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The synthesis of some azuleno[*c*]furans

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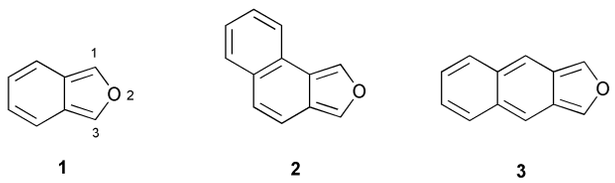
Azuleno[5,6-*c*]furan and 4-chloroazuleno[4,5-*c*]furan have been prepared by a tandem cycloaddition–cycloreversion strategy. These azulenofurans are qualitatively more stable than isobenzofuran and were characterised spectroscopically and as their Diels–Alder adducts with *N*-methylmaleimide.

Introduction

Isobenzofuran **1** and its derivatives are theoretically interesting compounds whose preparations and properties have been extensively reviewed.[1] Although **1** has been characterized spectroscopically,[2–5] it has only a brief lifetime at or near room temperature, and the reactivity of **1** can be attributed to its *o*-xylylenoid character, which results in the propensity for **1** to undergo addition across the 1,3-positions. The driving force for this addition is the generation of a benzenoid aromatic system.[6,7] Angular fusion of a benzene ring to **1**, as in naphtho[1,2-*c*]furan **2**, stabilises the system, whereas linear fusion, as in naphtho[2,3-*c*]furan **3**, leads to increased reactivity, since in the case of **2** only the second benzenoid ring of a naphthalene system is generated upon 1,3-addition, while in **3** a complete naphthalene moiety is created (Scheme 1).[6a]

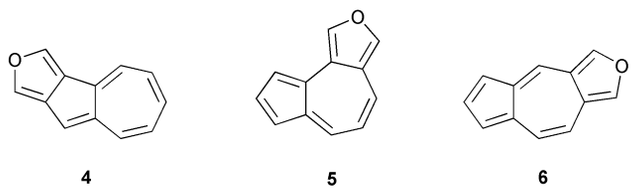


1 **2** **3**

Scheme 1

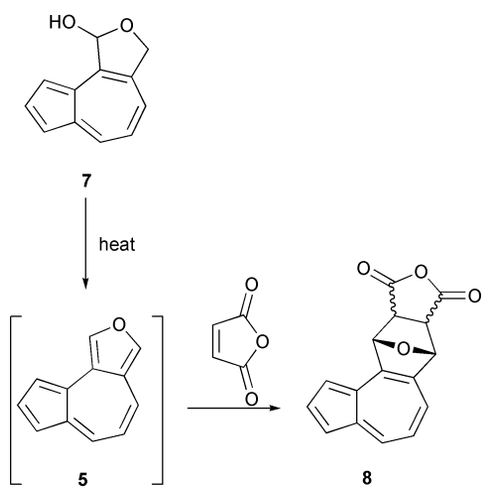
The fusion of the *c*-bond of furan to azulene generates three isomers: azuleno[1,2-*c*]furan **4**, azuleno[4,5-*c*]furan **5** and azuleno[5,6-*c*]furan **6**. On the basis of three different computational methods, Nikolic and co-workers concluded that **4** should be the least stable of these isomers.[8] However, the azulenofurans **4**, **5** and **6** may turn out to be less reactive than isobenzofuran and the naphtho[*c*]furans **2** and **3** as the resonance energy of azulene is lower than that of benzene and naphthalene.[9] Although there are many reported values for the resonance energy of azulene,[9a] on the basis of the Dewar model which uses 1,3-butadiene as a 'normal' reference polyene the resonance energy of azulene is 16.1 kcal mol^{-1}, while that of benzene is 26.1 kcal mol^{-1} and the value for naphthalene is 40.7 kcal mol^{-1}.[9b] In view of this, the driving force for the addition across the 1,3-positions of the furan moieties of **4**, **5** and **6** should be reduced compared to isobenzofuran and naphtho[2,3-*c*]furan **3**, possibly allowing for the isolation of these azuleno[*c*]furans under normal laboratory conditions (Scheme 2).

In contrast to the extensive literature pertaining to isobenzofuran and its benzo-fused derivatives,[1] little experimental work has been reported on azuleno[*c*]furans. Ebine and co-workers generated azuleno[4,5-*c*]furan **5** *in situ* by heating the hemiacetal **7** in the presence of maleic anhydride and obtained the *endo* and *exo* adducts **8** in 20 and 49% yield respectively (Scheme 3).[10] However, to date none of the azuleno[*c*]furans nor their derivatives have been isolated or characterised spectroscopically.



