Annelated Dehydroannulenes Fused with Azulene: Synthesis and Properties of Tetradehydro[14]- and -[16]annuleno[*a*]azulenes

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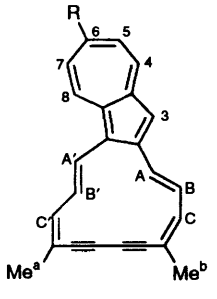
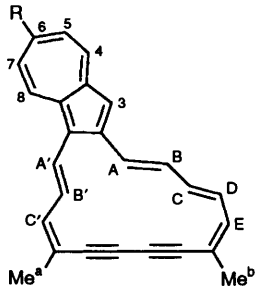
10,11,12,13-Tetradehydro-9,14-dimethyl[14]-, 10,11,12,13-tetradehydro-9,14-dimethyl[16]annuleno[*a*]azulene and their 3-isopropyl derivatives have been synthesized. The effect of annelation of a 10π-azulene ring onto the monocyclic $[4n + 2]\pi$- and $[4n]\pi$-electron systems is discussed on the basis of ^{1}H NMR and electronic spectra.

Annulenes and dehydroannulenes annelated with benzene or heterocycles have now been thoroughly investigated.[1] Annelated annulenes fused with another annulene (annulenoannulenes) have also been studied.[2] In contrast, annelated monocyclic annulenes fused with some nonbenzenoid aromatics other than annulene have not yet been reported.[1]



1 R = Pr^i
2 R = H



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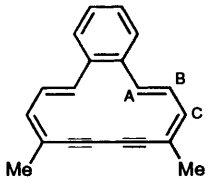
4 R = H



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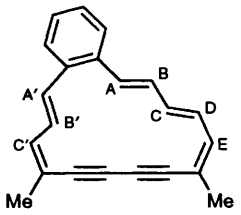

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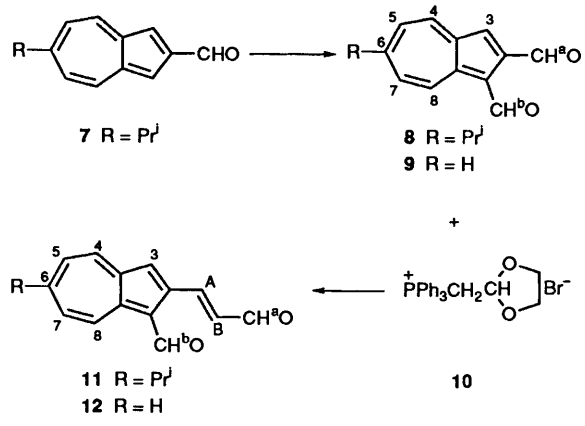
We now describe the synthesis of the title compounds, 10,11,12,13-tetradehydro-3-isopropyl-9,14-dimethyl[14]-**1**,† 10,11,12,13-tetradehydro-3-isopropyl-9,14-dimethyl[16]-annuleno[*a*]azulene **3**, and their respective 3-unsubstituted derivatives **2** and **4**, in which a conjugated 14- or 16-membered ring is fused to an azulene ring. The purpose of this investigation was to study the effect produced by annelation of a 10π-azulene ring onto macrocyclic $[4n + 2]\pi$- and $[4n]\pi$-systems by comparison with the closest available models **5** and **6** which were prepared by Sondheimer and co-workers.[3] It should be pointed out that the tetradehydro-[14]- **1**, **2** and -[16]-annuleno[*a*]azulenes **3**, **4** are the first examples of diatropic 14π- and paratropic 16π-electron neutral annulenes, respectively, fused with a nonbenzenoid compound, azulene.[4,5]

† The marked numerals 3–8 used in the structural formulae of compounds **1**–**4** and **23**, and as their ^{1}H NMR locants, are different from the locant numbering for their systematic nomenclature.

Results and Discussion

Synthesis.—We considered that the title compounds would be synthesized by application of the method used in the synthesis of the methano-bridged tetradehydroannulenes,[6] *i.e.*, the Wittig condensation of cyclohepta-1,3,5-triene-1,6-dicarbaldehyde or its vinylogues with (3-methylpent-2-en-4-ynyl)triphenylphosphonium bromide **13**,[7] followed by oxidative cyclization of the resulting acyclic diacetylenes. In addition, we expected that the 3-isopropyl derivatives **1** and **3** would be more stable than the 3-unsubstituted homologues **2** and **4**, due to the electron-donating property of an isopropyl group on the electron-deficient seven-membered ring of azulene.[8] Thus, we planned to use 6-isopropylazulene-1,2-dicarbaldehyde **8** and its monovinylogue **11** as the starting materials for the synthesis.

Compounds **8** and **11** were prepared as illustrated in Scheme 1. Formylation of 6-isopropylazulene-2-carbaldehyde **7**[9] by Vilsmeier procedure afforded the dialdehyde **8** (63% yield). The dialdehyde **8** gave the homologous vinylogue **11** in 67% yield by Wittig condensation with 1.3 mol equiv. of [(1,3-dioxolan-2-yl)methyl]triphenylphosphonium bromide **10**[10] and lithium



7 R = Pr^i
8 R = Pr^i
9 R = H
11 R = Pr^i
12 R = H
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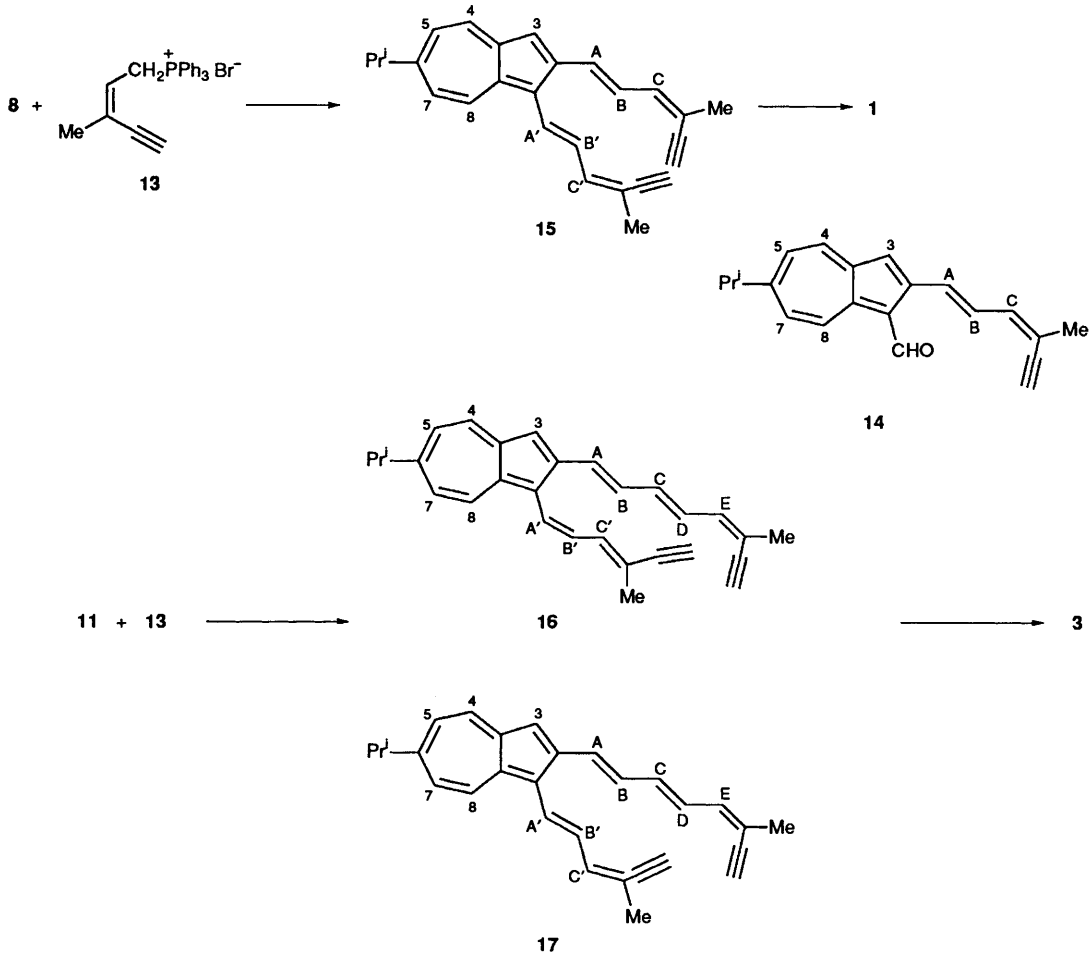
Scheme 1



Scheme 2

methoxide in *N,N*-dimethylformamide (DMF) at 65 °C, followed by hydrolysis of the resulting acetal of compound **11** with dil. hydrochloric acid in ethanol at room temperature.[11] The sole formation of compound **11** suggests that the formyl group at the 2-position of the azulene ring is more reactive than that at the 1-position. The 6-unsubstituted vinylogous dialdehyde **12** was similarly prepared by homologation of the known azulene-1,2-dicarbaldehyde **9**[12,*] in 59% yield.

The synthesis of compounds **1** and **3** is shown in Scheme 2. First, the Wittig reaction of the dialdehyde **8** with 5 mol equiv. of the salt **13** was carried out with butyllithium as a base in THF; however, the only product identified was a single condensation product, the aldehyde **14**, again indicating the higher reactivity of the formyl group at the 2-position than that at the 1-position. When the Wittig reaction of the dialdehyde **8** was carried out using 10 mol equiv. of the salt **13** with butyllithium in THF at −55 to −20 °C, the desired dicondensation product was obtained. The product was a stereoisomeric mixture of the acyclic diacetylenes, from which the *E,E*-isomer **15**† was isolated in 10% yield by chromatography on alumina. Oxidative coupling of the acyclic mixture containing compound **15** was carried out with anhydrous copper(II) acetate in a mixture of pyridine, diethyl ether and methanol under relatively dilute conditions,[3b] and gave rise to the desired monomeric cyclic compound, the tetradehydro-[14]annuleno[*a*]azulene **1**, in 20% yield.

Similarly, the Wittig reaction between the dialdehyde **11** and the salt **13** afforded a stereoisomeric mixture of the acyclic diacetylenes, from which the *E,Z*-isomer **16** (12% yield) and the *E,E*-isomer **17** (7%) were obtained by chromatography on alumina. Reaction of the mixture with anhydrous copper(II) acetate as before afforded the desired tetradehydro[16]-annuleno[*a*]azulene **3** in 16% yield.

