Synthesis and some properties of 7H-naphth[3,2,1-cd]azulen-7-ones and related compounds

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7H-Naphth[3,2,1-cd]azulen-7-ones are synthesized by the intramolecular Friedel–Crafts cyclization of diethyl 4-phenylazulene-1,3-dicarboxylate derivatives with polyphosphoric acid (PPA). Treatment of 7H-naphth[3,2,1-cd]-azulen-7-one with methyl trifluoromethanesulfonate or perchloric acid gives 7-methoxynaphth[3,2,1-cd]azulenium trifluoromethanesulfonate or 7-hydroxynaphth[3,2,1-cd]azulenium perchlorate. Both spectroscopic inspection and molecular orbital calculations for 7-hydroxynaphth[3,2,1-cd]azulenium ion show that the tropylium moiety is a main contributor to the ground state in the resonance structure. The syntheses of 7H-azuleno[1,8-bc]phenanthren-7-ones and 5,7-dihydrodinaphth[3,2,1-cd:1′,2′,3′-ij]azulene-5,7-diones are also described.
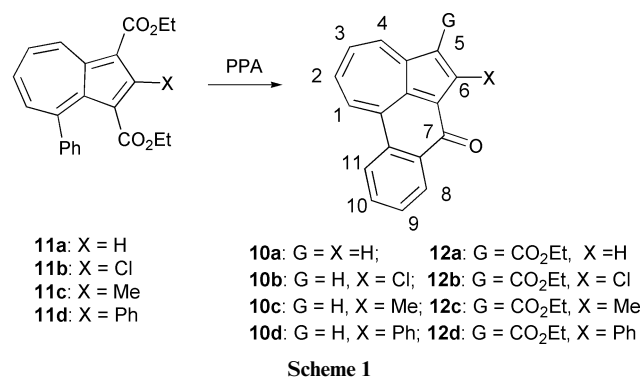
The benz[cd]azulenyl system **1**, a theoretically interesting odd non-alternant analog of the phenalenyl system **2**,[1] has attracted attention and some synthetic studies to the parent hydrocarbon **3**[2] and its alkyl derivatives,[3] and the ketonic and the iminic derivatives **4**–**7**[2,4–14] of this system were made. In connection with this series, the cyclohept[cd]-s-indacene **8**[15] and cyclohepta-[def]fluorene-4,8-dione **9**[16] were synthesized, and we also communicated the synthesis of 7H-naphth[3,2,1-cd]azulen-7-ones **10**[17,18] as a benzolog of the benz[cd]azulenyl system (see Chart 1). In this paper, we report the full details of the syn-

Chart 1
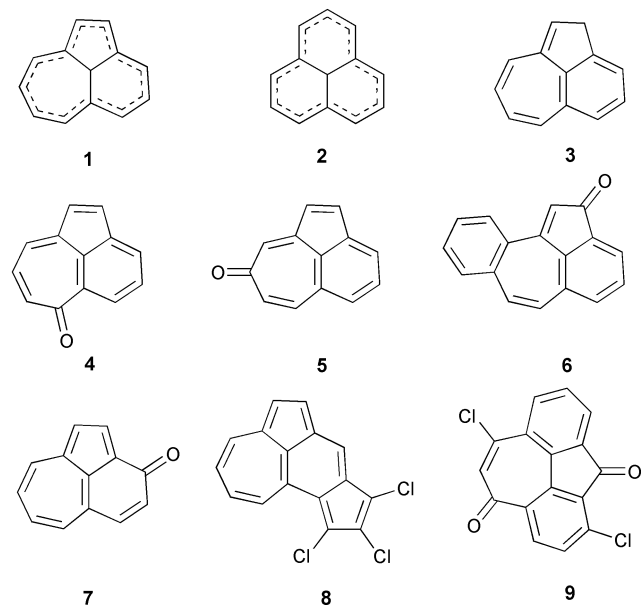
thesis and some properties of 7H-naphth[3,2,1-cd]azulen-7-ones and 7H-azuleno[1,8-bc]phenanthren-7-ones. Furthermore, the synthesis of the 5,7-dihydrodinaphth[3,2,1-cd:1′,2′,3′-ij]-azulene-5,7-dione system, which is a formally dibenz-annelated cyclohepta[def]fluorene-3,5-dione, is also described.

Results and discussion

Treatment of diethyl 4-phenylazulene-1,3-dicarboxylate[19,20] **11a** with polyphosphoric acid (PPA) at about 100 °C for 7 h gave two kinds of colored products, 7H-naphth[3,2,1-cd]azulen-7-one **10a** and ethyl 7-oxo-7H-naphth[3,2,1-cd]azulen-5-carboxyl-ate **12a**, in 10 and 60% yield respectively (Scheme 1). Alkaline

11a: X = H
11b: X = Cl
11c: X = Me
11d: X = Ph

10a: G = X =H; **12a**: G = CO₂Et, X =H
10b: G = H, X = Cl; **12b**: G = CO₂Et, X = Cl
10c: G = H, X = Me; **12c**: G = CO₂Et, X = Me
10d: G = H, X = Ph; **12d**: G = CO₂Et, X = Ph

Scheme 1

hydrolysis of **12a**, followed by decarboxylation upon heating at 300 °C gave **10a**. When the reaction of **11a** with PPA was performed at room temperature for 2 days, only compound **12a** was obtained, in 67% yield. Alkaline hydrolysis of **11a**, and successive treatment of the obtained carboxylic acid with hot PPA for 3 h, gave **10a** in 61%. The structures of these compounds were deduced by their spectroscopic data as well as elemental analysis and mass spectra. In a similar manner, compounds **11b**–**11d** were treated with PPA and gave 7H-naphth-[3,2,1-cd]azulen-7-one derivatives (**10b**–**10d** and **12b**–**12d**). The results are listed in Table 1.

In the IR spectra of 7H-naphth[3,2,1-cd]azulen-7-ones **10a**–**10d** and **12a**–**12d**, absorptions of the ring carbonyl were seen at 1620–1640 cm⁻¹. The lowering of the carbonyl frequency should arise from a high polarization of the carbonyl group. This is consistent with the fact that compounds **10a** and **12a** did not react with carbonyl reagents, such as hydroxylamine or phenylhydrazines.