4 **5** **6**

Scheme 2

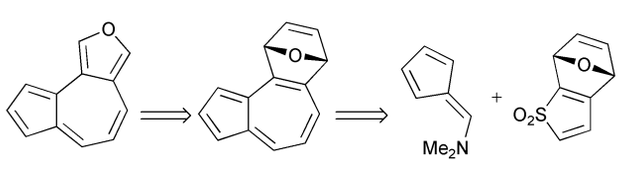


endo:*exo* 29:61

Scheme 3

Results and discussion

We envisaged that access to the azulenofurans **4**–**6** should in principle be possible through retro-Diels–Alder reaction of the appropriate epoxy-bridged dihydrobenzazulene. For example, extrusion of the etheno bridge from **9** should deliver azuleno[4,5-*c*]furan **5**, and we wondered whether compound **9** would in turn be accessible from a Houk–Leaver azulene synthesis[11] between the thiophene-1,1-dioxide **11** and 6-*N,N*-dimethylaminofulvene **10** (Scheme 4).



5 **9** **10** **11**

Scheme 4

Synthesis of 4-chloroazuleno[4,5-*c*]furan 27

In an initial effort to prepare the epoxy-bridged sulfone system of **11**, the dibromide **12**[12] was added slowly to a solution of

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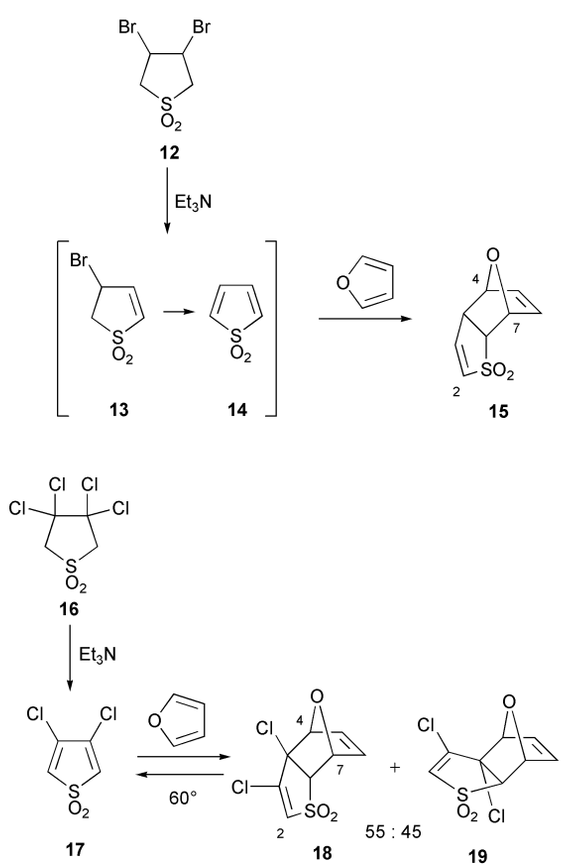
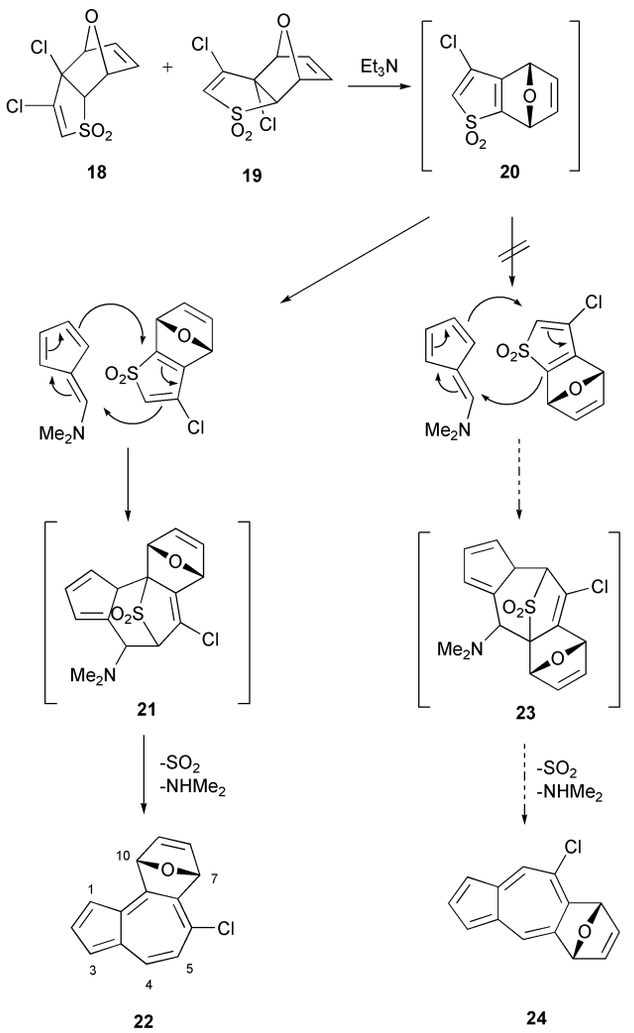
furan and triethylamine over 10 hours. This gave in 18% yield a single product identified as the *endo* adduct **15** since $^3J_{3a,4} = 4.7$ Hz and $^3J_{7,7a} = 4.8$ Hz, indicating an *exo* orientation of 3a-H and 7a-H within the 7-oxabicyclo[2.2.1]hept-2-enyl system. Adduct **15** arises either by trapping of the reactive thiophene-1,1-dioxide **14** by furan, or by dehydrobromination of the adduct derived from furan and the presumed intermediate **13**. It should be noted that Nakayama and co-workers found that thiophene-1,1-dioxide **14**, generated by oxidation of thiophene with dimethyldioxirane, preferentially dimerises rather than form an adduct with furan.[13] However, in the present case **14** was generated under conditions of high dilution in the presence of a large excess of furan, which should favour interception over dimerisation. Several attempts to convert adduct **15** into **11** by functionalisation α to the sulfone, followed by elimination, were unrewarding. Thus although **15** is not useful in the synthesis of azulenofurans, its formation suggests that **14** can be intercepted by furan when generated under conditions of high dilution that prevent dimerisation.