The 3-unsubstituted [14]- **2** and [16]-annuleno[*a*]azulene **4** were prepared similarly to compounds **1** and **3**, as shown in Scheme 3. Wittig reaction between the dialdehyde **9** and the salt **13** afforded the *E,Z*-isomer **18** (12%) and the *E,E*-isomer **19** (4%). The mixture of compounds **18** and **19** was subjected to the coupling reaction to afford the [14]annuleno[*a*]azulene **2** (16% yield) along with recovered diacetylene **18**. The Wittig reaction between compounds **12** and **13** afforded a mixture of the acyclic diacetylenes from which the *E,Z*-isomer **20** was isolated. Coupling of the stereoisomeric mixture containing compound **20** afforded the [16]annuleno[*a*]azulene **4** in 17% yield.

Both of the tetradehydro-[14]- **1**, **2** and the -[16]-annuleno-[*a*]azulenes **3** and **4** thus obtained formed coloured crystals and were thermally more stable than the corresponding acyclic diacetylenes, contrary to our expectation.

^{1}H *NMR Spectra.*—Chemical-shift assignments of the olefinic protons in compounds **1**–**4** and **14**–**20** were made as

* In this work, azulene-2-carbaldehyde was prepared by the reaction of 2*H*-cyclohepta[*b*]furan-2-one with 3,3-dimethoxy-2-pyrrolidinopropene followed by hydrolysis of the resulting 2-(dimethoxymethyl)-azulene [ref. 12(*b*)].

† The *E* and *Z* notations indicate the geometry of the double bonds adjacent to the azulene ring in compounds **15**–**20**, *i.e.*, $CH^A{=}CH^B$ and $CH^{A'}{=}CH^{B'}$.

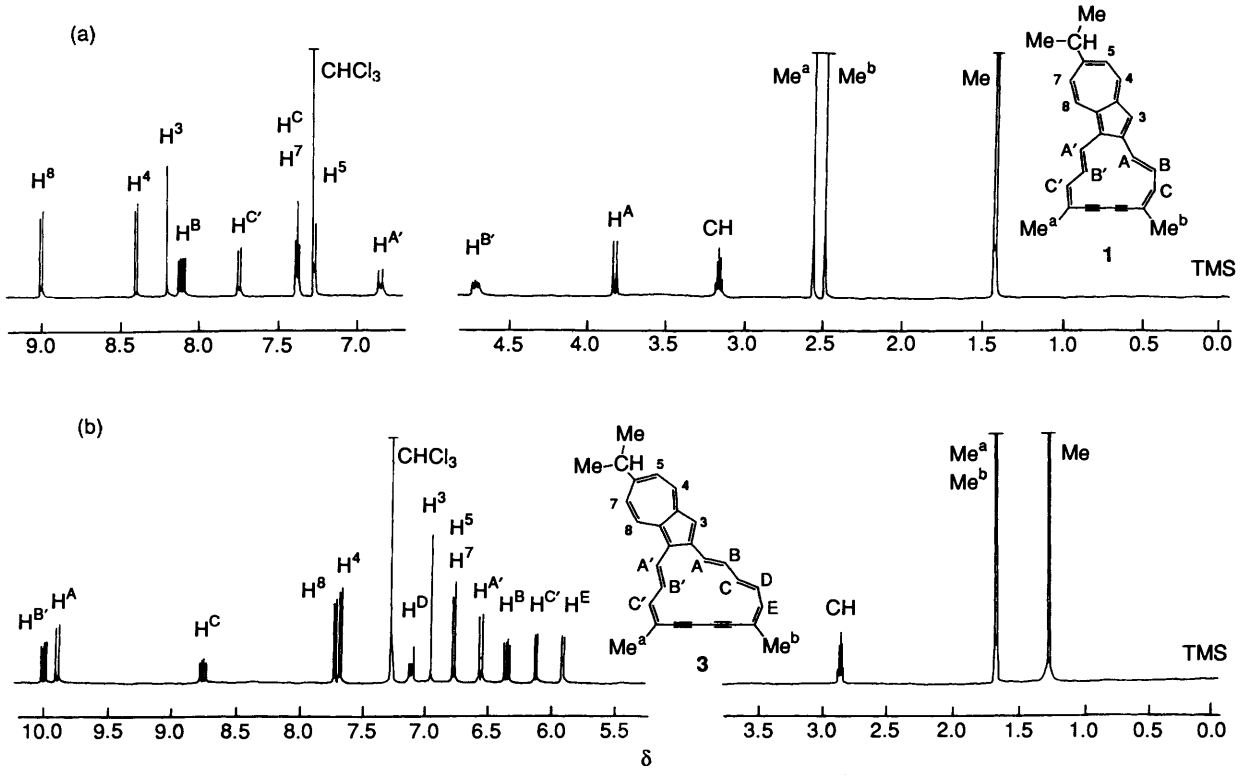
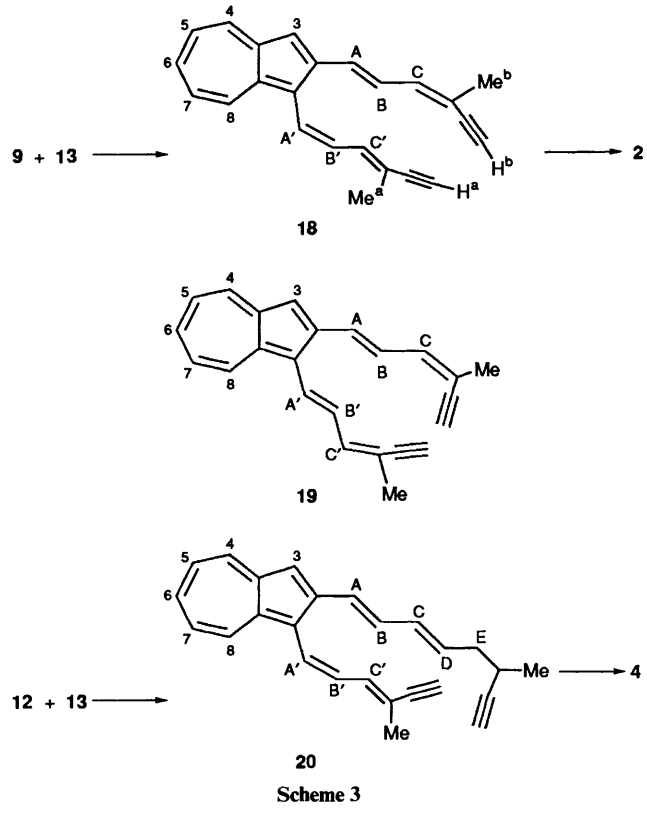


Fig. 1 600 MHz ^{1}H NMR spectra of compounds **1** (a) and **3** (b) in $CDCl_3$ at 25 °C (internal standard, Me_4Si)



Scheme 3

follows. Broad doublet signals were assigned to the protons adjacent to a methyl group, because the broadening was due to allylic coupling to the methyl protons as revealed by decoupling experiments, while sharp doublets were assigned to the protons adjacent to the azulene ring. Then the proton sequence along the polyene moiety was determined by successive decoupling experiments. Determination of the positions of the polyene moiety for the azulene ring was made on the basis of NOE experiments between the 3-H (or 8-H) proton and the olefinic proton adjacent to the azulene ring. Geometries are assigned using the magnitudes of the coupling constants; 14–16 Hz for an *E* double bond, 9–11 Hz for a *Z* double bond, 10–12 Hz for an s-*trans* single bond between two double bonds and 5–7 Hz for an s-*cis* single bond.[13]

Irradiation of the methyl signals in compounds **1**–**4** caused an intensity enhancement (NOE) of the doublet signals due to the respective adjacent olefinic protons, *i.e.*, H^C and $H^{C'}$ in compounds **1** and **2**, and $H^{C'}$ and H^E in compounds **3** and **4**, further confirming that these protons are located outside the macrocyclic ring.

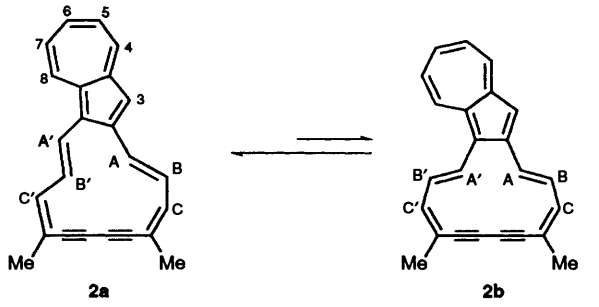
The 600 MHz ^{1}H NMR spectra of the tetradehydro-[14]- **1** and -[16]-annuleno[*a*]azulene **3**, taken in $CDCl_3$ at 25 °C, are presented in Figs. 1(*a*) and (*b*), respectively, together with the signal assignments. It is evident from Fig. 1(*a*) that the signals of the inner olefinic (H^A and $H^{B'}$) protons of compound **1** appear at high field, while those of the outer ($H^{A'}$, H^B, H^C and $H^{C'}$) protons as well as the signals of the azulene-ring protons (see later) are at low field, indicating that compound **1** is diatropic, as expected either for the 14π-electron system in the annulene part or for the peripheral 22π-system in the whole molecule. In contrast, as is seen from Fig. 1(*b*), the inner olefinic (H^A, $H^{B'}$ and H^C) protons of compound **3** appear at low field, while those of the outer ($H^{A'}$, H^B, $H^{C'}$, H^D and H^E) protons as well as the signals of the azulene-ring protons appear at high field, indicating that compound **3** is paratropic as expected for the 16π-annulene or as the 24π-peripheral system.

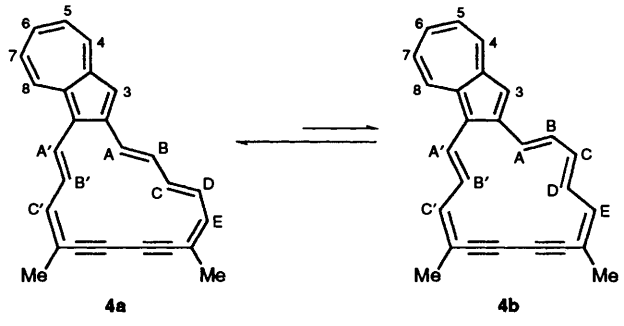
The ^{1}H NMR data for the annulene part of compounds **1**–**4** are listed in Table 1 together with those of the closely related compounds **5** and **6**. These spectral features are consistent with the structures given as **1**–**4**, respectively. From Table 1, the 3-unsubstituted annulenes **2** and **4** are also diatropic and paratropic, respectively, because they show almost the same chemical-shift data for the corresponding protons as those of compounds **1** and **3**, respectively.