Table 1 Cyclizations of diethyl 4-phenylazulene-1,3-dicarboxylates

Run	Compound	Method[a]	Products	Yield (%)
1	**11a**	a	**10a** (10)	**12a** (60)
2	**11a**	b	**10a** (—)	**12a** (67)
3	**11a**	c	**10a** (61)	**12a** (—)
4	**11b**	a	**10b** (14)	**12b** (68)
5	**11b**	b	**10b** (—)	**12b** (99)
6	**11b**	c	**10b** (90)	**12b** (—)
7	**11c**	a	**10c** (26)	**12c** (54)
8	**11d**	a	**10d** (21)	**12d** (51)
9	**11d**	b	**10d** (—)	**12d** (99)
10	**11d**	c	**10d** (78)	**12d** (—)
11	**16a**	a	**17a** (10)	**18a** (60)
12	**16a**	b	**17a** (—)	**18a** (85)
13	**16a**	c	**17a** (47)	**18a** (—)
14	**16b**	a	**17b** (7)	**18b** (76)

[a] Method a: PPA, heat at 100 °C for 7 h. Method b: PPA, room temperature for 2 days. Method c: 1) KOH, reflux, 2) PPA, 100 °C for 3 h.

The ^{1}H NMR spectra of 7*H*-naphth[3,2,1-*cd*]azulen-7-ones **10a**–**10d** and **12a**–**12d** are listed in Table 2. The ^{1}H NMR spectrum of **10a** in trifluoroacetic acid shows a downfield shift of the ring protons, especially those of the seven-membered ring. In addition, its electronic spectrum in acid is remarkably different from that in neutral solvent. These results suggest that **10a** exists as the naphth[3,2,1-*cd*]azulenium ion **13** in acidic medium (Scheme 2).

Scheme 2
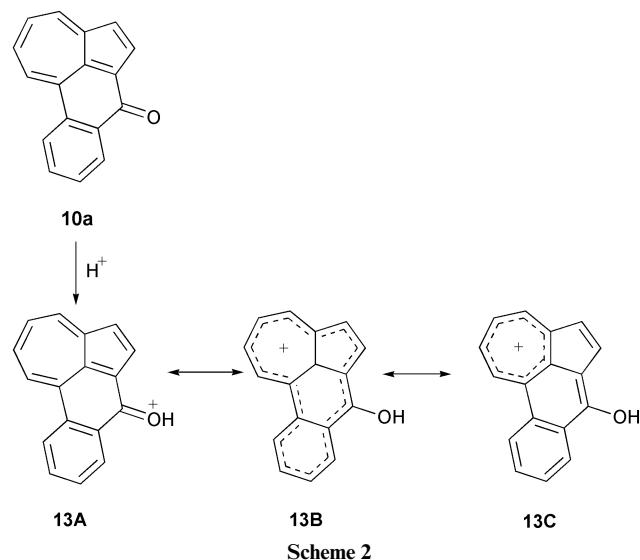
Methylation of compound **10a** with methyl trifluoro-methanesulfonate and perchloric acid gave 7-methoxy-naphth[3,2,1-*cd*]azulenium perchlorate **14**. The ^{1}H NMR spectrum of **14** resembles that of **10a** in trifluoroacetic acid except for the OMe signal. 6-Chloro-7-hydroxynaphth-[3,2,1-*cd*]azulenium perchlorate **15** was isolated by treatment of **10b** with trifluoroacetic acid–70% perchloric acid. In the IR spectrum of **15**, the OH signal at 3100 cm^{-1} together with the rather weak signal at 1610 cm^{-1} assignable to a carbonyl were seen. The result suggests that the cation **15** maintains a partial C=O$^+$–H character.

In order to gain insight into the structures of 7*H*-naphth-[3,2,1-*cd*]azulen-7-one and its cationic system (**10a** and **13**), *ab initio* molecular orbital calculations by Gaussian 98 using RHF/6-31G* were performed; we have previously presented the calculation of π-electron density of naphth[3,2,1-*cd*]azulenium cation.[17] The molecular diagrams (bond lengths and total atomic charges) of **10a** and **13** are shown in Fig. 1. The bond lengths of **10a** show the existence of bond-alternation in the seven-membered ring, and the total atomic charges show that

Table 2 The ^{1}H NMR chemical shifts of 7*H*-naphth[3,2,1-*cd*]azulen-7-ones **10a**–**10d**, and **12a**–**12d** and 7*H*-naphth[3,2,1-*cd*]azulenium cations **14** and **15**. δ/ppm (pattern, coupling constant *J*/Hz)

Compound	H-1	H-2	H-3	H-4	H-5	H-6	H-8	H-9	H-10	H-11	Others
10a (CDCl₃)	8.40–8.60 (m)	7.78 (dd, 10.0, 2.2)	7.46 (br t, 10.0)	8.26 (td, 10.0, 2.2)	7.14 (d, 4.2)	8.26 (d, 4.2)	8.10–8.30 (m)	7.40–7.70 (m)	7.40–7.70 (m)	8.40–8.60 (m)	
10a (CF₃CO₂H)	9.00 (br d, 10.0)	8.90 (br t, 10.0)	8.88 (br t, 10.0)	8.94 (br d, 10.0)	7.53 (d, 5.2)	8.41 (d, 5.2)	8.60–8.80 (m)	7.90–8.20 (m)	7.90–8.20 (m)	9.60–9.80 (m)	
10b (CDCl₃)	8.00–8.50 (m)	7.81 (td, 10.0, 2.0)	7.40–7.70 (m)	8.00–8.50 (m)	6.98 (s)		8.00–8.50 (m)	7.40–7.70 (m)	7.40–7.70 (m)	8.00–8.50 (m)	
10b (CF₃CO₂H)		8.70–9.20 (m)	8.70–9.20 (m)		7.60 (s)		8.70–9.20 (m)	8.10–8.40 (m)	8.10–8.40 (m)	9.80–10.10 (m)	
10c (CDCl₃)	8.40–9.00 (m)	7.30–8.30 (m)	8.10–8.40 (m)	8.40–9.00 (m)	7.02 (s)		7.30–8.30 (m)	7.30–8.30 (m)	7.30–8.30 (m)	8.40–9.00 (m)	2.94 (s, Me)
10d (CDCl₃)		7.40–8.60 (m)			7.29 (s)		7.40–8.60 (m)				7.40–8.60 (m, Ph)
14 (CF₃CO₂H)		8.60–9.30 (m)			7.78 (d, 5.7)	8.65 (d, 5.7)	8.60–9.30 (m)	8.00–8.35 (m)	8.00–8.35 (m)	9.80–10.10 (1H, m)	4.95 (s, OMe)
15 (CF₃CO₂H)		8.70–9.30 (m)			7.66 (s)		8.70–9.30 (m)	8.00–8.40 (m)	8.00–8.40 (m)	9.70–10.00 (m)	
12a (CDCl₃)	8.27 (br d, 9.8)	7.78 (br t, 9.8)	7.56 (br t, 9.8)	9.41 (br d, 9.8)		8.55 (s)	7.95–8.15 (m)	7.40–7.60 (m)	7.40–7.60 (m)	8.15–8.35 (m)	1.46 (t, *J* 7.0, Me), 4.37 (q, 7.0, CH₂)
12b (CDCl₃)		7.30–8.40 (m)		9.00–9.20 (1H, m)			7.30–8.40 (m)				1.50 (t, 7.2, Me), 4.47 (q, 7.2, CH₂)
12c (CDCl₃)	7.70–8.40 (m)	7.30–7.60 (m)		9.00–9.30 (m)			7.70–8.40 (m)	7.30–7.60 (m)	7.30–7.60 (m)	7.70–8.40 (m)	1.46 (t, 7.2, Me), 2.95 (s, Me), 4.42 (q, 7.2, CH₂)
12d (CDCl₃)	7.70–8.40 (m)	7.50–8.10 (m)		9.40–9.60 (m)			7.70–8.40 (m)	7.50–8.10 (m)	7.70–8.40 (m)	7.70–8.40 (m)	0.97 (t, 7.1, Me), 4.14 (q, 7.1, CH₂), 7.52 (br s, Ph)