The cycloaddition between the more stable 3,4-dichlorothiophene-1,1-dioxide **17**[14] (generated *in situ*) and furan was complete in 4 hours at room temperature, giving a mixture of *endo* and *exo* adducts **18** and **19** in a ratio of 55 : 45 in 75% yield (Scheme 5). The adducts did not undergo dehydrochlorination with triethylamine in dichloromethane at room temperature, conditions previously observed to be effective for the adducts derived from 3,4-dichlorothiophene-1,1-dioxide **17** and 2-diazopropane.[15] At elevated temperatures (>60 °C), cycloreversion to **17** and furan was observed. However, a purple azulene was formed in 25% yield when a solution of the adducts **18** and **19** and 6-*N,N*-dimethylaminofulvene in triethylamine–acetonitrile (1 : 1) was kept at room temperature for four days.



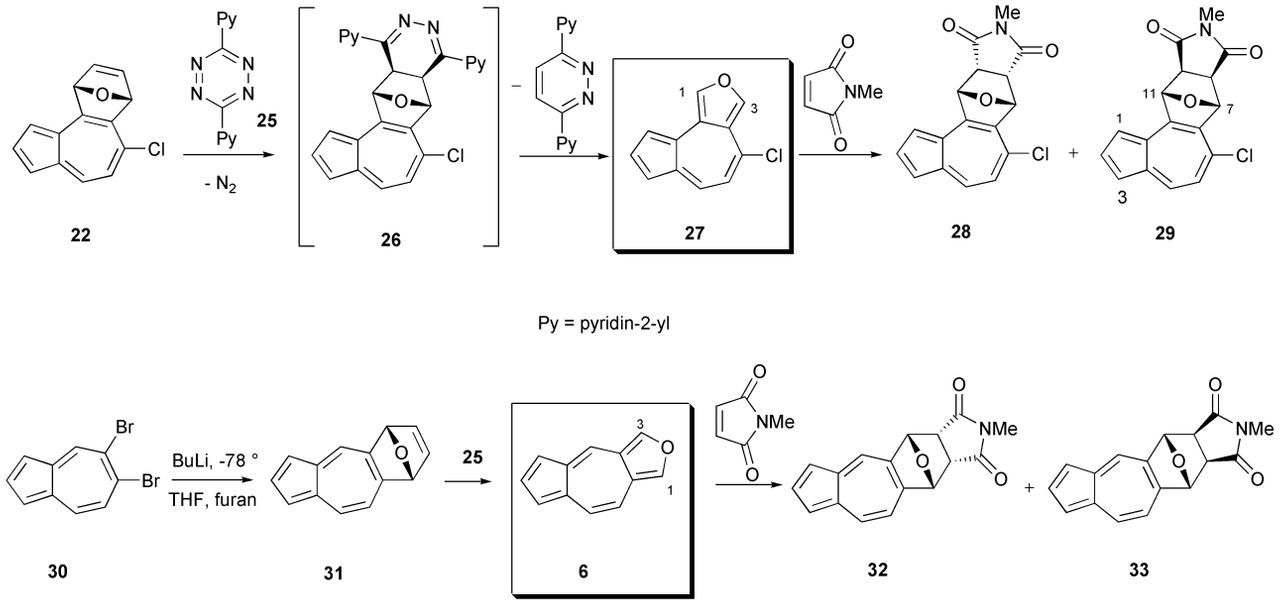
Scheme 5

The azulenic product was identified as the regioisomer **22** by its ^{1}H NMR spectrum. Thus, the 7-oxabicyclo[2.2.1]hepta-2,5-dienyl moiety shows a 4 spin system with 8-H and 9-H (7.07 or 7.17 ppm), $^3J_{8,9} = 5.5$ Hz, coupled to 7-H and 10-H (6.24 or 6.19 ppm), $^3J_{7,8} = {}^3J_{9,10} = 1.8$ Hz. Within the azulene ring system, 2-H, 1-H and 3-H appear as an AMX pattern with coupling constants of 3.9 and 4.3 Hz. The coupling constant between 5-H (6.96 ppm) and 4-H (7.93 ppm), $^3J_{4,5} = 11.2$ Hz, establishes structure **22** and rules out **24** since the magnitude of this coupling constant is typical of a vicinal coupling as required for **22**. The formation of **22** indicates that the [6 + 4] cycloaddition of 6-*N,N*-dimethylaminofulvene **10** and the thiophene dioxide **20** occurred in the regiochemical sense shown in Scheme 6.