Table 1 ^{1}H NMR data [δ_H(*J*/Hz)] for the annulene part of compounds **1**–**6** (in $CDCl_3$) at 600 MHz, determined at 25 °C

Compound	H^A	$H^{A'}$	H^B	$H^{B'}$	H^C	$H^{C'}$	H^D	H^E	Me[a]	Me[b]
1	3.81d	6.83d	8.10dd	4.70dd	7.36d	7.74d			2.55s	2.48s
	(16.2)	(16.2)	(16.2, 8.1)	(16.2, 9.4)	(8.1)	(9.4)				
2	3.89d	6.92d	8.10dd	4.66dd	7.35d	7.72d			2.47s	2.55s
	(16.1)	(16.1)	(16.1, 8.1)	(16.1, 9.5)	(8.1)	(9.5)				
5[a]	4.99		7.44		7.08				2.36	
$\Delta\delta$(**2** − **5**)					0.27				0.11–0.19	
3	9.89d	6.55d	6.35dd	10.00dd	8.75dd	6.11d	7.12dd	5.90d	1.66s	1.65s
	(15.5)	(15.5)	(15.5, 10.0)	(15.5, 10.5)	(15.0, 10.0)	(10.5)	(15.0, 7.5)	(7.5)		
4	9.85d	6.57d	6.38dd	9.97dd	8.77dd	6.12d	7.07dd	5.91d	1.67s	1.65s
	(15.5)	(15.9)	(15.5, 9.8)	(15.9, 11.0)	(15.5, 9.8)	(11.0)	(15.5, 7.2)	(7.2)		
6[a]	8.90	6.11	6.20	9.45	9.42	6.07	5.73	5.94	1.70	
$\Delta\delta$(**4** − **6**)						0.05		−0.03	−0.03 to −0.05	

[a] Taken from ref. 3.

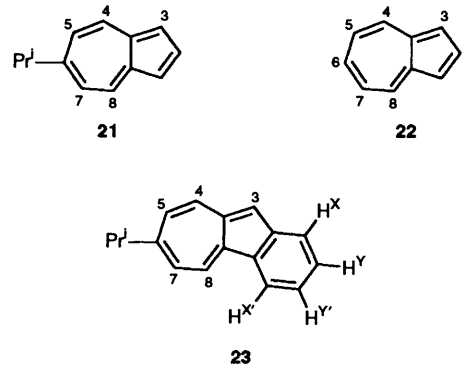




It was pointed out by Sondheimer and co-workers[3,14] that the best ring-current probe for the annulene part of annelated annulenes such as compounds **5** and **6** of the tetradehydrodimethylannulene type is provided by the chemical-shift data of the outer H^C in compound **5**, and $H^{C'}$ and H^E in compound **6**, and the methyl protons, since these protons are furthest from the point of fusion and must be conformationally fixed. In fact, as described below, although compounds **2** and **4** existed in the conformers **2a** and **4a**, respectively, at ambient temperature, it was found that the outer proton H^C in compound **2a**, and $H^{C'}$ and H^E in compound **4a**, remain outside the annulene ring between 25 °C and −100 °C, and their chemical shifts vary little in comparison with the other protons over this temperature range (Tables 1 and 3).

In order to examine the difference in the effects of annelation on the tetradehydro-[14]- and [16]-annulene system, the chemical-shift differences ($\Delta\delta$) between compounds **2** and **5**, and between compounds **4** and **6** are also given in Table 1 as an approximate measure of the magnitude of ring current. The $\Delta\delta$-values show that the diatropicity of the 14-membered part decreases on going from compound **2** to compound **5**, but the paratropicity of the 16-membered part varies little between compounds **4** and **6**. This observation is in accord with the previous result that annelation of a benzenoid compound or an annulene ring results in larger suppression of the diatropicity of [4*n* + 2]annulenes than of the paratropicity of [4*n*]annulenes.[2,3,15]

It is also of interest to examine the effect on the azulene ring chemical-shifts caused by annelation of the macrocyclic π-systems. The ^{1}H NMR parameters of the azulene part of compounds **1**–**4** obtained at ambient temperature are listed in Table 2 together with those of the model compounds 6-isopropylazulene **21**,[9] azulene **22**[16] and 7-isopropylbenz[*a*]azulene **23** which has very recently become available.[17] The chemical-shift differences of the corresponding respective protons among compounds **1**, **3**, **21** and **23**, and among the unsubstituted parent compounds **2**, **4** and **22** are also given. The $\Delta\delta$-values between compounds **21** and **1**, and between compounds **22** and **2**, show that all the protons of compounds **1** and **2** fused by a 14-membered ring resonate at lower field than do the corresponding protons of compounds **21** and **22**, revealing that these protons feel the deshielding effect of a [4*n* + 2]π- 14π-electron system. On the other hand, all the protons of compounds **3** and **4** fused by a 16-membered ring resonate at higher field than do the corresponding protons of compounds **21** and **22**, indicating that these protons feel the shielding effect of the fused [4*n*]π- 16π-electron system.



In addition, it is found that the deshielding effect of the 14-membered ring is greater for 3-H and 8-H protons than for 5-H and 6-H protons in compounds **1** and **2**, reflecting the effect of distance from the point of fusion. However, this situation does not hold for the shielding effect in compounds **3** and **4**.

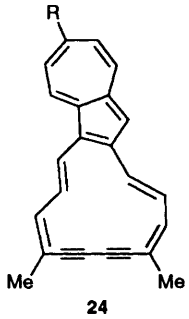
Also, the $\Delta\delta$-values between 7-isopropylbenz[*a*]azulene **23** and compound **1** show that all the azulene ring protons of compound **1** resonate at lower field than do the corresponding protons of compound **23**, albeit that the benzene ring in compound **23** should have a larger deshielding effect than the 14-membered ring in compound **1**. Furthermore, comparison

Table 2 ^{1}H NMR data [$\delta_H(J/Hz)$] of the azulene part of compounds **1–4** and **21–23** (in $CDCl_3$) at 600 MHz, determined at 25 °C

Compound	3-H	4-H	5-H	6-H	7-H	8-H	C*H*Me$_2$	CH*Me*$_2$
1	8.19s	8.39d	7.26d		7.38d	9.00d	3.15sept	1.41d
		(10.5)	(10.5)		(9.8)	(9.8)	(6.9)	(6.9)
3	6.94s	7.68d	6.76d		6.76d	7.72d	2.84sept	1.26d
		(10.5)	(10.5)		(10.5)	(10.5)	(7.0)	(7.0)
21[a]	7.32d	8.28d	7.10d		7.10d	8.28d	3.05sept	1.34d
	(3.7)	(10.4)	(10.4)		(10.4)	(10.4)	(6.9)	(6.9)
23[b]	7.20s	7.87d	6.74d		6.89dd	8.18d	2.86sept	1.25d
		(11.5)	(11.5, 1.5)		(8.0, 1.5)	(8.5)	(7.0)	(7.0)
Δδ(**21** − **1**)	−0.87	−0.11	−0.16		−0.28	−0.72	−0.10	−0.07
Δδ(**21** − **3**)	0.38	0.60	0.34		0.34	0.56	0.21	0.08
Δδ(**23** − **1**)	−0.99	−0.52	−0.52		−0.49	−0.82	−0.29	−0.16
2	8.24s	8.42d	7.29t	7.65dd	7.43t	9.03d		
		(10.0)	(9.6)	(10.1, 9.3)	(9.8)	(9.3)		
4	7.02s	7.73d	6.80t	7.16t	6.81t	7.76d		
		(9.8)	(9.8)	(9.8)	(9.8)	(9.8)		
22[c]	7.30d	8.23d	7.05dd	7.45dd	7.05dd	8.23d		
	(4.0)	(9.5)	(10.0, 10.0)	(10.0, 9.5)	(10.0, 9.5)	(9.5)		
Δδ(**22** − **2**)	−0.94	−0.19	−0.24	−0.20	−0.38	−0.80		
Δδ(**22** − **4**)	0.28	0.50	0.25	0.29	0.24	0.47		

[a] Taken from ref. 9. [b] Taken from ref. 17. [c] Taken from ref. 16.

of the coupling constants in compounds **23** and **1** (and in compounds **2–4**) suggests that the azulene ring in compound **1** (and in compounds **2–4**) is a more delocalized system than that of tricycle **23**, since the coupling constants of the former show less bond alternation than do those of the latter. These results might suggest that compound **1**, as well as compounds **2–4**, cannot be regarded as being composed of an azulene-annulene type π-system, but rather as a peripherally conjugated system, although we had described the opposite viewpoint in a preliminary report.[5]



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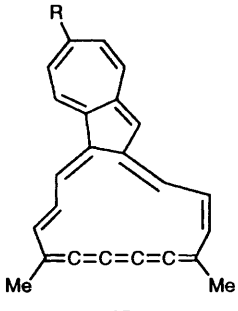

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From this study it was found that the fusion of an azulene ring (having smaller resonance energy) suppresses the diatropicity of the [4*n* + 2]π- 14π-electron system to a smaller extent than does a benzene ring (having larger resonance energy), as has been observed in monocyclic annelated annulenes fused with benzenoid or annulene systems.[2,3] However, this may be due to the fact that, unlike compound **5**, the tetradehydro[14]annuleno[*a*]azulenes **1** and **2** possess two more Kekulé structures, **24** and **25**.

Careful inspection of the ^{1}H NMR spectra of these annuleno[*a*]azulenes at 25 °C, however, revealed that the signals assigned to $H^{A'}$ and $H^{B'}$ in compounds **1** and **2** and those of H^C and H^D in compounds **3** and **4** were somewhat broadened. This suggested that these compounds existed as a rapidly interconverting mixture of conformers. Therefore, ^{1}H NMR spectra of 3-unsubstituted compounds **2** and **4** were examined at low temperatures by using CD_2Cl_2 as the solvent.

