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Synthesis and Stereochemical Aspects of 2,6-Disubstituted Perhydroazulenes – Core Units for a New Class of Liquid Crystalline Materials

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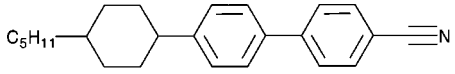
A novel approach for the synthesis of *cis*/*trans*-fused perhydroazulenes **13**–**19** is reported. The stereochemistry of the derivatives of carbene addition products **9a**–**c**/**20**–**22**, of the 2,6-disubstituted perhydroazulenes **12a**–**c**/**23**–**25**, and that of compounds **26**–**27** has been studied by single-crystal X-ray crystallography. The hydrogenation of the tropylidene to the perhydroazulene skeleton under various conditions is described.

Introduction

The liquid crystals used in TN and STN display devices are calamitic liquid crystals. A number of such liquid crystals have been synthesised and used in practical displays.[1,2] Compound **1** is a typical calamitic liquid crystalline material. The disadvantage of these types of devices is the narrow and non-uniform view cone which affects their performance. The use of the multidomain technique,[3] the introduction of an optical compensator to reduce the amount of light leakage in the dark state,[4] the use of an electrical field parallel to the plane of the substrates,[5] the use of amorphous twisted nematic liquid crystals,[6] and various modifications in the calamitic liquid crystals with a phenyl(bicyclohexyl) moiety,[7–11] have enhanced and optimized their performance.



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However, there is still a growing need for more and newer materials to be synthesised and tested for their LC properties. Desired features include wider viewing angles and enhanced brightness, lower driving voltages and less power consumption, faster response times and reduced manufacturing costs. Moreover, it is known that the switching behaviour of nematics for display applications is basically governed by their birefringence (Δn), dielectric anisotropy ($\Delta\varepsilon$), rotational viscosity (γ_1) and elastic constants (K_1, K_2, K_3), anisotropic properties depending on the chemical structure and size of a molecule. Various modifications in the basic cyclohexyl, bicyclohexyl and phenyl(bicyclohexyl) structures have been made recently in order to overcome problems of electrooptic and viscoelastic parameters. Kirsch et al.[12] showed that perfluorination of the central ethylene link in bis(cyclohexyl)ethane derivatives resulted in a dramatic increase of the clearing temperatures. Fluorinated ring materials have far lower rotational viscosities, making them interesting as mixture components in order to reduce the switching time of the display. Lateral fluorination is effective for increasing the value of the dielectric anisotropy by three to four times. Materials with terminal trifluoromethoxy groups possess higher clearing temperatures, allowing the operating temperature range for LCDs to be extended accordingly. It has also been demonstrated that the insertion of a difluorooxymethylene bridge into a specific location of the mesogenic core structure of phenylbicyclohexyl[13] results not only in a broader nematic phase, a higher dielectric anisotropy, and a lower rotational viscosity, but also in a higher specific resistivity and voltage holding ratio.

Therefore, by modification of the basic structures, a wide range of change of properties affecting the liquid crystal behaviour of these materials can be produced. The core unit presently used in most of the calamitic LC is cyclohexane, phenylcyclohexane etc.; a typical example is compound **1**.

In this paper, we introduce a completely new core unit – the perhydroazulene ring system. It is flat, allows numerous introductions of substituents, and its stereochemistry can

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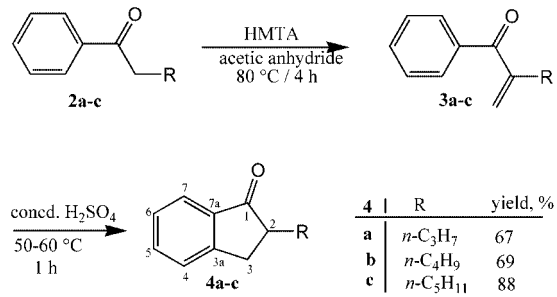
be influenced by the central junction as well as the relative orientation of the substituents. We report here the synthesis and stereochemistry of 2,6-disubstituted perhydroazulenes.

Results and Discussion

Two synthetic pathways to hydroazulenes are recognized, starting from 2-indanecarboxylates or from 5-substituted tropolones.[14] In 1951 the ring expansion of indanes was reported to give 2,6-substituted azulenes, but only in very low yields.[15] Later, Keehn et al.[16] improved this approach by using reduced indanes followed by a dehydrogenation sequence. At about the same time, 2,6-disubstituted azulenes were synthesized by the reaction of suitable tropolone precursors with cyanoacetates.[17] Thus, 2,6-disubstituted perhydroazulenes are not easily accessed, and a synthetic protocol giving satisfactory yields of these derivatives with a minimum number of steps would be highly desirable.

Our synthetic route started from the 2-alkylindan-1-ones **4a**–**c**, which were prepared by a Mannich type reaction from the commercially available **2a**–**c**. There are many reports[18] of the synthetic utility of the Mannich reaction for the preparation of 2-alkyl-1-indanones. However, because of the often lengthy procedure and poor yields, we used the procedure of Bhattacharya et al.,[19] which employs hexamethylenetetramine (HMTA) as the Mannich base, resulting in a simple procedure with satisfactory yields. A mixture of the ketones **2a**–**c**, hexamethylenetetramine and acetic anhydride was heated at 80 °C for 5 h under nitrogen. Aqueous work-up produced the acrylophenones **3a**–**c**, which were not isolated but directly underwent acid-catalyzed cyclization (H_2SO_4, 50–60 °C) to produce the corresponding indanones **4a**–**c** (Scheme 1) in good to excellent yields (67–88%). All derivatives **4a**–**c** were characterized by their usual spectroscopic and analytical data which have only been reported incompletely in the literature.[20]



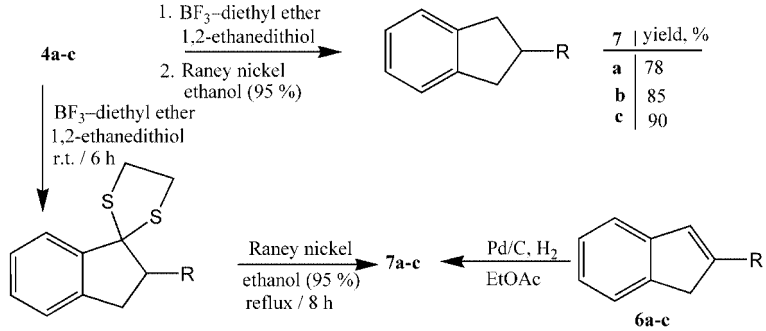
4	R	yield, %
a	n-C_3H_7	67
b	n-C_4H_9	69
c	n-C_5H_{11}	88

Scheme 1. Preparation of the aromatic ketones **4a**–**c**.

In the next step, the carbonyl group of **4a**–**c** was reduced to give the hydrocarbons **7a**–**c**. At first, the Clemmensen reduction with amalgamated zinc and then catalytic reduction[21] with hydrogen in the presence of acid were tried, but both approaches resulted in poor yields (ca. 10–20%). Later, the procedure of Mitra et al.[22] was employed, whereby the carbonyl group is first protected with 1,2-ethanedithiol in the presence of BF_3–diethyl ether for 6 hours at room temperature to yield the thioketals **5a**–**c**. Reductive desulfurisation with Raney-Nickel in ethanol finally resulted in **7a**–**c**. Sometimes, in addition to **7a**–**c**, the indene derivatives **6a**–**c** (yield ca. 15–20%) were also produced. These were converted to **7a**–**c** in quantitative yields by further catalytic hydrogenation in the presence of Pd/C.

The Birch reduction[23] of the 2-alkylindanes **7a**–**c** (Scheme 2) was next carried out in liquid ammonia in the presence of sodium metal in anhydrous ethanol and THF to provide the 2-alkyl-4,7-dihydroindane derivatives **8a**–**c** in 85–97% yields. It is important to note that **8a**–**c** are slowly oxidized back to **7a**–**c** at room temperature, so they were immediately used for further reactions.

Continuing the synthesis, **8a**–**c** were treated with ethyl diazoacetate[24] and a copper catalyst ($CuSO_4$) in refluxing cyclohexane to afford the carbene adducts **9a**–**c** in acceptable yields (54–64%); the addition resulted in higher yields when the time of addition was increased. The slightly higher yield in the case of **8c**, with its long carbon chain at position

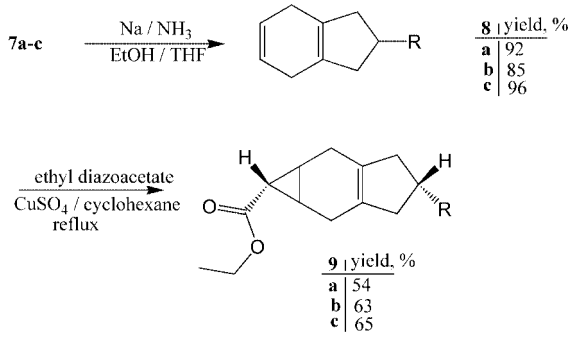


7	yield, %
a	78
b	85
c	90

5	yield, %
a	71
b	76
c	73

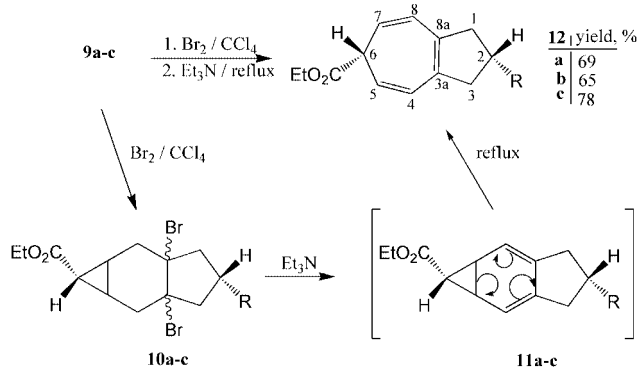
Scheme 2. Preparation of 2-alkylindanes **7a**–**c**.

2, could be due to the repulsive effect for the carbene addition to the inner carbon double bond, in spite of the fact that the central carbon double bond is more electron rich and hence in principle more susceptible to such additions. The compounds **9a**–**c** were found to contain impurities with similar retention times, which could be separated by chromatography on a silver nitrate impregnated silica gel column with pentane as an eluent, whereby its polarity was gradually increased by addition of dichloromethane. The column was prepared according to the procedure of Li et al.[25] For good separation, 50 g of adsorbent for each gram of mixture was required. The compounds **9a**–**c** were obtained as colourless liquids that solidified below 0 °C. The disappearance of a broad singlet due to the protons of the outer double bond in **8a**–**c** and the appearance of a small coupling constant of 4.33 Hz (for a triplet) at δ = 1.45 ppm between the protons on the cyclopropyl ring, and the presence of a quartet at 4.1 ppm (^3J = 7.12 Hz) from the methylene protons of the ester group, indicated that structures of **9a**–**c** had indeed been formed (Scheme 3). It is important to mention that GC analysis of these compounds showed overlapping signals, indicating the presence of a second isomer, in each case, but it was not possible to separate them because of closely similar retention times. Furthermore, NMR signals also did not help in identifying the second isomer. However, final confirmation of the stereochemistry of these structures was obtained from the X-ray data of their corresponding acids (see below).



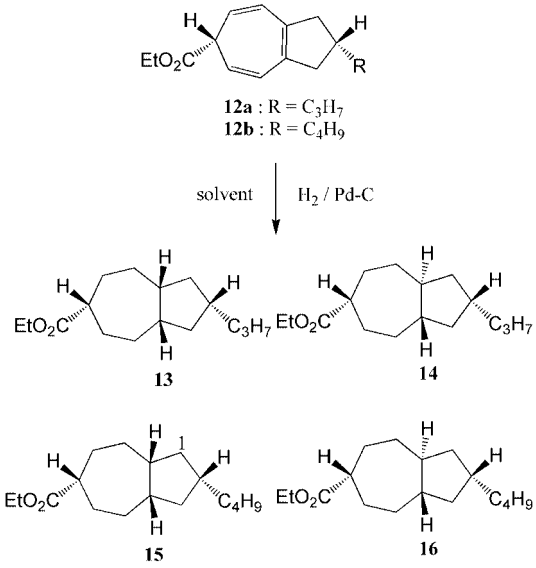
Scheme 3. Synthetic route to cyclopropane derivatives **9a**–**c**.

The next step involved the ring opening of **9a**–**c** to the cycloheptatrienes **12a**–**c**. The carbene adducts **9a**–**c** were first treated with bromine[16] in carbon tetrachloride, resulting in the formation of the dibromides **10a**–**c**. After complete addition of bromine, triethylamine was added slowly, giving triethylamine hydrobromide and in situ formation of the norcaradiene intermediates **11a**–**c**, which were converted into the tropylidenes **12a**–**c** as pale bluish liquids when refluxed overnight. The compounds **12a**–**c** were again contaminated by small amounts of impurities (as seen by the colour!), which were separated with a silver nitrate impregnated column of silica gel with pentane and dichloromethane as eluents, as described for **9a**–**c**. The pure **12a**–**c** were again a mixture of two isomers, as clearly indicated by the presence of overlapping ^{13}C signals (see experimental section). It was possible to separate the *cis* isomer in an analytically pure form by chromatography on a silver nitrate impregnated column. However, the second isomer was always contaminated with small amounts of the first component. The presence of a multiplet at δ = 2.67 ppm in the ^{1}H NMR spectrum for 6-H, doublets at 6.17–6.21 ppm with J = 9.1 Hz for 4/8-H and a singlet at δ = 141.8 ppm in the ^{13}C NMR spectrum for C-3a/8a indicated the formation of **12a**–**c**; the spectroscopic data did not allow the structure elucidation of the second isomers. However, it is likely that they differ by different orientation of the terminal groups at position 2 and 6 in **12a**–**c**. The position of the double bonds as well as the orientation of the terminal groups in one of the isomers of the cycloheptatrienes **12a**–**c** was established by the X-ray structures of the acids **23** and **25** (see below), confirming the stereochemistry shown for **12a**–**c** (Scheme 4).