Scheme 6

The azulene **22** was treated with 3,6-di(pyridin-2′-yl)-1,2,4,5-tetrazine **25** at room temperature to give 4-chloroazuleno[4,5-*c*]-furan **27** as a yellow–olive green crystalline product in 70% yield *via* the usual cycloaddition–cycloreversion sequence.[2,16] The furan **27** was stable towards rapid radial chromatography, but decomposed within several hours at room temperature. It was fully characterised spectroscopically (see below) and reacted rapidly with *N*-methylmaleimide to give adducts **28** and **29** in a 1 : 1 ratio. The ^{1}H NMR spectrum of the *exo* isomer **29** showed two doublets at 6.21 ppm ($J = 1.0$ Hz) and 6.07 ppm ($J = 1.0$ Hz) ascribable to the two bridgehead protons 7-H and 11-H which mutually couple through a four-bond pathway, and two doublets for 7a-H and 10a-H at 3.24 ppm ($J = 6.7$ Hz) and 3.13 ppm ($J = 6.7$ Hz). The absence of coupling between 7-H, 7a-H and 10a-H, 11-H shows that the dihedral angle between these hydrogens is about 90° by using the Karplus curve. The ^{1}H NMR spectrum of the *endo* adduct **28** showed the bridgehead protons as second order multiplets at δ 6.26 and 6.16 ppm, and 7a-H and 10a-H were observed as a multiplet centered around 3.97 ppm. A further key difference in the ^{1}H NMR spectral properties of **28** and **29** rests in the chemical shifts of the



Scheme 7

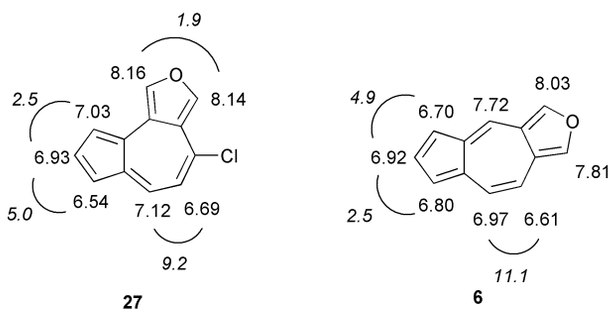
N-methyl groups. Thus the values for **28** (2.18 ppm) and **29** (3.07 ppm) show a difference similar to that observed between the analogous shifts in the *endo* adduct of isobenzofuran and *N*-methylmaleimide (2.39 ppm) and the corresponding *exo* adduct (3.20 ppm) (Scheme 7).[17]

Synthesis of azuleno[5,6-*c*]furan 6

Lemal and coworkers recently reported the preparation of adduct **31** by trapping of 5,6-didehydroazulene with furan.[18] We find that the yield of **31** can be increased from the reported 22 to 42% by using butyllithium instead of phenyllithium as the debrominating agent, and carrying out the reaction at −78 °C instead of ambient temperature. Gratifyingly, treatment of adduct **31** with 3,6-di(pyridin-2′-yl)-1,2,4,5-tetrazine **25** again effected ready extrusion of the etheno bridge and gave azuleno[5,6-*c*]furan **6** as a red crystalline solid in 81% yield. Adducts **32** and **33** were obtained in a 77 : 23 ratio on reaction of **6** with *N*-methylmaleimide.

Spectroscopic properties of 4-chloroazuleno[4,5-*c*]furan 27 and azuleno[5,6-*c*]furan 6

Full assignments of the ^{1}H and ^{13}C NMR signals of **27** and **6** were made with the aid of 2D NMR techniques and the key features of the ^{1}H spectra are summarised in Scheme 8. For **27**, 1-H (8.16 ppm) and 3-H (8.14 ppm) appear as an AB pattern with $^{4}J_{1,3}$ = 1.9 Hz. Similar 4 bond coupling values have been observed between 1-H and 3-H in naphtho[1,2-*c*]furan **2** where $^{4}J_{1,3}$ = 1.5 Hz[6a] although the analogous long range coupling was not observed for **6** due to slight line-broadening. The average value for the aromatic ^{1}H shifts for the precursor **22** (7.52 ppm) has been shifted upfield in **27** (6.86 ppm), showing a reduction in diatropic character of **27** relative to the azulenoid ring system. A similar trend is observed in a comparison of the average shift of the azulenoid protons in **31** (7.72 ppm) and azuleno[5,6-*c*]furan **6** (6.95 ppm). The fixed nature of the double bonds in the ring systems of **27** and **6** is apparent from the large difference observed between $^{3}J_{7,8}$ = 5.0 Hz and $^{3}J_{8,9}$ = 2.5 Hz in the five-membered carbocyclic ring of **27** and the analogous difference between $^{3}J_{6,7}$ = 2.5 Hz and $^{3}J_{7,8}$ = 4.9 Hz for **6**. This can be contrasted with the analogous 3 bond coupling constants observed within a true azulenoid system. For example, in the precursor **22**, J = 3.6 and 4.3 Hz for the related protons, and in azulene itself, $^{3}J_{1,2}$ = 4.0 Hz. The value of 2.5 Hz observed for the coupling constant across the apparent single bonds in the five-membered carbocyclic rings of **27** and **6** is not