The spectra of compound **2** at different temperatures are illustrated in Fig. 2. On lowering the temperature, the $H^{A'}$ and $H^{B'}$ signals broadened (at −20 °C) and disappeared under the baseline at −40 °C, while the other signals also broadened on further cooling. Splitting and resharpening of the signals was observed below ~ −70 °C and the spectrum at −95 °C, the lowest temperature examined, indicated that this compound existed as a mixture of two conformers in the ratio 78:22, although the interconversion was not completely frozen on the NMR timescale. From careful analysis of the temperature dependence of the spectra, structures **2a** and **2b** were assigned to the major and minor isomers, respectively. The interconversion between the two takes place by rotation of the $CH^{A'}=CH^{B'}$ moiety about the adjacent single bonds and the free energy of activation for the minor-to-major conversion was estimated to be ~ 8.8 kcal mol^{-1} * at −80 °C judging from the coalescence of the 8-H signal.[18]

The chemical shifts of the two isomers of compound **2** were assigned as given in Table 3. The protons located inside the annulene ring resonate at high field, δ 1.9–3.8, while the outer olefinic protons resonate at low field, δ 7.2–9.2, indicating

Table 3 ^{1}H NMR chemical shifts of compounds **2** and **4** at low temperature (600 MHz, δ values)[a]

Compound	**2**		**4**	
isomer	**2a**	**2b**	**4a**	**4b**
proportion (%)	78	22	85	15
H^A	2.94	3.72[b]	9.33	11.41
H^B	8.31	7.95	6.32	6.15
H^C	7.41	7.41	9.82	5.44
H^D			5.64	10.93
H^E			5.86	5.79
$H^{A'}$	8.73	3.77[b]	6.52	6.15
$H^{B'}$	1.94	~7.7[c]	9.66	11.30
$H^{C'}$	8.05	~7.4[c]	6.11	5.79
3-H	8.36	8.00	6.91	6.83
4-H	8.44	8.44	7.73	7.46
5-H	7.34	7.34	6.83	6.66
6-H	7.72	7.72	7.21	7.02
7-H	7.48	7.48	6.83	6.66
8-H	8.91	9.23	7.73	7.46
Me	2.45,	2.50,	1.62,	1.47,
	2.59	2.50	1.62	1.47

[a] Obtained in CD_2CCl_2 at −95 °C for compound **2** and at −100 °C for compound **4**. Coupling constants are not shown. [b,c] Mutually interchangeable.

* 1 cal = 4.184 J.

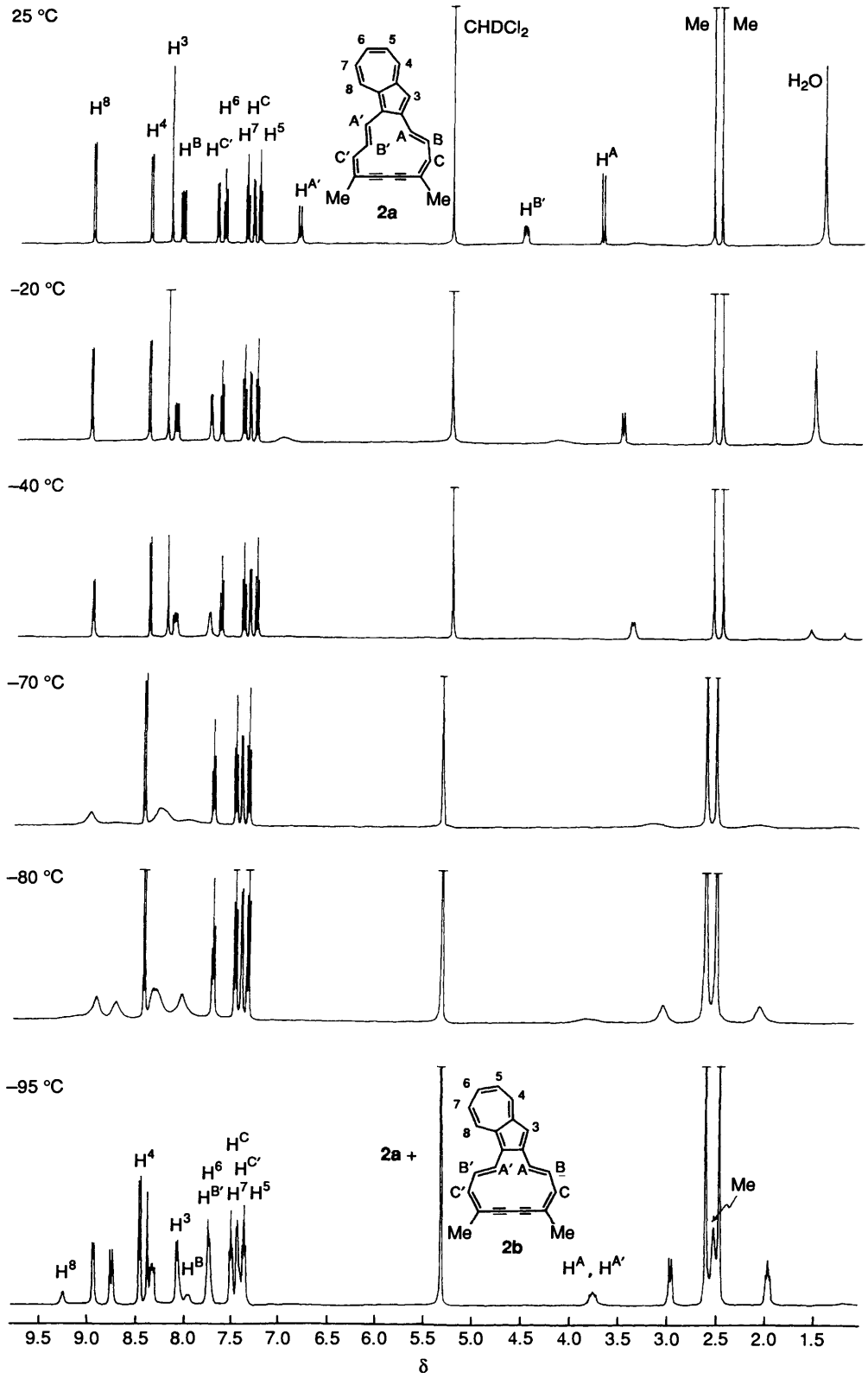

Fig. 2 600 MHz ^{1}H NMR spectra of compound **2** in CD_2Cl_2 at different temperatures (internal standard, Me_4Si). Assignment of the signals is given only for conformer **2b** at −95 °C.

the diatropicity of this compound as described above. The methyl signals of the two isomers have almost the same chemical shifts, and this suggests that the magnitudes of diatropicity are quite similar between these isomers.

The [16]annuleno[*a*]azulene **4** also showed temperature-dependent ^{1}H NMR spectra, and similar behaviour to that of compound **2** on lowering the temperature, as illustrated in Fig. 3. The H^C and H^D signals broadened at −10 °C and disappeared under the baseline at −40 °C, while the other signals also broadened at −70 °C. Splitting and resharpening of the signals were observed at −80 °C. At −100 °C, two isomers are present in the ratio 85:15. The interconversion is

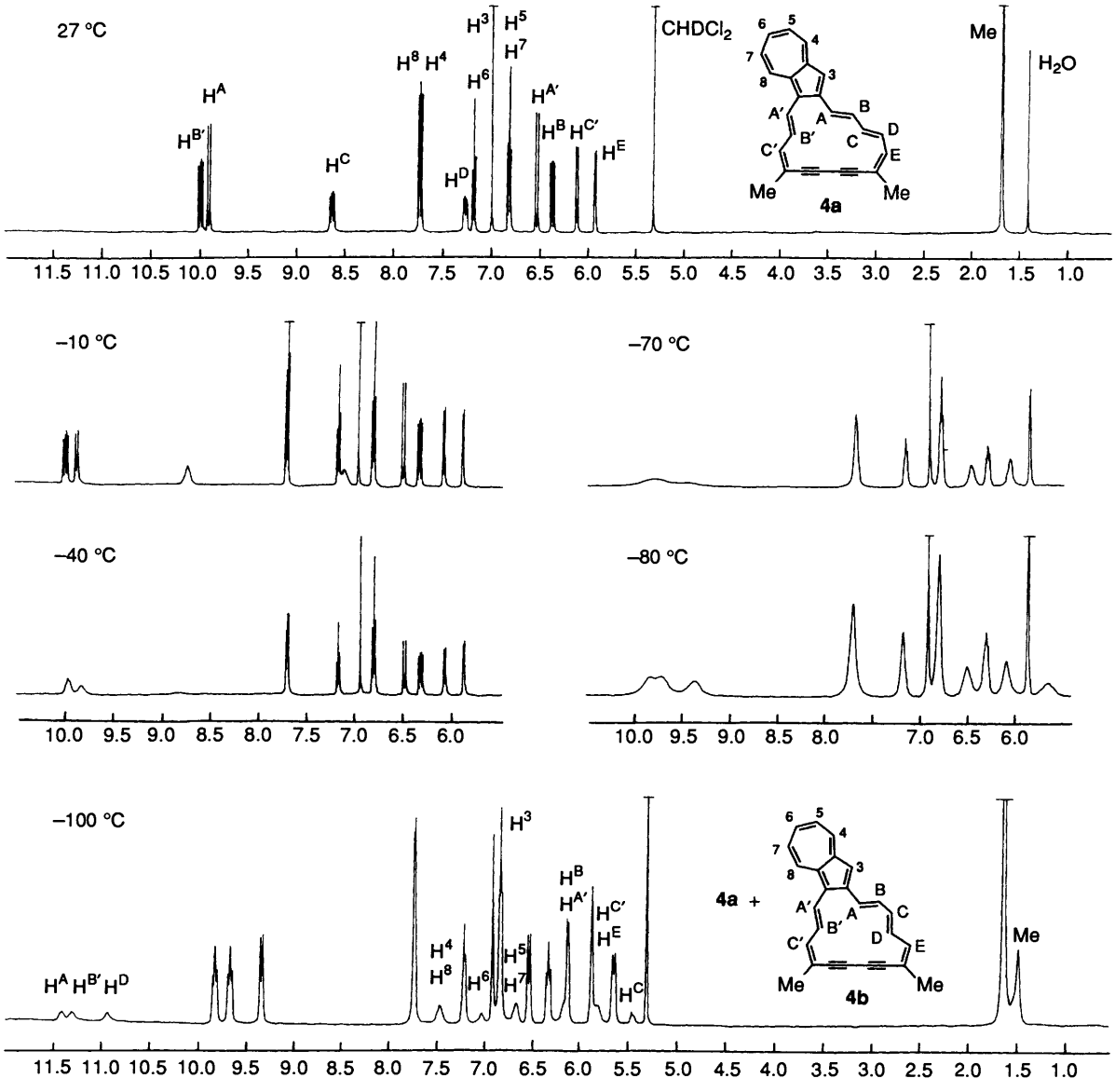

Fig. 3 600 MHz ^{1}H NMR spectra of compound **4** in CD_2Cl_2 at different temperatures (internal standard, Me_4Si). Assignment of the signals is given only for conformer **4b** at −100 °C.