E(RHF) = −724.818349969   E(RHF) = −724.428312757

Bond lengths   Bond lengths
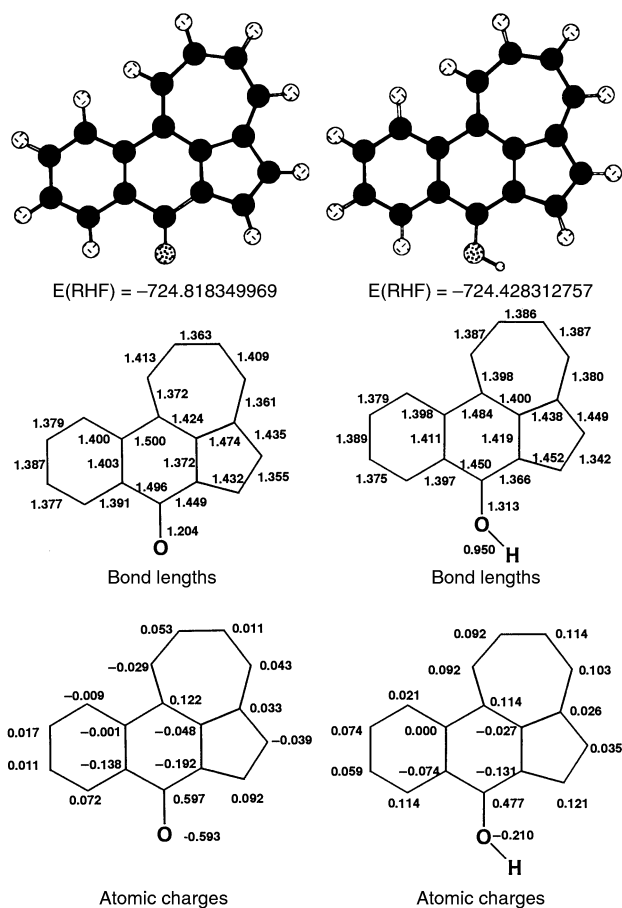
Atomic charges   Atomic charges

Fig. 1 Calculated bond lengths and total atomic charges for optimized structures of 7*H*-naphth[3,2,1-*cd*]azulen-7-one **10a** (left) and its protonated structure **13** (right) by Gaussian 98 using RHF/6-31G*.
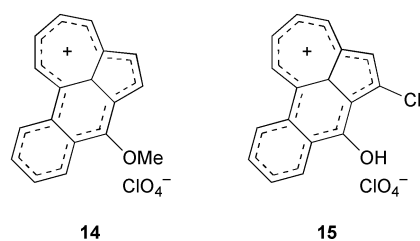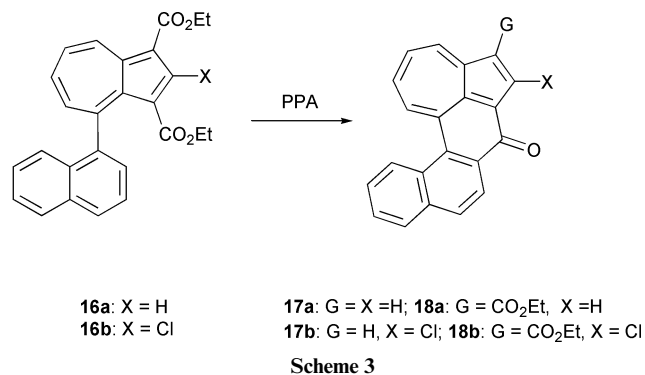

**14**   **15**

Chart 2

the seven-membered ring has slightly cationic character; the results indicate that **10a** has some heptafulvene character as well as dipolar character. The atomic charges of **10a** suggest that the C-5 position (−0.039) would be reactive towards electrophiles, and C-2 (0.053), C-3 (0.011) and C-4 (0.043) towards nucleophiles. In the molecular diagram of **13**, the bond length of C=O was lengthened (1.313 Å). The bond lengths of the seven-membered ring (1.380–1.398 Å) did not show any bond alternation, and the atomic charges of the carbons of the seven-membered ring are cationic. These inspections of the bond lengths and the total atomic charges of the cation **13** show that a resonance form **13C** is the main contributor to the ground state of **13**. This supports the interpretation of the spectral data.

