The azulene ring as a structural element in liquid crystals

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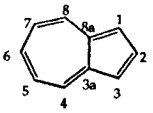
A new approach to the synthesis of azulene liquid crystals is described based on Hafner's procedure involving reaction of a pyridinium salt with a cyclopentadienide. The preparation of a variety of liquid crystalline materials using this method is described. Variants are reported with single substituents on the azulene ring in the 6-position and doubly substituted in the 2, 6-positions. The effect of the azulene ring as a core or dipolar terminal structural element is explored. 6-(5-Alkyl-1,3-dioxan-2-yl)azulenes are shown to exhibit smectic A phases and 2-cyclohexyl-6-(5-tridecyl-1,3-dioxan-2-yl)azulene show smectic A and B phases. Phase characterisation of the materials is recorded together with X-ray measurements on the smectic A phase of one representative compound. Results of dichroism studies on the azulene mesogens are also briefly reviewed.

The essential structure of a calamitic mesogen incorporates a rigid core with a flexible terminal chain, and often a polar end group, and mesophase behaviour is strongly dependent on the nature of the core. In the search for new mesogenic structures, the azulene ring system potentially opens up a whole new range of liquid crystal types. The azulene ring $C_{10}H_{10}$ is a non-benzenoid aromatic hydrocarbon with an intrinsic dipole moment (1.08 D) which is delocalised over the whole ring.[1] Azulenes are chromophores: the deep blue colour of the parent compound arises from the electronic transition from the highest occupied molecular orbital to the lowest unoccupied antibonding orbital (the ^1L_b band).[2] The azulene ring system is planar and thermodynamically stable, although the 10π electrons display the reactivity expected of an aromatic system. Substitution of the ring can alter the wavelength of this absorption band resulting in different colours for different azulene derivatives.



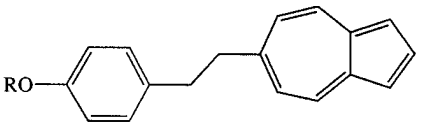
Praefcke and Schmidt[3] reported the synthesis of substituted azulenes linked to nematogenic alkylcyclohexanes by an ester group following the Nozoe procedure.[4] We have also used this route to produce mesogenic azulenes[5] with alkylbiphenyls as the mesogenic moiety. In 1990, a series of patents by Mitsubishi described the synthesis of a range of 2-substituted,[6] 6-substituted[7] and 2,6-disubstituted azulenes[8–10] using the Nozoe route, some of which were mesogenic. Only limited data were presented on the mesophase behaviour of these compounds which were mostly examined as solutes in a nematic host material. The mesophase properties of previously reported azulene based liquid crystals are summarised in Table 1.

Synthesis

In order to prepare potentially mesogenic azulenes without ester linkages, we adopted the Hafner synthesis[11] where an *N*-alkyl-4-methylpyridinium salt was reacted with sodium cyclopentadienide to give 6-methylazulene (see Schemes 1 and 2). In a similar way we prepared 6-(diethoxymethyl)azulene **1a** by reaction of sodium cyclopentadienide with 4-(diethoxymethyl)pyridinium bromide. Alternatively, reaction with monosubstituted sodium cyclopentadienides gave a mixture of 1,6- and 2,6-disubstituted azulenes which, in some cases, were separable by HPLC. Transacetalation of the diethoxymethyl group with 2-substituted propane-1,3-diols then gave substituted azulenes, some of which were mesogenic.

Simple alkyl propane-1,3-diols were prepared by reacting diethyl malonate with the appropriate alkyl halide and then reducing the ester groups with $LiAlH_4$; 2-(4-alkyloxyphenyl)-propane-1,3-diols were prepared by reacting ethyl 4-alkoxyphenylacetates with diethyl oxalate; the product was then decarbonylated and reduced with $LiAlH_4$.

The products derived from Scheme 1 were a mixture of *cis* and *trans* isomers which were separable by MPLC or HPLC, and were assigned by the characteristic ^1H NMR spectra for the two CH_2 groups on the dioxan-2-yl ring. For the *cis*-isomers, the chemical shift difference between the axial and equatorial hydrogens is small whereas a large chemical shift difference is observed for the *trans* isomers and this characteristic pattern agrees with previously published results.[12]



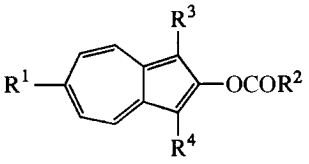
2a R = C_6H_{13}
b R = $C_{10}H_{21}$

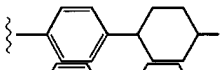
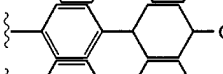
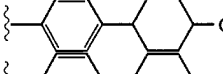
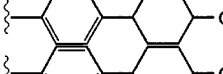
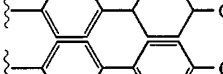
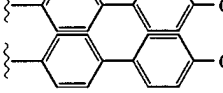
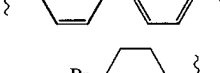
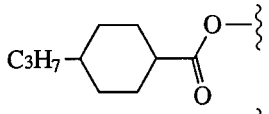
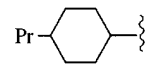
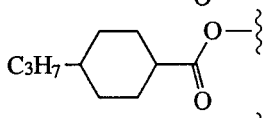
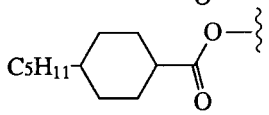
Attempts were also made to prepare mesogenic azulenes with a phenyl ring instead of the dioxan-2-yl ring. Two homologues **2a,b** were prepared by different methods. Deprotection of **1a** with dilute hydrochloric acid gives azulene-6-carbaldehyde which was reacted with the appropriate Wadsworth–Emmons reagent to give 6-(4-hexyloxystryryl)-azulene, which rapidly decomposed. Reduction of the double bond gave **2a**. The C_{10} analogue, **2b** was prepared by reducing the double bond of the appropriate stilbazole, quaternising the product with 1-bromobutane and reacting the resulting pyridinium salt with sodium cyclopentadienide.

Mesophase Behaviour

Of the compounds synthesised, the *trans* isomers of **1e–k**, **1n** and **1p** were mesogenic. Table 2 shows the transition temperatures for compounds **1e–k** which showed a monotropic smectic A phase. These *trans* isomers exhibited two crystal forms (K_1 and K_2) which melted at different temperatures. The observed phase sequence is shown in Fig. 1 and illustrates the trends in melting points of the two crystal forms and the S_A phase. (For the two metastable crystal states: K_1 corresponds to the melting point on initially heating the crystal from room temperature,

Table 1 Transition temperatures and wavelengths of visible absorption of mesogenic azulenes previously reported in the literature



					transition temp[a]/°C						
R_1	R_2	R_3	R_4	λ_{max}/nm	K		N		I		ref.
H		CO_2Et	CO_2Et		●	136	●	(110.5)	●		3
H		CO_2Me	CO_2Me		●	149	●	(121.9)	●		3
H		CO_2Et	CO_2Et	480	●	123.7	●	(115.9)	●		3
H		CO_2Pr	CO_2Pr		●	104.5	●	(89.3)	●		3
H		CO_2Et	H	510	●	86.1	●	153.2	●		3
H		CO_2Et	CO_2Et		●	144	●	(78.6)	●		5
H		CO_2Et	H		●	146	●	(145)	●		5
		CO_2Et	CO_2Et	475	●	122	●	(111)	●		8
	H	H	H	476	●	118	●	(122.6)	●		7
	H	H	H	566	●	106.7	●	119.4	●		7

[a]Parentheses indicate a monotropic transition.

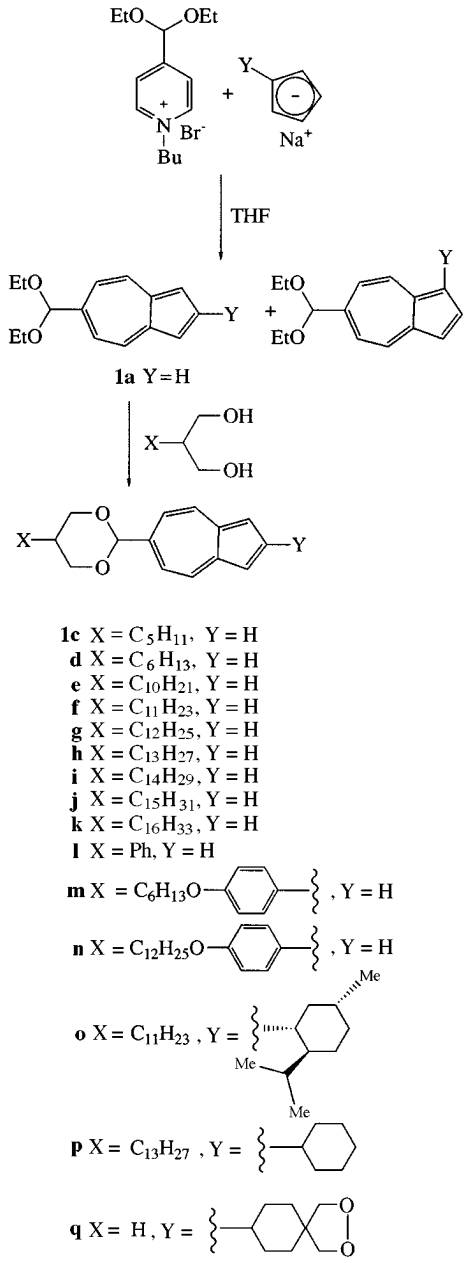
and K_2 is the melting point when heating the crystal phase formed on cooling). For compounds where K_2 is lower than the monotropic smectic A transition temperature an enantiotropic S_A phase is observed.

The *trans* isomer of **1n** showed a crystal B phase at around 170 °C and was identified by the lancet texture observed on cooling from the isotropic phase. For compound **1p**, where the 2-substituent is an unsubstituted cyclohexyl ring, smectic A (144 °C) and smectic hexatic B (117 °C) phases were observed. Compound **1q** was prepared as it was hoped that the molecular length could then be extended with a collinear chain on the cyclohexyl ring; however the *cis* and *trans* isomers were inseparable by HPLC.

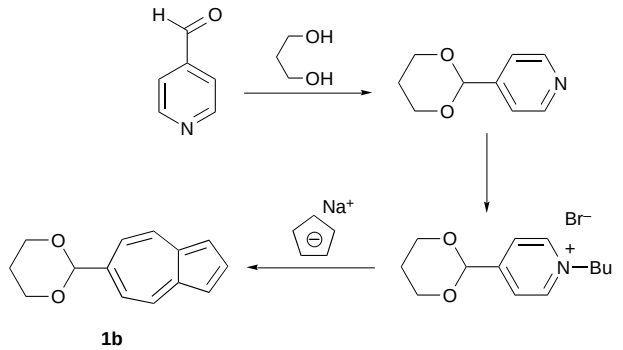
Addition of a 2-cyclohexyl substituent (compound **1p**) increases the thermal stability of the S_A phase compared to the singly substituted 6-(tridecyl-1,3-dioxan-2-yl)azulene, **1h** which showed a monotropic smectic A phase, such that an enantiotropic phase is now observed. This molecule incorporates an aromatic ring with saturated cyclic groups either side of it, which traditionally has been considered unfavourable for mesogenic behaviour. Potentially, this molecule opens up a new series of mesogens and it is expected that the addition of a terminal alkyl chain on to the cyclohexyl ring will lower the clearing points and transition temperatures of the observed mesophases.