not completely frozen at this temperature, and the signals are still broad, and especially those due to the minor isomer are structureless. The free energy of activation for the minor-to-major conversion is estimated to be ~8.5 kcal mol^{-1} at −88 °C.[18] Structures **4a** and **4b** are assigned to the major and minor isomers, respectively, and the chemical-shift assignments are shown in Table 3, where those for the minor isomer may be somewhat ambiguous. The protons of the azulene moiety of both isomers appear at δ 6.6–7.7 and the outer olefinic protons of the annulene moiety resonate at high field, δ 5.4–6.6, while the inner olefinic protons resonate at low field, below δ 9.3. These features clearly suggest the paratropicity of this compound as described above. The inner protons of the minor isomer **4b** resonate at lower field than do those of the major isomer **4a**, while the methyl signals of isomer **4b** are more shielded than are those of isomer **4a**. This seems to suggest that isomer **4b** is more paratropic than is isomer **4a**.

Electronic Spectra.—The electronic absorption spectra, measured in THF, of the tetradehydro-3-isopropyl-[14]- **1** and -[16]-annuleno[*a*]azulene **3** are illustrated in Fig. 4, together with that of 6-isopropylazulene **21**.

It is noted that the spectrum of the [16]annuleno[*a*]azulene **3** shows a rather broad absorption curve as compared with those of the [14]annuleno[*a*]azulene **1** and 6-isopropylazulene **21**, demonstrating that compound **3** is a [4*n*]π-electron system, as recognized in the spectra of [4*n*]π-annulenes and dehydroannulenes.[1] Also, the end absorption of compound **3** tails to a longer wavelength than that of compound **1**, an effect recently pointed out for the spectra of [4*n*]annulenes.[19]

Experimental

M.p.s were determined on a hot-stage apparatus and are uncorrected. IR spectra were taken with a Hitachi 260-50 spectrophotometer as KBr discs and were calibrated against polystyrene; only significant maxima are described. Electronic spectra were measured in THF solution and run with a Hitachi 220A spectrophotometer. Mass spectra were recorded with a JEOL JMS-D 300 spectrometer operating at 75 eV using a direct-inlet system. ^{1}H NMR spectra at ambient temperature were recorded in $CDCl_3$ with a JEOL FX-90Q (90 MHz), a JEOL GX-270 (270 MHz) or a Bruker AM-600 (600 MHz) spectrometer, $SiMe_4$ (TMS) being used as internal standard.

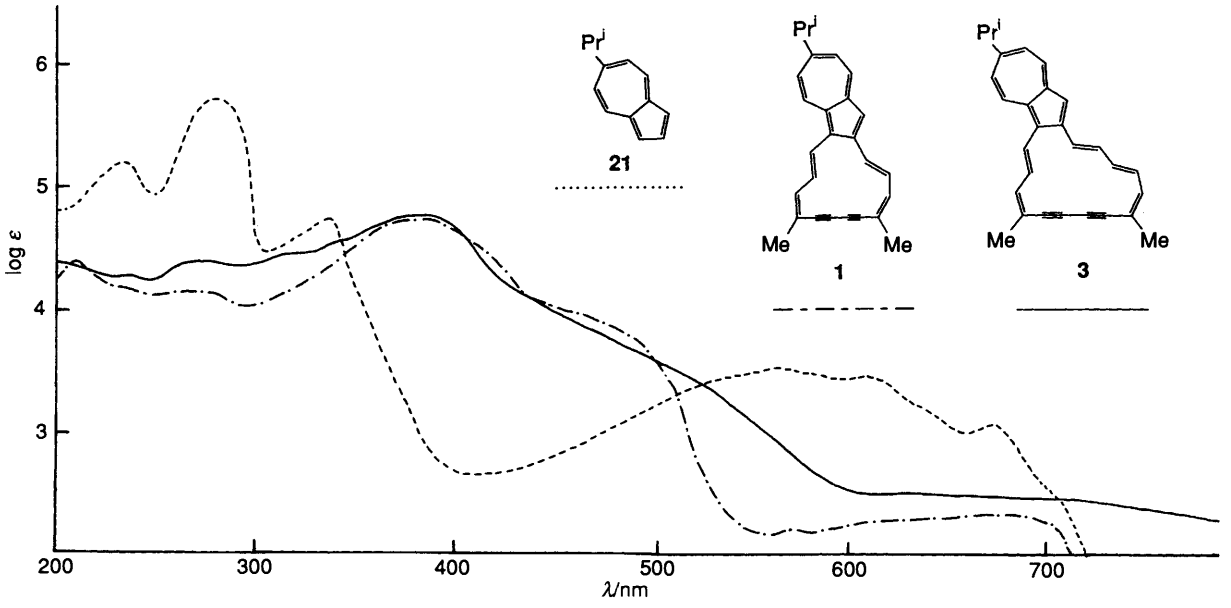

Fig. 4 Electronic absorption spectra of the tetradehydro-3-isopropyl-[14]annuleno[*a*]azulene **1** (— · — · —), -[16]annuleno[*a*]azulene **3** (———) and 6-isopropylazulene **21** (- - - - - -) in THF

J Values are given in Hz. Assignments were clarified by the use of decoupling and NOE experiments where necessary. NMR locants follow the non-systematic numbering schemes shown in the structural formulae. Variable-temperature ^{1}H NMR measurements were made on the AM-600. Merck alumina (activity II–III) or silica gel (Daiso Gel 1001 W or Daiso Gel 1002 W) was used for column chromatography, and preparative TLC (PLC) was carried out on 20 × 20 cm alumina plates (Merck, 0.5 or 2 mm thick). Progress of all reactions was followed by TLC using Merck precoated silica gel.

THF was distilled from sodium benzophenone ketyl under nitrogen before use. Organic extracts with benzene were washed with saturated aq. sodium chloride (except where stated otherwise) and dried over anhydrous sodium sulfate prior to removal of the solvent. Solvents were evaporated under water-pump pressure. Ether refers to diethyl ether.

6-*Isopropylazulene*-1,2-*dicarbaldehyde* **8**.—To a stirred solution of the aldehyde **7**[9] (2.54 g, 12.8 mmol) in DMF (25 cm^3) was added, during 1 h, a solution of phosphorus trichloride oxide (3.94 g, 25.6 mmol) in DMF (25 cm^3) at −2 °C. After being stirred for 8 h at −6 °C, the reaction mixture was poured onto water. To the solution was added aq. potassium hydroxide until it turned alkaline to litmus (pH 10). Then the mixture was extracted with benzene. The combined extracts were washed and dried. The residue obtained after removal of solvent was chromatographed on silica gel (3.8 × 11.5 cm). The fractions eluted with hexane–ether (3:2) afforded the *dialdehyde* **8** (1.83 g, 63%) as dark violet needles, m.p. 97–98 °C (from hexane–benzene); *m*/*z* 226 (M^+, 100%) ($C_{15}H_{14}O_2$ requires M, 226.2); λ_{max}/nm 237 (ε/dm^3 mol^{-1} cm^{-1} 4600), 291 (7900), 303sh (9400), 316sh (12 200), 326 (13 400), 360 (3400), 385sh (1700), 546sh (240), 583 (285) and 637sh (150); ν_{max}/cm^{-1} 2840 (CHO), 1680 and 1645 (C=O); δ_H(90 MHz) 10.89 (1 H, s, CH^{b}O), 10.72 (1 H, s, CH^{a}O), 9.72 (1 H, d, *J* 11, 8-H), 8.60 (1 H, d, *J* 10, 4-H), 7.73 (1 H, s, 3-H), 7.66 (1 H, d, *J* 11, 7-H), 7.56 (1 H, d, *J* 10, 5-H), 3.21 (1 H, sept, *J* 7, C*H*Me$_2$) and 1.41 (6 H, d, *J* 7, Me) (Found: C, 79.8; H, 6.3. $C_{15}H_{14}O_2$ requires C, 79.6; H, 6.2%).

2-(2-*Formylvinyl*)-6-*isopropylazulene*-1-*carbaldehyde* **11**.—To a stirred solution of the dialdehyde **8** (416 mg, 1.84 mmol) and the salt **10**[10] (1.02 g, 2.39 mmol) in DMF (120 cm^3) was added dropwise methanolic lithium methoxide, prepared from lithium (17 mg, 2.39 mmol) and methanol (10 cm^3), during 50 min at 66 °C under argon. After being stirred for 5.5 h at 66 °C, the mixture was poured onto water and extracted with benzene. The combined extracts were washed and dried. The residue obtained after removal of solvent was chromatographed on alumina (3.2 × 4.5 cm). The fractions eluted with 5% ether in hexane afforded the acetal (286 mg, 52%) of the dialdehyde **11**.