Scheme 8 δ_{H} and J values (Hz) for azulenofurans **27** and **6**.

that dissimilar to the corresponding value $^{3}J_{3,4}$ = 1.9 Hz seen in cyclopentadiene[19] and 1.95 Hz in fulvene.[20] In addition, CNDO/2 calculations on azuleno[4,5-*c*]furan **5** reveal the π-HOMO coefficients of the five-membered carbocyclic and furan rings of **5** to resemble those of fulvene and butadiene respectively.[10] Thus although **27** and **6** each contain peripheral 14π electron systems and are aromatic by extension of Hückel's rule, the presence of the furan ring imparts bond fixation on the azulene moiety.

Conclusion

In summary, the general strategy shown in Scheme 4 has resulted in the synthesis and characterisation of 4-chloroazuleno[4,5-*c*]furan **27** and azuleno[5,6-*c*]furan **6**, the first azulene analogues of isobenzofuran. NMR spectral evidence indicates double bond fixation within the azulene moieties of these compounds. Qualitatively, **27** and **6** are more stable than isobenzofuran, but behave in a similar manner with respect to Diels–Alder cycloaddition.

Experimental

Melting points were determined on a Kofler hot stage and are uncorrected. Microanalyses were performed by M. H. W. Laboratories, Phoenix, Arizona. NMR spectra were recorded on Bruker AM 300, ARX 500 and AV 600 spectrometers using $CDCl_3$ as solvent unless otherwise stated. J values are given in Hz. Routine ^{13}C assignments were made with the aid of DEPT experiments and full assignments of the ^{13}C and ^{1}H signals of the azuleno[*c*]furans were derived from HMBC and HsQC measurements. Mass spectra were recorded in the EI mode

using a VG Autospec instrument. Preparative radial chromatography was carried out using a Chromatotron model 7924T system (Harrison Research, Palo Alto, California) using plates coated with Kieselgel 60 PF_{254} gipshaltig (Merk Art. 7749), while rapid silica gel filtrations were performed under water aspirator vacuum using Fluka Kieselgel 60 as adsorbent packed on a sintered glass funnel. In both techniques increasing proportions of ethyl acetate in light petroleum were used as eluting solvents and fractions were monitored by TLC. Organic extracts were dried over anhydrous magnesium sulfate.

(3aα,4α,7α,7aα)-3a,4,7,7a-Tetrahydro-4,7-epoxybenzo[*b*]-thiophene-1,1-dioxide 15

A solution of 3,4-dibromo-2,3,4,5-tetrahydrothiophene-1,1-dioxide[12] (5.56 g, 20.0 mmol) in dichloromethane (70 mL) was slowly added dropwise to a stirred solution of triethylamine (16.7 ml, 0.12 mol) in furan (70 mL). After the addition was completed (*ca*. 10 hours) the mixture was heated under reflux for 30 minutes. The reaction mixture was washed with 1 M HCl solution, dried, concentrated under reduced pressure and subjected to silica gel filtration. Elution with 30% ethyl acetate–light petroleum gave the *adduct* (0.68 g, 18%), which crystallised from dichloromethane–light petroleum as colourless prisms, mp 119–124 °C (decomp.) (Found: C, 52.1; H, 4.5. $C_8H_8O_3S$ requires C, 52.2; H, 4.4%). δ_H (500 MHz) 6.60 (1H, dd, *J* 5.8, 1.7), 6.44 (1H, dd, *J* 6.7, 2.6), 6.31 (1H, dd, *J* 6.7, 1.8), 6.28 (1H, dd, *J* 5.8, 1.8), 5.29 (1H, br d, *J* 4.7), 5.12 (1H, br d, *J* 4.8), 3.89–3.95 (1H, m), 3.87 (1H, dd, *J* 7.7, 4.7). δ_C (75.5 MHz) 138.0 (CH), 134.5 (CH), 134.3 (CH), 133.1 (CH), 79.9 (CH), 79.1 (CH), 60.8 (CH), 50.3 (CH).

(3aα,4α,7α,7aα)-3,3a-Dichloro-3a,4,7,7a-tetrahydro-4,7-epoxybenzo[*b*]thiophene-1,1-dioxide 18 and (3aα,4β,7β,7aα)-3,3a-dichloro-3a,4,7,7a-tetrahydro-4,7-epoxybenzo[*b*]thiophene-1,1-dioxide 19

Triethylamine (15.4 ml, 0.111 mol) was added to a solution of 3,3,4,4-tetrachloro-2,3,4,5-tetrahydrothiophene-1,1-dioxide (11.45 g, 44.4 mmol) in furan (50 mL) and dichloromethane (50 mL) and the mixture stirred overnight. The mixture was poured into 0.5 M HCl solution and extracted with dichloromethane (2×). The organic extracts were washed with brine, dried and concentrated under reduced pressure to give a solid which was subjected to silica gel filtration. Elution with 10% ethyl acetate–light petroleum gave the *exo adduct* **19** (4.33 g, 41%) followed by the *endo adduct* **18** (3.55 g, 34%).