Small angle X-ray measurements were made for compound **1f**, 6-(5-undecyl-1,3-dioxan-2-yl)azulene. From the data obtained, an average value for the inter-layer spacing was calculated to be 27 Å. Molecular modelling calculations were then made in an attempt to describe the molecular arrangement. At 0 K, the molecular length was determined from MACROMODEL to be 27.56 Å, which is close to the observed value for the inter-layer spacing of this smectic A phase. An even closer value is obtained when part of the molecule is tilted with respect to the smectic layers; this has the effect of shortening the apparent length of the molecule and calculations predict a value of 26.9 Å at 300 K. However, modelling the molecule at 357 K, the value for the molecular length decreases to 23.65 Å. The entropy of the system is now greater, and this manifests itself in thermal agitation of the alkyl chain which is no longer fully extended. From this result it is possible to rule out a monolayer structure for this S_A phase, since for the temperatures at which the phase is observed, there will be some thermal agitation of the alkyl chain, and the measured molecular length must be less than the calculated value with a fully extended chain.

In considering how the molecules are arranged within the layers, the intermolecular interactions must also be considered. Azulene has a distributed dipole moment and dipolar resonance forms of azulene will contribute to the intermolecular interactions in the smectic mesophase. It has been reported in the literature[13,14] that only *anti*-azulenophanes of the type shown (Fig. 2) can be formed, since this minimises the energy of both the resonance and electrostatic interactions between the interacting azulene pairs. For the corresponding *syn*-azulenophase these interactions would be repulsive. It is



Scheme 1



Scheme 2

expected that in the observed mesophase the azulene rings would adopt a packing arrangement which minimises the energy of these types of interactions, resulting in an anti-parallel bilayer structure as illustrated (Fig. 3). A similar type of alignment is observed in mesogens with strongly polar groups.[15] Our proposed structure for the S_A phase is a bilayer that involves extensive interdigitation of the alkyl chains, which accounts for both the dipolar interactions of the azulene ring and the thermal disorder of the alkyl chains.

Linear Dichroism

Since azulene derivatives are coloured, their use as dichroic materials in liquid crystal devices is of some interest. Measurement of the linear dichroism of a number of non-mesogenic and mesogenic compounds dissolved in suitable nematic host materials have been reported.[16] Measurements were also carried out on three compounds prepared in this work. From these studies it is possible to determine the degree of order of the host azulene molecules and the angle made by the transition moment to the long molecular axis. For the parent azulene, the transition moment responsible for the characteristic blue colour is polarized perpendicular to the axis[2] through carbon atoms 2 and 6. Substitution of the azulene ring and attachment of different terminal groups change the absorption frequency and the angle of the transition moment with respect to the molecular axis. Consequently, it is possible to make azulene liquid crystal mixtures having different colours and with either positive or negative linear dichroism. In Table 3 absorption frequencies and dichroic ratios are summarised for a range of azulene derivatives: a dichroic ratio of less than one indicates that the optical absorption perpendicular to the azulene molecular axis is larger than along the axis.

Conclusions

New 6-substituted azulenes were successfully synthesised by reacting functionalised *N*-alkylpyridinium salts with sodium cyclopentadienide to give mesogenic azulenes where the azulene ring was incorporated as an end group. The preparation of 6-(diethoxymethyl)azulene **1a** and azulene-6-carbaldehyde was significant as they are functionalised azulenes which may be reacted further to give new 6-substituted azulene compounds. The development of the transacetalation reaction of 6-(diethoxymethyl)azulene led to a new homologous series of mesogenic azulenes which exhibited monotropic smectic A phases in the range 78 to 86 °C. These compounds are the first reported azulenes to show a smectic phase. In these compounds it may be argued that the azulene ring has a dual role, and is behaving both as part of the core and as a polar end group. Molecular modelling substantiated the claim that the dipolar interactions of adjacent azulene rings are important in determining the intermolecular interactions which results in the observed smectic A layered structure, with the alkyl chains extensively interdigitated.

Attempts to extend the core led to the synthesis of 6-[5-(4-dodecyloxyphenyl)-1,3-dioxan-2-yl]azulene, **1n**. A crystal B phase was observed in the range 170–190 °C. This contrasts with related compounds without a phenyl group as part of the core, which form a smectic A phase approximately 100 °C lower. It was also possible to prepare potential azulene mesogens by hydrogenation of a stilbazole and reacting the quarternised salt with sodium cyclopentadienide. Unfortunately, the resultant 6-(4-decyloxyphenethyl)azulene, **2b** was not mesogenic, which can be attributed to the separation of the aromatic rings by a flexible dimethylene linkage. (However, the intermediate 4-(4′-decyloxyphenethyl)pyridine was mesogenic, and exhibited a smectic A phase in the range 159–222 °C.)

New 1,6- and 2,6-disubstituted azulenes were synthesised by the reaction of functionalised *N*-alkylpyridinum salts with sodium monosubstituted cyclopentadienides. The synthesis of 2-cyclohexyl-6-(tridecyl-1,3-dioxan-2-yl)azulene **1p** gave a mesogen which showed a smectic A and a smectic B phase in the range 95–144 °C. All previously reported azulene mesogens

Table 2 Mesophase behaviour of azulene liquid crystals

compound	*cis* mp	transition temperatures (microscopy)			transition data (DSC)		
		K_1 mp/°C	K_2 mp/°C	(S_A/I)/°C	ΔH/kJ mol^{-1}	T_{onset}/°C	ΔS J K^{-1} mol^{-1}
1c	81.4	100.1	—	—			
1d	83.6	99.6	—	—			
1e	94.5	94.5	76.8	83.9	4350	82	12.3
1f	96.9	97.8	—	(84.1)	3350	79	9.5
1g	97.5	98.5	78.5	85.0	3440	79	9.8
1h	99.7	101.1	80.0	84.0	3150	79	9.0
1i	100.2	102.1	86.0	(83.9)	4210	80	11.9
1j	102.1	102.8	88.0	(79.5)	3290	77	9.4
1k	103.4	103.9	90.0	(78.9)	4000	75	11.5

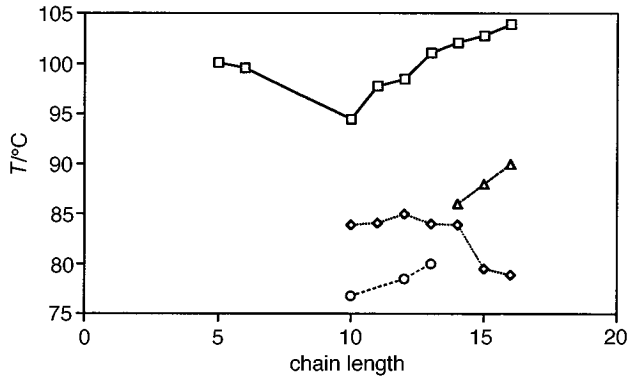


Fig. 1 Phase diagram of compounds **1c–k**: (□) K_1–I; (◇) S_A–I; (○) K_2–S_A; (△) K_2–I

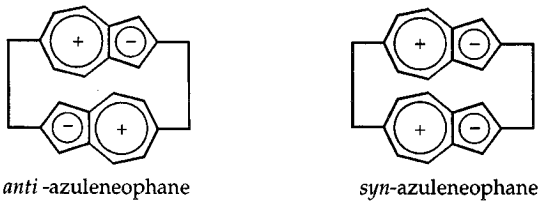


Fig. 2 Structures of the azuleneophanes

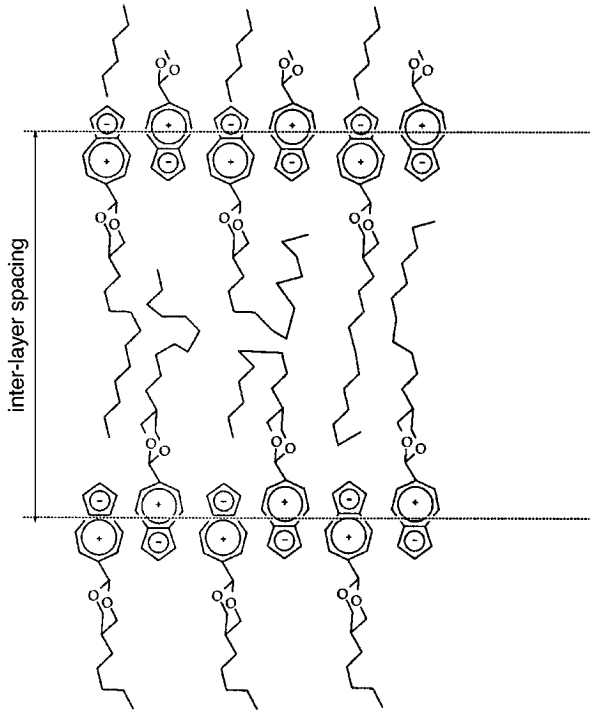


Fig. 3 Proposed layer structure of the smectic A phase involving extensive interdigitation

are linked through ester groups. It is anticipated that substitution of the cyclohexyl ring by an alkyl chain will lead to a new homologous series with lower clearing points and transition temperatures.

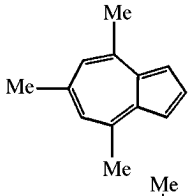
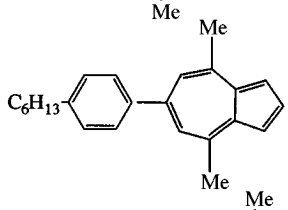
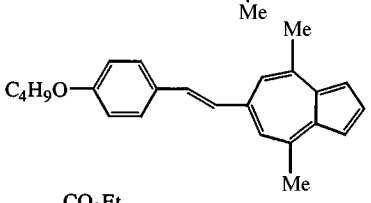
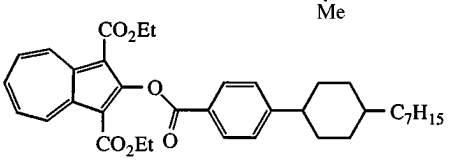
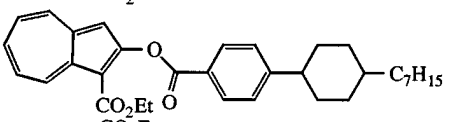
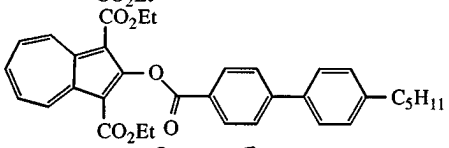
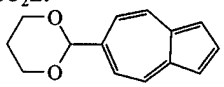
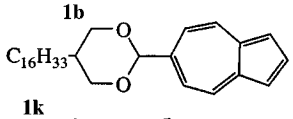
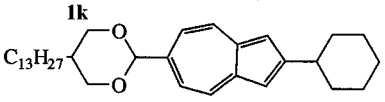
The linear dichroism of some azulene mesogens was determined by measuring the order parameter of these compounds as dyes in liquid crystal hosts. The optical order parameters were low as a result of the large angle which the transition moment makes with the molecular axis; in some cases this angle was close to the magic angle of 54°44′ at which the dichroism is zero. As a result of the large angle, it was possible to vary the sign of the dichroism by varying the substituents on the azulene ring. However, these compounds are not suitable for use in guest–host displays despite the high extinction coefficients.

Various aspects of the synthesis and physical properties of azulene liquid crystals have been explored in this work. It is evident that the synthesis of azulene is difficult and having tried a number of routes, the most successful method for this work involved the reaction of *N*-alkylpyridinium salts with sodium cyclopentadienide. However, the development of new azulene based liquid crystals is restricted by the limited synthetic routes currently available.