We next examined the cyclization of two diethyl 4-(α-naphthyl)azulene-1,3-dicarboxylates (**16a**, **16b**). Treatment of **16a** with hot PPA for 6 h gave 7*H*-azuleno[1,8-*bc*]phenanthren-7-ones (**17a** and **18a**) in 7% and 60% yield, respectively (Scheme 3). In the ¹H NMR spectrum of **17a**, a couple of AB doublets were seen at δ 8.07 and 8.63 (*J* 8.4 Hz) and this shows that the condensation occurred at the 2-position of the naphthalene moiety of **16a**. In the IR spectra of **17a** and **18a**, the lower-lying ring-carbonyl absorptions were again seen at

16a: X = H
16b: X = Cl

17a: G = X =H; **18a**: G = CO₂Et, X =H
17b: G = H, X = Cl; **18b**: G = CO₂Et, X = Cl

Scheme 3

1610 and 1627 cm⁻¹. These findings are consistent with the assignments of **17a** and **18a** as 7*H*-azuleno[1,8-*bc*]phenanthren-7-ones. Similarly, treatment of **16b** with PPA gave **17b** and **18b**. The results of some reactions of **16a** and **16b** are listed in Table 1.

In similar manner, we examined a cyclization of diethyl 4,8-diphenylazulene-1,3-dicarboxylates. Treatment of **19a** with PPA at 100 °C for 5 h gave the desired 6-methyl-5,7-dihydro-dinaphth[3,2,1-*cd*:1′,2′,3′-*ij*]azulene-5,7-dione **20a** in 68% yield (Scheme 4). The mass spectrum of **20a** showed a

19a : R = Me
19b : R = Cl

20a : R = Me
20b : R = Cl
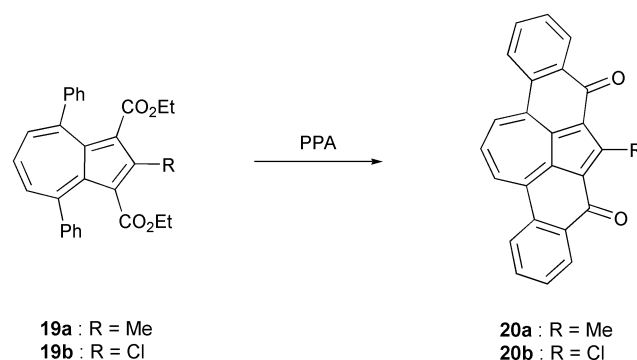
Scheme 4

molecular-ion peak at *m/z* 346, and in the IR spectrum two coupled carbonyl signals were seen at *ν* 1642 and 1621 cm⁻¹. In the ¹H NMR spectrum, signals appeared at δ 3.83 (3H, s), 7.20–7.80 (6H, m), 7.83 (1H, t, *J* 10.4) and 8.20–8.60 (4H, m). These were consistent with the structure assigned. Similar treatment of **19b** with PPA gave **20b** in only 10% yield.

To increase the yield, we next examined the cyclization of ethyl 4,6-diphenyl-7-oxo-7*H*-naphth[3,2,1-*cd*]azulene-5-carboxylate **21** with PPA and obtained 6-phenyl-5,7-dihydro-dinaphth[3,2,1-*cd*: 1′,2′,3′-*ij*]azulene-5,7-dione **20c** in 70% yield (Scheme 5).

21

20c : R = Ph
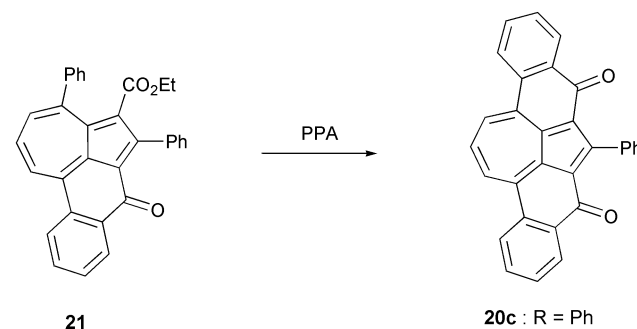
Scheme 5

The electronic spectrum of **20a** in trifluoroacetic acid differs from that in chloroform and resembles that of 7*H*-naphth-[3,2,1-*cd*]azulen-7-one **10a** in conc. sulfuric acid. The spectrum

of **20a** in conc. sulfuric acid differs from that in trifluoroacetic acid; the maxima of longest wavelength shifted to shorter wavelength and strengthened. These suggest the generation of both monocation and dication species. In the ^{1}H NMR spectrum of **20c** in trifluoroacetic acid, the ring signals resonated at rather low field, except for the phenyl group at C-6, at δ 7.90–8.20 (4H, m, H-2, -3, -9 and -10), 8.50–9.00 (4H, m, H-1, -4, -8 and -11), 8.99 (1H, t, J 11.0, H-13) and 9.73 (2H, d, J 11.0, H-12 and -14), whereas those of **20c** in sulfuric acid resonated at slightly higher field then those of the monocation, at δ 7.60–8.60 (8H, m, ArH), 8.85 (1H, t, J 11.0, H-13) and 9.45 (2H, d, J 11.0, H-12 and -14). This suggests that the dication has the nature of an antiaromatic pericyclic conjugated 20π system.

To complement our analysis of the nature of the monocation and the dication, the structures of **20a**, the monoprotonated cation **22** and the diprotonated cation **23** were studied by *ab initio* molecular orbital calculations by Gaussian 98 using RHF/6-31G*. The bond lengths and the atomic charges show that **20a** deviates slightly from symmetry and that the bond alternation is small. In addition the bond lengths of the carbonyl groups are both 1.024 Å. Total atomic charge showed that the seven-membered ring is slightly positive. These data show that **20a** has inherently a 1,3-dibenzoylazulene-like character rather than peripheral conjugation. When consideration of the molecular orbital calculations on the monocation **22**, the bond length of C=O$^+$–H was lengthened into 1.314 Å and that of C=O was shortened to 1.198 Å. The divergence of the bond lengths of the seven-membered ring is very small (1.383–1.397 Å). These data suggest that the contribution of the resonance form **22B** is large. The structure of dication **23** has a symmetric feature and the bond lengths of C=O$^+$–H are both 1.297 Å; the bond length of the C=O bond of the protonated carbonyl is lengthened. The cationic charge is distributed over all of the ring carbons including the benzene ring, and the atomic charge on the oxygen is only -0.164. These suggest that the resonance form **23B**, a 20π peripheral structure, contributes to the ground state as does **23** (see Chart 3).