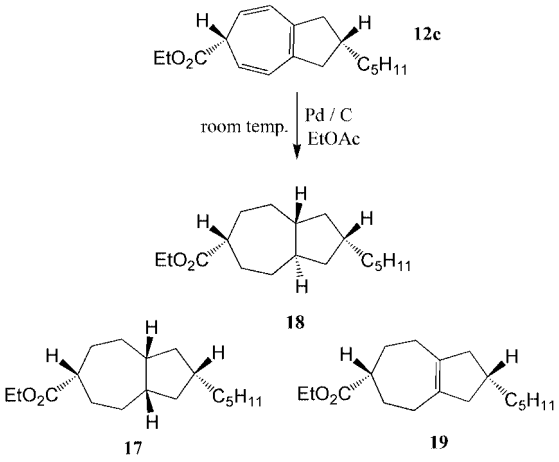
Scheme 4. Synthesis of cycloheptatriene derivatives **12a**–**c**.

In the final step (see Schemes 5 and 6), the precursors **12a**–**c** were hydrogenated. Catalytic hydrogenation of **12a** by using Pd/C in EtOAc resulted in a mixture of two isomers **13** and **14**, clearly indicated by GC and NMR analysis. The isomer mixture was separated by column chromatog-



Scheme 5. Hydrogenation of **12a/12b**.

raphy. Because of the almost identical retention times of the two isomers, it was a tedious job to elute them. Using pentane whose polarity had been slightly increased by the addition of dichloromethane (1–10%) as eluent, the separation of these isomers still took many hours.



Scheme 6. Hydrogenation of **12c**.

In the case of the butyl derivative **12b**, hydrogenation yielded the compounds **15** and **16**, which were separated in the same way as described for **13** and **14**.

It is important to note that the *cis* isomer in all cases was found to elute faster than the *trans* isomer, although not by a large margin, and it was possible to obtain the pure *cis* compound in appreciable quantity (> 60%) from the mixture. However, the completely pure *trans* isomer could not be obtained, as it was contaminated by the *cis* compound in all cases. After complete characterization of **12a**–**c** by their usual spectroscopic, analytical and X-ray data, it was possible to elucidate the structures of the fully hydrogenated azulene systems **13**–**16**. The disappearance of the doublets at 6.1 ppm with coupling constants of 9.1 Hz for the 4/8 protons in **12a**–**c** and the appearance of multiplets for these protons was indicative of the formation of **13**–**16**. Further confirmation of the structures of all these derivatives was provided by the 2D NMR spectroscopic data coupled with various analytical data, which can be found separately in the experimental section. The stereochemistry of the *cis*-fused systems was confirmed by the X-ray structures of the acids **26** and **27** derived from esters **13** and **15**, respectively.

Following the same procedure as described for **12a** and **12b**, **12c** was hydrogenated in order to obtain the perhydroazulene systems **17** and **18**. In the case of the propyl and butyl derivatives, **12a** and **12b**, respectively, the hydrogenation always resulted in completely reduced products. However, in the case of **12c**, hydrogenation with Pd/C in EtOAc at room temperature yielded, in addition to **17** and **18**, the partially reduced ester **19**. The formation of **19** was not expected; however, it was considered to be an important side product having a double bond at the ring junction and thus avoiding the problem of *cis,trans* isomerism at this part of the molecule. The formation of **19** can possibly be explained by considering the steric effect of the long pentyl chain at position 2, which resulted in slow hydrogenation at room temperature. Hydrogenating **12c** at elevated pressure and for longer times led to the completely reduced system. The elucidation of the structure of **19** was performed largely by NMR spectroscopy and MS analysis. Derivatives **17/18** gave a molecular ion peak at 280, whereas the peak for **19** was at 278. The disappearance of the ^{13}C signal for C-3a/8a of **17/18** at 42.96 ppm (2 d) and the appearance of this signal for **19** at 135.85 ppm (2 × s) was indicative of the formation of **19**. The structure was confirmed by 2D NMR spectroscopy as described in the experimental section. As the stereochemistry for **13** and **15** was established by X-ray structural analysis of their respective acids, the stereochemistry of **17**–**19** was assumed to be the same as that described for **12c**. The complete spectroscopic data of **17**–**19** are given in the experimental section.

As the pure isomers were required for further synthetic work, various hydrogenation methods were investigated in order to obtain one isomer exclusively. There are numerous reports[26] of the catalytic hydrogenation of C–C double bonds over Pd/C and the problem of controlling the stereochemistry of the reduction product and of minimizing the formation of *cis,trans* isomers. Platinum is often found to be an excellent choice to give the *cis* adduct, whereas palladium often yields the *trans* isomers. We studied the effect of various solvents and reducing agents on the formation of the *cis*- and *trans* isomers; it was found that in most cases the ratio of *cis,trans* isomers remained ca. 4:1 and one isomer could not be obtained exclusively (Table 1).

It is worthwhile to note here that the reduction of the indane ring, followed by the addition of a carbene, was

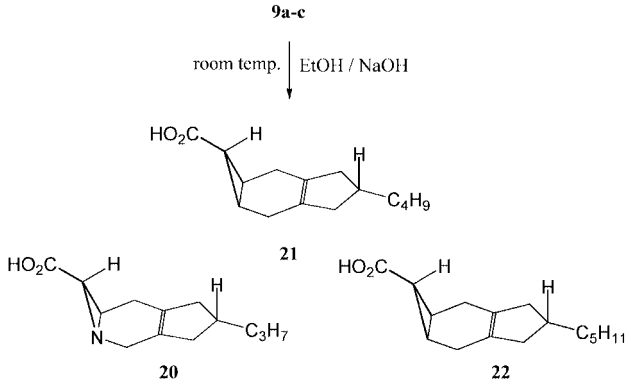
Table 1. Effect of hydrogenation conditions on the *cis,trans* isomer ratio of **12a**.

Catalyst	Solvent	Substrate/temp. [°C]	Pressure [atm]	*cis* Isomer [%] [a]	*trans* Isomer [%] [a]
10% Pd/C	EtOAc	**12a**/room temp.	< 1	70	30
10% Pt/C	EtOAc	**12a**/room temp.	< 1	72	28
10% Pt/C	AcOH	**12a**/room temp.	< 1	70	30
10% Pt/C	EtOH	**12a**/room temp.	1	74	26
PtO_2	EtOAc	**12a**/room temp.	< 1	86	14
PtO_2	EtOAc	**12a**/room temp.	1	75	25
PtO_2	EtOH	**12a**/room temp.	< 1	85	15
PtO_2	EtOH	**12a**/0	< 1	85	15
PtO_2	cyclohexane	**12a**/room temp.	1	70	30

[a] Analysis by GC.

found to be an improvement of the Buchner[27] method and can be used as a general route to a variety of novel substituted perhydroazulenes.

In order to investigate the exact stereochemistry of the esters **9a**–**c** (Scheme 7), their hydrolysis[28] was carried out in ethanol in the presence of sodium hydroxide; the resulting acids **20**–**22** were recrystallized from hexane and dichloromethane and provided single crystals suitable for X-ray studies. All of the acids obtained were characterized by their spectroscopic and analytical data, which are given separately in the experimental section.



Scheme 7. Hydrolysis of the esters **9a**–**c**.

As shown in Figures 1, 2 and 3, the cyclohexene rings in each of the three compounds are only slightly folded by 6.1(1)° to 13.7(2)° (folding calculated as angles between the planes C2/C1A/C6A/C6 to C2/C2A/C5A/C6 in molecule **20** and equivalent planes in **21** and **22**). The cyclopropyl groups are strongly folded to their neighbouring planes of the four adjacent atoms from the six-membered ring units by 72.4(1)° to 73.4(1)°. The carboxyl groups of **20** to **22** are all in the *exo*-position with nearly bisecting orientations of the carboxyl groups to the three-membered rings from 85.2(1)° to 89.4(1)°.

As a consequence of this nearly optimal orbital overlap, relatively long vicinal bonds from 1.523(2) Å to 1.531(2) Å and short distal bonds from 1.492(2) to 1.494(2) Å in the cyclopropyl subunits were found. The carboxylic groups of all three crystals build dimeric pairs (Figure 4) by hydrogen bonding across the inversion centres. Disorder effects were found at the envelope vertices of the five-membered rings, which point in complementary directions (Figures 1, 2 and 3 show only one of the disordered positions). Associated disorder effects were found in the alkyl side chains of **21** and **22**.

It is noteworthy that, during the recrystallization of acid **20**, we obtained single crystals of **23**, which were different (triclinic) from the previous ones (monoclinic) in **20**. The X-ray crystallographic data indicated the presence of a different isomer, having both alkyl group and the three-membered ring pointing up from the molecular plane. We did not obtain such isomers in the case of **21** and **22** and, because of the overlapping signals in the chromatogram; it was not possible to separate the mixture of two isomers. It

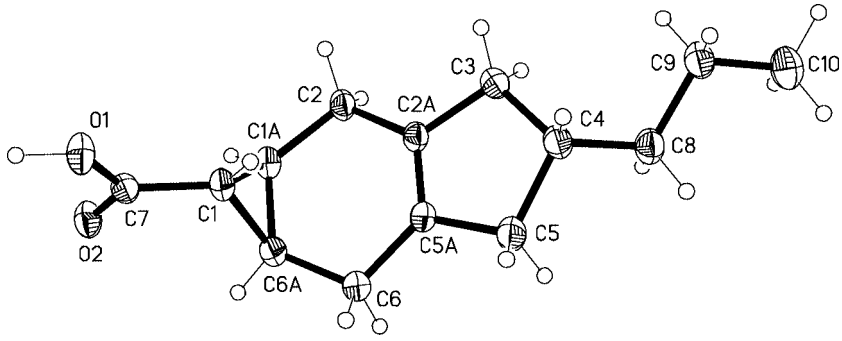


Figure 1. Structure of **20** in the crystal. The minor disorder component of C4,8,9,10 is omitted.

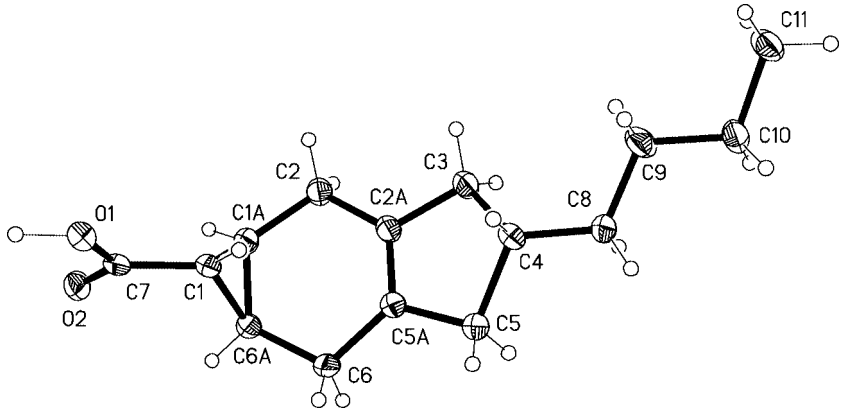


Figure 2. Structure of **21** in the crystal. The minor disorder component of C4,8,9,10,11 is omitted.

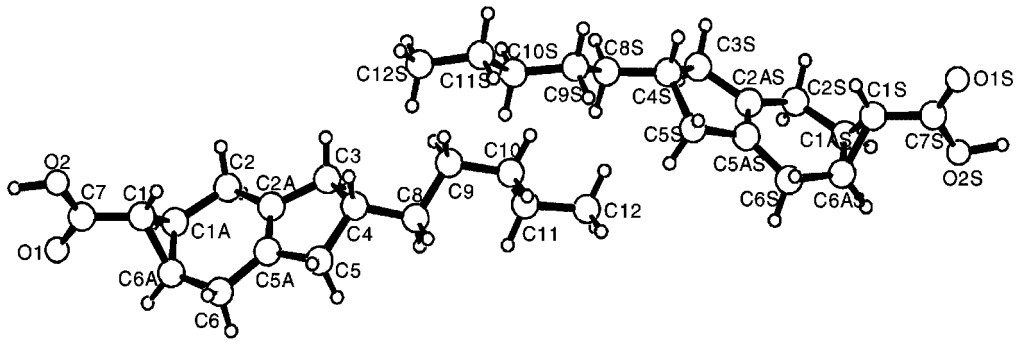


Figure 3. Structure of **22** in the crystal. Only one of the disorder positions is shown.

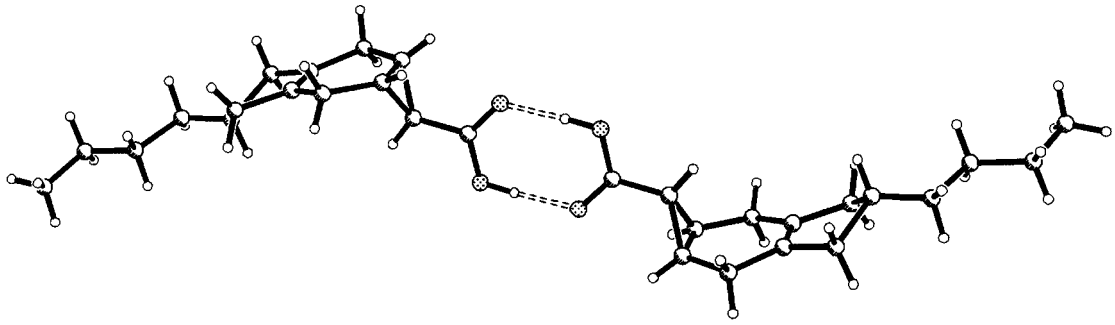


Figure 4. Section of crystal packing of compound **21** showing hydrogen bonding.

is clear that the crystallized form of **20** contains two isomers.

The general geometry of **23** (Figure 5 and 6) is similar to that established above for **20**–**22**. The fold angle of the cyclohexene ring is 12.7(1)°, and the cyclopropyl ring makes interplanar angles of 72.8(1)° to C1A/C2/C6/C6A and 90.0(1)° to the carboxylic acid group.

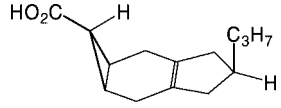


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Figure 5. Molecular structure of **23**.