Experimental

Reactions sensitive to moisture and air were carried out in flame-dried glassware under nitrogen or argon using freshly distilled solvents. Solvents were dried and purified according to literature methods. Thin-layer chromatography on TLC aluminium sheets pre-coated with silica gel (Merck 69) F_{254} was used to monitor reactions and to establish the purity of samples. TLC plates were inspected using UV light or developed with iodine vapour. Oil-free sodium hydride was obtained by washing with dry light petroleum in an argon atmosphere. Amberlyst 15 (H^+) ion-exchange resin was used in transacetalation reactions. Column chromatography separations were performed on silica gel (Merck 60) or neutral silica (Merck, 60) as the stationary phase. Loading of the sample was carried out either as a concentrated solution of the mixture in the solvent used for the mobile phase, or whenever the mixture was only sparingly soluble in the eluent, it was supported on silica gel by dissolving in a solvent, adding silica and evaporating the slurry to dryness to leave a powder which was poured on to the top of the column. Organic solutions were dried over magnesium sulfate unless otherwise stated. Melting points were determined using either a Reichert-Köfler hot-stage apparatus or a Zeiss-Labpol microscope equipped with crossed polarisers and a Linkam hot-stage with integrated temperature controller, and are uncorrected. Elemental analyses were performed by the University of Sheffield Microanalytical Service. Low resolution mass spectra were recorded using a Kratos MS 25 mass spectrometer. High resolution mass spectra was recorded using a Kratos MS 60 mass spectrometer to give accurate mass values. ^1H and ^{13}C NMR spectra were recorded

Table 3 Absorption frequencies and dichroic ratios for a range of azulene derivatives

compound	λ_{max}/nm	ε_{max}/cm^2 mol^{-1}	dichroic ratio $A_{\parallel}/A_{\perp}$	ref.
	548	280000	1.0	17
	565	340000	1.0	17
	590	440000	1.44	17
	480	720000	1.8[a]	3
	510	630000	2.1[a]	3
	468	560000	2.4	5
 **1b**	595	320000	0.72	—
 **1k**	550	354000	0.64	—
 **1p**	565	340000	0.50	—

[a]Extrapolated from literature values.

using $SiMe_4$ as an internal standard in stated solvents. Multiplicities are represented by the following abbreviations: s, singlet; d, doublet; t, triplet, q, quartet; m, multiplet; br, broad signal. Coupling constants, (J) are given in Hz.

4-(Diethoxymethyl)pyridine

This compound was prepared by adapting the procedure of Popp and McEwen,[17] but full experimental details are given below. A 13.5% solution of hydrogen bromide in ethanol was prepared by cooling ethanol (88 ml) to 0 °C under nitrogen and adding acetyl bromide (12 ml) dropwise. To a portion of this solution (52 ml) pyridine-4-carbaldehyde (11.2 g, 105 mmol) was added to give a white precipitate and a yellow solution which was stirred at 20 °C for 90 h. Dry benzene (100 ml) was then added and any water formed during the reaction, removed by azeotropic distillation through a Soxhlet extractor containing $MgSO_4$, over a period of 24 h. Benzene and ethanol were evaporated under reduced pressure to give an orange solid which was made alkaline (pH 9) by adding 10% K_2CO_3 solution (75 ml). This was extracted with diethyl ether (3 × 50 ml), dried and reduced to leave a colourless oil. Purification by vacuum distillation gave unreacted pyridine-4-carbaldehyde, bp 73–74 °C, 0.5 mmHg and 4-(diethoxymethyl)-pyridine as a colourless oil, bp 75–76 °C, 0.5 mmHg, 19 g, 81%; δ_H (250 MHz, $CDCl_3$) 1.25(t, 6H, J 7, 2Me); 3.58[m, 4H, 2(OCH_2Me)]; 5.50[s, 1H, pyridine-CH-$(OEt)_2$]; 7.40(d, 2H, J 6, pyridine); 8.70(d, 2H, J 6, pyridine); δ_C (63 MHz, $CDCl_3$) 15.0(q, 2C, 2Me); 61.2[t, 2C, 2(OCH_2Me]; 99.8[d, 1C, pyridine-CH-$(OEt)_2$]; 121.6(d, 2C, pyridine); 147.6(s, 1C, pyridine); 149.9(d, 2C, pyridine); m/z (EI) 181(M^+, 90%).

N-Butyl-4-(diethoxymethyl)pyridinium bromide

4-(Diethoxymethyl)pyridine (4 g, 22.0 mmol) was dissolved in dry ethanol (10 ml) and 1-bromobutane (4.56 g, 33.0 mmol) added. The mixture was heated at reflux for 16 h. The ethanol and excess 1-bromobutane were evaporated under reduced pressure. The resulting yellow oil was left under high vacuum to remove any remaining solvent to give *N*-butyl-4-(diethoxy-

methyl)pyridinium bromide, (6.0 g, 85%), δ_H (250 MHz, $CDCl_3$) 0.95[t, 3H, $N(CH_2)_3CH_3$]; 1.25[t, 6H, $2(OCH_2CH_3)$]; 1.45[m, 2H, $N(CH_2)_2CH_2Me$]; 2.05(m, 2H, $NCH_2CH_2C_2H_5$); 2.70(2H, br s, H_2O); 3.65[q, 4H, $2(OCH_2CH_3)$]; 5.05(t, 2H, $NCH_2C_3H_7$); 5.70(s, 1H, $(OEt)_2$-C*H*-pyridine); 8.15(d, 2H, pyridine); 9.60(d, 2H, pyridine); δ_C (63 MHz, $CHCl_3$) 12.7(q, 1C, $C_3H_7CH_3$); 14.2[q, 2C, $2(OCH_2CH_3)$]; 18.4(t, 1C, CH_2); 32.9(t, 1C, CH_2); 33.0(t, 1C, CH_2); 60.2(t, 1C, CH_2); 61.5[t, 2C, $2(OCH_2CH_3)$]; 91.3(d, 1C, $(OEt)_2$-*C*H-pyridine); 97.4(d, 2C, 2-pyridine); 125.3(d, 2C, 3-pyridine); 156.7(s, 1C, 4-pyridine); *m/z* (+ve FAB MS) $C_{14}H_{24}NO_2$ 238 (M^+, 100%).

6-(Diethoxymethyl)azulene, 1a

Freshly distilled cyclopentadiene (2.42 g, 36.6 mmol) was added dropwise over 30 min to sodium hydride (0.88 g, 36.6 mmol) in THF (70 ml) at 0 °C and then allowed to warm to 20 °C. *N*-butyl-4-(diethoxymethyl)pyridinium bromide (17.5 g, 55.0 mmol) dissolved in THF (50 ml) was then added to the pinkish solution which went dark red and then brown. The mixture was heated at reflux for 3 h, a blue spot being indicated by TLC. THF was evaporated under reduced pressure to leave a black viscous oil to which silica was added. Purification by column chromatography using light petroleum (bp 40–60 °C) as eluent gave 6-(diethoxymethyl)azulene as a dark blue oil (2.72 g, 32%). Further purification using a Kügelrohr apparatus gave **1a** (Found: C, 78.0; H, 7.9. $C_{15}H_{18}O_2$ calculated: C, 78.2, H, 7.9%), δ_H (250 MHz, $CDCl_3$) 1.25(t, 6H, 2Me); 3.6[m, 4H, $2(OCH_2CH_3)$]; 5.45[s, 1H, $HC(OEt)_2$]; 7.40(m, 4H, azulene *H*-$C^{1,3,5,7}$); 7.90(t, 1H, *J* 4, azulene H-C^2); 8.35 (d, 2H, azulene *H*-$C^{4,8}$); δ_C (60 MHz, $CDCL_3$) 15.2 (q, 1C, Me); 61.8[t, 2C, $(OCH_2Me)_2$]; 104.4[d, 1C, H-*C*$(OEt)_2$]; 118.1(d, 2C, azulene $C^{1,3}$); 121.4(d, 2C, azulene $C^{5,7}$); 135.8(d, 2C, azulene $C^{4,8}$); 137.3(s, 1C, azulene C^2); 139.9(s, 2C, azulene $C^{3a,8a}$); 147.3(s, 1C, azulene C^6); *m/z* (EI) 230 (M^+, 80%).

4-(1,3-Dioxan-2-yl)pyridine

A 13.5% solution of HBr in propane-1,3-diol was prepared by cooling propane-1,3-diol (88 ml) to 0 °C under nitrogen and adding acetyl bromide (12 ml) dropwise. To a portion of this solution (52 ml) was added pyridine-4-carbaldehyde (11.2 g, 105 mmol) and the solution was stirred at 20 °C for 90 h. Dry benzene (100 ml) was then added and any water formed during the reaction, removed by azeotropic distillation through a Soxhlet extractor containing $MgSO_4$, over a period of 24 h. Benzene and ethanol were then evaporated under reduced pressure to give an orange solid which was made alkaline (pH 9) by adding 10% K_2CO_3 solution (75 ml). This was extracted with diethyl ether (3×50 ml), dried and reduced to leave a brown oil. Purification by vacuum distillation gave unreacted pyridine-4-carbaldehyde and a small amount of product, bp 68–71 °C at 0.6 mmHg (3.62 g, 21%) as a mixture of 4-(1,3-dioxan-2-yl)pyridine (1.05 g, 6.1% from ^1H NMR) and propane-1,3-diol as a colourless oil at 71–100 °C at 0.6 mmHg, δ_H (220 MHz, $CDCl_3$); 1.70(m, 2H, $OCH_2CH_2CH_2O$); 4.0(m, 4H, $OCH_2CH_2CH_2O$); 5.50(s, 1H 1,3-dioxan-2-yl-C*H*-pyridine); 7.70(d, 2H, 2-pyridine); 8.70(d, 2H, 3-pyridine); and signals for propane-1,3-diol; *m/z* (+CI) $C_9H_{11}NO_2$ 165 (M^+, 100%).

N-Butyl-4-(1,3-dioxan-2-yl)pyridinium bromide

The crude mixture of 4-(1,3-dioxan-2-yl)pyridine (1.05 g, 6.36 mmol) and 1-bromobutane (4.5 g, 33.0 mmol) was added to dry ethanol (10 ml) and heated at reflux for 16 h, the reaction being followed by TLC. The ethanol was evaporated under reduced pressure but the product *N*-butyl-4-(1,3-dioxan-2-yl)pyridinium bromide remained contaminated with propane-1,3-diol, *m/z* (+ve FAB MS) $C_{13}H_{20}NO_2$ 222 (M^+, 100%).