Experimental

Mps are uncorrected. ^{1}H NMR spectra (60 MHz) were recorded on a Varian A-60D spectrometer (60 MHz) and a Varian HA100 spectrometer (100 MHz), and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400S (100.6 MHz) using deuteriochloroform as solvent with tetramethylsilane as internal standard unless otherwise stated; *J*-values are recorded in Hz. Electronic spectra were taken with an Hitachi EPS-3 spectrophotometer. IR spectra were recorded for KBr pellets on a Shimadzu IR-27 infracord unless otherwise stated. Mass spectra were taken with an Hitachi RMU-6D mass spectrometer at 25 eV. Kieselgel 60 and Wako-gel C-200 were used for column chromatography.

Cyclization of diethyl 4-phenylazulene-1,3-dicarboxylates with PPA

Typical procedure. (a) A solution of diethyl 4-phenylazulene-1,3-dicarboxylate [19,20] **11a** (0.110 g) in PPA (5 ml) was heated on a water-bath at 100 °C for 7 h. Water was added to the mixture which was then extracted with chloroform; then the extract was washed with water, dried over sodium sulfate, and evaporated. The residue was subjected to silica gel column chromatography. Elution with chloroform gave 7*H*-naphth-[3,2,1-*cd*]azulen-7-one **10a** (0.007 g, 10%) and ethyl 7-oxo-7*H*-naphth[3,2,1-*cd*]azulene-5-carboxylate **12a** (0.041 g, 60%), successively.

(b) A solution of diethyl 4-phenylazulene-1,3-dicarboxylate **11a** (0.220 g) in PPA (5 ml) was set aside for 2 days at room temperature, and worked up as above. Chromatography of the residue with chloroform gave **10a** (0.170 g, 67%).

Chart 3
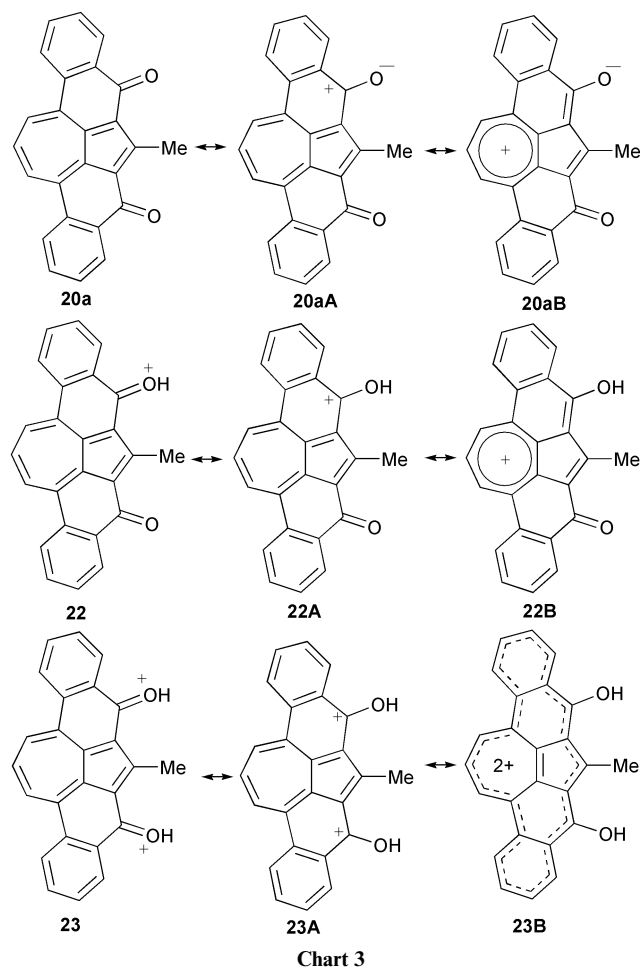
(c) A mixture of **11a** (0.900 g) in ethanol (100 ml) and potassium hydroxide (1.00 g) in water (20 ml) was refluxed for 1 h, then neutralized with hydrochloric acid. The resultant precipitate was collected by filtration and dried *in vacuo*. A mixture of the solid and PPA was heated on a water-bath at 100 °C for 3 h, and worked up as above. Chromatography of the residue with chloroform gave **10a** (0.360 g, 61%).

10a: Blue needles (from cyclohexane), mp 146.5–147 °C; δ_C 122.60, 125.67, 125.82, 126.18, 127.97, 130.21, 130.96, 131.72, 136.11, 136.15, 136.42, 137.27, 137.92, 137.97, 138.36, 147.39 and 179.22; ν_{max}/cm^{-1} 1629 (C=O); λ_{max} (chloroform)/nm (log ε) 260 (4.40), 264 (4.41), 287 (4.31), 300 (4.28), 308 (4.24), 355 (3.71), 373 (3.89), 393 (3.97), 418 (3.60), 570 (2.91), 585 (2.90), 614 (2.89) and 670 (2.54); λ_{max} (conc. H$_2$SO$_4$) nm (log ε) 230 (4.37), 257 (4.38, sh), 276 (4.74), 322 (4.18), 352 (3.81, sh), 399 (3.97), 437 (3.86) and 496 (3.52); *m/z* (rel. intensity) 230 (M$^+$, 100), 202 (70), 201 (17), 200 (27), 199 (6), 198 (5), 176 (6), 175 (6) and 174 (7) (Found: C, 88.3; H, 5.2. C$_{17}$H$_{10}$O requires C, 88.7; H, 4.9%).

12a: Violet prisms (from ethanol), mp 185–187 °C; δ_C 14.87, 60.74, 121.14, 124.14, 126.03, 128.19, 128.30, 131.53, 132.40, 133.08, 135.72, 136.19, 138.82, 139.44, 139.66, 140.01, 142.32, 145.56, 165.32 and 179.49; ν_{max}/cm^{-1} 1704 and 1637 (C=O); λ_{max} (chloroform)/nm (log ε) 271 (4.73), 298 (4.71), 312 (4.53), 375 (4.21), 391 (4.26), 550 (3.15), 578 (3.19) and 625 (2.89); λ_{max} (conc. H$_2$SO$_4$)/nm (log ε) 257 (4.39), 283 (4.77), 295 (4.71), 328 (4.43), 395 (3.98), 435 (3.97) and 485 (3.77); *m/z* (rel. intensity) 302 (M$^+$, 74), 274 (16), 257 (100), 246 (3), 230 (30), 229 (18), 202 (14), 201 (35), 200 (57) and 174 (8) (Found: C, 79.1; H, 4.9. C$_{20}$H$_{14}$O$_3$ requires C, 79.4; H, 4.7%).