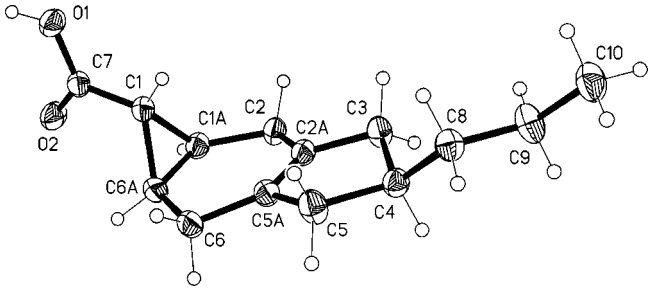
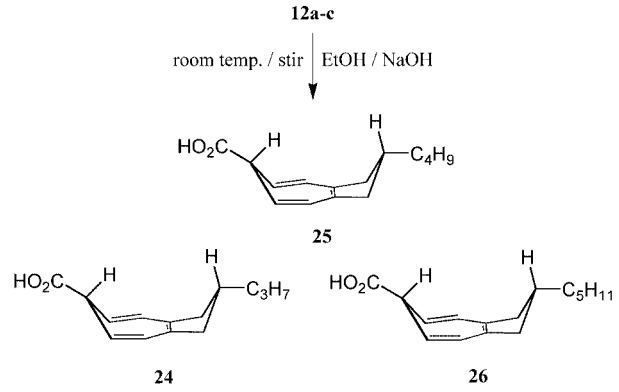


Figure 6. Structure of **23** in the crystal. The minor disorder component of C4,8,9,10 is omitted.

In summary, these results show that the carbene has added to the outer double bond of **8a**–**c** "away" from the alkyl group (*trans*) and with the ester/acid function pointing to the outer side (*exo*) of the molecule. Both arrangements are in accordance with expectations.

In order to confirm the structures of the tropylidene derivatives **12a**–**c**, their hydrolysis was carried out in an ethanol/sodium hydroxide mixture to yield the acids **24**–**26**, which were recrystallized from a hexane/dichloromethane mixture to provide single crystals of **24** and **26** suitable for X-ray analysis, whereas compound **25** could not be recrystallized. All of these derivatives were also characterized by their spectroscopic and analytical data, and from the similarity of these data we assume that **25** has comparable stereochemistry as **24** and **26** as shown in Scheme 8.



Scheme 8. Hydrolysis of esters **12a**–**c**.

Due to the partial hydrogenation of the azulene skeleton in the compounds **24** and **26**, the cycloheptatriene subunits were found in a boat-shape conformation. The interplanar

angles between the calculated planes C5/C6/C7 to C4/C5/C7/C8 are 55.5(1)° and 52.1(7)°, the comparable angles between C4/C3A/C8A/C8 to C4/C5/C7/C8 are 28.6(1)° and 28.5(1)° for **24** and **26**, respectively (Figure 7 and 8). A slight envelope-conformation was noticed in the five-membered ring of **24** with 21.7(2)° between C1/C2/C3 and C1/C3/C3A/C8A. In the analogous hydroazulene derivative **26** C2 was found at two positions, each with 50% multiplicity, both indicating an envelope shape for the corresponding five-membered ring, its top atom pointing in opposite directions. As mentioned in the discussion of the crystal structures of **20** to **22**, the similarly paired carboxylic groups in **24** are linked together through hydrogen bonds across a centre of symmetry. Comparable dimeric connections were found in the packing arrangement of **26** too.

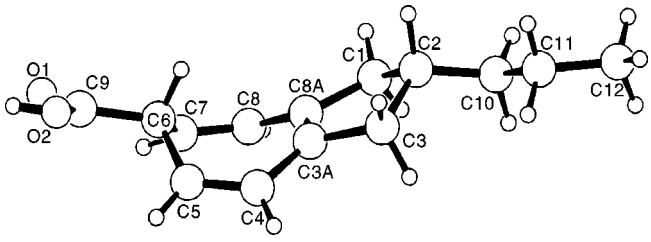
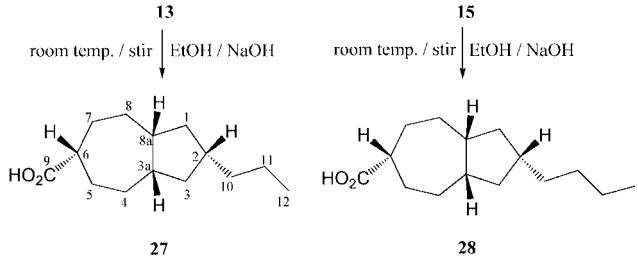


Figure 7. Structure of **24**. Only one position of the disordered carboxyl group and the terminal methyl group is shown, respectively.

In principle, the double bonds in the seven-membered rings of these derivatives could be arranged in different order, the various isomers being connected by symmetry-allowed 1,7-hydrogen shifts. The exclusive generation of the particular isomers is probably associated with their greater thermodynamic stability: with a double bond at the ring junction, an isomer results that possesses the most highly substituted double bond possible.

Finally, we wished to investigate the *cis*-fused isomers of the perhydroazulenes, which led us to hydrolyse the esters **13** and **15** (Scheme 9) employing the same procedure as mentioned above. This provided the acids **27** (Figure 9) and **28** in the form of colourless solids that on recrystallization from hexane/dichloromethane yielded suitable crystals for X-ray analysis. The data show that in both acids, protons at 3a/8a are pointing in the same direction giving rise to *cis*-fused systems as required. The cycloheptane rings display closely similar conformations with local mirror symmetry through C6 and the midpoint of C3A–C8A; the torsion angle about this bond is approximately zero and the other angles alternate +/– around the ring. Hydrogen bonding between the acids produces the usual dimeric forms, but for **28**, unusually, the two molecules involved are not related by symmetry but are crystallographically independent, although virtually identical (r.m.s. deviation of a least-squares fit is 0.04 Å) (Figure 10). The complete spectroscopic and analytical data of the acids **27** and **28** can be found in the experimental section.



Scheme 9. Hydrolysis of perhydroazulene systems **13** and **15**.

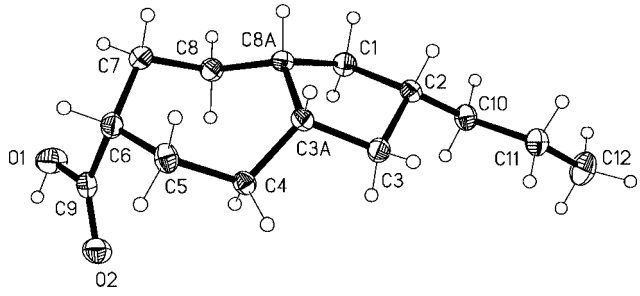


Figure 9. Structure of **27** in the crystal.

With these experiments the stereostructures of our most important intermediates are firmly established.

In order to confirm the stereochemistry of **19** (Schemes 6 and 10), this unsaturated ester was hydrolyzed as described above to obtain the acid **29**. However, this acid could not be recrystallized to provide single crystals suitable for X-ray analysis. Nonetheless, the disappearance of a quartet at δ = 4.14 ppm and of one triplet at δ = 60.09 ppm in the ^{1}H and ^{13}C spectra, respectively, arising from the methylene protons of the ester group, indicate the formation of **29**. Complete spectroscopic and analytical data of this acid can be found in the experimental section.

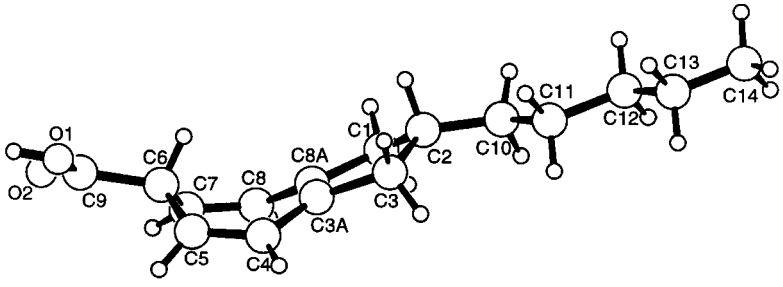


Figure 8. Structure of **26** in the crystal. Only one of the disordered positions of C2 is shown.

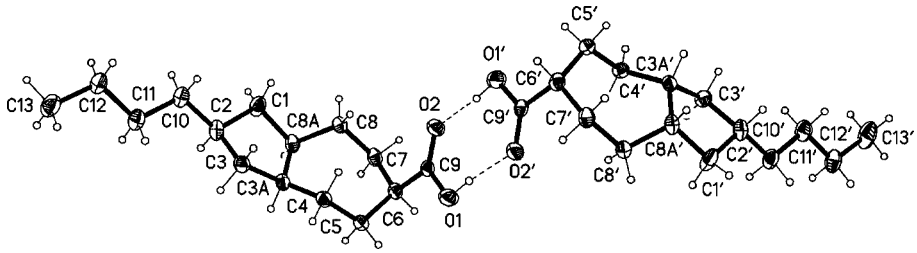
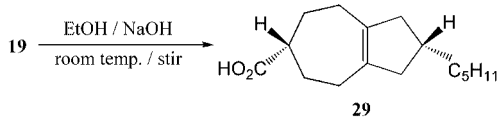


Figure 10. Structure of **28** in the crystal.



Scheme 10. Hydrolysis of ester **19**.

The incorporation of the novel core units into liquid-crystalline materials will be reported in our following publications.

Experimental Section

General: TLC: precoated plastic plates, PolyGram Sil G/UV_{254}. Column chromatography: Silica gel 60 (70–230 mesh) Merck (Darmstadt). M.p. below 200 °C: Büchi 510 melting point apparatus, above 200 °C: Kofler-Heiztischmikroskop, uncorrected. ^1H and ^{13}C NMR: Bruker AC 200, ^1H NMR (200.1 MHz). ^{13}C NMR (50.3 MHz); Bruker DRX-400, ^1H NMR (400.1 MHz). ^{13}C NMR (100.6 MHz); chemical shifts (δ) are expressed in parts per million (ppm) downfield from tetramethylsilane or using the residual non-deuterated solvent as internal standards ($CDCl_3$: ^1H: δ = 7.26; ^{13}C: δ = 77.00 ppm). IR: Nicolet 320 FT-IR and Bruker Tensor 27 spectrometer. Samples were prepared either as KBr pellets or as thin films. UV: in acetonitrile and methanol with a Beckman UV 5230 or a HP 8452A Diode Array spectrophotometer. MS: Finnigan MAT 8430 using the electron ionization method (EI, 70 eV). GC/MS: Finnigan MAT 4515 (EI = 40 eV) mass spectrometer attached to a Carlo–Erba HRGC 5160 (DB 1–0.25 μm fused-silica capillary column; 30 m × 0.31 mm ID. Elemental analyses: Institut für Pharmazeutische Chemie, TU Braunschweig. CH_2Cl_2 and Et_3N were distilled from CaH_2 under nitrogen, whereas THF and Et_2O were distilled from Na and benzophenone under nitrogen prior to use. All other chemicals were of reagent qualidy and used as obtained from the manufacturers. Reactions were carried out under dried N_2 when necessary.

2-Propylindan-1-one (4a): A mixture of valerophenone (**2a**, 25 g, 0.154 mol), hexamethylenetetramine (36 g, 0.26 mol) and acetic anhydride (34 g, 0.33 mol) was heated at 80 °C for 5 h under nitrogen. The reaction mixture was cooled to 30 °C and poured into a stirred mixture of dichloromethane (150 mL) and sodium hydroxide (150 mL of a 2 N solution). The organic layer was separated and washed with aqueous HCl (80 mL of 1 N solution). The dichloromethane solution containing pent-1-en-2-yl phenyl ketone (**3a**) was dried by azeotropic distillation, the CH_2Cl_2 being reduced to approximately 50 mL. The solution was used without further purification in the next step. It was added to concd. H_2SO_4 (110 mL) at a rate such that the reaction temperature was maintained between 50 and 60 °C. The solvent was removed by the sweep of nitrogen as soon as it was added. The reaction mixture was stirred at 50–60 °C for 1 h, cooled to 20 °C and quenched with a stirred mixture of CH_2Cl_2 (150 mL) and water (150 mL). After separating of the aqueous layer, the organic layer was concentrated in a rotary evaporator, dried with $MgSO_4$ and filtered through silica gel to produce 18 g (67%) of 2-propylindan-1-one (**4a**) as a light yellow oil. B.p. 108–110 °C/5 mm (ref.[20b] 110 °C/5 mm). ^1H NMR (400.1 MHz, $CDCl_3$): δ = 0.95 (t, ^3J = 7.1 Hz, 3 H, 10-H), 1.39–1.48/1.90–1.94 (m, 4 H, side-chain protons), 2.61–2.81 (m, 2 H, 3-H), 3.26–3.32 (m, 1 H, 2-H), 7.31–7.35 (m, 1 H, 6-H), 7.42–7.44 (d, ^3J = 7.66 Hz, 1 H, 4-H), 7.53–7.57 (m, 1 H, 5-H), 7.71–7.73 (d, ^3J = 7.64 Hz, 1 H, 7-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 208.77 (s, C-1), 32.64 (t, C-3), 47.05 (d, C-2), 123.55 (d, C-6), 127.06 (d, C-7), 126.35 (d, C-4), 134.39 (d, C-5), 153.56 (s, C-7a), 136.62 (s, C-3a), 13.86 (q, C-10), 20.44 (t, C-9), 33.40 (t, C-8) ppm. IR (film): $\tilde{\nu}$ = 1710 cm^{-1} (s, C=O), 2933, 2960 (s, CH-stretching), 3073, 3033 (w, CH-stretching, aromatic) 1610 (m, C=C aromatic), 1328 (m, CH_3 deformation). UV (CH_3CN): λ_{max} (lg ε) = 236 nm (3.42), 250 (4.03), 246 (4.06), 280 (3.26), 288 (3.41), 296 (3.39). MS (EI = 70 eV): *m/z* (%) = 174 (2) [M^+], 145 (5) [$M^+ - C_2H_5$], 132 (100) [$M^+ - C_3H_6$], 131 (14) [$M^+ - C_3H_7$], 115 (12) [131 – O], 103 (6.5) [131 – CO].