6-(1,3-Dioxan-2-yl)azulene, 1b

Freshly distilled cyclopentadiene (2.19 ml, 33.2 mmol) was added dropwise to sodium hydride (0.40 g, 16.7 mmol) in THF (30 ml) at 0 °C over 30 min and then allowed to warm to 20 °C. Crude *N*-butyl-4-(1,3-dioxan-2-yl)pyridinium bromide (1.9 g, 6.28 mmol), dissolved in THF (10 ml), was then added to the pink solution giving a colour change to dark orange and then brown. The mixture was heated at reflux for 3 h. Water (50 ml) was then added and the mixture extracted with dichloromethane (4×50 ml): the combined organic layers were dried and solvent evaporated under reduced pressure. Purification by column chromatography on silica using dichloromethane as eluent gave 6-(1,3-dioxan-2-yl)azulene as dark blue microprisms. Recrystallisation from pentane gave the pure product, (0.195 g, 15%), mp 110–111 °C (Found: C, 78.3; H, 6.6; $C_{14}H_{14}O_2$ calculated: C, 78.5; H, 6.6%); δ_H (250 MHz, $CDCl_3$) 1.45(m, 1H, dioxanyl); 2.25(m, 1H, dioxanyl); 4.00(m, 2H, dioxanyl); 4.30(m, 2H, dioxanyl); 5.50(s, 1H, *H*-C-azulene); 7.40(d, 2H, *J* 10, azulene H-$C^{1,3}$); 7.40(d, 2H, *J* 4, azulene H-$C^{5,7}$); 7.90(t, 1H, *J* 4, azulene H-C^2); 8.40(d, 2H, *J* 10, azulene H-C^4); δ_C (60 MHz, $CDCl_3$) 25.7(t, 1C, CH_2); 67.6 [t, 2C, $(OCH_2)_2$]; 104.3(d, 1C, H-*C*-azulene); 118.1(d, 2C, azulene $C^{1,3}$); 121.1(d, 2C, azulene $C^{5,7}$); 135.2(d, 2C, azulene $C^{4,8}$); 135.9(d, 1C, azulene C^2); 140.1(s, 2C, azulene $C^{3a,8a}$); 146.0(s, 1C, azulene C^6); *m/z* (EI) 214 (M^+, 83%).

cis- and *trans*-6-(5-Pentyl-1,3-dioxan-2-yl)azulene, 1c

Compound **1a** (0.35 g, 1.52 mmol) and 2-pentylpropane-1,3-diol (0.33 g, 2.28 mmol) were stirred together in dry benzene (10 ml) with an ion exchange resin (catalytic amount) at 100 °C for 6 h and the reaction was followed by TLC. Purification of the products was attempted by column chromatography on silica using hexane–dichloromethane (3:1) as eluent which gave the mixture of isomers as blue microprisms (170 mg, 39%). These were shown, by analytical HPLC, to be a mixture of the *cis*- and *trans*-forms in a ratio of 2:3. Separation was achieved using reverse phase HPLC to give the pure isomers, *cis*-6-(5-pentyl-1,3-dioxan-2-yl)azulene, mp 81.4 °C; (M^+ Found: 284.1785, $C_{19}H_{24}O_2$ requires: 284.17762); δ_H (250 MHz, CD_2Cl_2) 0.9(t, 3H, *J* 7, Me); 1.35[m, 7H, $CH_2(CH_2)_3Me$, C-HC_5H_9]; 1.83(m, 2H, $CH_2C_4H_9$); 4.10(m, 4H, $(OCH_2)_2$]; 5.52(s, 1H, *H*-C-azulene); 7.38(d, 2H, *J* 4, azulene H-$C^{1,3}$); 7.38(d, 2H, *J* 10, azulene H-$C^{5,7}$); 7.90(t, 1H, *J* 4, azulene H-C^2); 8.37(d, 2H, *J* 10, azulene H-$C^{4,8}$); δ_C (63 MHz, CD_2Cl_2) 14.1(q, 1C, Me); 22.7(t, 1C, CH_2); 27.3(t, 1C, CH_2) 29.6(t, 1C, CH); 32.0(t, 1C, CH_2); 34.4[d, 1C, $HC(CH_2O)_2$]; 71.0(t, 2C, $(CH_2O)_2$]; 104.7(d, 1C, H-*C*-azulene); 118.2(d, 2C, azulene $C^{1,3}$); 121.2(d, 2C, azulene $C^{5,7}$); 136.1(d, 2C, azulene $C^{4,8}$); 137.6(d, 1C, azulene C^2); 140.1(s, 2C, azulene $C^{3a,8a}$); 146.0(s, 1C, azulene C^6); *m/z* (EI) 284 (M^+, 92%); and *trans*-6-(5-pentyl-1,3-dioxan-2-yl) azulene, mp 100.1 °C; (M^+ Found: 284.1783, $C_{19}H_{24}O_2$ requires: 284.17762); δ_H (250 MHz, CD_2Cl_2) 0.90(t, 3H, *J* 7, Me); 1.10(m, 2H, $C_3H_7CH_2Me$); 1.30[m, 6H, $(CH_2)_3C_2H_5$]; 2.20(m, 1H, C-HC_5H_9); 3.58(t, 2H, *J* 12, OCH_2); 4.28(q, 2H, *J* 4.5, OCH_2); 5.45(s, 1H, *H*-C-azulene); 7.38(d, 2H, *J* 4, azulene H-$C^{1,3}$); 7.38(d, 2H, *J* 10, azulene H-$C^{5,7}$); 7.90(t, 1H, *J* 4, azulene H-C^2); 8.35(d, 2H, *J* 10, azulene H-$C^{4,8}$); δ_C (63 MHz, CD_2Cl_2) 14.1(q, 1C, Me); 22.5(t, 1C, CH_2); 26.0(t, 1C, CH_2); 28.2(t, 1C, CH); 32.0(t, 1C, CH_2); 34.2[d, 1C, $HC(CH_2O)_2$]; 72.9[t, 2C, $(CH_2O)_2$]; 104.3(d, 1C, H-*C*-azulene); 118.2(d, 2C, azulene $C^{1,3}$); 121.2 (d, 2C, azulene $C^{5,7}$); 136.0(d, 2C, azulene $C^{4,8}$); 137.6(d, 1C, azulene C^2); 140.1(s, 2C, azulene $C^{3a,8a}$); 145.9(s, 1C, azulene C^6); *m/z* (EI) 284 (M^+, 100%).

The series of homologues were all prepared in a similar manner and the reaction conditions are outlined in Table A.

Table A

compound	catalyst	solvent	temperature/°C, time/h	yield (%)	*cis*:*trans* ratio
1d	TsOH	—	55/48	22	2:3
1e	i-e resin	Benzene	80/20	16	2:5
1f	i-e resin	CH_2Cl_2	50/20	13	1:3
1g	i-e resin	Benzene	reflux/4	23	1:3
1h	i-e resin	Benzene	reflux/8	6	1:3
1i	i-e resin	Benzene	100/8	26	1:3
1j	i-e resin	Toluene	reflux/4	41	1:3
1k	i-e resin	Toluene	100/8	39	1:3

All the above compounds gave ^{1}H NMR, ^{13}C NMR and mass spectra analogous to those for the 6-(5-pentyl-1,3-dioxan-2-yl)azulene isomers described above.

The high resolution mass spectra values for each compound are given in Table B.

Table B

compound	molecular formula	calc.	found *cis*	found *trans*
1d	$C_{20}H_{26}O_2$	298.1933	298.1941	298.1926
1e	$C_{24}H_{34}O_2$	354.2559	354.2542	354.2547
1f	$C_{25}H_{36}O_2$	368.2715	368.2719	368.2711
1g	$C_{26}H_{38}O_2$	382.2872	382.2882	382.2862
1h	$C_{27}H_{40}O_2$	396.3028	396.3046	396.3012
1i	$C_{28}H_{42}O_2$	410.3185	410.3178	410.3166
1j	$C_{29}H_{44}O_2$	424.3341	424.3348	424.3346
1k	$C_{30}H_{46}O_2$	438.3498	438.3489	438.3490

cis- and *trans*-6-(5-Phenyl-1,3-dioxan-2-yl)azulene, 1l

Compound **1a** and 2-phenylpropane-1,3-diol (0.5 g, 3.26 mmol) were stirred together with the ion-exchange catalyst at 60 °C in dry THF (5 ml) for 2 h. The reaction was monitored by TLC; when all the starting material had disappeared the reaction mixture was filtered to remove the resin and the product washed through with ethyl acetate. Purification by column chromatography on silica, using light petroleum (bp 40–60 °C)–ethyl acetate, 4:1, as eluent gave a mixture of the *cis*- and *trans*-isomers as dark blue microprisms, 0.532 g, 53%. These were shown, by analytical HPLC to be a mixture of the *cis*- and *trans*-forms in a ratio 1:2. Separation of the isomers was achieved by reverse phase chromatography; recrystallisation from diethyl ether–light petroleum gave the pure isomers; *cis*-6-(5-phenyl-1,3-dioxan-2-yl)azulene, mp 123 °C (M^+ Found: 290.1302, $C_{20}H_{18}O_2$ calculated: 290.1307); δ_H (250 MHz, $CDCl_3$) 2.75(m, 1H, dioxanyl); 4.4(m, 4H, dioxanyl); 5.79(s, 1H, H-C-azulene); 7.7(m, 2H, phenyl); 7.47(d, 2H, *J* 11, azulene H-C^{5,7}); 7.35(m, 5H, phenyl and azulene H-C^{1,3}); 7.9(t, 1H, *J* 4, azulene H-C^2); 8.45(d, 2H, *J* 11, azulene H-C^{4,8}); δ_C (63 MHz, $^2H_6$ acetone) 39.5(d, 1C, H-*C*-Ph); 72.1[t, 2C, (O*C*H$_2$)$_2$]; 104.9(d, 1C, H-*C*-azulene); 118.8(d, 2C, azulene C^{1,3}); 122.2(d, 2C, azulene C^{5,7}); 126.9(d, 1C, Ph); 128.9(d, 2C, Ph); 129.2(d, 2C, Ph); 136.5(d, 2C, azulene C^{4,8}); 138.1(s, 1C, Ph); 140.8(d, 1C, azulene C^2); 144.3(s, 2C, azulene C^{3a,8a}); 147.4(s, 1C, azulene C^6); *m*/*z* (EI) 290 (M^+, 45%); and *trans*-6-(5-phenyl-1,3-dioxan-2-yl)azulene, mp 193 °C (M^+ Found: 290.1302, $C_{20}H_{18}O_2$ calculated: 290.1307); δ_H (250 MHz, $CDCl_3$) 3.45(m, 1H, dioxanyl); 4.10(t, 2H, dioxanyl); 4.45(q, 2H, dioxanyl); 5.65(s, 1H, H-C-azulene); 7.30(m, 9H, azulene H-C^{1,3,5,7} and phenyl); 7.95(t, 1H azulene H-C^2); 8.45(d, 2H, azulene H-C^{4,8}); δ_C (63 MHz, $CDCl_3$) 41.1(d, 1C, H-*C*-Ph); 72.6[t, 2C, (O*C*H$_2$)$_2$]; 104.2(d, 1C, H-*C*-azulene); 118.3(d, 2C, azulene C^{1,3}); 121.2(d, 2C, azulene C^{5,7}); 127.6(d, 1C, Ph); 127.7(d, 2C, Ph); 128.9(d, 2C, Ph); 136.0(d, 2C, azulene C^{4,8}); 137.4(s, 1C, Ph) 137.7(d, 1C, azulene C^2); 140.2(s, 2C, azulene C^{3a,8a}); 145.6(s, 1C, azulene C^6); *m*/*z* (EI) 290 (M^+, 85%).

