyanthracene was added, with stirring, to 20 mL dimethylformamide containing *c.* 0·13 g of sodium hydride. After hydrogen evolution ceased, 0·7 mL of ethyl 4-bromobutanoate (Aldrich, distilled before use) was added to the solution. After stirring for 48 h under a dry atmosphere, 50 mL of water were added to the reaction mixture. It was extracted with methylene chloride (5 × 50 mL), and the combined organic layers were washed with 50 mL of 10 per cent aqueous sodium carbonate and water (4 × 50 mL), and then dried over anhydrous magnesium sulphate. After evaporating the solvent, the crude product was recrystallized thrice from 95 per cent ethanol to yield 0·80 g (50 per cent) of crystals, mp. 128·5–129°C. I.R. (KBr): 1735 (ester carbonyl), 1625, 1455, 1430, 1390, 1380, 1300–1270, 1200–1180, 1080, 1050, 1010, 880, 800, 740 cm^{-1}. ^1H NMR ($CDCl_3$/TMS): δ 8·35 (1 H, s, anthracenyl meso proton), 8·15 (1 H, s, anthracenyl meso proton), 7·7–8·0 (3 H, m, oxyanthracenyl

protons), 7·0–7·5 (4H, m, oxyanthracenyl protons), 4·0–4·3 (4H, m, CH_3CH_2– and $ArOCH_2$), 2·0–2·7 (4H, m, $-CH_2CH_2COO$), 1·25 (3H, *t*, $J = 7·2$ Hz, $CHCH_2$–). Elemental analysis: calculated for $C_{20}H_{20}O_3$: C 78·00, H 6·54. Found: C 78·02, H: 6·54.

3.5. *4-(2-Anthryoxyl)butanoic acid*

Ethyl 4-(2-anthryloxy)butanoate (0·15 g; 0·5 mmol) was dissolved in 10 mL of hot 95 per cent ethanol, and the solution was added to 20 mL aqueous 5 per cent NaOH. The turbid mixture was boiled so as to allow the ethanol to evaporate slowly and water was added constantly to retain the original volume of solution. When the vapours no longer contained the smell of alcohol, *c.* 500 mL hot water were added. The resulting clear solution was acidified with dil. HCl until a precipitate formed. The precipitate was extracted with chloroform (3 × 50 mL) and the combined extracts were evaporated (rotary evaporator) to yield a yellow solid. The residue was recrystallized from toluene to yield 0·09 g (66 per cent) of yellow needle crystals, m.p. 190–193°C. I.R. (KBr): 2500–3000, 1705 (acid carbonyl), 1630, 1470, 1455, 1430, 1410, 1300–1345, 1200–1180, 1045–1020, 880, 800, 780, 735 cm^{-1}. ^1H NMR ($CDCl_3$/TMS): δ 8·35 (1H, s, anthracenyl meso proton), 8·20 (1H, s, anthracenyl meso proton), 7·7–8·0 (3H, m, oxyanthracenyl protons), 7·0–7·5 (4H, m, oxyanthracenyl protons), 4·3 (2H, t, $ArOCH_2CH_2$–), 2·7 (2H, t, $-CH_2CH_2COO$), 2·3 (2H, quintet, $ArOCH_2CH_2CH_2COO$).

3.6. *Cholesteryl 4-(2-anthryloxy)butanoate (CAB)*

A mixture of 4-(2-anthryloxy)butanoic acid (0·17 g; 0·70 mmol), 10 ml dry benzene, and 0·5 mL oxalyl chloride was stirred and heated (bath temperature *c.* 50–60°C) under a dry atmosphere for *c.* 2·5 h. Benzene and excess oxalyl chloride were distilled under vacuum. More benzene (10–15 mL) was added three times; after each, it was distilled under vacuum to remove traces of oxalyl chloride. The yellow residue was mixed with a solution of 25 mL benzene, 0·24 g cholesterol, and a trace of pyridine. After *c.* 16 h of stirring under a dry atmosphere at *c.* 50°C, the solvent was evaporated (rotary evaporator) and the solid was recrystallized thrice from *tert*-amyl alcohol and thrice from methanol/chloroform. The resulting white crystals, 0·22 g (79 per cent), m.p. 204–206°C, showed a monotropic cholesteric liquid-crystalline phase (196–160°C). I.R. (KBr): 1735 (ester), 1630, 1455, 1410, 1375, 1280–1245, 1170, 1050, 1020, 1000, 880, 800, 740 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$/TMS): δ 8·32 (1H, s, anthracenyl meso proton), 8·24 (1H, s, anthracenyl meso proton), 7·83–8·00 (3H, m, oxyanthracenyl protons) 7·35–7·46 (2H, m, oxyanthracenyl protons), 7·10–7·24 (2H, m, oxyanthracenyl protons), 5·36 (1H, s, alkenyl), 4·60–4·70 (1H, m, oxycyclohexyl), 4·17 (2H, t, $J = 5·86$ Hz, $ArOCH_2$–), 2·56 (2H, t, $J = 6·88$ Hz, $-CH_2COO$), 0·67, 0·82, 0·90–2·2 (45H, m, methylene and cholesteryl protons). Elemental analysis: calculated for $C_{45}H_{60}O_3$: C 83·29, H 9·31. Found: C 83·51, H 9·50.