(3aα,4β,7β,7aα)-3,3a-Dichloro-3a,4,7,7a-tetrahydro-4,7-epoxybenzo[*b*]thiophene-1,1-dioxide **19** was recrystallised from dichloromethane–light petroleum to give colourless prisms, mp 168–170 °C (Found: C, 38.4; H, 2.1. $C_8H_6Cl_2O_2S$ requires C, 38.0; H, 2.4%). δ_H (300 MHz) 6.79 (1H, s), 6.70 (1H, dd, *J* 5.8, 1.7), 6.67 (1H, dd, *J* 5.8, 1.7), 5.55 (1H, br s), 5.20 (1H, br s), 3.49 (1H, s). δ_C (75.5 MHz) 146.2 (C), 136.5 (CH), 135.4 (CH), 132.1 (CH), 82.4 (CH), 81.4 (CH), 74.8 (C), 72.3 (CH).

(3aα,4α,7α,7aα)-3,3a-Dichloro-3a,4,7,7a-tetrahydro-4,7-epoxybenzo[*b*]thiophene-1,1-dioxide **18** was recrystallised from dichloromethane–light petroleum to give colourless prisms, mp 126–127 °C (Found: C, 37.9; H, 2.3. $C_8H_6Cl_2O_2S$ requires C, 38.0; H, 2.4%). δ_H (300 MHz) 6.78 (1H, dd, *J* 5.8, 1.7), 6.52 (1H, dd, *J* 5.8, 1.8), 6.47 (1H, d, *J* 1.0), 5.43 (1H, ddd, *J* 4.7, 1.7, 1.1), 5.10 (1H, dd, *J* 1.8, 1.1), 4.32 (1H, dd, *J* 4.7, 1.0). δ_C (75.5 MHz) 145.4 (C), 137.3 (CH), 132.9 (CH), 131.6 (CH), 88.1 (CH), 80.5 (CH), 78.2 (C), 73.7 (CH).

6-Chloro-7,10-dihydro-7,10-epoxybenz[*e*]azulene 22

A solution of the adducts **18** and **19** (0.90 g, 3.80 mmol) and 6-*N*,*N*-dimethylaminofulvene (0.45 g, 3.72 mmol) in acetonitrile (3 mL) and triethylamine (3 mL) was allowed to stand in the dark for 4 days. The resulting black mixture was adsorbed onto silica and subjected to silica gel filtration (2.5% ethyl acetate–light petroleum) to give the *azulene* as a purple oil (221 mg, 25%). An analytical sample was obtained by crystallisation from light petroleum to give purple prisms, mp 50–51 °C (Found: C, 73.7; H, 4.2. $C_{14}H_9ClO$ requires C, 73.5; H, 4.0%). Mass spectrum *m*/*z* 230 (M + 2, 20%), 228 (M, 62), 204 (12), 202 (45), 201 (21), 200 (24), 199 (58), 166 (14), 165 (100), 164 (43), 163 (49), 162 (13), 160 (21), 139 (26), 96 (27), 84 (36). δ_H (300 MHz) 7.93 (1H, d, *J* 11.2), 7.75 (1H, dd, *J* 3.6, 4.3), 7.37 (1H, d, *J* 3.6), 7.28 (1H, d, *J* 4.3), 7.17 (1H, dd, *J* 5.5, 1.8), 7.07 (1H, dd, *J* 5.5, 1.8), 6.96 (1H, d, *J* 11.2), 6.24 (1H, dd, *J* 1.8, 1.5), 6.19 (1H, dd, *J* 1.8, 1.5). δ_C (75.5 MHz) 152.9 (C), 142.2 (CH), 139.2 (CH), 138.2 (C), 137.0 (CH), 136.8 (C), 134.8 (C), 132.9 (C), 132.0 (CH), 122.7 (CH), 121.5 (CH), 114.1 (CH), 84.7 (CH), 84.3 (CH).

4-Chloroazuleno[4,5-*c*]furan 27

3,6-Di(pyridin-2′-yl)-1,2,4,5-tetrazine **25** (70 mg, 0.30 mmol) was added to a solution of 6-chloro-7,10-dihydro-7,10-epoxybenz[*e*]azulene **22** (63 mg, 0.28 mmol) in dry dichloromethane (10 mL) and the solution stirred until the starting material was consumed (*ca*. 30 minutes). The reaction mixture was concentrated without heating and subjected to rapid radial chromatography. Elution with light petroleum gave the *furan* as a yellow–green crystalline solid (39 mg, 70%) of indefinite mp (Found: *M* 202.0189. $C_{12}H_7ClO$ requires 202.0185). Mass spectrum *m*/*z* 204 (M + 2, 33%), 203 (13), 202 (M, 100), 173 (12), 139 (76), 138 (17), 137 (10), 71 (16), 69 (15), 57 (44), 56 (53). δ_H (600 MHz) 8.16 (1H, d, *J* 1.9, 1-H), 8.14 (1H, d, *J* 1.9, 3-H), 7.11 (1H, d, *J* 9.2, 6-H), 7.01–7.04 (1H, m, 9-H), 6.93 (1H, dd, *J* 5.0, 2.5, 8-H), 6.69 (1H, d, *J* 9.2, 5-H), 6.55 (1H, dd, *J* 5.0, 1.4, 7-H). δ_C (151 MHz) 145.1 (C, C-6a), 144.7 (CH, C-3), 138.9 (CH, C-1), 134.7 (C, C-4), 132.4 (CH, C-8), 131.1 (CH, C-6), 123.3 (C, C-3a), 123.1 (C, C-9a), 122.3 (CH, C-7), 121.7 (CH, C-9), 121.6 (CH, C-5), 119.8 (C, C-9b). Electronic spectrum (hexane) λ_{max} (log ε) 231 (4.13), 250 (4.08), 258 (4.09), 285 (4.06), 390 (3.90), 410 (3.93), 434 (3.72), 547 (2.31) nm.