This procedure was used to prepare **1m** and **1n** (Table C) by reaction with the appropriate diol.

cis- and *trans*-6-[5-(4-Hexyloxyphenyl)-1,3-dioxan-2-yl]-azulene, 1m

cis-6-[5-Hexyloxyphenyl)-1,3-dioxan-2-yl]azulene, mp 143 °C (decomp.) and the *trans*-6-[5-(4-hexyloxyphenyl)-1,3-dioxan-2-yl]azulene, mp 225 °C, δ_H (250 MHz, CD_2Cl_2) 0.89(t, 3H, *J* 7, Me); 1.40[m, 6H, $C_2H_4(CH_2)_3Me$]; 1.75(m, 2H, $CH_2CH_2C_4H_9$); 3.33(m, 1H, H-C-phenyl); 3.92(t, 2H, *J* 7, dioxanyl CH_2); 4.02(t, 2H, *J* 11.5, $OCH_2C_5H_{11}$); 4.32(q, 2H, *J* 11.5, dioxanyl CH_2); 5.6(s, 1H, *H*-C-azulene); 6.86(d, 2H, *J* 8.5, phenyl); 7.16(d, 2H, *J* 8.5, phenyl); 7.38(d, 2H, *J* 4.5, azulene H-C^{1,3}); 7.42(d, 2H, *J* 10.5, azulene H-C^{5,7}); 7.9(t, 1H, *J* 4.5, azulene H-C^2); 8.39(d, 2H, *J* 10.5, azulene H-C^{4,8}); δ_C (63 MHz, CD_2Cl_2) 14.2(q, 1C, Me); 23.0(t, 1C, CH_2); 26.1(t, 1C, CH_2); 29.6(t, 1C, CH_2); 32.0(t, 1C, CH_2); 40.7[t, 1C, H-C-(OCH_2)]; 68.5(t, 1C, OCH_2); 73.1[d, 2C, dioxanyl 2(OCH_2)]; 104.3(d, 1C, H-C-azulene); 115.1(d, 2C, phenyl); 118.5(d, 2C, azulene C^{1,3}); 121.6(d, 2C, azulene C^{5,7}); 129.0(d, 2C, phenyl); 129.6(s, 1C, phenyl); 136.2(d, 2C, azulene C^{4,8}); 138.0(d, 1C, azulene C^2); 140.4(s, 2C, azulene C^{3a,8a}); 146.4(s, 1C, phenyl); 158.9(s, 1C, azulene C^6); *m*/*z* (EI) 390 (M^+, 62%).

cis- and *trans*-6-[5-(4-dodecyloxyphenyl)-1,3-dioxan-2-yl]-azulene, 1n

cis-6-[5-(4-Dodecyloxyphenyl)-1,3-dioxan-2-yl]azulene, mp 127 °C (M^+ Found: 474.3139, $C_{32}H_{42}O_3$ calculated: 474.3134); δ_H (250 MHz, CD_2Cl_2) 0.86(t, 3H, *J* 7, Me); 1.26[m, 18H, $CH_2(CH_2)_9Me$]; 1.75(m, 2H, $CH_2CH_2C_9H_{18}Me$); 2.75(m, 1H, C*H*-phenyl-$OC_{12}H_{25}$); 3.94(t, 2H, $OCH_2C_{11}H_{23}$); 4.38[m, 4H, 2(dioxanyl CH_2)]; 5.68(s, 1H, dioxanyl—C*H*—azulene); 6.89(d, 2H, *J* 9, phenyl); 7.39(m, 4H, azulene H-C^{1,3,5,7}); 7.53(d, 2H, *J* 9, phenyl); 7.90(t, 1H, *J* 4, azulene H-C^2); 8.39(d, 2H, *J* 11, azulene H-C^{4,8}); δ_C (63 MHz, CD_2Cl_2) 14.25(q, 1C, Me); 23.1(t, 1C, CH_2); 26.4(t, 1C, CH_2); 29.7[t, 2C, 2(CH_2)]; 29.8[t, 4C, 4(CH_2)]; 30.0(t, 1C, CH_2); 32.3(t, 1C, CH_2); 38.6(t, 1C, dioxanyl-CH phenyl-$OC_{12}H_{25}$); 68.4(t, 1C, $OCH_2C_{11}H_{23}$); 72.2[d, 2C, dioxanyl 2(OCH_2)]; 104.8(d, 1C, dioxanyl-HC-azulene); 114.6(d, 2C, phenyl); 118.5(d, 2C, azulene C^{1,3}); 121.6(d, 2C, azulene C^{5,7}); 129.7(d, 2C, phenyl); 135.2(s, 1C, phenyl); 136.3(d, 2C, azulene C^{4,8}); 138.0(d, 1C, azulene C^2); 140.4(s, 2C, azulene C^{3a,8a}); 146.5(s, 1C, phenyl); 158.3(s, 1C, azulene C^6); *m*/*z* (EI) 474 (M^+, 100%); and *trans*-6-[5-(4-dodecyloxyphenyl)-1,3-dioxan-2-yl]azulene, mp 206 °C (crystal S_B) (M^+ Found: 474.3123, $C_{32}H_{42}O_3$ calculated: 474.3134); δ_H (250 MHz, CD_2Cl_2) 0.88(t, 3H, *J* 7, Me); 1.30[m, 18H, $CH_2(CH_2)_9Me$]; 1.75(m, 2H, $CH_2CH_2C_9H_{18}Me$); 3.34(m, 1H, C*H*-phenyl-$OC_{12}H_{25}$); 3.94(t, 2H, *J* 7, $OCH_2C_{11}H_{23}$); 4.04(t, 2H, *J* 11.5, dioxanyl CH_2); 4.34(q, *H*, *J* 4.5, dioxanyl CH_2); 5.68(s, 1H, dioxanyl-C*H*-azulene); 6.88(d, 2H, *J* 9, phenyl); 7.17(d, 2H, *J* 9, phenyl); 7.42(m, 4H, azulene H-C^{1,3,5,7}); 7.92(t, 1H, *J* 4, azulene H-C^2); 8.40(d, 2H, *J* 11, azulene H-C^{4,8}); δ_C (63 MHz, CD_2Cl_2) 14.24(q, 1C, Me); 23.1(t, 1C, CH_2); 26.4(t,

Table C

compound	alkyl chain	catalyst	solvent	temperature/°C, time/h	yield (%)	*cis*:*trans*
1m	OC_6H_{13}	i-e resin	THF	60/48	7	1:4
1n	$OC_{12}H_{25}$	i-e resin	THF	100/8	14	1:3

1C, CH_2); 26.4(t, 1C, CH_2); 29.6[t, 2C, 2(CH_2)]; 29.7[t, 4C, 4(CH_2)]; 30.0(t, 1C, CH_2); 32.3(t, 1C, CH_2); 40.7(t, 1C, dioxanyl-HC phenyl-$OC_{12}H_{25}$); 68.4(t, 1C, $OCH_2C_{11}H_{23}$); 73.1(d, 2C, dioxanyl 2(OCH_2)); 104.3(d, 1C, dioxanyl-HC-azulene); 115.1(d, 2C, phenyl); 118.5(d, 2C, azulene $C^{1,3}$); 121.6(d, 2C, azulene $C^{5,7}$); 129.0(d, 2C, phenyl); 129.6(s, 1C, phenyl); 136.2(d, 2C, azulene $C^{4,8}$); 138.0(d, 1C, azulene C^2); 140.4(s, 2C, azulene $C^{3a,8a}$); 146.4(s, 1C, phenyl); 158.9(s, 1C, azulene C^6); *m/z* (EI) 474 (M^+, 100%).

2-(+)-Neomenthyl-6-(diethoxymethyl)azulene

(+)-Neomenthylcyclopentadiene[18] (2 g, 9.8 mmol, 1.1 equiv.) was added to sodium hydride (0.21 g, 8.90 mmol, 1 equiv.) in dry THF (30 ml) at 20 °C to give a slightly pink solution. After 30 min, when no further reaction was observed, *N*-butyl-4-(diethoxymenthyl)pyridinium bromide (5.0 g, 15.0 mmol, 2 equiv.) in THF (20 ml) was added to give a dark brown solution which was heated at reflux for 16 h. Solvent was evaporated under reduced pressure and alumina added. Purification by column chromatography was attempted on basic alumina using hexane as eluent to give an unidentified yellow oil and 2-(+)-neomenthyl-6-(diethoxymenthyl)azulene as a dark blue oil 0.74 g, 22.6% (Found: 368.2706, $C_{25}H_{36}O_2$ calculated: 368.2715); δ_H (250 MHz, $CDCl_3$) 0.8(t, 6H, 2Me); 1.30(m, 18H, neomenthyl); 2.20(m, 1H, neomenthyl *H*-C-azulene); 3.60(t, 2H, OCH_2); 3.55[m, 4H, 2(OCH_2Me)]; 7.30(s, 2H, azulene H-$C^{1,3}$); 7.35(d, 2H, azulene H-$C^{5,7}$); 8.25(d, 2H, azulene H-$C^{4,8}$); δ_C (63 MHz, $CDCl_3$) 15.2(q, 2C, Me); 21.3(q, 1C, Me); 21.4(q, 1C, Me): 22.8(q, 1C, Me); 26.5(t, 1C, CH_2); 26.9(d, 1C, CH); 30.5(d, 1C, CH); 35.7(t, 1C, CH_2); 39.6(d, 1C, CH); 43.0(t, 1C, CH_2); 48.2[d, 1C, (+)-neomenthyl H-*C*-azulene]; 61.9[t, 2C, 2(OCH_2)Me]; 104.5(d, 1C, diethoxy H-*C*-azulene); 119.6(d, 2C, azulene $C^{1,3}$); 121.5(d, 2C, azulene $C^{5,7}$); 133.6(d, 2C, azulene $C^{4,8}$); 139.5(s, 2C, azulene $C^{3a,8a}$); 145.3(s, 1C, azulene C^6); 158.3(s, 1C, azulene C^2); *m/z* (EI) 368 (M^+, 50%).

***cis*- and *trans*-2-Neomenthyl-6-(5-undecyl-1,3-dioxan-2-yl)-azulene, 1o**

2-Neomenthyl-6-(diethoxymethyl)azulene (0.6 g, 1.63 mmol) and 2-undecylpropane-1,3-diol (0.6 g, 2.61 mmol) were heated to 60 °C together with an ion-exchange resin (catalytic amount) in dry ethyl acetate (3 ml) for 1 h. The reaction was monitored by TLC and solvent evaporated under reduced pressure when starting material had disappeared. Purification was achieved by column chromatography on neutral silica using light petroleum–diethyl ether, 4:1, as eluent to give the mixture of isomers as blue microprisms, 150 mg, 18%. Separation of the isomers (*cis*/*trans*: 1/3) was achieved by HPLC to give *cis*-2-neomenthyl-6-(5-undecyl-1,3-dioxan-2-yl)azulene, as a blue oil, δ_H (250 MHz, $CDCl_3$) 1.30(m, 43H, neomenthyl and $C_{11}H_{23}$); 4.05[s, 4H, 2(OCH_2)]; 5.45(s, 1H, dioxanyl *H*-C-azulene); 7.20(s, 2H, azulene H-$C^{1,3}$); 7.25(d, 2H, azulene H-$C^{5,7}$); 8.25(d, 2H, azulene H-$C^{4,8}$); δ_C (63 MHz, $CDCl_3$) 14.1(q, 1C, Me); 21.2(q, 1C, Me); 21.4(q, 1C, Me); 22.7(q, 1C, Me); 22.8(t, 1C, CH_2); 26.4 (t, 1C, CH_2); 26.9 (t, 1C, CH_2); 27.6 (t, 1C, CH_2); 28.2 (t, 1C, CH_2); 29.4(t, 1C, CH_2); 29.7[t, 5C, 5(CH_2)]; 30.5(d, 1C, CH); 31.9(t, 1C, CH_2); 34.4(d, 2C, CH); 35.7(t, 1C, CH_2); 39.6(d, 1C, CH); 42.9[t, 1C, H-*C*($CH_2O)_2$]; 48.2(d, 1C, neomenthyl H-*C*-azulene); 70.9[t, 2C, 2(OCH_2Me)]; 104.9(d, 1C, dioxanyl H-*C*-azulene); 119.6(d, 2C, azulene $C^{1,3}$); 121.2(d, 2C, azulene $C^{5,7}$); 133.8(d, 2C, azulene $C^{4,8}$); 139.7(s, 2C, azulene $C^{3a,8a}$); 144.2(s, 1C, azulene C^6); 158.5(s, 1C, azulene C^2); and *trans*-2-neomenthyl-6-(5-undecyl-1,3-dioxan-2-yl)azulene, as blue microprisms, mp 53–43 °C, δ_H (250 MHz, $CDCl_3$) 1.30(m, 42H, neomenthyl and $C_{11}H_{23}$); 2.20(m, 1H, neomenthyl *H*-C-azulene); 3.60(t, 2H, OCH_2); 4.30(q, 2H, OCH_2); 5.45(s, 1H, dioxanyl *H*-C-azulene); 7.30(s, 2H, azulene H-$C^{1,3}$); 7.35(d, 2H, azulene H-$C^{5,7}$); 8.25(d, 2H, azulene H-$C^{4,8}$); δ_C (63 MHz, $CDCl_3$) 14.1(q, 1C, Me); 21.3(q, 1C, Me); 21.4(q, 1C, Me); 22.7(q, 1C, Me); 22.8(t, 1C, CH_2); 26.4(t, 1C, CH_2); 26.9(t, 1C, CH_2); 28.2(t, 1C, CH_2); 29.4(t, 1C, CH_2); 29.5(t, 1C, CH_2); 29.7(t, 4C, CH_2); 29.8(t, 1C, CH_2); 30.5(d, 1C, CH); 31.9(t, 1C, CH_2); 34.2(d, 1C, CH); 35.7(t, 1C, CH_2); 39.6(d, 1C, CH); 42.9[t, 1C, H-*C*($CH_2O)_2$]; 48.2(d, 1C, neomenthyl H-*C*-azulene); 72.9[t, 2C, 2(OCH_2Me)]; 104.6(d, 1C, dioxanyl H-*C*-azulene); 119.6(d, 2C, azulene $C^{1,3}$); 121.2(d, 2C, azulene $C^{5,7}$); 133.7(d, 2C, azulene, $C^{4,8}$); 139.7(s, 2C, azulene $C^{3a,8a}$); 144.0(s, 1C, azulene C^6); 158.5(s, 1C, azulene C^2); *m/z* (EI) 506 (M^+, 18%).