2-Butylindane-1-one (4b): From **2b** (25 g, 0.142 mol), **4b** was prepared by the same route as described above for **4a**. Yield: 18.5 g (69%). B.p. 154 °C/14 Torr (ref.[20c] 154 °C/14 Torr). ^1H NMR (400.1 MHz, $CDCl_3$): δ = 0.94 (t, ^3J = 7.1 Hz, 3 H, 11-H), 1.34–1.53 (m, 6 H, side-chain protons), 1.95–2.02 (m, 2 H, 3-H), 2.64–2.71 (m, 1 H, 2-H), 7.30–7.39 (m, 1 H, 6-H), 7.46–7.47 (d, ^3J = 7.71 Hz, 1 H, 4-H), 7.57–7.61 (m, 1 H, 5-H), 7.76–7.78 (d, ^3J = 7.71 Hz, 1 H, 7-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 209.03 (s, C-1), 153.72 (s, C-7a), 136.78 (s, C-3a), 134.53 (d, C-5), 127.21 (d, C-7), 126.46 (d, C-4), 123.76 (d, C-6), 47.37 (d, C-2), 32.79 (t, C-8), 31.09 (t, C-3), 29.51 (t, C-9), 22.63 (t, C-10), 13.89 (q, C-11) ppm. IR (film): $\tilde{\nu}$ = 3072, 3031 cm^{-1} (w, C–H stretching, aromatic), 2957, 2858 (s, C–H stretching, aliphatic), 1465, 1434 (w), 1712 (s, C=O). UV (CH_3CN): λ_{max} (lg ε) = 206 nm (4.51), 242 (4.10), 286 (3.44), 294 (3.43), 248 (4.03), 272 (3.14), 304 (2.79). MS (EI = 70 eV): *m/z* (%) = 188 (35) [M^+], 145 (13) [$M^+ - C_3H_7$], 132 (100) [$M^+ - C_4H_8$], 91 (7) [$C_7H_7^+$], 77 (7) [$C_6H_5^+$].

2-Pentylindane-1-one (4c): From **2c** (32.25 g, 0.169 mol), **4c** was prepared by the same route as described above for **4a**. Yield: 18 g (88%). b. p. 166 °C/14 Torr (ref.[13c] 166 °C/14 Torr). ^1H NMR (200.1 MHz, $CDCl_3$): δ = 0.85 (t, ^3J = 6.5 Hz, 3 H, 12-H), 1.21–1.50 (m, 8 H, side-chain protons), 2.60–2.81 (m, 2 H, 3-H), 3.21–3.30 (m, 1 H, 2-H), 7.30–7.72 (m, 4 H, aromatic protons) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 13.97 (q, C-12), 22.46 (t, C-11), 27.03 (t, C-9), 31.38 (t, C-8), 31.77 (t, C-10), 32.82 (t, C-3), 47.42 (d, C-2), 208.93 (s, C-1), 123.74 (d, C-7), 126.48 (d, C-4), 127.21 (d, C-6), 134.53 (d, C-5), 136.81 (s, C-7a), 153.71 (s, C-3a) ppm. IR (film): $\tilde{\nu}$ = 3072, 3032 cm^{-1} (w, C–H stretching, aromatic), 2956, 2930, 2871 (s, C–H stretching, aliphatic), 1713 (s, C=O), 1464 (w, C–H deformation). UV (CH_3CN): λ_{max} (lg ε) = 208 nm (3.99), 242

(3.79), 286 (3.09), 294 (3.09), 204 (3.88). MS (EI = 70 eV): *m/z* (%) = 202.1 (1) [M^+], 200 (1) [$M^+ - H_2$], 145 (14) [$M^+ - C_4H_9$], 132 (100) [$M^+ - C_5H_{10}$], 131 (6) [132-H].

1,3-Dithiolan of 2-Propylindanone, 5a: A solution of 2-propylindan-1-one (**4a**, 18 g, 0.106 mol) in boron trifluoride–diethyl ether (30 g, 27.25 mL, 0.217 mol) was treated with ethanedithiol (10.02 g, 0.106 mol) and the mixture stirred at room temp. for 6 h. The mixture was diluted with methanol (60 mL) and the organic layer was separated. The solvent was removed by rotary evaporation and the residue purified by column chromatography on silica gel (pentane/CH_2Cl_2, 2:1) to furnish 18.9 g (71%) of **5a** as colourless liquid. B.p. 188–190 °C/1 Torr. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 0.84 (t, ^3J = 7.2 Hz, 3 H, 10-H), 1.24–1.76 (m, 4 H, side-chain protons), 2.37–2.50 (m, 2 H, 3-H), 2.78–2.85 (m, 1 H, 2-H), 3.09–3.42 (m, 4 H, 11-,11a-H), 6.98–7.39 (m, 4 H, aromatic protons) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.50 (q, C-10), 21.43 (t, C-9), 31.64 (t, C-3), 36.58 (t, C-8), 40.53/40.01 (2 t, C-11,-11a), 54.50 (d, C-2), 124.25/124.38 (2 d, C-5,-6), 127.14/127.77 (2 × d, C-4,-7), 140.70 (s, C-1), 148.45 (s, C-3a,-7a) ppm. IR (film): $\tilde{\nu}$ = 3022 cm^{-1} (m, CH stretching, aromatic), 2956, 2925, 2869 (s, CH stretching, aliphatic), 1603 (m, C=C conjugated), 1378 (m, CH_3 deformation). UV (CH_3CN): λ_{max} (lg ε) = 242 nm (3.39), 232 (2.84), 260 (3.17), 264 (3.16), 272 (3.15), 280 (3.06). MS (GC/MS): *m/z* (%) = 250 (28) [M^+], 222 (99) [$M^+ - C_2H_4$], 179 (47) [222 – C_3H_7], 147 (56) [179 – S], 129 (62), 115 (100) [179 – S_2], 103 (8) [179 – CS_2].

1,3-Dithiolan of 2-Butylindanone, 5b: From **4b** (19 g, 0.101 mol), **5b** was prepared by the same route as described above for **5a**. Yield: 19 g (76%). B.p. 216 °C/5 Torr. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.98 (t, ^3J = 6.98 Hz, 3 H, 11-H), 1.39–1.57 (m, 6 H, side-chain protons), 2.54–2.68 (m, 2 H, 3-H), 3.05 (m, 1 H, 2-H), 3.30–3.63 (m, 4 H, 12-,12a-H), 7.57–7.18 (m, 4 H, aromatic protons) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 148.41 (s, C-3a,-7a), 140.68 (s, C-1), 127.72, 127.10 (2 d, C-4,-7), 124.31, 124.21 (2 d, C-5,-6), 54.62 (d, C-2), 40.95, 40.49 (2 t, C-12,-12-a), 36.58 (t, C-8), 30.43 (t, C-3), 29.05 (t, C-9), 23.00 (t, C-10), 14.13 (q, C-11) ppm. IR (film): $\tilde{\nu}$ = 3068 cm^{-1} (w, C–H stretching, aromatic), 3022 (w, C–H stretching, aromatic), 2955–2856 (s, C–H stretching, aliphatic), 1470, 1459 (w), 1275 (w). UV (CH_3CN): λ_{max} (lg ε) = 194 nm (4.55), 192 (4.53), 196 (4.54), 206 (4.27), 212 (4.18), 216 (4.06), 230 (3.58). MS (EI = 70 eV): *m/z* (%) = 264 (46) [M^+], 265 (7) [M^+ + 1], 266 (3) [M^+ + 2], 236 (100) [$M^+ - C_2H_4$], 169 (51) [$M^+ - C_2H_4S_2$], 105 (57) [$M^+ - C_{12}H_{16}$], 77 (24) [$C_6H_5^+$].

1,3-Dithiolan of 2-Pentylindanone, 5c: From **4c** (18 g, 0.089 mol), **5c** was prepared by the same route as described above for **5a**. Yield: 18 g (73%). B.p. 220 °C/5 Torr. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.97 (t, ^3J = 6.0 Hz, 3 H, 12-H), 1.39–1.98 (m, 8 H, side-chain protons), 2.56–2.80 (m, 2 H, 3-H), 3.02–3.07 (m, 1 H, 2-H), 3.31–3.61 (m, 4 H, 13-,13a-H), 7.17–7.30 (m, 4 H, aromatic protons) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.07 (q, C-12), 22.66 (t, C-11), 27.86 (t, C-9), 29.32 (t, C-8), 32.14 (t, C-10), 36.58 (t, C-3), 40.48, 40.93 (2 t, C-13,-13a), 54.64 (d, C-2), 124.20 (d, C-7), 124.31 (d, C-4), 127.08 (d, C-8), 127.74 (d, C-5), 140.67 (s, C-7a), 148.41 (s, C-3a) ppm. IR (film): $\tilde{\nu}$ = 3037, 3022 cm^{-1} (w, C–H stretching, aromatic), 2955, 2925 (s, C–H stretching, aliphatic), 1470, 1459 (m), 1275, 747 (s). UV (CH_3CN): λ_{max} (lg ε) = 196 nm (4.05), 212 (4.05), 258 (2.95), 264 (2.94), 270 (2.95), 278 (2.88), 324 (2.09), 366 (2.00). MS (EI = 70 eV): *m/z* (%) = 278 (44) [M^+], 250 (73) [$M^+ - C_2H_4$], 217 (40) [250 – SH], 186 (9) [250 – S_2], 179 (71) [250 – C_5H_{11}], 115 (76) [179 – S_2], 103 (5) [115 – 12], 43 (100) [C_3H_7].

2-Propylindane (7a): A mixture of **5a** (18 g, 0.072 mol) and Raney nickel (100 g) in ethanol (300 mL, 95%) was refluxed for 8 h. The cooled mixture was filtered and the filtrate diluted with water (100 mL), extracted with diethyl ether (2 × 100 mL) and the combined ether extracts were washed with water. The dried (Na_2SO_4) extract was concentrated and purified by passing it through a small column of silica gel to get 8.98 g (78%) of 2-propylindane (**7a**) as a colourless liquid. B.p. 85–90 °C/1 Torr (ref.[22] 85–90 °C/1 Torr). ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.04 (t, ^3J = 7.07 Hz, 3 H, 10-H), 1.43–1.61 (m, 5 H, side-chain protons, 2-H), 2.50–3.18 (m, 4 H, 1-,3-H), 7.17–7.29 (m, 4 H, aromatic protons) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.3 (q, C-10), 21.57 (t, C-9), 38.14 (t, C-3), 39.40 (2 t, C-1,-3), 40.07 (d, C-8), 124.40 (2 d, C-5,-6), 126.02 (2 d, C-4,-7), 143.73 (2 s, C-3a,-7a) ppm. IR (film): $\tilde{\nu}$ = 2956 cm^{-1} (s, CH-stretching, aliphatic), 2928 (s, C–H stretching, aliphatic), (3043, 3022 (m, CH-stretching, aromatic), 1378 (m, CH_3 deformation), 1601 (s, C=C aromatic). UV (CH_3CN): λ_{max} (lg ε) = 194 nm (4.50), 196 (4.50), 198 (4.42), 202 (3.97), 204 (3.85), 208 (3.80), 216 (3.73), 264 (2.75), 268 (2.93), 274 (2.96). MS (EI = 70 eV): *m/z* (%) = 160 (67) [M^+], 131 (64) [$M^+ - C_2H_5$], 117 (100) [$M^+ - C_3H_7$], 104 (63) [117 – CH]. HRMS ($C_{12}H_{16}$): calcd. 160.1252; found 160.1245 ± 2 ppm.

2-Butylindane (7b): From **5b** (18 g, 0.068 mol), **7b** was prepared by the same route as described above for **7a**. Yield: 10 g (85%). B.p. 120 °C/14 Torr (ref.[20b,20c] 120 °C/14 Torr). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.98 (t, ^3J = 6.92 Hz, 3 H, 11-H), 1.37–1.59 (m, 6 H, side-chain protons), 2.44–2.50 (m, 1 H, 2-H), 2.60–3.12 (m, 4 H, 1-,3-H), 7.15–7.35 (m, 4 H, aromatic protons) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.13 (q, C-11), 22.87 (t, C-10), 30.65 (t, C-9), 35.51 (t, C-8), 39.36 (2 t, C-1,-3), 40.24 (d, C-2), 124.34 (2 d, C-5,-6), 125.94 (2 d, C-4,-7), 143.70 (2 s, C-3a,-7a) ppm. IR (film): $\tilde{\nu}$ = 3096 cm^{-1} (w, C–H stretching, aromatic), 3022 (w, C–H stretching, aromatic), 2956, 2852 (s, C–H stretching, aliphatic), 1459, 1482 (w). UV (CH_3CN): λ_{max} (lg ε) = 196 nm (4.59), 194 (4.57), 198 (4.54), 204 (3.99), 208 (3.90), 216 (3.84), 220 (3.63), 224 (3.17), 268 (3.05), 274 (3.06). MS (EI = 70 eV): *m/z* (%) = 174 (73) [M^+], 117 (100) [$M^+ - C_4H_9$], 131 (51) [$M^+ - C_3H_7$], 104 (78) [$M^+ - C_5H_{10}$], 91 (35) [$C_7H_7^+$], 77 (13) [$C_6H_5^+$].

2-Pentylindane (7c): From **5c** (16.50 g, 0.059 mol), **7c** was prepared by the same route as described above for **7a**. Yield: 10.0 g (90%). B.p. 134 °C/14 Torr (ref.[20c] 134 °C/14 Torr). ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 0.95 (t, ^3J = 6.6 Hz, 3 H, 12-H), 1.31–1.56 (m, 9 H, side-chain protons, 2-H), 2.56–3.13 (m, 4 H, 1-,3-H), 7.13–7.25 (m, 4 H, aromatic protons) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.10 (q, C-12), 22.71 (t, C-11), 28.12 (t, C-9), 32.07 (t, C-8), 35.82 (t, C-10), 39.39 (2 t, C-1,-3), 40.29 (d, C-2), 124.35 (2 d, C-4,-7), 125.96 (2 d, C-5,-6), 143.69 (2 s, C-3a,-7a) ppm. IR (film): $\tilde{\nu}$ = 3071 cm^{-1} (w, C–H stretching, aromatic), 3044 (w, C–H stretching aromatic), 2956, 2924 (s, C–H stretching, aliphatic), 1482, 1459 (w), 739 (s). UV (CH_3CN): λ_{max} (lg ε) = 196 nm (4.13), 214 (3.78), 268 (2.93), 274 (2.94), 324 (2.25), 346 (2.21), 374 (2.16). MS (EI = 70 eV): *m/z* (%) = 188.1 (88) [M^+], 173 (1) [$M^+ - CH_3$], 159 (1) [$M^+ - C_2H_5$], 145 (6) [$M^+ - C_3H_7$], 131 (50) [$M^+ - C_4H_9$], 117 (100) [$M^+ - C_5H_{11}$], 104 (60) [117 – CH].