Diels–Alder cycloaddition between 4-chloroazuleno[4,5-*c*]furan 27 and *N*-methylmaleimide

N-Methylmaleimide (26 mg, 0.23 mmol) was added to a solution of 4-chloroazuleno[4,5-*c*]furan (46 mg, 0.23 mmol) in anhydrous dichloromethane (5 mL), and the solution was stirred at room temperature for 1 hour during which the colour changed from green to blue. The reaction mixture was concentrated under reduced pressure and subjected to radial chromatography. Elution with 20–50% ethyl acetate–light petroleum gave the *exo adduct* **29** as a blue crystalline solid (32 mg, 44%) and the *endo adduct* **28** as a purple–blue crystalline solid (31 mg, 43%).

(7α,7aβ,10aβ,10α)-6-Chloro-9-methyl-7,7a,10a,11-tetrahydro-7,11-epoxy-9*H*-azuleno[4,5-*f*]isoindole-8,10-dione **29** was recrystallised from ethyl acetate–light petroleum to give blue prisms, mp 239–241 °C (Found: M 313.0504. $C_{17}H_{12}ClNO_3$ requires 313.0506). Mass spectrum *m*/*z* 315 (M + 2, 11%), 313 (M, 30), 285 (11), 204 (32), 203 (100), 165 (12), 163 (11), 139 (40), 86 (10), 82 (13), 69 (11), 57 (10). δ_H (300 MHz) 8.14 (1H, d, *J* 10.8), 7.95 (1H, dd, *J* 3.6, 4.0), 7.52 (1H, br d, *J* 4.0), 7.48 (1H, br d, *J* 3.6), 7.21 (1H, d, *J* 10.8), 6.21 (1H, d, *J* 1.0), 6.06 (1H, d, *J* 1.0), 3.24 (1H, d, *J* 6.7), 3.13 (1H, d, *J* 6.7), 3.07 (3H, s). δ_C (75.5 MHz) 175.6 (CO), 175.2 (CO), 147.0 (C), 138.9 (CH), 138.3 (C), 136.3 (C), 134.7 (C), 133.6 (CH), 129.8 (C), 122.5 (CH), 122.1 (CH), 115.7 (CH), 84.2 (CH), 84.1 (CH), 50.0 (CH), 48.3 (CH), 25.5 (CH_3).

(7α,7aα,10aα,10α)-6-Chloro-9-methyl-7,7a,10a,11-tetrahydro-7,11-epoxy-9*H*-azuleno[4,5-*f*]isoindole-8,10-dione **28** was recrystallised from ethyl acetate–light petroleum to give blue prisms, mp 234–235 °C (Found: *M* 313.0496. $C_{17}H_{12}ClNO_3$ requires 313.0506). Mass spectrum *m*/*z* 315 (M + 2, 11%), 313

(M, 31), 285 (11), 205 (11), 204 (34), 203 (14), 202 (100), 200 (11), 165 (15), 163 (11), 139 (42), 86 (12), 84 (23), 82 (14), 81 (10), 69 (18), 57 (19). δ_H (300 MHz) 8.07 (1H, d, *J* 10.8), 7.93 (1H, dd, *J* 3.8, 3.8), 7.38–7.47 (2H, m), 7.15 (1H, d, *J* 10.8), 6.22–6.31 (1H, m), 6.12–6.20 (1H, m), 3.92–4.03 (2H, m), 2.18 (3H, s). δ_C (300 MHz) 173.0 (CO), 172.6 (CO), 144.1 (C), 139.2 (CH), 137.9 (C), 136.6 (C), 133.4 (CH), 132.3 (C), 130.6 (C), 122.5 (CH), 121.8 (CH), 117.2 (CH), 83.1 (CH), 82.9 (CH), 50.1 (CH), 48.6 (CH), 24.0 (CH_3).