1-Cyclohexyl-6-(diethoxymethyl)azulene and 2-cyclohexyl-6-(diethoxymethyl)azulene

Cyclohexylcyclopentadiene, (1 g, 6.76 mmol) was added to sodium hydride (0.2 , 8.33 mmol) in THF (30 ml) and heated gently until the reaction had completed, to give a red solution. Butyl-4-(diethoxymethyl)pyridine bromide (5.0 g, 15.0 mmol) was added in THF (25 ml) and heated at reflux for 90 h. Solvent was evaporated under reduced pressure and neutral silica added to the dark brown oil. Purification by column chromatography on neutral silica using light petroleum as eluent gave a colourless oil identified as *N*-butyl-(4-ethoxycarbonyl-4-ethyl)dihydropyridine, 0.5 ml, 14%, δ_H (250 MHz, $CDCl_3$) 0.81(t, 3H, *J* 7.5, CH_2CH_3); 0.89(t, 3H, *J* 7.5, $NC_3H_6CH_3$); 1.24(t, 3H, *J* 7.5, $COOCH_2CH_3$); 1.27(m, 2H, $NC_2H_4CH_2$Me); 1.44(m, 2H, $NCH_2CH_2C_2H_5$); 1.49(q, 2H, *J* 7.5, CH_2Me); 3.20(t, 2H, *J* 7, $NCH_2C_3H_7$); 4.13(q, 2H, *J* 7, $COOCH_2$Me); 4.40(d, 2H, *J* 8, β-dihydropyridine); 5.93(d, 2H, *J* 8, α-dihydropyridine); δ_C (63 MHz, $CDCl_3$) 8.5(q, 1C, CH_2CH_3); 13.8(q, 1C, $NC_3H_6CH_3$); 14.1(q, 1C, $COOCH_2CH_3$); 19.7(t, 1C, $NC_2H_4CH_2$Me); 32.3(d, 1C, $NCH_2CH_2C_2H_5$); 35.1(t, 1C, CH_2Me); 46.6(s, 1C, γ-dihydropyridine); 53.1(t, 1C, $NCH_2C_3H_7$); 60.4(t, 1C, OCH_2Me); 98.4(d, 2C, β-dihydropyridine); 130.2(d, 2C, α-dihydropyridine); 176.5(s, 1C, COOEt), and a mixture of the isomers as a dark-blue oil, 0.533 g, 25%. Separation of the isomers was achieved by MPLC to give 1-cyclohexyl-6-(diethoxymethyl)azulene, as a purple–blue oil, (Found: 312.2103, $C_{21}H_{28}O_2$ calculated: 312.2089); δ_H (250 MHz, CD_2Cl_2) 1.30[t, 6H, 2(OCH_2Me)]; 1.70(m, 10H, cyclohexyl); 3.25(m, 1H, azulene C*H*-cyclohexyl); 3.55[m, 4H, 2(OCH_2Me)]; 5.35[s, 1H, $(EtO)_2CH$-azulene]; 7.15(d, 2H, azulene H-$C^{5,7}$); 7.2(d, 1H, azulene H-C^3); 7.75(d, 1H, azulene H-C^2); 8.15(d, 1H, azulene H-C^4); 8.25(d, 1H, azulene H-C^4); δ_C (63 MHz, CD_2Cl_2) 15.4[q, 2C, 2(OCH*Me*)]; 26.8(t, 1C, cyclohexyl); 27.6(t, 2C, cyclohexyl); 35.6(t, 2C, cyclohexyl); 37.0(d, 1C, azulene *C*H-cyclohexyl); 62.4[t, 2C, 2(OCH_2Me)]; 105.1[d, 1C, $(EtO)_2C$H-azulene]; 117.3(d, 1C, azulene C^3); 120.1(d, 1C, azulene C^5); 120.8(d, 1C, azulene C^7); 132.6(d, 1C, azulene C^2); 134.6(s, 1C, azulene C^1); 135.1(d, 1C, azulene C^4); 135.8(d, 1C, azulene C^8); 137.9(s, 1C, azulene C^{3a}); 140.6(s, 1C, azulene C^{8a}); 148.0(s, 1C, azulene C^6); *m/z* (EI) 312 (M^+, 100%), and 2-cyclohexyl-6-(diethoxymethyl)-azulene, as blue microprisms, mp 58–59 °C (Found 312.2074, $C_{21}H_{28}O_2$ calculated: 312.2089); δ_H (250 MHz, CD_2Cl_2) 0.90[t, 6H, 2(OCH_2Me)]; 1.80(m, 10H, cyclohexyl); 2.90(m, 1H, azulene C*H*-cyclohexyl); 3.65[m, 4H, 2(OCH_2Me)]; 4.45 [s, 1H, $(EtO)_2CH$-azulene]; 7.20(s, 2H, azulene H-$C^{1,3}$); 7.30(d, 2H, azulene H-$C^{5,7}$); 8.20(d, 2H, azulene H-$C^{4,8}$); δ_C (63 MHz, CD_2Cl_2) 5.2[q, 2C, 2(OCH_2Me)]; 16.6(t, 1C, cyclohexyl); 16.9(t, 2C, cyclohexyl); 24.5(t, 2C, cyclohexyl); 30.3(d, 1C, azulene *C*H-cyclohexyl); 94.9[t, 2C, 2(OCH_2Me)]; 106.0[d, 1C, $(EtO)_2CH$-azulene]; 111.7(d, 2C, azulene $C^{1,3}$); 123.9(d, 2C, azulene, $C^{5,7}$); 130.3(d, 2C, azulene $C^{4,8}$); 130.3(s, 2C, azulene $C^{3a,8a}$); 135.9(s, 1C, azulene C^6); 151.4(s, 1C, azulene C^2); *m/z* (EI) 312 (M^+, 100%).

cis*- and *trans*-2-Cyclohexyl-6-(5-tridecyl-1,3-dioxan-2-yl)-azulene, *1p

2-Cyclohexyl-6-(diethoxymethyl)azulene (0.28 g, 0.90 mmol) and tridecylpropane-1,3-diol (0.3 g, 1.15 mmol) were dissolved

in dry benzene (20 ml) and heated at 80 °C with an ion exchange resin (catalytic amount) for 3 h. Solvent was evaporated under reduced pressure to leave a black product. Purification was attempted by column chromatography on neutral silica using light petroleum with 1% diethyl ether as eluent to give the pure *trans*-2-cyclohexyl-6-(5-tridecyl-1,3-dioxan-2-yl)azulene, as blue microprisms (Found: C, 82.73; H, 10.80; $C_{33}H_{50}O_2$ calculated: C, 82.79; H, 10.52%); δ_H (250 MHz, CD_2Cl_2) 0.80(t, 3H, *J* 7, Me); 1.1(m, 2H, cyclohexyl CH_2); 1.20(m, 22H, $C_{11}H_{22}C_2H_5$); 1.45(m, 6H, cyclohexyl); 1.70(m, 4H, cyclohexyl); 2.05(m, 1H, *H*C-$C_{13}H_{27}$); 2.85(m, 1H, azulene C*H*-cyclohexyl); 3.46(t, 2H, *J* 11 Hz, OCH_2); 4.16(q, 2H, *J* 5, OCH_2); 5.70(s, 1H, dioxanyl *H*C-azulene); 7.14(s, 2H, azulene H-$C^{1,3}$); 7.21(d, 2H, *J* 10.5, azulene H-$C^{5,7}$); 8.13(d, 2H, *J* 10.5 Hz), azulene H-$C^{4,8}$); δ_C (63 MHz, CD_2Cl_2) 14.3(q, 1C, Me), 23.1(t, 1C, CH_2); 26.7(t, 1C, cyclohexyl); 27.1(t, 2C, cyclohexyl); 28.5(t, 1C, CH_2); 29.7(t, 1C, CH_2); 29.9[t, 8C, 8(CH_2)]; 30.1(t, 1C, CH_2); 32.3(t, 2C, cyclohexyl); 34.6(d, 1C, H*C*-$C_{13}H_{27}$); 40.5(d, 1C, azulene *C*H-cyclohexyl); 73.2[t, 2C, 2(OCH_2)]; 104.7(d, 1C, dioxanyl H*C*-azulene); 116.2(d, 2C, azulene $C^{1,3}$); 121.7(d, 2C, azulene $C^{5,7}$); 134.1(d, 2C, azulene $C^{4,8}$); 140.6(s, 2C, azulene $C^{3a,8a}$); 144.7(s, 1C, azulene C^6); 161.9(s, 1C, azulene C^2); *m/z* (EI) 478 (M^+, 100%). MPLC on silica gave the pure *cis*-2-cyclohexyl-6-(5-tridecyl-1,3-dioxan-2-yl)azulene, as purple microprisms, mp 86–87 °C (M^+, calculated: 479.3882, $C_{33}H_{50}O_2$ found: 479.3889); δ_H (250 MHz, CD_2Cl_2) 0.86(t, 3H, *J* 7, Me); 1.1(m, 2H, cyclohexyl CH_2); 1.30(m, 22H, $C_{11}H_{22}C_2H_5$); 1.50(m, 6H, cyclohexyl); 1.80(m, 4H, cyclohexyl); 2.08(m, 1H, *H*C-$C_{13}H_{27}$); 2.92(m, 1H, azulene C*H*-cyclohexyl); 4.09[m, 4H, 2(OCH_2)]; 5.40(s, 1H, dioxanyl *H*C-azulene); 7.20(s, 2H, azulene H-$C^{1,3}$); 7.30(d, 2H, *J* 10.5, azulene H-$C^{5,7}$); 8.20(d, 2H, *J* 10.5), azulene H-$C^{4,8}$); δ_C (63 MHz, CD_2Cl_2) 14.3(q, 1C, Me), 23.1(t, 1C, CH_2); 26.7(t, 1C, cyclohexyl); 27.1(t, 2C, cyclohexyl); 28.5(t, 1C, CH_2); 29.7(t, 1C, CH_2); 29.8[t, 7C, 7(CH_2)]; 30.0(t, 1C, CH_2); 30.2(t, 1C, CH_2); 32.3(t, 2C, cyclohexyl); 34.6(d, 1C, H*C*-$C_{13}H_{27}$); 40.4(d, 1C, azulene *C*H-cyclohexyl); 71.3[t, 2C, 2(OCH_2)]; 105.2(d, 1C, dioxanyl H*C*-azulene); 116.1(d, 2C, azulene $C^{1,3}$); 121.7(d, 2C, azulene $C^{5,7}$); 134.1(d, 2C, azulene $C^{4,8}$); 140.6(s, 2C, azulene $C^{3a,8a}$); 144.7(s, 1C, azulene C^6); 161.9(s, 1C, azulene C^2); *m/z* (EI) 479 (M^+, 100%).