4,7-Dihydro-2-propylindane (8a): 2-Propylindane (**7a**, 14.5 g, 90.62 mmol), liquid NH_3 (87 mL), EtOH (100 mL) and THF (60 mL, dry) were placed in a 500-mL three-necked flask equipped with a mechanical stirrer and the temperature maintained at –75 °C with a methanol-liquid nitrogen bath. Sodium metal was added until the blue colour persisted for 20 min. The NH_3 was allowed to evaporate overnight. The remaining residue was partitioned between ether and water. The ether layer was evaporated and the resulting liquid was again partitioned between ether and water. The ether layer was dried with $MgSO_4$ and the solvent evaporated to

give crude 4,7-dihydro-2-propylindane (**8a**) (13.55 g, 92%) as a colourless liquid. The product was rather unstable and on standing slowly re-oxidized to 2-propylindane, it was thus quickly used for further reaction. B.p. 52–54 °C/7 Torr. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 0.90 (t, ^3J = 7.0 Hz, 3 H, 10-H), 1.28–1.41 (m, 5 H, side-chain protons, 2-H), 1.87–2.40 (m, 4 H, 1-,3-H), 2.61 (br. s, 4 H, 4-,7-H), 5.74 (br. s, 2 H, 5-,6-H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.25 (q, C-10), 21.37 (t, C-9), 27.51 (2 t, C-4,-7), 35.9 (d, C-2), 39.28 (t, C-8), 42.13 (2 t, C-1,-3), 124.73 (2 d, C-5,-6), 130.92 (s, C-3a,-7a) ppm. IR (film): $\tilde{\nu}$ = 3026 cm^{-1} (m, C–H stretching), 2956, 2915, 2874 (s, CH-stretching), 1377 (m, CH_3 deformation). UV (CH_3CN): λ_{max} (lg ε) = 192 nm (3.88), 194 (3.88), 208 (3.56), 224 (2.98), 230 (2.70), 240 (2.13), 274 (1.94), 296 (1.97). MS (GC/MS): *m/z* (%) = 162 (95) [M$^+$], 119 (81) [M$^+$ – C_3H_7], 92 (100) [C_7H_8], 91 (95), 79 (22).

4,7-Dihydro-2-butylindane (8b): From **7b** (14 g, 0.080 mol), **8b** was prepared by the same route as described above for **8a**. Yield: 12 g (85%). B.p. 78 °C/5 Torr. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.94 (t, ^3J = 6.84 Hz, 3 H, 11-H), 1.31–1.47 (m, 7 H, side-chain protons, 2-H), 1.95–2.47 (m, 4 H, 1-,3-H), 2.66 (br. s, 4 H, 4-,7-H), 5.79 (s, 2 H, 5-,6-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.16 (q, C-11), 22.90 (t, C-10), 27.54 (2 t, C-1,-3), 30.62 (t, C-9), 36.19 (t, C-2), 36.72 (d, C-8), 42.20 (2 t, C-4,-7), 124.75 (2 d, C-5,-6), 130.96 (s, C-3a,-7a) ppm. IR (film): $\tilde{\nu}$ = 3026 cm^{-1} (s, C–H-stretching), 2957, 2721 (s), 1466, 1428 (w), 1644 (w), 926, 955 (w). UV (CH_3CN): λ_{max} (lg ε) = 194 nm (3.96), 200 (3.83), 208 (3.52), 218 (3.25), 228 (2.68), 268 (2.21), 274 (2.22). MS (EI = 70 eV): *m/z* (%) = 176 (67) [M$^+$], 174 (30) [M$^+$ – H_2], 119 (78) [M$^+$ – C_4H_9], 92 (100) [$C_7H_8^+$].

4,7-Dihydro-2-pentylindane (8c): From **7c** (14.5 g, 0.077 mol), **8c** was prepared by the same route as described above for **8a**. Yield: 14.0 g (96%). B.p. 138 °C/2 Torr. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.9 (t, ^3J = 6.8 Hz, 3 H, 12-H), 1.29–1.43 (m, 9 H, side-chain protons, 2-H), 1.94–2.44 (m, 4 H, 1-,3-H), 2.66 (br. s, 4 H, 4-,7-H), 5.78 (s, 2 H, 5-,6-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.09 (q, C-12), 22.71 (t, C-11), 27.55 (2 t, C-1,-3), 28.05 (t, C-9), 32.10 (t, C-8), 37.0 (t, C-10), 36.24 (d, C-2), 42.21 (2 t, C-4,-7), 124.76 (2 d, C-5,-6), 130.96 (s, C-3a,-7a) ppm. IR (film): $\tilde{\nu}$ = 3026 cm^{-1} (m, CH-stretching), 2956, 2922, 2873, 2851 (s, C–H stretching), 1645, 1465, 1459, 1443 (w), 661 (m). UV (CH_3CN): λ_{max} (lg ε) = 196 nm (3.78), 212 (3.46), 252 (1.65), 266 (1.70), 324 (2.33), 360 (2.27). MS (EI = 70 eV): *m/z* (%) = 190.1 (66) [M$^+$], 175 (1) [M$^+$ – CH_3], 161 (2) [M$^+$ – C_2H_5], 147 (3) [M$^+$ – C_3H_7], 133 (9) [M$^+$ – C_4H_9], 119 (100) [M$^+$ – C_5H_{11}], 105 (13) [119 – CH_2], 92 (97) [119 – C_2H_3], 91 (88) [119 – C_2H_4].

Ethyl 4-Propyl-1,1a,2,3,4,5,6,6a-octahydrocyclopropa[*f*]indene-1-carboxylate (9a): To a refluxing suspension of **8a** (14.5 g, 89.50 mmol), $CuSO_4$ (anhydrous, 7.5 g) and cyclohexane (anhydrous, 70 mL) was added dropwise with stirring over a period of 5 h a solution of ethyl diazoacetate (34.69 g, 304.0 mmol) in 150 mL of anhydrous cyclohexane with a dropping funnel. The mixture was refluxed for further 60 min and filtered to remove the $CuSO_4$. The solution was concentrated and the product was separated by column chromatography on silica gel using pentane as solvent increasing its polarity with dichloromethane. Some unreacted starting material eluted from the column first, followed by **9a** (12 g, 54%), and finally by diethyl fumarate, a side product. The small impurities which eluted with the product were further separated with the help of a silver nitrate impregnated silica gel column with pentane as an eluent, increasing its polarity with dichloromethane. An aqueous solution of 5.5 g of silver nitrate in 30 mL of distilled water was mixed with 50 g of 200–300-mesh silica and ground for 5 min in a mortar. The mixture was then dried in an oven at 150 °C for 1 h. The resulting powder was almost white, stored in a beaker wrapped with dark paper and dried with phosphorus pentoxide in a vacuum desiccator. The adsorbent could be stored for several months without significant darkening or decrease of activity. The column was packed in the same way as an ordinary silica gel column but was wrapped with dark paper. The adduct (11.2 g, 50%) was a colourless liquid which on keeping it below room temperature solidified. M.p. 15 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.90 (t, ^3J = 7.0 Hz, 3 H, 10-H), 1.27 (t, ^3J = 7.15 Hz, 3 H, 12-H), 1.25–1.35 (m, 6 H, 8/9-H, 1a-,6a-H), 1.45 (t, ^3J = 4.33 Hz, 1 H, 1-H), 1.76–1.81 (br. s, 4 H, 2-,6-H), 2.14–2.23 (m, 1 H, 4-H), 2.31 (br. s, 4 H, 3-,5-H), 4.12–4.14 (q, ^3J = 7.1 Hz, 2 H, 11-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.50, 14.56 (2 × q, C-10,-12), 21.60 (t, C-9), 22.49 (2 d, C-1a,-6a), 24.41 (d, C-4), 24.46 (2 t, C-2,-6), 36.23 (d, C-1), 39.36 (t, C-8), 42.71 (2 t, C-3,-5), 60.44 (t, C-11), 129.26 (2 s, C-2a,-5a), 175.30 (s, C-7) ppm. IR (film): $\tilde{\nu}$ = 2956 cm^{-1} (m, CH-stretching), 1724 (s, C=O), 1376 (m, CH_3 deformation), 1213, 1172 (s, C–O). UV (CH_3CN): λ_{max} (lg ε) = 192 nm (3.93), 238 (1.30), 268 (1.28), 282 (0.89), 296 (1.31), 380 (1.31). MS (EI = 70 eV): *m/z* (%) = 248 (100) [M$^+$], 220 (5) [M$^+$ – CO], 219 (22) [M$^+$ – C_2H_5], 203 (30) [M$^+$ – C_2H_5O], 194 (20), 175 (33) [M$^+$ – $C_3H_5O_2$], 162 (72) [175 – CH], 131 (53), 112 (90), 105 (32). $C_{16}H_{24}O_2$ (248.8): calcd. C 77.36, H 9.75; found C 76.92, H 10.11.

Ethyl 4-Butyl-1,1a,2,3,4,5,6,6a-octahydrocyclopropa[*f*]indene-1-carboxylate (9b): From **8b** (14 g, 0.079 mol), **9b** was prepared by the same route as described above for **9a**. Yield: 13.0 g (63%). Compound **9b** melts at room temperature. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.79 (t, ^3J = 7.01 Hz, 3 H, 11-H), 1.18 (t, ^3J = 7.13 Hz, 3 H, 13-H), 1.10–1.31 (m, 8 H, side-chain protons, 1a-,6a-H), 1.23 (t, ^3J = 4.87 Hz, 1 H, 1-H), 1.47–1.74 (m, 4 H, 2-,6-H), 2.05–2.10 (m, 1 H, 4-H), 2.23 (br. s, 4 H, 3-,5-H), 4.03 (q, ^3J = 7.12 Hz, 2 H, 12-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.09 (q, C-11), 14.26 (q, C-13), 22.19 (2 d, C-1a,-6a), 22.81 (t, C-10), 26.12 (d, C-4), 30.05 (2 t, C-2,-6), 30.49 (t, C-9), 36.15 (d, C-1), 36.47 (t, C-8), 42.45 (2 t, C-3,-5), 60.16 (t, C-12), 128.96 (2 s, C-2a,-5a), 174.99 (s, C-7) ppm. IR (film): $\tilde{\nu}$ = 3025 cm^{-1} (w), 2977, 2722 (s, CH stretching), 1445, 1465 (w), 1725 (s, C=O), 1172, 1287 (s). UV (CH_3CN): λ_{max} (lg ε) = 192 nm (3.93), 204 (3.69), 216 (3.23), 228 (2.70), 240 (2.31), 294 (2.21), 342 (2.16). MS (EI = 70 eV): *m/z* (%) = 262 (88) [M$^+$], 233 (18) [M$^+$ – C_2H_5], 217 (28) [M$^+$ – C_2H_5O], 149 (12) [M$^+$ – $C_6H_9O_2$], 112 (100) [M$^+$ – $C_{11}H_{18}$].

Ethyl 4-Pentyl-1,1a,2,3,4,5,6,6a-Octahydrocyclopropa[*f*]indene-1-carboxylate (9c): From **8c** (14.3 g, 0.075 mol), **9c** was prepared by the same route as described above for **9a**. Yield: 13.5 g (65%). M.p. above 5 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.91 (t, ^3J = 6.8 Hz, 3 H, 12-H), 1.28 (t, ^3J = 7.1 Hz, 3 H, 14-H), 1.24–1.42 (m, 10 H, side-chain protons, 1a-,6a-H), 1.46 (t, ^3J = 4.27 Hz, 1 H, 1-H), 1.70–1.92 (m, 4 H, 2-,6-H), 2.20 –2.24 (m, 1 H, 4-H), 2.32 (br. s, 4 H, 3-,5-H), 4.15 (q, ^3J = 7.2 Hz, 2 H, 13-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.37 (q, C-12), 14.60 (q, C-14), 22.54 (2 d, C-1a,-6a), 22.97 (t, C-11), 23.65 (d, C-1), 24.50 (2 t, C-2,-6), 28.25 (t, C-10), 32.33 (t, C-9), 36.52 (d, C-4), 37.28 (t, C-8), 42.79 (2 t, C-3,-5), 60.49 (t, C-13), 129.30 (2 s, C-2a,-5a), 175.7 (s, C=O) ppm. IR (film): $\tilde{\nu}$ = 2982 cm^{-1} (s, C–H stretching aliphatic), 1724 (s, C=O), 1465, 1445, 1368 (m), 1297, 1260, 1224 (s), 1173, 1155 (s), 1142, 1037 (s). UV (CH_3CN): λ_{max} (lg ε) = 198 nm (3.66), 214 (4.13), 324 (2.67), 350 (2.62). MS (EI = 70 eV): *m/z* (%) = 276 (51) [M$^+$], 247 (18) [M$^+$ – C_2H_5], 231 (18) [M$^+$ – C_2H_5O], 203 (25) [M$^+$ – $C_2H_5CO_2$], 188 (35) [203 – CH_3], 205 (16) [M$^+$ – C_5H_{11}], 159 (20) [205 – C_2H_6O], 131 (70) [159 – CO], 117 (35) [131 – CH_2], 112 (100) [$C_6H_8O_2$], 105 (38) [131 – C_2H_2], 91 (58) [105 – CH_2].