To a stirred solution of the acetal (286 mg, 0.96 mmol) in ethanol (100 cm^3) was added 8% HCl (130 cm^3) in one portion at room temperature. After being stirred for 15 min at room temperature, the mixture was poured onto water and extracted with benzene. The combined extracts were washed with aq. sodium hydrogen carbonate and dried. The residue was chromatographed on silica gel (2.6 × 6.0 cm). The fractions eluted with benzene–dichloromethane (1:4) afforded the *dialdehyde* **11** (163 mg, 67%) as green needles, m.p. 108–109 °C (from hexane–benzene); *m*/*z* 252 (M^+, 4%) and 223 (100) ($C_{17}H_{16}O_2$ requires M, 252.3); λ_{max}/nm 215 (ε 18 600), 253 (14 300), 262 (13 700), 316sh (53 700), 330 (59 300), 345 (56 600), 381sh (20 400), 402 (12 700), 542sh (1090), 576 (1340) and 626sh (730); ν_{max}/cm^{-1} 2810, 2725 (CHO), 1670, 1635 (C=O) and 970 [(*E*)-HC=CH]; δ_H(90 MHz) 10.69 (1 H, s, CH^{b}O), 9.85 (1 H, d, *J* 8, CH^{a}O), 9.28 (1 H, d, *J* 10.5, 8-H), 8.56 (1 H, d, *J* 16, H^A), 8.43 (1 H, d, *J* 10, 4-H), 7.59 (1 H, d, *J* 10.5, 7-H), 7.54 (1 H, s, 3-H), 7.50 (1 H, d, *J* 10, 5-H), 6.93 (1 H, dd, *J* 16 and 8, H^B), 3.18 (1 H, sept, *J* 7, C*H*Me$_2$) and 1.40 (6 H, d, *J* 7, Me) (Found: C, 80.7; H, 6.3. $C_{17}H_{16}O_2$ requires C, 80.9; H, 6.4%).

2-(2-*Formylvinyl*)*azulene*-1-*carbaldehyde* **12**.—To a stirred solution of the dialdehyde **9**[12] (400 mg, 2.17 mmol) and the salt **10** (1.21 g, 2.82 mmol) in DMF (140 cm^3) was added dropwise methanolic lithium methoxide, prepared from lithium (20 mg, 2.88 mmol) and methanol (12 cm^3), during 1 h at 60 °C under argon. After being stirred for 3.5 h at 60 °C, the mixture was worked up as for the isolation of the acetal of compound **11**. The product was chromatographed on alumina (3.2 × 5.0 cm). The fractions eluted with hexane–ether (3:7) afforded the acetal of the dialdehyde **12**.

To a stirred solution of the acetal in ethanol (200 cm^3) was added 8% HCl (150 cm^3) in one portion at room temperature. After being stirred for 10 min at room temperature, the mixture was worked up as for the isolation of compound **11**. The

product was chromatographed on silica gel (2.6 × 8.0 cm). The fractions eluted with benzene–dichloromethane (1:1) afforded the *dialdehyde* **12** (270 mg, 59%) as green needles, m.p. 172–173 °C (from hexane–benzene); *m/z* 210 (M^+, 4%) and 181 (100) ($C_{14}H_{10}O_2$ requires M, 210.2); λ_{max}/nm 215 (ε 15 300), 252 (15 100), 257sh (14 900), 313 (48 100), 327 (49 600), 343 (42 400), 370sh (15 900), 380sh (13 900), 399sh (7270), 554sh (845), 591 (976) and 645sh (538); ν_{max}/cm^{-1} 2820 and 2740 (CHO), 1675 and 1635 (C=O) and 985 and 970 [(*E*)-HC=CH]; δ_H(90 MHz) 10.74 (1 H, s, CH^bO), 9.87 (1 H, d, *J* 8, CH^aO), 9.37 (1 H, d, *J* 10, 8-H), 8.58 (1 H, d, *J* 16, H^A), 8.50 (1 H, d, *J* 10, 4-H), 8.02–7.45 (3 H, m, 5-, 6- and 7-H), 7.62 (1 H, s, 3-H) and 6.97 (1 H, dd, *J* 16 and 8, H^B) (Found: C, 80.2; H, 4.9. $C_{14}H_{10}O_2$ requires C, 80.0; H, 4.8%).

6-*Isopropyl*-2-(4-*methylhexa*-1,3-*dien*-5-*ynyl*)*azulene*-1-*carbaldehyde* **14**.—To a stirred suspension of the salt **13**[7] (1.35 g, 3.2 mmol) in dry THF (50 cm^3) was added dropwise a solution of butyllithium in hexane (1.6 mol dm^{-3}; 2.0 cm^3, 3.2 mmol) by a syringe during 15 min at −70 °C under argon. After stirring of the mixture for 30 min at −70 °C, a solution of the dialdehyde **8** (150 mg, 0.66 mmol) in dry THF (25 cm^3) was added dropwise during 2 h at −70 °C and the mixture was stirred for 30 min at −70 °C. Then the temperature was allowed to rise to −10 °C and the mixture was stirred for 1 h at −10 °C. After addition of ethyl acetate (8.5 cm^3), the mixture was poured onto water and extracted with benzene. The extracts were washed and dried. The residue was chromatographed on alumina (2.8 × 8.0 cm). The fractions eluted with hexane–ether (2:3) gave a solid, which was purified by PLC with hexane–ether (2:1). The fast moving, second band afforded the *aldehyde* **14** (12 mg, 6.3%) as brown needles, m.p. 117–119 °C (decomp.) (from hexane–benzene); *m/z* 288 (M^+, 100%) ($C_{21}H_{20}O_2$ requires M, 288.3); λ_{max}/nm 214 (ε 22 500), 229sh (20 600), 270sh (14 300), 287sh (18 400), 297sh (20 900), 348 (58 200), 371 (43 300), 405sh (24 700), 427sh (22 600), 454sh (11 800), 533sh (1100), 568 (1280) and 619sh (693); ν_{max}/cm^{-1} 3290 (C≡CH), 2740 (CHO), 2090 (C≡C), 1640 (C=O) and 970 [(*E*)-HC=CH]; δ_H(270 MHz) 10.58 (1 H, s, CHO), 9.24 (1 H, d, *J* 10.3, 8-H), 8.24 (1 H, d, *J* 10.3, 4-H), 7.59 (1 H, dd, *J* 15.6 and 7.5, H^B), 7.58 (1 H, d, *J* 7.5, H^C), 7.47 (1 H, s, 3-H), 7.45 (1 H, d, *J* 10.3, 7-H), 7.37 (1 H, d, *J* 10.5, 5-H), 6.62 (1 H, d, *J* 15.6, H^A), 3.47 (1 H, s, C≡CH), 3.10 (1 H, sept, *J* 5.9, $CHMe_2$), 2.05 (3 H, s, Me) and 1.36 (6 H, d, *J* 5.9, $CHMe_2$) (Found: C, 87.2; H, 6.9. $C_{21}H_{20}O_2$ requires C, 87.5; H, 7.0%).

6-*Isopropyl*-1,2-*bis*(4-*methylhexa*-1,3-*dien*-5-*ynyl*)*azulene* **15**.—To a stirred suspension of the salt **13** (2.20 g, 5.01 mmol) in dry THF (40 cm^3) was added a solution of butyllithium in hexane (1.6 mol dm^{-3}; 3.1 cm^3, 5.01 mmol) by a syringe during 20 min at −60 °C under argon. After the mixture had been stirred for 1 h at −60 °C, a solution of the dialaldehyde **8** (113 mg, 0.50 mmol) in dry THF (10 cm^3) was added dropwise during 1.5 h at −55 °C and the mixture was then stirred for 5 h at −20 °C. After addition of ethyl acetate (2 cm^3) and benzene (10 cm^3), the mixture was worked up as for the isolation of compound **14**. The product was chromatographed on alumina (3.2 × 5.0 cm). The initial fractions eluted with hexane–ether (1:1) afforded a mixture of the *Z,Z*- and *E,Z*-isomer* of compound **15** (30 mg, 17%) as a dark green liquid; *m/z* 350 (M^+, 100%) ($C_{27}H_{26}$ requires M, 350.4). The later fractions eluted with hexane–ether (1:4) afforded the E,E-*isomer* **15** (18 mg, 10%) as a green liquid; *m/z* 350.1963 ($C_{27}H_{26}$ requires M, 350.2031); λ_{max}/nm 256 (ε 3300), 361 (16 000), 439sh (4700), 468sh (2000) and 646 (290); ν_{max}/cm^{-1} 3280 (C≡CH), 2100 (C≡C) and 1000 [(*E*)-HC=CH]; δ_H(270 MHz) 8.28 (1 H, d, *J* 10.3, 8-H), 8.02 (1 H, d, *J* 10.3, 4-H), 7.49 (1 H, dd, *J* 15.5 and 11.0, H^B or $H^{B'}$), 7.45 (1 H, s, 3-H), 7.19–7.03 (3 H, m, $H^{B'}$ or H^B, H^A and $H^{A'}$), 7.04 (1 H, d, *J* 10.3, 7-H), 6.99 (1 H, d, *J* 10.3, 5-H), 6.58 (2 H, br d, *J* 11.0, H^C and $H^{C'}$), 3.43 (1 H, s, C≡CH), 3.33 (1 H, s, C≡CH), 2.98 (1 H, sept, *J* 7, $CHMe_2$), 2.03 (6 H, s, Me) and 1.32 (6 H, d, *J* 7, $CHMe_2$).

10,11,12,13-*Tetradehydro*-3-*isopropyl*-9,14-*dimethyl*[14]*annuleno*[a]*azulene* **1**.—A solution of a stereoisomeric mixture containing compound **15** (90 mg, 0.26 mmol) in a mixture of pyridine (25 cm^3), ether (10 cm^3) and methanol (10 cm^3) was added dropwise during 5 h to a stirred solution of copper(II) acetate monohydrate (2.0 g) in a mixture of pyridine (100 cm^3), ether (40 cm^3) and methanol (35 cm^3) at 60 °C. The mixture was stirred for a further 30 min, then was poured onto water and extracted with benzene. The combined extracts were washed with dil. HCl until they turned acidic to litmus, and then with aq. sodium hydrogen carbonate and dried. The residue obtained after removal of solvent was chromatographed on silica gel (1.8 × 10.0 cm). The fractions eluted with hexane afforded the [14]*annuleno*[a]*azulene* **1** (18 mg, 20%) as a solid. The solid was purified by PLC with hexane–benzene (6:1). The fast moving, second band gave a purple solid. It formed black-purple needles, m.p. 189–190 °C (decomp.) (from hexane–benzene); *m/z* 348 (M^+, 100%) ($C_{27}H_{24}$ requires M, 348.4); λ_{max}/nm 275 (ε 13 400), 380 (49 700), 482sh (6400) and 680 (220); and see Fig. 4; ν_{max}/cm^{-1} 2120 (C≡C) and 970 and 950 [(*E*)-HC=CH]; for ^1H NMR data see Tables 1, 2 and Fig. 1(*a*) (Found: C, 93.1; H, 6.7. $C_{27}H_{24}$ requires C, 93.1; H, 6.9%).