4-(Ethylenedioxy)cyclohexanol

4-(Ethylenedioxy)cyclohexanone (5.0 g, 32 mmol, 1 equiv.) in dry THF (25 ml) was added dropwise to $LiAlH_4$ (3.0 g, 79 mmol, 2.2 equiv.) in dry THF (20 ml). When the reaction had ceased, the mixture was heated at reflux for a further 3 h and allowed to cool. Excess $LiAlH_4$ was destroyed by the careful addition of wet diethyl ether and then water. The white suspension was then filtered through Celite which was washed with copious amounts of diethyl ether. The organic portions were combined, dried and solvent was evaporated under reduced pressure to leave crude 4-(ethylenedioxy)cyclohexanol as a yellow oil, 5 g, 99%, δ_H (250 MHz, $CDCl_3$) 1.75(m, 8H cyclohexyl CH_2s); 3.80(m, 1H, *H*COH); 4.00(s, 4H, ketal CH_2s).

4-(Ethylenedioxy)cyclohexyl tosylate

This was prepared by following the procedure of Winstein *et al.*[12] but full experimental details are given below. 4-(Ethylenedioxy)cyclohexanol, (5 g, 31.6 mmol, 1 equiv.) was dissolved in dry pyridine and tosyl chloride (9.0 g, 47.2 mmol, 1.5 equiv.) added in small portions. The reaction mixture was stirred vigorously for 30 min and then kept at 0 °C for 16 h. The crystals which appeared were collected and extracted into diethyl ether (50 ml). The ethereal portion was then washed with 2 M HCl (30 ml), water (100 ml) and 10% aqueous potassium carbonate (20 ml). Solvent was evaporated under reduced pressure to leave a viscous oil. This was left at 0 °C with seeding until crystals had formed, which were collected to give colourless crystals of 4-(ethylenedioxy)cyclohexyl tosylate, 7.2 g, 73%, δ_H (250 MHz, $CDCl_3$) 1.75(m, 8H, cyclohexyl CH_2s); 2.45(s, 3H, Me); 3.90(m, 4H, ketal CH_2s); 4.60(m, 1H, HCOTs); 7.30(d, 2H, phenyl); 7.80(d, 2H, phenyl): *m/z* (EI) 211 (M^+, 25%).

4-(Ethylenedioxy)cyclohexylcyclopentadiene

This was prepared by following the literature procedure for the synthesis of (+)-neomenthylcyclopentadiene by Cesarotti and Kagan,[19] but full experimental details are given below.

Freshly distilled cyclopentadiene (12 ml, 0.177 M) was added dropwise to sodium hydride (3.4 g, 0.142 M) in THF (25 ml) at 0 °C to give a pink solution. When the reaction had completed this was syringed into a solution of 4-(ethylenedioxy)cyclohexyl tosylate (11 g, 35.5 mmol) in THF (50 ml) and heated at reflux for 16 h to leave dark red colour. Water was then added, the now dark brown solution filtered through a Büchner funnel and solvent evaporated from the filtrate under reduced pressure to leave a brown oil. Purification by vacuum distillation (0.5 mmHg, 140 °C) gave 4-(ethylenedioxy)cyclohexylcyclopentadiene as a yellow oil, 2.5 g, 34%, δ_H (250 MHz, $CDCl_3$) 1.75(m, 8H, cyclohexyl CH_2s); 2.30[m, 1H, cyclopentadienyl-C*H*(cyclohexyl)]; 2.95(m, 2H, cyclopentadiene; 3.95(m, 4H, ketal CH_2s); 6.00–6.50(m, 3H, cyclopentadiene).

1-[4-(Ethylenedioxy)cyclohexyl]-6-(diethoxymethyl)azulene and 2-[4-(ethylenedioxy)cyclohexyl]-6-(diethoxymethyl)azulene

4-(Ethylenedioxy)cyclohexylcyclopentadiene, (1.5 g, 7.28 mmol) was added to sodium hydride (0.2 g, 8.00 mmol) in THF (30 ml) and heated gently until the reaction had completed to give a red solution. A solution of *N*-butyl-4-(diethoxymethyl)-pyridinium bromide (5.0 g, 15.0 mmol) in THF (25 ml) was then added leaving a colourless solution which was heated at reflux for 48 h; the reaction turning red and then dark brown. Solvent was evaporated under reduced pressure and neutral silica added to the dark brown oil. Purification by column chromatography on neutral silica using light petroleum–diethyl ether, 3:2, as eluent gave *N*-butyl-(4-ethoxycarbonyl-4-ethyl)dihydropyridine as a colourless oil and a mixture of the isomers as a dark blue oil. Separation of the isomers was attempted by HPLC and reverse phase HPLC but led to decomposition and a small amount of pure 1-[4-(ethylenedioxy)cyclohexyl]-6-(diethoxymethyl)azulene as a blue oil, (M^+ Found: 370.2130, $C_{23}H_{30}O_4$ calculated: 370.2144); δ_H (250 MHz, CD_2Cl_2) 1.2 [t, 6H, *J* 7, 2(*CH*$_3$)]; 1.85(m, 8H, cyclohexyl); 3.23(m, 1H, azulene *H*C-cyclohexyl); 3.60[m, 4H, 2(OCH_2CH$_3$)]; 3.95(s, 4H, O-CH_2-CH_2-O); 5.4 [s, 1H, (EtO)$_2$-*H*C-azulene]; 7.25(m, 3H, azulene H-$C^{3,5,7}$); 7.81(d, 1H, *J* 4, azulene H-C^2); 8.24(d, 1H, *J* 10, azulene H-C^4); 8.33(d, 1H, *J* 10, azulene H-C^8); δ_C (63 MHz, CD_2Cl_2) 15.3[q, 2C, 2(OCH$_2$*Me*)]; 32.5(t, 2C, cyclohexyl); 35.6(d, 1C, azulene *C*H-cyclohexyl); 62.3[t, 2C, 2(O*C*H$_2$Me)]; 64.6(t, 1C, O*C*H$_2$CH$_2$-O); 64.6(t, 1C, O-CH$_2$-*C*H$_2$-O); 104.9[d, 1C, (EtO)$_2$*C*H-azulene]; 108.8(s, 1C, cyclohexyl-*C*-ketal); 117.2(d, 1C, azulene C^3); 120.2(d, 1C, azulene C^5); 120.9(d, 1C, azulene C^7); 132.5(d, 1C, azulene C^2); 134.7(s, 1C, azulene C^1); 135.0(d, 1C, azulene C^4); 135.9(d, 1C, azulene C^8); 136.1(s, 1C, azulene C^{3a}); 140.5(s, 1C, azulene C^{8a}); 147.9(s, 1C, azulene C^6); *m/z* (EI) 270 (M^+, 50%); and 2-[4-(ethylenedioxy)cyclohexyl]-6-(diethoxymethyl)-azulene as blue microprisms, mp 53–54 °C (M^+ Found: 370.2151, $C_{23}H_{30}O_4$ calculated: 370.2144); δ_H (250 MHz, CD_2Cl_2) 1.20[t, 6H, 2(OCH$_2$*Me*)]; 1.80(m, 8H, cyclohexyl); 2.95(m, 1H, azulene C*H*-cyclohexyl); 3.58[m, 4H, 2(OCH$_2$Me)]; 3.93(s, 4H, O-CH_2-CH_2-O); 5.42 [s, 1H, (EtO)$_2$C*H*-azulene]; 7.22(s, 2H, azulene H-$C^{1,3}$); 7.32(d, 2H, *J* 10.5, azulene H-$C^{5,7}$); 8.20(d, 2H, *J* 10, azulene H-$C^{4,8}$); δ_C (63 MHz, CD_2Cl_2) 15.4[q, 2C, 2(OCH$_2$*Me*)]; 31.8(t, 2C, cyclohexyl); 35.3(t, 2C, cylcohexyl); 39.1(d, 1C, azulene *C*H-cyclohexyl); 62.3[t, 2C, 2(O*C*H$_2$Me)]; 64.6(t, 1C, O-*C*H$_2$-CH$_2$-O);

64.7(t, 1C, O-CH_2-CH_2-O); 105.0[d, 1C, $(EtO)_2CH$-azulene]; 108.9(s, 1C, cyclohexyl-*C*-ketal); 116.2(d, 2C, azulene $C^{1,3}$); 122.0(d, 2C, azulene $C^{5,7}$); 134.2(d, 2C, azulene $C^{4,8}$); 140.5(s, 2C, azulene $C^{3a,8a}$); 146.3(s, 1C, azulene C^6); 160.0(s, 1C, azulene C^2); *m/z* (EI) 370 (M^+, 100%).

Azulene-6-carbaldehyde

Compound **1a** (0.5 g, 2.17 mmol) was dissolved in dichloromethane (100 ml) and 2 M hydrochloric acid (50 ml) added. The mixture was stirred and the reaction monitored by TLC. When all the 6-(diethoxymethyl)azulene had disappeared as judged by TLC, the mixture was separated and the organic layer dried and the solvent evaporated under reduced pressure. Recrystallisation from light petroleum gave azulene-6-carbaldehyde as green–turquoise crystals, 0.27 g, 80%, mp 44–45 °C (M^+ Found: 156.0579, $C_{11}H_8O_2$ calculated: 156.0575); δ_H (250 MHz, $CDCl_3$) 7.50(d, 2H, *J* 3.5, azulene H-$C^{1,3}$); 7.70(d, 2H, *J* 10, azulene H-$C^{5,7}$); 8.10(t, 1H, *J* 3.5, azulene H-C^2); 8.50(d, 2H *J* 10, azulene H-$C^{4,8}$); 10.1 (s, 1H, *CH*O); δ_C (63 MHz, $CDCl_3$) 119.8 (d, 2C, azulene $C^{1,3}$); 123.7(d, 2C, azulene $C^{5,7}$); 135.2 (d, 2C, azulene $C^{4,8}$); 137.1(s, 1C, azulene C^2); 140.3(s, 2C, azulene $C^{3a,8a}$); 141.7(s, 1C, azulene C^6); 194.6(d, 1C, *C*HO); *m/z* (EI) 156 (M^+, 100%).