4-Propyl-1,1a,2,3,4,5,6,6a-octahydrocyclopropa[*f*]indene-1-carboxylic Acid (20): In a 250-mL round-bottomed flask EtOH (100 mL) and NaOH (1 M, 60 mL) were placed. The mixture was left to stir for a while and the ethyl ester **9a** (2.0 g, 8.064 mmol) was added slowly; the mixture was kept at room temp. and stirred for 4–6 h. When TLC analysis showed no more starting material to be present, the mixture was acidified with 1 M HCl. The EtOH was evaporated and the residual water extracted twice with ethyl acetate and once with CH_2Cl_2. The organic parts were combined, washed with water and dried ($MgSO_4$). The solvent was evaporated and the residue purified by column chromatography on silica gel by first eluting the impurities with CH_2Cl_2 and finally washing the column with Et_2O to yield 1.5 g (84%) of **20** as a colourless solid which was recrystallized from hexane/dichloromethane to yield analytically pure cubes. M.p. 80–83 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.92 (t, ^3J = 7.0 Hz, 3 H, 10-H), 1.27–1.37 (m, 6 H, 8-,9-H, 1a-,6a-H), 1.47 (t, ^3J = 4.2 Hz, 1 H, 1-H), 1.85–1.89 (br. s, 4 H, 2- 6-H), 2.25 (m, 1 H, 4-H), 2.33 (br. s, 4 H, 3-,5-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.22 (q, C-10), 21.30 (t, C-9), 23.31 (d, C-4), 23.34 (2 d, C-1a,-6a), 24.14 (2 t, C-2,-6), 35.91 (d, C-1), 39.08 (t, C-8), 42.38 (2 t, C-3,-5), 128.89 (2 s, C-2a,-5a), 181.63 (s, C-7) ppm. IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1} (s, C–H stretching), 2877, 2835 (m), 2674, 2624, 2580 (w), 1686 (s, C=O), 1466, 1452, 1434, 1347 (m), 1303, 1217 (m), 1013 (w). UV (CH_3CN): λ_{max} (lg ε) = 192 nm (4.00). MS (EI = 70 eV): *m*/*z* (%) = 220 (53) [M$^+$], 202 (11) [M$^+$ – H_2O], 177 (30) [M$^+$ – C_3H_7], 160 (41) [177 – OH], 131 (75) [177 – HCOOH], 105 (55) [C_8H_9], 91 (100) [105 – CH_2]. $C_{14}H_{20}O_2$ (220.31): calcd. C 76.33, H 9.15, O 14.52; found C 76.31, H 9.18.

4-Butyl-1,1a,2,3,4,5,6,6a-octahydrocyclopropa[*f*]indene-1-carboxylic Acid (21): From **9b** (2 g, 7.63 mmol), **21** was prepared by the same route as described above for **20**. Yield: 1.5 g (84%). M.p. 78–80 °C (recrystallized from hexane/dichloromethane to get colourless needles). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.92 (t, ^3J = 6.9 Hz, 3 H, 11-H), 1.25–1.38 (m, 8 H, side-chain protons, 1a-,6a-H), 1.43 (t, ^3J = 4.24 Hz, 1 H, 1-H), 1.85 (br. s, 4 H, 2-,6-H), 2.16–2.25 (m, 1 H, 4-H), 2.34 (br. s, 4 H, 3-,5-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.12 (q, C-11), 22.83 (t, C-10), 23.29 (d, C-4), 23.35 (2 d, C-1a,-6a), 24.15 (2 t, C-3,-5), 30.50 (t, C-9), 36.14 (d, C-1), 36.49 (t, C-8), 42.43 (2 t, C-2,-6), 128.89 (2 s, C-2a,-5a), 181.58 (s, C-7) ppm. IR (KBr): $\tilde{\nu}$ = 2954 cm^{-1} (s, C–H stretching), 1686 (s, C=O), 1655, 1648 (w), 1466, 1458, 1445 (m), 1344 (w), 1299, 1213(m). UV (CH_3CN): λ_{max} (lg ε) = 198 nm (4.18), 202 (4.15), 206 (4.13), 244 (2.29), 254 (2.47). MS (EI = 70 eV): *m*/*z* (%) = 234 (55) [M$^+$], 216 (9) [M$^+$ – H_2O], 205 (5) [M$^+$ – C_2H_5], 189 (21) [M$^+$ – CO_2H], 177 (69) [M$^+$ – C_4H_9], 159 (29) [177 – H_2O], 131 (85) [177 – HCOOH], 117 (66) [131 – CH_2], 105 (66) [C_8H_9], 91 (100) [131 – C_3H_4]. $C_{15}H_{22}O_2$ (234.34): calcd. C 77.21, H 9.07, O 13.71; found C 77.56, H 9.10.

4-Pentyl-1,1a,2,3,4,5,6,6a-octahydrocyclopropa[*f*]indene-1-carboxylic Acid (22): From **9c** (2.0 g, 7.25 mmol), **22** was prepared by the same route as described above for **20**. Yield: 1.4 g (80%). M.p. 72–74 °C (recrystallized from hexane/dichloromethane to yield colourless irregular crystals). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.80 (t, ^3J = 6.8 Hz, 3 H, 12-H), 1.13–1.31 (m, 10 H, side-chain protons, 1a-,6a-H), 1.37 (t, ^3J = 4.23 Hz, 1 H, 1-H), 1.74 (br. s, 4 H, 2-,6-H), 2.05–2.14 (m, 1 H, 4-H), 2.23 (br. s, 4 H, 3-,5-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.07 (q, C-12), 22.67 (t, C-11), 23.20 (d, C-1), 23.34 (2 d, C-1a,-6a), 24.16 (2 t, C-3,-5), 27.92 (t, C-10), 32.02 (t, C-9), 36.18 (d, C-4), 36.77 (t, C-8), 42.44 (2 t, C-2,-6), 128.90 (2 s, C-2a,-5a), 181.05 (s, C=O) ppm. IR (KBr): $\tilde{\nu}$ = 2956 cm^{-1} (s, C–H stretching), 1690 (s, C=O), 1686 (s), 1448 (m), 1384 (m), 1298 (m), 1209 (m). UV (CH_3CN): λ_{max} (lg ε) = 196 nm (4.05), 212 (3.95), 244 (3.08), 250 (3.02), 258 (2.95), 324 (2.65), 354 (2.60), 374 (2.57). MS (EI = 70 eV): *m*/*z* (%) = 249 (13) [M$^+$ + 1], 248 (91) [M$^+$], 230 (8) [M$^+$ – H_2O], 201 (20) [230 – C_2H_5], 188 (28) [201 – CH], 177 (67) [M$^+$ – C_5H_{11}], 131 (87) [177 – HCOOH], 117 (55) [131 – CH_2], 105 (59) [131 – C_2H_2], 91 (100) [131 – C_3H_4]. $C_{16}H_{24}O_2$ (248.37): calcd. C 77.38, H 9.74; found C 77.45, H 9.87.

Ethyl 2-Propyl-1,2,3,6-tetrahydro-6-azulenecarboxylate (12a): Ethyl 4-propyl-1,1a,2,3,4,5,6,6a-octahydrocyclopropa[*f*]indene-1-carboxylate (**9a**, 8.0 g, 32.3 mmol) was dissolved in CCl_4 (400 mL) and the solution cooled with an ice bath. Bromine (5.16 g, 32.3 mmol) dissolved in CCl_4 (18 mL) was added dropwise with stirring. When the addition was complete, triethylamine, 16.0 g (158.1 mmol) was added. Triethylamine hydrobromide began to form immediately. The mixture was refluxed for 18 h, cooled and the hydrobromide was filtered off. The filtrate was evaporated and the resulting oil partitioned between benzene and dilute aqueous acid (HCl). The benzene layer was washed with water and dried with $MgSO_4$ and filtered to get the crude product. The product was purified by column chromatography on silica gel using pentane as solvent and increasing the polarity with dichloromethane. The product **12a** (5.5 g, 69%), a clear bluish liquid, eluted with 1% dichloromethane. B.p. 124–126 °C/5 Torr. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.92 (t, ^3J = 7.2 Hz, 3 H, 12-H), 1.30 (t, ^3J = 7.14 Hz, 3 H, 14-H), 1.33–1.37 (m, 4 H, 10-,11-H), 2.34 (m, 1 H, 2-H), 2.38–2.41/2.79–2.85 (m, 4 H, 1-,3-H), 2.67–2.71 (m, 1 H, 6-H), 4.22–4.27 (q, ^3J = 7.14 Hz, 2 H, 13-H), 5.34–5.41 (m, 2 H, 5-,7-H), 6.17–6.21 (2 d, ^3J = 9.1 Hz, 2 H, 4-,8-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.23 (2 × q, C-12,-14), 21.39 (t, C-11), 37.06 (d, C-2), 38.20 (t, C-10), 42.75 (2 t, C-1,-3), 45.20(d, C-6), 60.93 (t, C-13), 115.99, 116.63 (2 d, C-5,-7), 125.29, 125.44 (2 d, C-4,-8), 141.81 (s, C-3a,-8a), 173.27 (s, C-9) ppm. IR (film): $\tilde{\nu}$ = 2958 cm^{-1} (m, CH stretching), 1738 (s, C=O), 1610 (w), 1465, 1447 (w), 1392 (w), 1368, 1301, 1292, 1274 (m), 1255, 1193, 1179, 1164 (m), 1105, 1069 (w). UV (CH_3CN): λ_{max} (lg ε) = 228 nm (3.77), 236 (3.68), 246 (3.66), 264 (3.50), 288 (3.44), 300 (3.31), 318 (3.02). MS (EI = 70 eV): *m*/*z* (%) = 246 (10) [M$^+$], 217 (10) [M$^+$ – C_2H_5], 218 (4) [M$^+$ – CO], 173 (100) [M$^+$ – $C_3H_5O_2$], 129 (7) [173 – C_3H_8].

Ethyl 2-Butyl-1,2,3,6-tetrahydro-6-azulenecarboxylate (12b): From **9b** (8.0 g, 30.53 mmol), **12b** was prepared by the same route as described above for **12a**. Yield: 5.2 g (65%). B.p. 135 °C/5 Torr. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.96 (t, ^3J = 7.1 Hz, 3 H, 13-H), 1.34 (t, ^3J = 7.16 Hz, 3 H, 15-H), 1.37–1.51 (m, 6 H, side-chain protons), 2.19–2.21 (m, 1 H, 2-H), 2.37–2.43/2.85–2.88 (m, 4 H, 1-,3-H), 2.72–2.83 (m, 1 H, 6-H), 4.16 (q, ^3J = 7.13 Hz, 2 H, 14-H), 5.38–5.45 (m, 2 H, 5-,7-H), 6.21–6.24 (2 d, ^3J = 9.02 Hz, 2 H, 4-,8-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.08 (q, C-13), 14.20 (q, C-15), 22.81 (t, C-12), 30.53 (t, C-11), 35.62 (t, C-10), 37.27 (d, C-2), 42.78 (2 t, C-1,-3), 45.18 (d, C-6), 60.89 (t, C-14), 116.60 (2 d, C-5,-7), 125.41 (2 d, C-4,-8), 141.77 (s, C-3a,-8a), 173.24 (s, C-9) ppm. IR (film): $\tilde{\nu}$ = 3024 cm^{-1} (w), 2957, 2852 cm^{-1} (s, CH stretching), 1466, 1447 (w) 1739 (s, C=O), 1193, 1259 (s, C–O). UV (CH_3CN): λ_{max} (lg ε) = 206 nm (4.31), 208 (4.30), 254 (3.50), 268 (3.57), 292 (3.38), 310 (3.01), 342 (2.39). MS (EI = 70 eV): *m*/*z* (%) = 260 (13) [M$^+$], 231 (6) [M$^+$ – C_2H_5], 232 (1) [M$^+$ – CO], 87 (100) [M$^+$ – $C_3H_5O_2$], 129 (8) [187 – C_4H_{10}], 88 (16) [129 – C_3H_5].

Ethyl 2-Pentyl-1,2,3,6-tetrahydro-6-azulenecarboxylate (12c): From **9c** (8 g, 28.98 mmol), **12c** was prepared by the same route as described above for **12a**. Yield: 6.2 g (78%). B.p. >260 °C/2 Torr. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.92 (t, ^3J = 7.0 Hz, 3 H, 14-H), 1.29–1.34 (t, ^3J = 7.1 Hz, 3 H, 16-H), 1.31–1.38 (m, 8 H, side-chain protons), 1.62–1.74/2.42–2.47 (m, 4 H, 1-,3-H), 2.38–2.41 (m, 1 H, 2-H), 2.83 (m, 1 H, 6-H), 4.30 (q, ^3J = 7.1 Hz, 2 H, 15-H), 5.41–

5.45 (m, 2 H, 5-,7-H), 6.21 (2 d, ^3J = 9.10 Hz, 2 H, 4-,8-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.07 (q, C-14), 14.24 (q, C-16), 22.66 (t, C-13), 26.02 (t, C-12), 33.01 (t, C-11), 35.92 (t, C-10), 37.32 (d, C-2), 42.80 (2 t, C-1,-3), 45.20 (d, C-6), 60.93 (t, C-15), 115.97, 116.63 (2 d, C-5,-7), 125.30, 125.45 (2 d, C-4,-8), 141.81 (s, C-3a,-8a), 173.28 (s, C-9) ppm. IR (film): $\tilde{\nu}$ = 3023 cm^{-1} (w, C–H stretching), 2956, 2925 (s, C–H stretching aliphatic), 1737 (s, C=O), 1465, 1447, 1367, 1301 (w), 1256 (m), 1223 (w), 1192, 1175, 1161 (m). UV (CH_3CN): λ_{max} (lg ε) = 206 nm (4.14), 274 (3.64), 288 (3.64), 312 (3.50), 344 (3.30), 374 (2.98). MS (EI = 70 eV): *m/z* (%) = 274 (5) [M$^+$], 245 (5) [M$^+$ – C_2H_5], 228 (2) [245 – OH], 201 (100) [M$^+$ – $C_3H_5O_2$], 129 (10) [201 – C_5H_{12}].