Isomeric 6-*Isopropyl*-1-(4-*methylhexa*-1,3-*dien*-5-*ynyl*)-2-(6-*methylocta*-1,3,5-*trien*-7-*ynyl*)*azulenes* **16** *and* **17**.—To a stirred suspension of the salt **13** (15.2 g, 36.0 mmol) in dry THF (100 cm^3) was added a solution of butyllithium in hexane (1.6 mol dm^{-3}; 22.5 cm^3, 36.0 mmol) by a syringe during 25 min at −65 °C under argon. After the mixture had been stirred for 1 h at −55 °C, a solution of the dialdehyde **11** (808 mg, 3.20 mmol) in dry THF (30 cm^3) was added dropwise during 2 h at −50 °C and the mixture was stirred for 5 h at −22 °C. After addition of ethyl acetate (3 cm^3) and benzene (8 cm^3), the mixture was worked up as for the isolation of compound **14**. The product was chromatographed on alumina (2.6 × 8.9 cm). The fractions eluted with hexane–ether (9:1) afforded the E,Z-*isomer* **16** (96 mg, 12%) as a yellow-green liquid; *m/z* 376.2164 ($C_{29}H_{28}$ requires M, 376.2189); λ_{max}/nm 261 (ε 10 300), 285sh (6300), 352 (9400), 428 (4900), 460sh (3300), 493sh (1100), 599 (870) and 634sh (800); ν_{max}/cm^{-1} 3280 (C≡CH), 2090 (C≡C), 990 [(*E*)-HC=CH] and 680 and 660 [(*Z*)-HC=CH]; δ_H(90 MHz) 8.06 (1 H, d, *J* 11, 8-H), 7.94 (1 H, d, *J* 11, 4-H), 7.47 (1 H, s, 3-H), 7.34–6.75 (7 H, m, 5- and 7-H, H^A, $H^{A'}$, H^B, H^C and H^D), 6.50 (1 H, dd, *J* 12 and 11, $H^{B'}$), 6.40 (1 H, d, *J* 11, $H^{C'}$), 6.29 (1 H, d, *J* 9, H^E), 3.39 (2 H, s, C≡CH), 3.00 (1 H, m, $CHMe_2$), 1.99 (3 H, s, Me), 1.84 (3 H, s, Me) and 1.32 (6 H, d, *J* 6.8, $CHMe_2$).

The later fractions eluted with hexane–ether (9:1) afforded the *E,E*-isomer **17** (54 mg, 7%) as a yellow-green liquid; *m/z* 376 (M^+, 3%) and 277 (100) ($C_{29}H_{28}$ requires M, 376.5); λ_{max}/nm 261 (ε 6600), 371 (12 700), 435sh (5400), 468sh (3300), 500sh (1100) and 638 (100); ν_{max}/cm^{-1} 3280 (C≡CH), 2090 (C≡C), 990 and 970 [(*E*)-HC=CH]; δ_H(270 MHz) 8.06 (1 H, d, *J* 10.5, 8-H), 7.94 (1 H, d, *J* 10.5, 4-H), 7.42 (1 H, s, 3-H), 7.16 (1 H, dd, *J* 15.6 and 11.2, H^B), 7.02 (2 H, d, *J* 10.5, 5- and 7-H), 6.98–6.83 (3 H, m, $H^{A'}$, $H^{B'}$ and H^D), 6.86 (1 H, d, *J* 15.6, H^A), 6.51 (1 H, dd, *J* 14.6 and 11.2, H^C), 6.42 (1 H, d, *J* 11.0, $H^{C'}$ or H^E), 6.31 (1 H, d,

* The *E* and *Z* notations indicate the geometry of the double bonds adjacent to the azulene ring in compounds **15**–**20**, *i.e.*, CH^A=CH^B and $CH^{A'}$=CH^B.

J 10.5, H^E or $H^{C'}$), 3.40 (1 H, s, C≡CH), 3.39 (1 H, s, C≡CH), 3.00 (1 H, sept, *J* 6.8, C*H*Me_2), 1.99 (3 H, s, Me), 1.84 (3 H, s, Me) and 1.32 (6 H, d, *J* 6.8, CHMe_2).

10,11,12,13-*Tetradehydro*-3-*isopropyl*-9,14-*dimethyl*[16]*annuleno*[a]*azulene* **3**.—A solution of compounds **16** and **17** (143 mg, 0.356 mmol) in a mixture of pyridine (15 cm^3) and ether (5 cm^3) was added dropwise during 1.5 h to a stirred solution of anhydrous copper(II) acetate (1.20 g) in a mixture of pyridine (36 cm^3) and ether (12 cm^3) at 45 °C. After being stirred for a further 2 h at 45 °C, the mixture was worked up as for the isolation of compound **1**. The product was chromatographed on alumina (2.6 × 7 cm). The fractions eluted with hexane–benzene (9:1) afforded the [16]*annuleno*[a]*azulene* **3** (24 mg, 16%) as dark brown microcrystals, m.p. 200–203 °C (decomp.) (from hexane–benzene); *m/z* 374 (M^+, 100%) ($C_{29}H_{26}$ requires M, 374.5); λ_{max}/nm 268 (ε 23 800), 315 (27 700), 385 (55 400) and 656 (280); and see Fig. 4; ν_{max}/cm^{-1} 2170 (C≡C) and 970 [(*E*)–HC=CH]; for ^1H NMR data see Tables 1, 2 and Fig. 1(*b*) (Found: C, 92.9; H, 7.0. $C_{29}H_{26}$ requires C, 93.0; H, 7.0%).

Isomeric 1,2-*Bis*(4-*methylhexa*-1,3-*dien*-5-*ynyl*)*azulenes* **18** *and* **19**.—To a stirred suspension of the salt **13** (7.0 g, 16.3 mmol) in dry THF (50 cm^3) was added a solution of butyllithium in hexane (1.6 mol dm^{-3}; 11 cm^3, 17.0 mmol) by a syringe during 50 min at −44 °C under argon. After the mixture had been stirred for 1.5 h at 0 °C, a solution of the dialdehyde **9** (300 mg, 1.63 mmol) in dry THF (60 cm^3) was added dropwise during 2 h at −40 °C and the mixture was stirred for a further 1 h at −30 °C. After addition of ethyl acetate (2 cm^3) and benzene (30 cm^3), the mixture was worked up as for the isolation of compound **14**. The product was chromatographed on alumina (3.2 × 16 cm). The fractions eluted with 15% benzene in hexane afforded a stereoisomeric mixture of the desired acyclic diacetylenes (122 mg, 24%) as a green liquid. The liquid was again chromatographed on alumina (1.6 × 41 cm). The initial fractions eluted with 10% benzene in hexane afforded the E,Z-*isomer* **18** (58 mg, 12%) as green needles, m.p. 132–134 °C (decomp.) (from hexane); *m/z* 308 (M^+, 100%) ($C_{24}H_{20}$ requires M, 308.4); λ_{max}/nm 251 (ε 23 400), 283 (16 100), 341 (40 300), 402 (15 100), 427 (15 500), 454 (9050), 617 (393) and 653 (396); ν_{max}/cm^{-1} 3250 (C≡CH), 2060 (C≡C), 980 [(*E*)–HC=CH] and 730 [(*Z*)-HC=CH]; δ_H(600 MHz) 8.14 (1 H, d, *J* 9.8, 4-H), 8.01 (1 H, d, *J* 9.8, 8-H), 7.56 (1 H, s, 3-H), 7.55 (1 H, dd, *J* 16.0 and 11.0, H^B), 7.43 (1 H, t, *J* 9.8, 6-H), 7.08 (2 H, t, *J* 9.8, 5- and 7-H), 6.97 (1 H, t, *J* 11.0, $H^{B'}$), 6.89 (1 H, d, *J* 16.0, H^A), 6.87 (1 H, d, *J* 11.0, $H^{A'}$), 6.55 (1 H, d, *J* 11.0, H^C), 6.27 (1 H, d, *J* 11.0, $H^{C'}$), 3.46 (1 H, s, C≡CH^b), 3.39 (1 H, s, C≡CH^a), 2.03 (3 H, s, Me^b) and 1.84 (3 H, s, Me^a) (Found: C, 93.4; H, 6.7. $C_{24}H_{20}$ requires C, 93.5; H, 6.5%).

The later fractions eluted with 15% benzene in hexane afforded the E,E-*isomer* **19** (21 mg, 4%) as dark green plates, m.p. 91–92 °C (decomp.) (from hexane); *m/z* 308 (M^+, 100%) ($C_{24}H_{20}$ requires M, 308.4); λ_{max}/nm 253 (ε 25 900), 258sh (17 000), 360 (59 600), 438sh (18 800), 469sh (10 100) and 644 (1360); ν_{max}/cm^{-1} 3260 (C≡CH), 2070 (C≡C) and 960 [(*E*)-HC=CH]; δ_H(600 MHz) 8.35 (1 H, d, *J* 9.8, 8-H), 8.09 (1 H, d, *J* 9.8, 4-H), 7.54 (1 H, s, 3-H), 7.53 (1 H, dd, *J* 16.0 and 10.0, H^B), 7.41 (1 H, dd, *J* 10.0 and 9.8, 6-H), 7.17 (1 H, d, *J* 16.0, $H^{A'}$), 7.16 (1 H, d, *J* 16.0, H^A), 7.09 (1 H, dd, *J* 16.0 and 10.0, $H^{B'}$), 7.08 (1 H, t, *J* 10.0, 7-H), 7.03 (1 H, d, *J* 9.8, 5-H), 6.60 (2 H, br d, *J* 10.0, H^C and $H^{C'}$), 3.46 (1 H, s, C≡CH), 3.34 (1 H, s, C≡CH), 2.04 (3 H, s, Me) and 2.03 (3 H, s, Me) (Found: C, 93.05; H, 6.5%).