3.7. *1,2-Di(4-(2-anthryloxy)butanoyloxy)ethane*

A mixture of 4-(2-anthryloxy)butanoic acid (1·0 g; 3·6 mmol), 125 mL dry benzene, and 1 mL oxalyl chloride was stirred and heated (bath temperature *c.* 50–60°C) under a dry atmosphere for *c.* 2·5 h. Benzene and excess oxalyl chloride were distilled under vacuum. Benzene (15 mL) was added three times and after each, it was

removed under vacuum. The yellow residue was mixed with a solution of 50 mL benzene, 0·1 mL ethylene glycol (vacuum distilled shortly before use), and 3 mL dimethylformamide. After *c.* 72 h of stirring under a dry atmosphere at *c.* 60°C, 100 mL distilled water was added. The mixture was extracted with methylene chloride (2 × 100 mL), and the combined organic layers were evaporated (rotary evaporator) to give a yellow solid. It was chromatographed on a silica gel column with chloroform, and the fraction corresponding to RF = 0·35 on a TLC plate (eluted by chloroform) was collected. The products were then recrystallized from 95 per cent EtOH and *tert*-amyl alcohol to yield 0·5 g (23 per cent), mp. 167–171°C. I.R. (KBr): 1725–1750 cm^{-1} (ester carbonyl). ^1H NMR ($CDCl_3$/TMS): δ 8·19 (2 H, s, meso proton of anthracenyl group, position 9), 8·28 (4 H, s, meso proton of anthracenyl group, position 10), 7·83–8·00 (6 H, m, oxyanthracenyl protons) 7·12–7·42 (8 H, m, oxyanthracenyl protons), 4·33 (4 H, s, $-OCH_2CH_2O-$), 4·08 (4 H, t, $ArOCH_2CH_2-$), 2·59 (4 H, t, $-CH_2CH_2COO-$), 2·17 (4 H, quintet, $ArOCH_2CH_2CH_2COO-$). U.V. (methylene chloride): λ_{max} 390 (ε 7100), 370 (ε 7600), 348 (ε 8200), 330 (ε 7200), 315 nm (ε 4100).

3.8. *Intramolecular photodimerization of 1,2-di(4-(2-anthryloxy)butanoyloxy)ethane*

A solution of 100 mg of 1,2-di(4-(2-anthryloxy)butanoyloxy)ethane dissolved in 1050 mL methylene chloride was distributed equally among 12 Pyrex test tubes. After deaerating the aliquots by bubbling with nitrogen for 20 min, the septum sealed tubes were irradiated for 2·5 h with a 450 W medium pressure mercury arc equipped with a Pyrex filter. Sample tubes were *c.* 1 cm from the lamp. The degree of photodimerization was monitored by U.V. analyses periodically. Disappearance of the absorption band of the anthracenyl chromaphore at 400–300 nm was assumed to provide a direct measure of the extent of dimer formation.

The reaction mixtures after 2·5 h irradiation were combined and the solvent was removed (rotary evaporator) to give a brown solid. It was column chromatographed on silica gel with 96/4 (by volume) of $CHCl_3$/EtOAc as eluent. Fractions that correspond to RF = 0·39–0·46 by analytical TLC were collected to yield a white solid. ^1H NMR ($CDCl_3$/TMS): δ 6·82–6·26 (14 H, m, phenyl); 4·43 (4 H, s, bridge protons); 4·35 (4 H, s, $-OCH_2CH_2O-$); 3·79–3·98 (4 H, two triplets superimposed to make a quartet, $ArOCH_2CH_2-$); 2·48–2·34 (4 H, t, $-CH_2CH_2COO-$); 2·23–1·91 (4 H, quintet, $-CH_2CH_2CH_2-$).

3.9. *Preparation of DHH*

The solid above (0·030 g) was dissolved in 150 mL of hot 95 per cent ethanol, and the solution was added to 20 mL aqueous 5 per cent NaOH. The turbid mixture was boiled to allow the ethanol to evaporate slowly and water was added constantly to retain the total volume of solution. When the vapours no longer contained the smell of alcohol, *c.* 300 mL hot water were added. The resulting clear solution was acidified with dil. HCl until a precipitate formed. The precipitate was extracted with methylene chloride (3 × 100 mL) and the combined extracts were evaporated (rotary evaporator) after being dried over anhydrous $MgSO_4$ to yield 0·025 g of a white solid, m.p. 195–212°C. It was insoluble in benzene, cold 95 per cent EtOH, and diethyl ether, but soluble in toluene, methylene chloride, and chloroform.