2-Propyl-1,2,3,6-tetrahydroazulene-6-carboxylic Acid (24): From **12a** (0.70 g, 2.85 mmol), **24** was prepared by the same route as described above for **20**. The acid was recrystallized from hexane/dichloromethane mixture to yield colourless irregular crystals. Yield: 0.5 g (81%). M.p. 118–120 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.96 (t, ^3J = 7.1 Hz, 3 H, 12-H), 1.36–1.50 (m, 4 H, side-chain protons), 2.29 (m, 1 H, 2-H), 2.39–2.44/2.82–2.88 (m, 4 H, 1-,3-H), 2.89–2.90 (m, 1 H, 6-H), 5.43–5.46 (dd, $^3J_{5,4}$ = $^3J_{7,8}$ = 9.07*Hz*, $^3J_{5,6}$ = $^3J_{7,6}$ = 5.6 Hz, 2 H, 5-,7-H), 6.24–6.27 (2 d, ^3J = 9.1 Hz, 2 H, 4-,8-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.23 (q, C-12), 21.39 (t, C-11), 37.04 (d, C-2), 38.18 (t, C-10), 42.75 (2 t, C-1,-3), 44.72 (d, C-6), 115.74 (2 d, C-5,-7), 125.81 (2 d, C-4,-8), 141.95 (2 s, C-3a,-8a), 178.20 (s, C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3023 cm^{-1} (w, C–H stretching), 2964, 2950, 2924 (m, C–H stretching), 2834, 2871, 2829 (w), 2700 (w), 2596 (w), 1713 (s, C=O), 1686 (w), 1655 (w), 1419 (w), 1312, 1298, 1220 (w). UV (CH_3CN): λ_{max} (lg ε) = 206 nm (4.31), 268 (3.57). MS (EI = 70 eV): *m/z* (%) = 218 (14) [M$^+$], 200 (6) [M$^+$ – H_2O], 173 (100) [M$^+$ – CO_2H], 129 (17) [173 – C_3H_8]. $C_{14}H_{18}O_2$ (218.30): calcd. C 77.02, H 8.32; found C 77.08, H 8.17.

2-Butyl-1,2,3,6-tetrahydroazulene-6-carboxylic Acid (25): From **12b** (0.70 g, 2.69 mmol), **25** was prepared by the same route as described above for **20**. Yield: 0.49 g (78%). M.p. 78–81 °C (compound was obtained as an off-white solid). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.94 (t, ^3J = 6.86 Hz, 3 H, 13-H), 1.30–1.39 (m, 6 H, side-chain protons), 1.40–1.55 (m, 4 H, 1-,3-H), 2.27–2.30 (m, 1 H, 2-H), 2.83–2.87 (m, 1 H, 6-H), 5.39–5.43 (dd, $^3J_{5,4}$ = $^3J_{7,8}$ = 9.0 Hz, $^3J_{5,6}$ = $^3J_{7,6}$ = 5.7 Hz, 2 H, 5-,7-H), 6.24–6.27 (d, ^3J = 9.1 Hz, 2 H, 4-,8-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.11 (q, C-13), 22.82 (t, C-12), 30.54 (t, C-11), 35.82 (t, C-10), 37.79 (d, C-2), 42.98 (2 t, C-1,-3), 44.71 (d, C-6), 115.73 (2 d, C-5,-7), 125.62 (2 d, C-4,-8), 141.82 (2 s, C-3a,-8a), 179.20 (s, C-9) ppm. IR (KBr): $\tilde{\nu}$ = 3024 cm^{-1} (w, C–H stretching), 2956, 2924, 2872, 2853 (s, C–H stretching), 2695, 2596 (w), 1710 (s, C=O), 1612, 1466, 1455 (w), 1420, 1298 (m), 1211 (w). UV (CH_3CN): λ_{max} (lg ε) = 206 nm (4.31), 248 (3.56), 268 (3.47), 300 (3.04). MS (EI = 70 eV): *m/z* (%) = 232 (15) [M$^+$], 214 (8) [M$^+$ – H_2O], 187 (100) [M$^+$ – CO_2H], 129 (21) [187 – C_4H_{10}].

2-Pentyl-1,2,3,6-tetrahydroazulene-6-carboxylic Acid (26): From **12c** (0.68 g, 2.48 mmol), **26** was prepared by the same route as described above for **20**. Yield: 0.5 g (82%). M.p. 70–72 °C (from hexane/dichloromethane off-white needles). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.92 (t, ^3J = 5.9 Hz, 3 H, 14-H), 1.25–1.50 (m, 8 H, side-chain protons), 2.27–2.30 (m, 1 H, 2-H), 2.32–2.84 (m, 4 H, 1-,3-H), 2.87–2.90 (m, 1 H, 6-H), 5.43–5.46 (dd, $^3J_{5,4}$ = $^3J_{7,8}$ = 9.2 Hz, $^3J_{5,6}$ = $^3J_{7,6}$ = 5.7 Hz, 2 H, 5-,7-H), 6.25–6.28 (d, ^3J = 8.9 Hz, 2 H, 4-,8-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.07 (q, C-14), 22.67 (t, C-13), 27.98 (t, C-12), 32.0 (t, C-11), 35.90 (t, C-10), 37.30 (d, C-2), 42.98 (2 t, C-1,-3), 44.72 (d, C-6), 115.75 (2 d, C-5,-7), 125.81 (2 d, C-4,-8), 141.95 (2 s, C-3a,-8a), 178.17 (s, C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3023 cm^{-1} (w, C–H stretching), 2957, 2923, 2870, 2853 (m, C–H stretching), 2699, 2595 (m), 1712 (s, C=O), 1219 (m). UV (CH_3CN): λ_{max} (lg ε) = 206 nm (4.30), 268 (3.53). MS (EI = 70 eV): *m/z* (%) = 246 (12) [M$^+$], 228 (5) [M$^+$ – H_2O], 201 (100) [M$^+$ – CO_2H], 129 (21) [201 – C_5H_{12}].

Ethyl 2-Propyl Perhydro-6-azulenecarboxylate (13/14): Ethyl 2-propyl-1,2,3,6-tetrahydro-6-azulenecarboxylate (**12a**, 3.29 g, 13.37 mmol) was dissolved in ethyl acetate (300 mL) in a 500-mL flask and Pd/C (1.1 g) added to the mixture. A stream of H_2 was blown through the suspension after evacuation, and the flask was shaken for 2 h under hydrogen. The mixture was filtered to remove the catalyst and the solvent was evaporated to yield the product (3.09 g, 92%) as a colourless liquid. The product was obtained in the form of a mixture of isomers, which were later separated by column chromatography on silica gel with pentane. The *cis*-fused isomer (**13**, 2.6 g, 77%) eluted first followed by the *trans* isomer **14**. However, pure *trans*-fused material could not be separated as it always contained traces of the *cis*-fused derivative. The spectroscopic data for **13** are given below. B.p. 135–140 °C/5 Torr. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.90 (t, ^3J = 6.94 Hz, 3 H, 12-H), 1.28 (t, ^3J = 7.12 Hz, 3 H, 14-H), 1.30–1.33 (m, 4 H, side-chain protons), 1.51–1.53 (m, 2 H, 3a-,8a-H), 1.55–1.60 (m, 4 H, 4-,8-H), 1.67–1.72 (m, 1 H, 2-H), 0.82/1.89 (m, 4 H, 1-,3-H), 2.10–2.14 (m, 4 H, 5-,7-H), 2.64–2.67 (m, 1 H, 6-H), 4.15 (q, ^3J = 7.12 Hz, 2 H, 13-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.26 (q, C-12), 14.38 (q, C-14), 21.78 (t, C-11), 28.75 (2 t, C-4,-8), 29.56 (2 t, C-5,-7), 37.79 (t, C-10), 39.94 (d, C-2), 41.63 (2 t, C-1,-3), 41.87 (2 d, C-3a,-8a), 43.41 (d, C-6), 59.97 (t, C-13), 176.11 (s, C=O) ppm. IR (film): $\tilde{\nu}$ = 2932 cm^{-1}(s, CH-stretching), 1732 (s, C=O), 1463, 1450 (w), 1376, 1221 (w), 1183, 1143 (m), 1095, 1046, 1033 (w). UV (CH_3CN): λ_{max} (lg ε) = 204 nm (2.92), 216 (2.55), 234 (2.15), 284 (1.86), 312 (1.80), 342 (1.64), 374 (1.54). GC/MS (EI = 70 eV): *m/z* (%) = 252 (95) [M$^+$], 237 (5) [M$^+$ – CH_3], 223 (12) [M$^+$ – C_2H_5], 209 (29) [M$^+$ – C_3H_7], 206 (18) [223 – OH], 178 (15) [206 – CO], 163 (100) [206 – C_3H_7], 135 (57) [163 – CO], 109 (52) [135 – C_2H_2], 81 (49) [109 – C_2H_4]. HRMS ($C_{16}H_{28}O_2$): calcd.252.2089; found 252.20856 ± 0.5 ppm.

Ethyl 2-Butyl-perhydroazulene-6-carboxylate (15/16): From **12b** (1.07 g, 4.24 mmol), **15/16** was prepared by the same route as described above for **13** (colourless liquid). The spectroscopic and analytical data for **15** are given below. Yield: 0.86 g (76%). B.p. 146 °C/5 Torr. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.90 (t, ^3J = 6.74 Hz, 3 H, 13-H), 1.28 (t, ^3J = 7.12 Hz, 3 H, 15-H), 1.27–1.34 (m, 6 H, side-chain protons), 1.49–1.53 (m, 2 H, 3a-,8a-H), 1.53–1.59 (m, 4 H, 4-,8-H), 1.70 (m, 1 H, 2-H), 0.82/1.89 (m, 4 H, 1-,3-H), 2.09–2.16 (m, 4 H, 5-,7-H), 2.64–2.67 (m, 1 H, 6-H), 4.13–4.18 (q, ^3J = 7.12 Hz, 2 H, 14-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.09 (q, C-13), 14.25 (q, C-15), 22.96 (t, C-12), 28.75 (2 t, C-4,-8), 29.56 (2 t, C-5,-7), 30.96 (t, C-11), 35.16 (t, C-10), 40.18 (d, C-2), 41.67 (2 t, C-1,-3), 41.87 (2 d, C-3a,-8a), 43.41 (d, C-6), 59.96 (t, C-14), 176.08 (s, C-9) ppm. IR (film): $\tilde{\nu}$ = 2928 cm^{-1} (s, CH-stretching), 1462, 1378 (w), 1732 (s, C=O), 1182, 1160 (s, C–O). UV (CH_3CN): λ_{max} (lg ε) = 192 nm (3.95), 232 (2.60), 260 (2.37), 278 (2.30), 310 (2.18). MS (EI = 70 eV): *m/z* (%) = 266 (88) [M$^+$], 237 (45) [M$^+$ – C_2H_5], 220 (36) [237 – OH], 251 (19) [M$^+$ – CH_3], 209 (78) [M$^+$ – C_4H_9], 163 (100) [220 – C_4H_9], 135 (55) [163 – CO]. HRMS ($C_{17}H_{30}O_2$): calcd. 266.2246; found 266.22431 ± 5 ppm.

Ethyl 2-Pentyl-perhydroazulene-6-carboxylate (17/18): From **12c** (0.8 g, 2.91 mmol), **17/18** was prepared by the same route as described above for **13**. In addition to **17/18** (colourless liquid) partially reduced **19** was also isolated (164 mg, 20%) and characterized; on further hydrogenation it was quantitatively converted to

17/18. The spectroscopic and analytical data for **17** are given below. Yield: 0.6 g (73%). B.p. 152 °C/2 Torr. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.89 (t, ^3J = 6.9 Hz, 3 H, 14-H), 1.27 (t, ^3J = 7.0 Hz, 3 H, 16-H), 1.24–1.33 (m, 8 H, side-chain protons), 1.44–1.53 (m, 2 H, 3a-,8a-H), 1.54–1.66 (m, 4 H, 4-,8-H), 1.68–1.69 (m, 1 H, 2-H), 0.76/1.72 (m, 4 H, 1-,3-H), 1.91–2.10 (m, 4 H, 5-,7-H), 2.13–2.18 (m, 1 H, 6-H), 4.13 (q, ^3J = 7.1 Hz, 2 H, 15-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.04 (q, C-14), 14.24 (q, C-16), 22.63 (t, C-13), 22.65 (t, C-12), 25.99 (2 t, C-4,-8), 28.75 (2 t, C-5,-7), 31.11 (t, C-11), 32.98 (t, C-10), 41.87 (d, C-2), 42.45 (2 t, C-1, 3), 42.96 (2 d, C-3a,-8a), 43.40 (d, C-6), 59.99 (t, C-15), 176.49 (s, C-9) ppm. IR (film): $\tilde{\nu}$ = 2977 cm^{-1} (s, C–H stretching aliphatic), 1732 (s, C=O), 1462, 1449, 1378, 1298, 1288, 1236, 1221, 1201 (m), 1161 (s), 1035 (m). UV (CH_3CN): λ_{max} (lg ε) = 194 nm (3.78), 208 (3.45), 216 (3.32), 268 (2.06). MS (EI = 70 eV): *m*/*z* (%) = 280 (100) [M$^+$], 251 (65) [M$^+$ – C_2H_5], 235 (23) [M$^+$ – C_2H_5O], 209 (82) [M$^+$ – C_5H_{11}], 180 (13) [209 – C_2H_5], 165 (81) [209 – CO_2], 151 (11) [165.2 – CH_2], 135 (40) [165.2 – C_2H_6].