Similar treatment of **11b–11d**, **16a** and **16b** gave corresponding compounds (**10b–10d** and **12b–12d**, **17a**, **17b** and **18a**, **18b**), respectively. Results are listed in Table 1.

10b: Blue-violet needles (from ethanol), mp 190–191 °C; δ_C 121.39, 125.57, 126.93, 128.08, 131.02, 131.18, 131.27, 131.99, 135.62, 136.05, 137.11, 137.25, 143.46, 143.98 and 178.12; ν_{max}/cm^{-1} 1631 (C=O); λ_{max} (chloroform)/nm (log ε) 261 (4.88), 292 (4.80), 299 (4.28), 308 (4.91), 382 (4.43), 402 (4.49), 550 (3.19), 578 (3.24) and 673 (2.97); λ_{max} (conc. H$_2$SO$_4$)/nm (log ε) 230 (4.42), 255 (4.38), 277 (4.78), 327 (4.28), 408 (3.97), 437 (3.98) and 494 (3.51); m/z (rel. intensity) 266 (M$^+$, 38), 264 (M$^+$, 100), 238 (18), 236 (70), 202 (12), 201 (39), 200 (65), 199 (23), 198 (17), 176 (7), 175 (9) and 174 (17) (Found: C, 77.0; H, 3.4. C$_{17}$H$_9$ClO requires C, 77.4; H, 3.4%).

12b: Red-violet prisms (from ethanol), mp 202.5–204 °C; δ_C 14.84, 61.31, 118.76, 119.34, 125.74, 128.13, 129.01, 131.51, 132.37, 133.71, 135.15, 135.66, 136.92, 138.13, 138.44, 138.53, 143.49, 145.92, 164.42 and 178.08; ν_{max}/cm^{-1} 1692 and 1637 (C=O) ; λ_{max} (chloroform)/nm (log ε) 260 (4.51), 274 (4.63), 297 (4.67), 305 (4.77), 380 (4.12), 401 (4.20), 550 (3.23) and 685 (2.69); λ_{max} (conc. H$_2$SO$_4$)/nm (log ε) 255 (4.38), 284 (4.80), 324 (4.39), 408 (4.01), 436 (4.04) and 510 (3.61); m/z (rel. intensity) 338 (M$^+$, 23), 336 (M$^+$, 64), 310 (4), 308 (11), 293 (32), 291 (89), 266 (24), 265 (19), 264 (65), 263 (18), 238 (5), 237 (6), 236 (15), 235 (11), 201 (20), 200 (100), 199 (27) and 198 (20) (Found: C, 71.4; H, 3.8. C$_{20}$H$_{13}$ClO$_3$ requires C, 71.3; H, 3.9%).

10c: Blue needles (from ethanol), mp 142–143.5 °C; δ_C 18.02, 122.95, 123.24, 125.35, 125.74, 127.63, 130.40, 130.54, 131.46, 135.50, 135.88, 136.23, 136.39, 137.31, 145.92, 155.88 and 179.97; ν_{max}/cm^{-1} 1620 (C=O); λ_{max} (chloroform)/nm (log ε) 262 (4.46), 288 (4.41), 300 (4.39), 309 (4.39), 335 (3.80, sh), 358 (3.82), 377 (4.04), 399 (4.14), 416 (3.81), 559 (3.04), 598 (3.05), 633 (2.78, sh) and 653 (2.71, sh) (Found: C, 88.5; H, 5.0. C$_{18}$H$_{12}$O requires C, 88.5; H, 5.0%).

12c: Red-violet prisms (from ethanol), mp 180–181 °C; δ_C 14.93, 17.34, 60.75, 120.14, 122.30, 125.54, 127.85, 128.08, 130.99, 131.93, 133.07, 135.76, 136.13, 136.96, 137.17, 137.47, 138.56, 145.36, 160.03, 166.23 and 180.31; ν_{max}/cm^{-1} 1680 and 1628 (C=O) ; λ_{max} (chloroform)/nm (log ε) 272 (4.60), 301 (4.68), 308 (4.51, sh), 356, (3.91), 375 (4.11), 398 (4.20), 540 (3.08, sh), 563 (3.11) and 604 (2.88, sh) (Found: C, 79.7; H, 5.1. C$_{21}$H$_{16}$O$_3$ requires C, 79.6; H, 5.2%).

10d: Green needles (from ethanol), mp 194.5–146 °C; δ_C 121.53, 123.67, 125.47, 126.32, 128.10, 128.33, 129.31, 130.03, 130.61, 130.95, 131.63, 135.99, 136.55, 136.69, 137.15, 137.54, 137.78, 145.79, 155.57 and 179.06; ν_{max}/cm^{-1} 1623 (C=O); λ_{max} (chloroform)/nm (log ε) 263 (4.55), 290 (4.39), 312 (4.49), 390 (4.14), 410 (4.16), 564 (3.24), 603 (3.32) and 653 (3.04); m/z (rel. intensity) 306 (M$^+$, 53), 304 (100), 276 (7), 230 (1) and 202 (2) (Found: C, 90.2; H, 4.6. C$_{23}$H$_{14}$O requires C, 90.2; H, 4.6%).

12d: Violet prisms (from ethanol), mp 222–224 °C; δ_C 13.96, 60.68, 121.51, 121.76, 125.74, 127.90, 128.17, 128.84, 131.40, 132.13, 132.92, 135.76, 136.50, 137.57, 138.25, 138.95, 139.32, 144.71, 157.42, 166.20 and 179.21; ν_{max}/cm^{-1} 1686 and 1627 (C=O) ; λ_{max} (chloroform)/nm (log ε) 270 (4.56), 301 (4.62), 310 (4.52), 380 (4.08), 399 (4.13), 540 (3.10), 568 (3.16) and 610 (2.90); m/z (rel. intensity) 378 (M$^+$, 88), 377 (100), 350 (38), 349 (99), 333 (24), 306 (15), 305 (49) and 276 (6) (Found: C, 82.5; H, 4.8. C$_{26}$H$_{18}$O$_3$ requires C, 82.5; H, 4.7%).