10,11,12,13-*Tetradehydro*-9,14-*dimethyl*[14]*annuleno*[a]*azulene* **2**.—To a stirred solution of anhydrous copper(II) acetate (566 mg) in a mixture of pyridine (40 cm^3), ether (16 cm^3) and methanol (50 cm^3) was added dropwise during 4.5 h a solution of a mixture of compounds **18** and **19** (32 mg, 0.10 mmol) in a mixture of pyridine (15 cm^3), ether (6 cm^3) and methanol (6 cm^3) at 60 °C, and the reaction mixture was stirred for a further 2 h at 60 °C. Then the mixture was worked up as for the isolation of compound **1**. The product was chromatographed on alumina (2.0 × 11.4 cm). The fractions eluted with 5–7% benzene in hexane afforded the unchanged compound **18** (2 mg recovery).

The later fractions eluted with 20% benzene in hexane afforded the [14]*annuleno*[a]*azulene* **2** (5.0 mg, 16%) as brown microcrystals, m.p. 196–198 °C (decomp.) (from hexane–dichloromethane); *m/z* 306 (M^+, 72%) and 289 (100) ($C_{24}H_{18}$ requires M, 306.3); ν_{max}/nm 283 (ε 10 600), 379 (36 600), 488sh (3770) and 700 (533); ν_{max}/cm^{-1} 2115 (C≡C) and 960 [(*E*)-HC=CH]; for ^1H NMR data see Tables 1–3 and Fig. 2 (Found: C, 93.7; H, 6.5. $C_{24}H_{18}$ requires C, 94.1; H, 6.0%).

1-(4-*Methylhexa*-1,3-*dien*-5-*ynyl*)-2-(6-*methylocta*-1,3,5-*trien*-7-*ynyl*)*azulene* **20**.—To a stirred suspension of the salt **13** (4.20 g, 10 mmol) in dry THF (30 cm^3) was added a solution of butyllithium in hexane (1.6 mol dm^{-3}; 6.5 cm^3, 10.4 mmol) by a syringe during 1 h at −60 °C under argon. After stirring of the mixture for 30 min at −50 °C, a solution of the dialdehyde **12** (210 mg, 1 mmol) in dry THF (10 cm^3) was added dropwise during 2.5 h at −50 °C and the mixture was stirred for a further 2 h at −10 °C. After addition of ethyl acetate (3 cm^3) and benzene (20 cm^3), the mixture was worked up as for the isolation of compound **1**. The product was chromatographed on alumina (3.2 × 10 cm). The fractions eluted with hexane afforded a stereoisomeric mixture of the desired acyclic diacetylenes (76 mg, 23%) as a green solid. The solid was further purified by PLC with hexane–benzene (1:9). The fast moving, second band afforded the E,Z-*isomer* **20** (7 mg, 3%) as dark green needles, m.p. 84–86 °C (decomp.) (from hexane–benzene); *m/z* 334 (M^+, 8%) and 277 (100) ($C_{26}H_{22}$ requires M, 306.4); λ_{max}/nm 348 (ε 67 800), 427 (36 100), 456sh (23 800), 490sh (7050), 630 (230) and 671sh (220); ν_{max}/cm^{-1} 3255 (C≡CH), 2065 (C≡C), 985 [(*E*)-HC=CH] and 685 and 660 [(*Z*)-HC=CH]; δ_H(270 MHz) 8.12 (1 H, d, *J* 10.0, 4-H), 7.99 (1 H, d, *J* 10.0, 8-H), 7.49 (1 H, s, 3-H), 7.43 (1 H, t, *J* 10.0, 6-H), 7.20 (1 H, dd, *J* 16 and 11, H^B), 7.07 (2 H, t, *J* 10.0, 5- and 7-H), 6.97 (1 H, t, *J* 11, $H^{B'}$), 6.88 (1 H, dd, *J* 15 and 11, H^C), 6.87 (1 H, d, *J* 16, H^A), 6.86 (1 H, d, *J* 11, $H^{A'}$), 6.52 (1 H, dd, *J* 15 and 11, H^D), 6.42 (1 H, br d, *J* 11, H^E), 6.27 (1 H, br d, *J* 11, $H^{C'}$), 3.41 (1 H, s, C≡CH), 3.40 (1 H, s, C≡CH), 1.99 (3 H, s, Me) and 1.83 (3 H, s, Me) (Found: C, 93.6; H, 6.1. $C_{26}H_{22}$ requires C, 93.8; H, 6.2%).

10,11,12,13-*Tetradehydro*-9,14-*dimethyl*[16]*annuleno*[a]*azulene* **4**.—To a stirred solution of anhydrous copper(II) acetate (2.00 g) in a mixture of pyridine (120 cm^3), ether (60 cm^3) and methanol (30 cm^3) was added dropwise during 6 h a solution of the acyclic diacetylenes containing compound **20** (138 mg, 0.41 mol) in a mixture of pyridine (25 cm^3), ether (15 cm^3) and methanol (10 cm^3) at 50 °C. Then the mixture was worked up as for the isolation of compound **1**. The product was chromatographed on alumina (1.8 × 16 cm). The fractions eluted with hexane afforded the [16]*annuleno*[a]*azulene* **4** (22 mg, 17%) as black-purple plates, m.p. 192–193 °C (decomp.) (from hexane–benzene); *m/z* 332 (M^+, 68%) and 315 (100) ($C_{26}H_{20}$ requires M, 332.4); λ_{max}/nm 280 (ε 23 200), 316sh (31 000), 385 (57 000) and 678 (430); ν_{max}/cm^{-1} 2160 (C≡C), 990 and 965 [(*E*)-HC=CH]; for ^1H NMR data see Tables 1–3 and Fig. 3 (Found: C, 94.3; H, 6.2. $C_{26}H_{20}$ requires C, 94.0; H, 6.0%).

UV Data for 6-*Isopropylazulene* **21**.[9]—λ_{max}/nm 234 (ε 15 600), 279 (53 600), 285 (52 500), 322sh (3960), 328 (4760),

335 (4650), 344 (6250), 564 (341), 580sh (315), 608 (296) and 670 (114); and see Fig. 4.

^{1}H *NMR Data for 7-Isopropylbenz*[a]*azulene* **23**.[17]—δ_H(600 MHz) 8.27 (1 H, d, *J* 7.5 and 1.5, H^X), 8.18 (1 H, d, *J* 8.5, 8-H), 7.87 (1 H, d, *J* 11.5, 4-H), 7.77 (1 H, d, *J* 7.5 and 1.5, $H^{X'}$), 7.55 (1 H, dd, *J* 7.5 and 1.5, $H^{Y'}$), 7.37 (1 H, dd, *J* 7.5 and 1.5, H^Y), 7.20 (1 H, s, 3-H), 6.89 (1 H, d, *J* 8.0 and 1.5, 7-H), 6.74 (1 H, dd, *J* 11.5 and 1.5, 5-H), 2.86 (1 H, sept, *J* 7.0, CH) and 1.25 (6 H, d, *J* 7.0, Me); and see Table 2.

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References

1 A. T. Balaban, M. Banciu and V. Ciorba, *Annulenes, Benzo-, Hetero-, Homo-Derivatives, and Their Valence Isomers*, CRC Press, Florida, 1987, vol. 2, p. 115.
2 T. M. Cresp and F. Sondheimer, *J. Am. Chem. Soc.*, 1977, **99**, 194; M. Nakagawa, *Angew. Chem.*, 1979, **91**, 215.
3 (*a*) R. T. Weavers and F. Sondheimer, *Angew. Chem.*, 1974, **86**, 167; (*b*) N. Darby, T. M. Cresp and F. Sondheimer, *J. Org. Chem.*, 1977, **42**, 1960.
4 D. Lloyd, *Non-benzenoid Conjugated Carbocyclic Compounds*, Elsevier, Amsterdam, 1984, p. 331.
5 Part of this work has been reported in preliminary form; H. Higuchi, J. Ojima, M. Yasunami, K. Fujimori and M. Yoshifuji, *Tetrahedron Lett.*, 1994, **35**, 1259.
6 J. Ojima, E. Ejiri, T. Kato, S. Kuroda, S. Hirooka and M. Shibutani, *Tetrahedron Lett.*, 1986, **27**, 2467; J. Ojima, E. Ejiri, T. Kato, M. Nakamura, S. Kuroda, S. Hirooka and M. Shibutani, *J. Chem. Soc., Perkin Trans. 1*, 1987, 831.
7 M. Montavon, H. Lindler, R. Marbet, R. Rüegg, G. Saucy, P. Zeller and O. Isler, *Helv. Chim. Acta*, 1957, **40**, 1250.
8 P. J. Garratt, *Aromaticity*, Wiley, New York, 1986, p. 246.
9 M. Yasunami, T. Ueno, M. Yoshifuji, A. Okamoto and K. Hirotsu, *Chem. Lett.*, 1992, 1971.
10 T. M. Cresp, M. V. Sargent and P. Vogel, *J. Chem. Soc., Perkin Trans. 1*, 1974, 37.
11 J. Ojima, T. Hashimoto, J. Katsuyama, H. Miyashita, S. Fujita, S. Kuroda, Y. Kano and G. Yamamoto, *J. Chem. Soc., Perkin Trans. 1*, 1990, 333.
12 (*a*) M. Saito, T. Morita and K. Takase, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 3696; (*b*) M. Yasunami, M. Miyoshi and K. Takase, unpublished results.
13 L. M. Jackman and S. Sternhell, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, Pergamon Press, London, 1969, pp. 280–304.
14 R. H. Wightman and F. Sondheimer, *Tetrahedron Lett.*, 1975, 4179; R. R. Jones, J. M. Brown and F. Sondheimer, *Tetrahedron Lett.*, 1975, 4183.
15 Y. Aso, M. Iyoda and M. Nakagawa, *Tetrahedron Lett.*, 1981, **22**, 1993; Y. Yoshikawa, M. Iyoda and M. Nakagawa, *Tetrahedron Lett.*, 1981, **22**, 1989.
16 W. G. Schneider, H. J. Bernstein and J. A. Pople, *J. Am. Chem. Soc.*, 1958, **80**, 3497; D. J. Bertelli and P. Crews, *Tetrahedron*, 1970, **26**, 4717.
17 M. Yasunami, M. Shinba, T. Amemiya, Y. Kondoh, T. Sato, M. Yoshifuji and K. Takase, unpublished results.
18 D. Kost, E. H. Carlson and M. Raban, *Chem. Commun.*, 1971, 656.
19 J. Anthony, C. B. Knobler and F. Diederich, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 406.

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