2-Propyl-perhydroazulene-6-carboxylic Acid (27): From **13** (1.0 g, 3.978 mmol), **27** was prepared as described above for **20**. Acid **27** was recrystallized from hexane/dichloromethane mixture to yield colourless needles. Yield: 0.7 g (79%). M.p. 94–96 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.91 (t, ^3J = 6.96 Hz, 3 H, 12-H), 1.26–1.33 (m, 4 H, side-chain protons), 1.48–1.53 (m, 2 H, 3a-,8a-H), 1.56–1.63 (m, 4 H, 4-,8-H), 1.70–1.73 (m, 1 H, 2-H), 0.83/1.72 (m, 4 H, 1-,3-H), 2.11–2.19 (m, 4 H, 5-,7-H), 2.74 (m, 1 H, 6-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.39 (q, C-12), 21.78 (t, C-11), 28.78 (2 t, C-4,-8), 37.78 (t, C-10), 29.44 (2 t, C-5,-7), 41.71 (2 t, C-1,-3), 39.98 (d, C-2), 43.22 (d, C-6), 42.01 (2 s, C-3a,-8a), 182.25 (s, C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3027 cm^{-1}, 2952, 2931, 2915, 2904, 2888, 2866, 2843 (s, C–H stretching aliphatic), 3380 (m), 2730, 2682, 2651, 2631, 2600, 2587, 2552 (w), 1700 (s, C=O), 1656, 1648 (w), 1451, 1426, 1403 (m), 1324, 1309, 1301 (w), 1283, 1266, 1241, 1213, 1192, 1151 (m). UV (MeOH): λ_{max} (lg ε) = 206 nm (3.58), 244 (3.19), 288 (2.52), 236 (3.12), 274 (2.42), 308 (2.03). MS (EI = 70 eV): *m*/*z* (%) = 224 (40) [M$^+$], 206 (15) [M$^+$ – H_2O], 195 (30) [M$^+$ – C_2H_5], 181 (100) [M$^+$ – C_3H_7], 163 (25) [181 – H_2O], 137 (80) [181 – CO_2], 109 (45) [137 – C_2H_4]. $C_{14}H_{24}O_2$ (224.33): calcd. C 74.94, H 10.79; found C 74.92, H 10.89.

2-Butyl-perhydroazulene-6-carboxylic Acid (28): From **15** (50 mg, 0.188 mmol), **28** was prepared as described above for **20**; recrystallization from hexane/dichloromethane yielded colourless needles. Yield: 40 mg (89%). M.p. 78–80 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.80 (t, ^3J = 6.73 Hz, 3 H, 13-H), 1.17 –1.21 (m, 6 H, side-chain protons), 1.23–1.42 (m, 2 H, 3a-,8a-H), 1.45–1.50 (m, 4 H, 4-,8-H), 1.55–1.60 (m, 1 H, 2-H), 0.72/1.81 (m, 4 H, 1-,3-H), 2.00–2.28 (m, 4 H, 5-,7-H), 2.65 (m, 1 H, 6-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.12 (q, C-13), 22.98 (t, C-12), 28.78 (2 t, C-4,-8), 30.96 (t, C-10), 29.49 (2 t, C-5,-7), 35.17 (t, C-11), 41.75 (2 t, C-1,-3), 40.23 (d, C-2), 43.06 (d, C-6), 42.01 (2 s, C-3a,-8a), 180.93 (s, C-9) ppm. IR (KBr): $\tilde{\nu}$ = 2953 cm^{-1}, 2931, 2921, 2892, 2870, 2855 (s, C–H stretching aliphatic), 3432 (m), 1697 (s, C=O), 1456 (m), 1274, 1248 (m). UV (CH_3CN): λ_{max} (lg ε) = 254 nm (3.22), 266 (3.19), 192 (4.24), 208 (3.92), 216 (3.74), 224 (3.54), 232 (3.32), 280 (3.13), 312 (2.75). MS (EI = 70 eV): *m*/*z* (%) = 238 (49) [M$^+$], 220 (19) [M$^+$ – H_2O], 209 (44) [M$^+$ – C_2H_5], 181 (100) [M$^+$ – C_4H_9], 163 (34) [181 – H_2O], 135 (49) [181 – HCO_2H], 109 (50) [135 – C_2H_2].

Ethyl 2-Pentyl-1,2,3,4,5,6,7,8-Octahydroazulene-6-carboxylate (19): Compound **19** was obtained during the hydrogenation of **12c** to **17/18** in the presence of Pd-C/H_2 in EtOAc; by increasing the reaction time it was converted into the fully hydrogenated **17/18**. Compound **19** was obtained as a coloured liquid after purification by column chromatography on silica gel. Yield: 164 mg (20%). B.p. 170 °C/5 Torr. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.91 (t, ^3J = 6.88 Hz, 3 H, 14-H), 1.28 (t, ^3J = 7.0 Hz, 3 H, 16-H), 1.25–1.39 (m, 8 H, side-chain protons), 1.69–1.76 (m, 4 H, 4-,8-H), 1.77–1.81 (m, 1 H, 2-H), 1.01/1.99 (m, 4 H, 1-,3-H), 2.00–2.13 (m, 4 H, 5-,7-H), 2.15–2.25 (m, 1 H, 6-H), 4.14 (q, ^3J = 7.1 Hz, 2 H, 15-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.07 (q, C-14), 14.22 (q, C-16), 22.68 (t, C-13), 27.72 (2 t, C-4,-8), 26.15 (t, C-10), 32.05 (t, C-11), 29.56 (2 t, C-5,-7), 45.98 (2 t, C-1,-3), 33.01 (t, C-12), 36.67 (d, C-2), 46.27 (d, C-6), 60.09 (t, C-15), 135.85 (2 s, C-3a,-8a), 176.48 (s, C-9) ppm. IR (film): $\tilde{\nu}$ = 2977 cm^{-1}, 2979, 2925, 2853 (s, C–H stretching aliphatic), 1736 (s, C=O), 1449, 1377, 1368, 1287, 1260, 1235 (m), 1117 (w), 1034 (w). UV (CH_3CN): λ_{max} (lg ε) = 196 nm (3.75), 274 (2.50), 288 (2.50), 338 (2.30), 366 (2.28), 374 (2.25). MS (EI = 70 eV): *m*/*z* (%) = 278 (21) [M$^+$], 232 (28) [M$^+$ – C_2H_5OH], 204 (52) [234 – C_2H_4], 161 (74) [204 – C_3H_7], 133 (100) [204 – C_5H_{11}], 119 (15) [133 – CH_2], 105 (23) [119 – CH_2]. HRMS ($C_{18}H_{30}O_2$): calcd. 278.22458; found 278.22451 ± 3 ppm.

2-Pentyl-1,2,3,4,5,6,7,8-Octahydroazulene-6-carboxylic Acid (29): From **19** (100 mg, 0.36 mmol), **29** (off-coloured liquid) was prepared by the same route as described for **20**. Yield: 70 mg (77%). B.p. 245 °C/5 Torr. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.81 (t, ^3J = 6.88 Hz, 3 H, 14-H), 1.12–1.25 (m, 8 H, side-chain protons), 1.56–1.71 (m, 4 H, 4-,8-H), 1.72–1.74 (m, 1 H, 2-H), 0.90/1.92 (m, 4 H, 1-,3-H), 1.96–2.16 (m, 4 H, 5-,7-H), 2.31–2.37 (m, 1 H, 6-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.08 (q, C-14), 22.69 (t, C-13), 27.57 (2 t, C-4,-8), 25.98 (t, C-12), 29.28 (2 t, C-5,-7), 32.96 (t, C-11), 45.95 (2 t, C-1,-3), 36.69 (t, C-10), 36.73 (d, C-2), 46.13 (d, C-6), 135.83 (2 s, C-3a,-8a), 182.46 (s, C-9) ppm. IR (film): $\tilde{\nu}$ = 2924 cm^{-1}, 2871, 2854 (s, C–H stretching aliphatic), 1704 (s, C=O), 1450, 1417, 1298, 1265, 1235 (m), 1192 (w). UV (CH_3CN): λ_{max} (lg ε) = 196 nm (2.65). MS (EI = 70 eV): *m*/*z* (%) = 250 (32) [M$^+$], 204 (11) [M$^+$ – HCO_2H], 179 (100) [M$^+$ – C_5H_{11}], 161 (36) [179 – H_2O], 133 (67) [179 – HCO_2H], 107 (11) [133.1 – C_2H_2].

X-ray Structure Determinations. Compounds 20, 21, 23, 27, 28: (Table 2 and Table 3) Data were measured with a Bruker Smart 1000 CCD diffractometer using Mo-K_α radiation at –140 °C. Data collection and reduction were performed with the Smart and SAINT software.[29] Structures were refined anisotropically on F^2 using the program SHELXL-97[30]. Hydrogen atoms were treated as follows: OH hydrogen atoms freely refined, ordered methyl as rigid groups, other H using a riding model starting from calculated positions. Special features: In compounds **20**, **21** and **23** the atom C4 of the five-membered ring was disordered over two positions to the extent of 5%, 40%, 13%, respectively, with concomitant disorder of the alkyl side chain in **21** and **22**. Appropriate systems of restraints were used to improve stability of refinement, but dimensions of disordered groups should nonetheless be interpreted with caution.

Compounds 22, 24, 26: The reflections were collected with a Bruker Smart APEX-diffractometer (Mo-K_α-radiation, graphite monochromator). Data collection and reduction were performed with the Bruker Smart and SAINT software. The structures were solved by Direct Methods (SHELXTL).[31] Structural parameters of the non-hydrogen atoms were refined anisotropically according to a full-matrix least-squares technique (F^2). The atom C4S in **22**, which is the "top" atom of the envelope shaped five-membered ring was disordered over two positions (85:15% multiplicity). The outer 4 methylene/methyl groups in **22** were located at two positions (85:15%). The oxygen atoms of the carboxyl group in **24** were disordered over three positions with a multiplicity of 50:25:25%. The

Table 2. Crystallographic data for **20**–**23**.

Compound	**20**	**21**	**22**	**23**
Empirical formula	$C_{14}H_{20}O_2$	$C_{15}H_{22}O_2$	$C_{16}H_{24}O_2$	$C_{14}H_{20}O_2$
Molecular mass [g/mol]	220.30	234.33	248.35	220.30
Crystal size [mm]	$0.34 \times 0.26 \times 0.13$	$0.28 \times 0.25 \times 0.12$	$0.38 \times 0.22 \times 0.01$	$0.50 \times 0.30 \times 0.12$
Crystal habit	colourless tablet	colourless tablet	colourless, irregular	colourless tablet
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Crystal system	monoclinic	triclinic	triclinic	triclinic
a [Å]	8.0728(12)	8.210(3)	8.7947(7)	8.3587(11)
b [Å]	7.1900(11)	9.413(3)	8.9311(7)	9.0378(11)
c [Å]	20.872(3)	9.554(3)	18.359(1)	9.4675(12)
α [°]	90	105.078(10)	86.694(2)	111.761(4)
β [°]	93.379(8)	92.916(10)	89.283(2)	107.952(4)
γ [°]	90	107.986(10)	79.071(2)	94.265(4)
V [Å^3]	1209.4(3)	671.2(4)	1413.5(2)	617.34(14)
$D_{calcd.}$ [Mg/m^3]	1.210	1.160	1.17	1.185
Z	4	2	4	2
$F(000)$	480	256	544	240
Temperature [K]	133	133	100	133
θ range [°]	1.95–28.28	2.23–28.28	2.22–26.37	2.48–30.03
μ [mm^{-1}]	0.079	0.075	0.075	0.077
$T_{min.}$, $T_{max.}$	no correction	no correction	no correction	no correction
Reflections collected	8410	6751	9124	7121
Reflections unique	2999	3255	5726	3553
Reflections observed	2054	2164	4975	2949
R_{int}	0.044	0.104	0.018	0.039
Variables	155	204	503	167
Restraints	9	151	0	35
R_1 [$I > 2\sigma(I)$]	0.044	0.056	0.048	0.046
wR_2	0.120	0.163	0.121	0.124
S (Gof)	0.98	1.03	1.04	1.03
$(\Delta\rho)_{max}$ [e·Å^{-3}]	0.39	0.28	0.49	0.42

Table 3. Crystallographic data for **24**–**28**.

Compound	**24**	**26**	**27**	**28**
Empirical formula	$C_{14}H_{18}O_2$	$C_{16}H_{22}O_2$	$C_{14}H_{24}O_2$	$C_{15}H_{26}O_2$
Molecular mass [g/mol]	218.28	246.34	224.33	238.36
Crystal size [mm]	$0.35 \times 0.35 \times 0.30$	$0.15 \times 0.14 \times 0.03$	$0.55 \times 0.45 \times 0.30$	$0.48 \times 0.15 \times 0.15$
Crystal habit	colourless, irregular	colourless, irregular	colourless prism	colourless prism
Space group	$C2/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
a [Å]	31.154(3)	16.201(4)	5.2566(7)	5.2171(8)
b [Å]	4.3706(4)	4.589(1)	10.7213(14)	22.362(3)
c [Å]	20.266(2)	19.159(5)	22.655(3)	23.893(3)
α [°]	90	90	90	90
β [°]	114.919(2)	97.502(7)	91.383(3)	90.278(4)
γ [°]	90	90	90	90
V [Å^3]	2502.6(4)	1412.2(6)	1276.4(3)	2787.5(7)
$D_{calcd.}$ [Mg/m^3]	1.16	1.16	1.167	1.136
Z	8	4	4	8
$F(000)$	944	536	496	1056
Temperature [K]	295	100	133	133
θ range [°]	2.22–28.34	2.14–17.22	1.80–30.51	1.25–30.52
μ [mm^{-1}]	0.076	0.074	0.076	0.073
$T_{min.}$, $T_{max.}$	no correction	0.989, 0.998	no correction	no correction
Reflections collected	8609	2997	10392	22340
Reflections unique	3098	849	3900	8255
Reflections observed	2225	571	3435	5465
R_{int}	0.035	0.061	0.031	0.090
Variables	219	166	150	317
Restraints	0	0	0	0
R_1 [$I > 2\sigma(I)$]	0.060	0.064	0.038	0.052
wR_2	0.182	0.174	0.012	0.136
S (Gof)	1.06	1.03	1.04	0.99
$(\Delta\rho)_{max}$ [e·Å^{-3}]	0.37	0.24	0.37	0.41

terminal methyl group was likewise disordered at two positions with 70:30% occupancy. In **26** the atom C2 being the top atom of the five membered ring was disordered over two positions (50%:50%) and was refined only isotropically. All hydrogen atom positions of **26** were calculated. In **22** and **24** hydrogen atoms at disordered fragments were calculated, the hydrogen atoms at the acyclic methylene groups were refined with a "riding" thermal parameter, all other H atoms were refined isotropically. The C atoms with 15% multiplicity were only refined isotropically. Refinement was carried out with SHELXTL. CCDC-281640 (for **20**), -281641 (for **21**), -274776 (for **22**), -281642 (for **23**), -274777 (for **24**), -274778 (for **26**), -281643 (for **27**), and -281644 (for **28**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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