17a: Green needles (from ethanol), mp 216–217 °C; δ_H 7.29 (1H, d, J 6.6, H-9), 8.07 (1H, d, J 8.4, H-5), 8.48 (1H, d, J 6.6, H-8), 8.63 (1H, d, J 8.4, H-6), 7.50–7.80 (3H, m, H-2, -3 and -11), 7.85–8.20 (3H, m, H-1, -4, -12) and 8.30–8.80 (2H, m, H-10 and -13); ν_{max}/cm^{-1} 1610 (C=O); λ_{max} (chloroform)/nm (log ε) 271 (4.49), 292 (4.49), 332 (4.22), 390 (4.04, sh), 407 (4.22), 442 (3.75), 465 (3.74), 595 (3.05) and 640 (3.03); λ_{max} (conc. H$_2$SO$_4$)/ nm (log ε) 214 (4.57), 265 (4.65), 285 (4.51, sh), 366 (4.25), 390 (4.23) and 510 (3.85) (Found: C, 89.9; H, 4.1. C$_{21}$H$_{12}$O requires C, 90.0; H, 4.3%).

18a: Violet needles (from ethanol), mp 241–242.5 °C; δ_H 1.48 (3H, t, J 7.2, CH$_3$), 4.48 (2H, q, J 7.2, CH$_2$), 7.50–8.80 (7H, m, H-1, -2, -3, -4, -11, -12 and -13), 8.12 (1H, d, J 8.7, H-5), 8.63

(1H, d, J 8.7, H-6), 8.99 (1H, s, H-8) and 9.80–10.05 (1H, m, H-10); δ_H (CF$_3$CO$_2$H) 1.66 (3H, t, J 7.2, CH$_3$), 4.73 (2H, q, J 7.2, CH$_2$), 7.80–9.10 (6H, m, H-1, -2, -3, -4, -11 and -12), 7.98 (1H, d, J 8.0, H-5), 8.48 (1H, d, J 8.0, H-6), 9.20 (1H, s, H-8), 9.47–9.75 (1H, m, H-13) and 10.07–10.35 (1H, m, H-10); ν_{max}/cm^{-1} 1707 and 1627 (C=O); λ_{max} (chloroform)/nm (log ε) 281 (4.57), 303 (4.76), 315 (4.50, sh), 386 (4.08, sh), 403 (4.18), 470 (3.97), 560 (3.09), 590 (3.07, sh) and 650 (2.85, sh); λ_{max} (conc. H$_2$SO$_4$)/nm (log ε) 215 (4.52), 248 (4.39), 272 (4.43), 285 (4.43), 329 (4.52), 360 (4.40, sh), 398 (4.16, sh) and 511 (4.04) (Found: C, 82.2; H, 4.7. C$_{24}$H$_{16}$O$_3$ requires C, 81.8; H, 4.6%).

17b: Green needles (from ethanol), mp 210–211 °C; δ_H 7.13 (1H, s, H-9), 7.40–8.10 (5H, m, H-1, -2, -3, -4 and -11), 7.99 (1H, d, J 8.5, H-5), 8.20–8.60 (3H, m, H-10, -12 and -13) and 8.55 (1H, d, J 8.5, H-6); ν_{max}/cm^{-1} 1625 (C=O); λ_{max} (chloroform)/nm (log ε) 272 (4.46), 292 (4.44), 321 (4.24, sh), 336 (4.30), 395 (3.96, sh), 412 (4.04), 463 (3.89), 568 (3.06), 606 (3.04) and 652 (2.77, sh) (Found: C, 79.9; H, 3.7. C$_{21}$H$_{11}$ClO requires C, 80.1; H, 3.5%).

18b: Brown needles (from ethanol), mp 220–221 °C; δ_H 1.50 (3H, t, J 7.0, CH$_3$), 4.43 (2H, q, J 7.0, CH$_2$), 7.45–8.05 (5H, m, H-2, -3, -4, -11 and -12), 7.91 (1H, d, J 8.5, H-5), 8.10–8.70 (2H, m, H-1 and -13), 8.36 (1H, d, J 8.5, H-6) and 9.43–9.64 (1H, m, H-10); δ_C 14.84, 61.27, 117.98, 123.23, 127.82, 127.89, 128.89, 129.16, 129.46, 130.48, 132.09, 134.17, 135.11, 135.13, 135.73, 136.52, 136.85, 137.08, 137.25, 138.54, 139.02, 144.54, 164.52 and 177.79; ν_{max}/cm^{-1} 1681 and 1633 (C=O); λ_{max} (chloroform)/nm (log ε) 250 (4.41), 285 (4.47), 300 (4.61), 337 (4.28), 392 (3.80), 409 (3.89), 466 (3.82), 540 (3.01), 568 (3.01, sh) and 615 (2.69) (Found: C, 74.1; H, 4.0. C$_{24}$H$_{15}$ClO$_3$ requires C, 74.5; H, 3.9%).

Deesterification of 12a

A mixture of **12a** (0.100 g) in ethanol (60 ml) and potassium hydroxide (1.00 g) in water (10 ml) was refluxed for 1 h, then neutralized with hydrochloric acid. The resulting precipitate was collected by filtration and dried *in vacuo*. The precipitate was heated at 300 °C under reduced pressure for 30 min. The resulting brown powder was dissolved in chloroform, and chromatography of the solution gave **10a** (0.005 g, 7%).

Synthesis of 7-methoxynaphth[3,2,1-*cd*]azulenium perchlorate 14

A mixture of **10a** (0.070 g) and methyl trifluoromethane-sulfonate (1.50 g) in dichloromethane (20 ml) was stirred for 20 h at room temperature and a reddish brown precipitate (0.072 g) was obtained. The precipitate was dissolved in tri-fluoroacetic acid (3 ml), and the solution was added dropwise to a mixture of acetic acid–70% perchloric acid (10 ml) to give **14** (0.070 g) as red-brown prisms (from trifluoroacetic acid–acetic acid), mp >300 °C; ν_{max}/cm^{-1} 1590 (C=C) and 1082 (ClO$_4^-$) (Found: C, 62.4; H, 3.6. C$_{18}$H$_{13}$ClO$_5$ requires C, 62.7; H, 3.8%).