Esterification of the corresponding acid chloride (from 0·022 g of the above acids and 1 mL oxalyl chloride in 20 mL dry benzene) with 0·03 g cholesterol in 15 mL dry

benzene gave the esters. Details of the procedure followed that of *CAB*. The crude products were purified by preparative thin layer chromatography with 0·5/3/6·5 (by volume) EtOAc/$CHCl_3$/cyclohexane as eluent. The fraction with RF = 0·5 was separated as before and collected: m.p. 194–196°C. ^{1}H NMR ($CDCl_3$/TMS): δ 6·9–6·8, 6·78–6·74, 6·5–6·3 (14 H, m, phenyl), 4·45 (4 H, s, bridged protons), 5·40 (2 H, s, alkenyl), 4·5–4·7 (2 H, m, oxycyclohexyl), 3·9 (4 H, m, $ArOCH_2$–), 2·6 (4 H, t, J = 6·88 Hz, $-CH_2COO$), 0·67, 0·85–2·3 (90 H, m, methylene and cholesteryl protons). The U.V. absorption spectrum is shown in figure 3(*e*).

3.10. *Preparation and separation of CAB photodimers*

CAB, 0·062 g, was dissolved in 10 mL hot benzene, and the solution ($9·5 \times 10^{-3}$ M) was placed in a modified Kimax glass tube. The sample compartment was 3 cm × 1 cm (i.d.) and was connected to a 8 cm outlet tube with i.d. *c.* 4 mm. After being deaerated by passing nitrogen through the solution for 15 min, the tube was flame-sealed and irradiated with a 450 W medium mercury arc equipped with a Pyrex filter for 14 h at *c.* 39°C. The distance between the tube and the lamp was *c.* 2 cm.

Photodimers were separated by preparative thin layer chromatography (6/3·5/0·5 (by volume) heptane/$CHCl_3$/EtOAc as eluent). Fractions corresponding to R_f = 0·52–0·57 were removed from the plate and extracted with chloroform. The white solid that resulted after chloroform was evaporated was further separated into 3 fractions, *DHTA*, *DHTS*, and *D4HH*, by HPLC. Material from many injections on the analytical column were combined. The solvent from each fraction was evaporated carefully and further analyses were performed on solutions of the solid residues.

3.11. *Photodimerization in neat phases of CAB*

For the solid phase a 15 mL aliquot of *CAB* in chloroform (*c.* 10^{-2} M) was placed in a 50 mL Pyrex flask. After the solvent was evaporated on a rotary evaporator, *CAB* was coated inside the flask as a thin film. *CAB* was then flushed with nitrogen and the flask was sealed by a septum stopper. The flask was irradiated under a Pyrex-filtered 450 W medium mercury arc for 24 h.

For experiments in the cholesteric or neat isotropic phase, typically 1 mg of *CAB* was placed in either a Kimax capillary over a flattened capillary (1″ × 4 mm × 0·4 mm i.d.). After being degassed to *c.* 10^{-4} torr by three freeze–pump–thaw cycles and flame sealed, the capillary was irradiated in a home-made heating unit at the temperature of interest (± 0·5°) for 60 s after being warmed to its isotropic phase and cooled to the temperature of interest.

3.12. *Thermostability of CAB dimers*

The decomposition kinetics of *CAB* dimers were studied by monitoring the growth of the anthracenyl ^1L_a absorption (300–400 nm), or by using HPLC to monitor the decrease in dimers concentrations. For the former method, typically, *c.* 1 mg of sample was dissolved in 10 mL eicosane (Aldrich, 99 per cent), and the solution was equally allocated among 10 ampoules (1 mL in size), which were flame-sealed. The ampoules were then immersed in an oil bath at a temperature of interest and, periodically, one of them was removed and cooled immediately with ice water. The U.V. spectrum of the liquid was then recorded (at *c.* 40°C) by diluting with 3·5 equivalents of eicosane.

When using HPLC, as exemplified by the case of *DHTA*, 1 mg was dissolved in 10 mL hexadecane containing 1 drop (*c.* 1/50 mL) of benzyl alcohol (internal standard for HPLC analysis). The solution was equally allocated among 15 ampoules (1 mL in size), which were flame-sealed and then immersed in an oil bath at a temperature of interest. Periodically, an ampoule was removed and cooled immediately in an ice-water bath, and analysed by HPLC as before. The decreased amount of dimers was determined by comparison with the internal standard (peak areas), and the first order rate constants were calculated.

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