5,8-Dihydro-5,8-epoxybenz[*f*]azulene 31

n-Butyllithium in hexane (1.6 M, 0.85 mL, 1.36 mmol) was added dropwise to a stirred solution of 5,6-dibromoazulene[18] (379 mg, 1.33 mmol) in a mixture of anhydrous furan (25 mL) and tetrahydrofuran (25 mL) at −78 °C. After 15 min water (1 mL) was added and the mixture was allowed to warm to room temperature, diluted with water (50 mL) and extracted with ether (50 mL). Evaporation of the dried extract followed by radial chromatography and elution with 5% ethyl acetate in light petroleum gave the title adduct as a blue crystalline solid (109 mg, 42%), mp 137–141 °C (lit.[18] 139.5–140 °C) having the reported[18] spectral properties.

Azuleno[5,6-*c*]furan 6

3,6-Di(pyridin-2-yl)-*s*-tetrazine (53 mg, 0.22 mmol) was added in one portion to a solution of 5,8-dihydro-5,8-epoxybenz[*f*]-azulene (43 mg, 0.22 mmol) in dichloromethane (10 mL) and the resulting solution was stirred at room temperature for 40 min when TLC indicated that the starting material had been consumed. The reaction mixture was concentrated under reduced pressure without heating and the residue subjected to radial chromatography. Elution with light petroleum gave *azuleno[5,6-c]furan* as a red crystalline solid (30 mg, 81%) which recrystallised from light petroleum as red prisms, mp 110 °C (Found: M 168.0575. $C_{12}H_8O$ requires M 168.0578). Mass spectrum *m*/*z* 169 (M + 1, 13%), 168 (100, M), 140 (10), 139 (54). δ_H (600 MHz) 8.03 (1H, s, 3-H), 7.81 (1H, s, 1-H), 7.72 (1H, s, 4-H), 6.97 (1H, d, *J* 11.1, 8-H), 6.92 (1H, dd, *J* 4.9, 2.5, 6-H), 6.80 (1H, br s, 7-H), 6.70 (1H, d, *J* 4.9, 5-H), 6.61 (1H, d, *J* 11.1, 9-H). δ_C (151 MHz) 145.1 (CH, 3-C), 141.14 (CH, 1-C), 141.08 (C, 4a-C), 133.5 (C, 7a-C), 132.0 (CH, 6-C), 129.3 (CH, 7-C), 129.0 (CH, 4-C), 125.6 (CH, 8-C), 124.5 (C, 9a-C), 124.2 (CH, 5-C), 123.2 (C, 3a-C), 113.5 (CH, 9-C). Electronic spectrum (hexane) λ_{max} (log ε) 205 (4.59), 261 (5.17), 270 (5.15), 339 (4.18), 356 (4.16), 375 (3.94), 484 (3.43) nm.

Diels–Alder addition between azuleno[5,6-*c*]furan 6 and *N*-methylmaleimide

A solution of the furan (23 mg, 0.14 mmol) and *N*-methylmaleimide (16 mg, 0.144 mmol) in dichloromethane (10 mL) was kept at room temperature overnight. The resulting blue solution was concentrated under reduced pressure and the residue subjected to radial chromatography. Elution with 40% ethyl acetate–light petroleum gave the *exo*-adduct **33** (7 mg, 18%) followed by the *endo*-adduct **32** (23 mg, 60%).

Adduct **32** crystallised from dichloromethane–light petroleum as blue prisms mp 206 °C (Found: M 279.0893. $C_{17}H_{13}NO_3$ requires M 279.0895). Mass spectrum *m*/*z* 279 (M, 17%), 169 (13), 168 (100), 139 (23). δ_H (300 MHz) 8.26 (1H, d, *J* 9.1), 8.23 (1H, s), 7.90 (1H, dd, *J* 3.8, 3.8), 7.43 (1H, d, *J* 3.5), 7.12 (1H, d, *J* 9.1), 5.69–5.86 (2H, m), 2.15 (3H, s). δ_C (75.5 MHz) 174.2 (CO), 174.1 (CO), 147.2 (C), 140.0 (C), 137.7 (CH), 137.1 (C), 136.0 (CH), 132.5 (C), 128.6 (CH), 120.3 (CH), 120.1 (CH), 115.5 (CH), 84.0 (CH), 83.2 (CH), 48.9 (CH), 48.6 (CH), 23.9 (CH_3).

Adduct **33** crystallised from dichloromethane–light petroleum as blue prisms mp >260 °C (Found: M 279.0896. $C_{17}H_{13}NO_3$ requires M 279.0895). Mass spectrum *m*/*z* 279 (M, 17%), 169 (14), 168 (100), 139 (22). δ_H (300 MHz) 8.35 (1H, s), 8.33 (1H, d, *J* 9.0), 7.93 (dd, *J* 3.8, 3.8), 7.48–7.41 (2H, m), 7.27 (1H, d, *J* 9.0), 5.79 (1H, s), 5.72 (1H, s), 3.13 (1H, d, *J* 6.7), 3.07 (1H, d, *J* 6.7), 3.05 (3H, s). δ_C (75.5 MHz) 175.9 (2 × CO), 150.3 (C), 140.3 (C), 137.7 (CH), 137.4 (C), 136.5 (CH), 135.5 (C), 128.0 (CH), 120.4 (CH), 119.9 (CH), 114.8 (CH), 85.2 (CH), 84.5 (CH), 49.5 (CH), 48.7 (CH), 25.3 (CH_3).

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