Synthesis of 6-chloro-7-hydroxynaphth[3,2,1-*cd*]azulenium perchlorate 15

To a solution of **10b** (0.100 g) in dichloromethane (15 ml) was added 70% perchloric acid (3 ml). The resulting precipitate was collected by filtration, and recrystallized from trifluoroacetic acid–70% perchloric acid to give **15** as red prisms (110 mg), mp >300 °C; ν_{max}/cm^{-1} 3100 (OH), 1610 (C=O), 1593 (C=C) and 1080 (ClO$_4^-$) (Found: C, 56.1; H, 2.8. C$_{17}$H$_{12}$Cl$_2$O$_5$ requires C, 55.9; H, 2.8%).

Cyclization of diethyl 2-methyl-4,8-diphenylazulene-1,3-dicarboxylate 19a with PPA

A solution of **19a** (0.015 g) in PPA (10 ml) was heated on a water-bath at 100 °C for 5 h. Water was added to the mixture which was then extracted with chloroform, and the extract was

washed with water, dried over sodium sulfate, and evaporated. The residue was subjected to silica gel column chromatography. Elution with chloroform gave 6-methyl-5,7-dihydrodinaphth-[3,2,1-*cd*:1′,2′,3′-*ij*]azulene-5,7-dione **20a** (0.008 g, 68%) as green scales (from chloroform), mp >300 °C; δ_H 3.83 (3H, s, CH$_3$), 7.20–7.80 (6H, m, H-1, -2, -3, -9, -10 and -11), 7.83 (1H, t, *J* 10.4, H-13) and 8.20–8.60 (4H, m, H-4, -8, -12 and -14); ν_{max}/cm^{-1} 1642 and 1621 (C=O); λ_{max} (chloroform)/nm (log ε) 278 (4.70), 322 (4.69), 344 (4.40, sh), 375 (4.30), 394 (4.27), 450 (3.57, sh), 552 (3.24, sh), 577 (3.27) and 625 (3.04, sh); λ_{max} (CF$_3$CO$_2$H)/nm (log ε) 299 (4.78), 314 (4.69, sh), 342 (4.24, sh), 364 (4.22), 391 (4.28), 419 (4.12), 523 (3.56, sh), 546 (3.62) and 580 (3.47, sh); λ_{max} (conc. H$_2$SO$_4$)/nm (log ε) 237 (4.65), 305 (4.60, sh), 322 (4.70), 357 (4.31), 415 (4.22), 496 (3.90) and 563 (3.82); *m/z* (rel. intensity) 346 (M$^+$, 100), 318 (10) and 290 (25) (Found: C, 86.3; H, 4.2. C$_{25}$H$_{14}$O$_2$ requires C, 86.7; H, 4.1%).

Cyclization of diethyl 2-chloro-4,8-diphenylazulene-1,3-dicarboxylate 20b with PPA

A solution of **20b** (0.030 g) in PPA (10 ml) was heated on a water-bath at 100 °C for 10 h. Water was added to the mixture which was then extracted with chloroform, and the extract was washed with water, dried over sodium sulfate, and evaporated. The residue was subjected to silica gel column chromatography. Elution with chloroform gave 6-chloro-5,7-dihydrodinaphth-[3,2,1-*cd*:1′,2′,3′-*ij*]azulene-5,7-dione **20b** (0.004 g, 10%) as green needles (from chloroform), mp >300 °C; δ_H (CF$_3$CO$_2$H) 8.30–8.80 (6H, m, H-1, -2, -3, -9, -10 and -11) and 8.90–9.60 (5H, m, H-4, -8, -12, -13 and -14); ν_{max}/cm^{-1} 1655 and 1610 (C=O); *m/z* (rel. intensity) 368 (M$^+$, 38), 366 (M$^+$, 100), 340 (4), 338 (13), 312 (9) and 310 (27) (Found: C, 78.3; H, 3.2. C$_{24}$H$_{11}$ClO$_2$ requires C, 78.6; H, 3.0%).

Cyclization of ethyl 4,6-diphenyl-7-oxo-7*H*-naphth[3,2,1-*cd*]-azulene-5-carboxylate 21 with PPA

A solution of **21**[21] (0.180 g) in PPA (30 ml) was heated on a water-bath at 100 °C for 8 h. Water was added to the mixture which was then extracted with chloroform, and the extract was washed with water, dried over sodium sulfate, and evaporated. The residue was subjected to silica gel column chromatography. Elution with chloroform gave 6-phenyl-5,7-dihydrodinaphth-[3,2,1-*cd*; 1′,2′,3′-*ij*]azulene-5,7-dione **20c** (0.110 g, 70%) as green scales (from chloroform), mp >300 °C; δ_H (CF$_3$CO$_2$H) 7.90 (5H, br s, Ph), 7.90–8.20 (4H, m, H-2, -3, -9, -10), 8.50–9.00 (4H, m, H-1, -4, -8 and -11), 8.99 (1H, t, *J* 11.0 H-13) and 9.73 (2H, d, *J* 11.0, H-12 and -14); δ_H (H$_2$SO$_4$–DSS) 7.51 (5H, br s, Ph), 7.60–8.60 (8H, m, H-1, -2, -3, -4, -8, -9, -10 and -11), 8.85 (1H, t, *J* 11.0 H-13) and 9.45 (2H, d, *J* 11.0, H-12 and -14); ν_{max}/cm^{-1} 1650 and 1621 (C=O); λ_{max} (chloroform)/nm (log ε) 276 (4.35), 323 (4.26), 480 (2.93), 555 (2.80), 587 (2.91) and 630 (2.69); λ_{max} (CF$_3$CO$_2$H)/nm (log ε) 302 (4.66), 315 (4.58, sh), 373 (4.09, sh), 391 (4.16), 520 (3.52, sh), 553 (3.58) and 593 (3.40, sh); λ_{max} (conc H$_2$SO$_4$)/nm (log ε) 236 (4.14, sh), 305 (4.58, sh), 325 (4.76), 359 (4.26, sh), 413 (4.22), 525 (4.14, sh), 536 (4.14) and 578 (3.76); *m/z* (rel. intensity) 408 (M$^+$, 100), 407 (87) and 379 (17) (Found: C, 88.3; H, 4.2. C$_{30}$H$_{16}$O$_2$ requires C, 88.2; H, 4.0%).

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