6-(4-Hexyloxyphenethyl)azulene, 2a

Diethyl 4-(hexyloxybenzyl)phosphonate (1.00 g, 2.96 mmol) was dissolved in diethyl ether (30 ml) and potassium *tert*-butoxide added (0.33 g, 2.96 mmol) to give a yellow precipitate. When this had dissolved azulene-6-carbaldehyde was added. The reaction was then kept stirring at 20 °C in the dark and followed by TLC. After 30 min the aldehyde spot seemed to have disappeared and an upper green spot appeared. Purification was attempted by column chromatography on silica using hexane–CH_2Cl_2, 3 : 2, as eluent in the dark to give a green crystalline product of 6-(4-hexyloxystyryl)azulene, which rapidly decomposed on standing, mp 225 °C (decomp.), δ_H (250 MHz, $CDCl_3$) 0.90 (t, 3H, *J* 7, Me); 1.40[m, 6H, $CH_2(CH_2)_3Me$]; 1.80(m, 2H, $CH_2CH_2C_4H_9$); 3.99(t, 2H, *J* 7, $CH_2C_5H_{11}$); 6.92(d, 2H, *J* 9, phenyl); 7.18(s, 2H, -*CH*=C*H*-); 7.32(d, 2H, *J* 4, azulene H-$C^{1,3}$); 7.4(d, 2H, *J* 11, azulene H-$C^{5,7}$); 7.5(d, 2H, *J* 9, phenyl); 7.8(t, 1H, *J* 4, azulene H-C^2); 8.30(d, 2H, *J* 11, azulene H-$C^{4,8}$); *m/z* (EI) 330 (M^+, 100%). This green product was then taken up into dry THF (30 ml) and lithium aluminium hydride added carefully (0.2 g, 4.93 mmol); the mixture was heated at reflux for 3 h, then stirred for 16 h at 20 °C. An upper purple spot was observed on TLC. The solvent was evaporated under reduced pressure and then purification was attempted by column chromatography on silica, using CH_2Cl_2–hexane, 2 : 3, as eluent, to give 6-(4-hexyloxyphenethyl)azulene as purple microprisms, which were then recrystallised from hexane, 0.10 g, 15%, mp 105 °C; δ_H (250 MHz, $CDCl_3$) 0.9(t, 3H, *J* 7, Me); 1.3[m, 6H, $(CH_2)_2(CH_2)_3Me$]; 1.80(m, 2H, $CH_2CH_2C_4H_9$); 3.0(m, 4H, CH_2CH_2); 3.90(t, 2H, *J* 7, $CH_2C_5H_{11}$); 6.7(d, 2H, *J* 9, phenyl); 7.05(d, 2H, *J* 11, azulene H-$C^{5,7}$); 7.05(d, 2H, *J* 9, phenyl); 7.30(d, 2H, *J* 4, azulene H-$C^{1,3}$); 7.80(t, 1H, *J* 4, azulene H-C^2); 8.20(d, 2H, *J* 11, azulene H-$C^{4,8}$); δ_C (63 MHz, $CDCl_3$); 14.0 (q, 1C, Me); 22.6(t, 1C, CH_2); 25.7(t, 1C, CH_2); 29.3(t, 1C, CH_2); 31.6(t, 1C, CH_2); 38.0(t, 1C, CH_2); 44.6(t, 1C, CH_2); 68.1(t, 2C, CH_2CH_2); 114.5(d, 2C, phenyl); 117.9(d, 2C, azulene $C^{1,3}$); 124.1(d, 2C, phenyl); 129.4(d, 2C, azulene $C^{5,7}$); 133.0(s, 1C, phenyl); 135.8(d, 1C, azulene C^2); 135.9(d, 2C, azulene $C^{4,8}$); 138.9(s, 2C, azulene $C^{3a,8a}$); 152.5(s, 1C, phenyl); 157.6(s, 1C, azulene C^6); *m/z* (EI) 332 (M^+, 15%).

4-(4-Decyloxyphenethyl)pyridine

trans-4-Decyloxy-4′-stilbazole[19] (1.5 g, 4.45 mmol) was dissolved in glacial acetic acid (100 ml) to give a yellow solution. Palladium on charcoal (75 mg) was then added and the vessel kept under an atmosphere of hydrogen. The mixture was left stirring at 20 °C until 1 equiv. of hydrogen had been taken up. The now colourless solution was filtered through Celite to remove the catalyst and washed with copious amounts of water. The filtrate was extracted with dichloromethane (3 × 60 ml) and the combined organic extracts washed with aq. K_2CO_3 (20%) and water. The organic layer was then dried and solvent evaporated under reduced pressure to give a slightly yellow oil which crystallised on standing. Recrystallisation from acetone yielded 4-(4-decyloxyphenethyl)-pyridine, as colourless crystals, 1.42 g, 94%, mp 44–45 °C; δ_H (250 MHz, $CDCl_3$) 0.90(t, 3H, Me); 1.30 [m, 14H, $(CH_2)_2(CH_2)_7Me$]; 1.75 [m, 2H, $CH_2CH_2(CH_2)_7Me$]; 2.90(m, 4H, CH_2CH_2); 3.90[t, 2H, $CH_2(CH_2)_8Me$]; 6.75(d, 2H, phenyl); 7.05(d, 2H, phenyl); 7.10(d, 2H, pyridine); 8.45(d, 2H, pyridine); δ_C (63 MHz, $CDCl_3$) 14.1 (q, 1C, Me); 22.7(t, 1C, CH_2); 26.1(t, 1C, CH_2); 29.3[t, 2C, $(CH_2)_2$]; 29.4(t, 2C, $2CH_2$); 29.6(t, 1C, CH_2); 31.9(t, 1C, CH_2); 35.7(t, 1C, phenyl-CH_2-CH_2); 37.3(t, 1C, CH_2-CH_2-pyridine), 68.0(t, 1C, OCH_2); 114.5(d, 2C, phenyl); 124.0(d, 2C, pyridine); 129.3(d, 2C, phenyl); 132.5(s, 1C, phenyl); 149.5(d, 2C, pyridine); 150.8(s, 1C, phenyl); 157.6(s, 1C, pyridine); *m/z* (EI) 339 (M^+, 15%).

***N*-Butyl-4-(4-decyloxyphenethyl)pyridinium bromide**

4-(4-Decyloxyphenethyl)pyridine (2.7 g, 7.96 mmol) was dissolved in absolute ethanol (30 ml) and 1-bromobutane (4 g, 29.1 mmol, excess) added. The mixture was heated at reflux for 50 h and allowed to cool at which pale yellow crystals appeared in the yellow solution. Excess 1-bromobutane and ethanol were evaporated under reduced pressure and drying under high vacuum then gave crude yellow crystals, found by ^1H NMR spectroscopy to be mainly *N*-butyl-4-(4-decyloxyphenethyl)pyridinium bromide, 2.26 g, 60%; δ_H (250 MHz, $CDCl_3$) 0.80(t, 3H, Me); 0.95(t, 3H, Me); 1.25(m, 16H, $OC_2H_4C_7H_{14}Me$, $NC_2H_4CH_2Me$); 1.75(m, 2H, $OCH_2CH_2C_8H_{17}$); 2.00(m, 2H, $NCH_2CH_2C_2H_4$); 2.95(t, 2H, phenyl-CH_2-CH_2-pyridine); 3.2(t, 2H, phenyl-CH_2-CH_2-pyridine); 3.90(t, 2H, $OCH_2C_9H_{19}$); 4.90(t, 2H, $NCH_2C_3H_7$); 6.75(d, 2H, phenyl); 7.00(d, 2H, phenyl); 7.80(d, 2H, pyridine); 9.20(d, 2H, pyridine); *m/z* (EI) $C_{27}H_{42}ON$ 396 ($M^+ - Br$, 50%). A less soluble product was isolated after extraction of the crude yellow crystals with dry acetone, which gave cream crystals, and these were determined to be pure 4-(4-decyloxyphenethyl)pyridinium bromide (Found: C, 65.71; H, 7.99; N, 3.43; Br, 18.89: $C_{23}H_{34}NOBr$ calculated: C, 65.71; H, 8.15; N, 3.33; Br, 19.01); δ_H (250 MHz, $CDCl_3$) 0.80(t, 3H, Me); 1.25 (m, 14H, $OC_2H_4C_7H_{14}Me$); 1.70(m, 2H, $OCH_2CH_2C_8H_{17}$); 2.90(t, 2H, phenyl-CH_2-CH_2-pyridine); 3.15(t, 2H, phenyl-CH_2-CH_2-pyridine); 3.85(t, 2H, $OCH_2C_9H_{19}$); 6.75(d, 2H, phenyl); 6.90(d, 2H, phenyl); 7.65(d, 2H, pyridine); 8.70(d, 2H, pyridine); δ_C (63 MHz, $CDCl_3$) 14.1(q, 1C, Me); 22.7(t, 1C, CH_2); 26.0(t, 1C, CH_2); 29.3(t, 1C, CH_2); 29.4(t, 2C, $2CH_2$); 29.5(t, 2C, $2CH_2$); 31.9(t, 1C, CH_2); 35.0(t, 1C, phenyl-CH_2-CH_2); 38.3(t, 1C, CH_2-CH_2-pyridine); 68.1(t, 1C, OCH_2); 114.8(d, 2C, phenyl CH); 127.2(d, 2C, pyridine); 129.3(d, 2C, phenyl); 130.0(s, 1C, phenyl); 140.0(d, 2C, pyridine); 158.1(s, 1C, phenyl); 163.3(s, 1C, pyridine); *m/z* (EI) $C_{23}H_{34}ON$ 340 ($M^+ - Br$, 100%).

6-(4-Decyloxyphenethyl)azulene, 2b

Freshly distilled cyclopentadiene (2.00 g, 30.3 mmol) was added dropwise over 30 min to sodium hydride (0.75 g, 24.6 mmol) in THF (70 ml) at 0 °C and the mixture was then allowed to warm to 20 °C. *N*-Butyl-4-(4-decyloxyphenethyl)pyridinium bromide (5.36 g, 11.3 mmol) dissolved in dry THF (10 ml) was then added to the pink solution which turned red, then green, then blue, and finally brown. The mixture was heated at reflux for 90 h, a blue spot being indicated by TLC. THF was

evaporated under reduced pressure to leave a brown oil. Silica was added to the brown oil and purification by column chromatography using light petroleum (bp 40–60 °C) as eluent, gave a blue product. Recrystallisation from diethyl ether–methanol gave 6-(4-decyloxyphenethyl)azulene as blue crystals, 0.64 g, 15%, mp 100 °C, (Found: C, 86.55, H, 9.38; $C_{28}H_{36}O$ calculated: C, 86.55; H, 9.33%); δ_H (250 MHz, CD_2Cl_2) 0.9(t, 3H, *J* 7, Me); 1.3[m, 14H, $(CH_2)_2(CH_2)_7Me$]; 1.80(m, 2H, $CH_2CH_2C_8H_{17}$); 3.0(m, 4H, CH_2CH_2); 3.90(t, 2H, *J* 7, $CH_2C_9H_{19}$); 6.75(d, 2H, *J* 9, phenyl); 7.05(d, 2H, *J* 11, azulene H-$C^{5,7}$); 7.05(d, 2H, *J* 9, phenyl); 7.30(d, 2H, *J* 4, azulene H-$C^{1,3}$); 7.80(t, 1H, *J* 4, azulene H-C^2); 8.25(d, 2H, *J* 11, azulene H-$C^{4,8}$); δ_C (63 MHz, CD_2Cl_2); 14.3 (q, 1C, Me); 23.1(t, 1C, CH_2); 26.5(t, 1C, CH_2); 29.8(t, 1C, CH_2); 30.0[t, 2C, $(CH_2)_2$]; 32.3(t, 1C, CH_2); 38.3(t, 1C, CH_2); 44.9(t, 1C, CH_2); 68.5(t, 2C, CH_2CH_2); 114.8(d, 2C, phenyl); 118.2(d, 2C, azulene $C^{1,3}$); 124.5(d, 2C, phenyl); 129.8(d, 2C, azulene $C^{5,7}$); 133.5(s, 1C, phenyl); 136.1(d, 1C, azulene C^2); 136.3(d, 2C, azulene $C^{4,8}$); 139.3(s, 2C, azulene $C^{3a,8a}$); 153.1(s, 1C, phenyl); 158.1(s, 1C, azulene C^6); *m*/*z* (EI) 388 (M^+, 20%).

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