Synthesis and some reactions of *N*-amino-2-methoxy-1-azaazulenium salt: leading to 3,3a-diazacyclopent[*a*]azulene and 2a,3-diazabenz[*cd*]azulene systems

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***N*-Amino-2-methoxy-1-azaazulenium salt 2 has been synthesized from 2-methoxy-1-azaazulene with *O*-mesitylenesulfonylhydroxylamine and its structure has been characterized by X-ray crystal analysis. The salt 2 reacts with ethyl cyanoacetate in the presence of potassium carbonate in acetonitrile to give ethyl (1-amino-1,2-dihydro-1-azaazulen-2-ylidene)cyanoacetate 4, which undergoes cyclization with potassium carbonate in ethanol to give ethyl 2-amino-3,3a-diazacyclopent[*a*]azulene-1-carboxylate. Reaction of 2 with diethyl ethoxymethylenemalonate in the presence of potassium carbonate in acetonitrile gives ethyl 2-methoxy-2a,3-diazabenz[*cd*]azulene-5-carboxylate and ethyl 3,3a-diazacyclopent[*a*]azulene-1-carboxylate as cyclization products. Cycloaddition of the salt 2 with an acetylenic ester proceeds regioselectively and gives 3,3a-diazacyclopent[*a*]azulene derivatives and 2a,3-diazabenz[*cd*]azulene derivatives.**

Introduction

Heterocyclic *N*-imides, which are highly useful synthetic intermediates for preparation of fused nitrogen-bridgehead heterocycles, have been investigated extensively.[1] Almost all the studies reported have been concerned with the alternant systems, no such investigations on non-alternant systems such as azaazulenes[2] having appeared so far; and this, despite the potential ability of the latter for the formation of novel fused heterocycles with their associated interesting chemistry. Since *N*-alkylations of 1-azaazulenes and 1,3-diazaazulenes are known in azaazulene chemistry,[3] we considered that the direct introduction of an amino group on N-1 of 1-azaazulenes would be possible for the formation of 1-azaazulene *N*-imide. As an aminating reagent, we adopted *O*-mesitylenesulfonylhydroxylamine (MSH), an excellent reagent for an amination of nitrogen heterocycles,[1] and achieved the formation of 1-azaazulene *N*-imide. We report herein a first synthesis and some reactions of *N*-amino-2-methoxy-1-azaazulenium salt together with an X-ray structural analysis.

Results and discussion

Since it is expected that the presence of an electron-donating group at C-2 position of 1-azaazulene enhances the nucleophilicity of N-1, we employed 2-methoxy-1-azaazulene **1** as a reactant. Thus, the treatment of **1** with MSH in dichloromethane yielded a stable *N*-amino-2-methoxy-1-azaazulenium salt **2** in 89% yield. The structure of **2** was deduced from the inspection of the spectroscopic data as well as elemental analysis, and finally determined by an X-ray crystal structure analysis. An ORTEP drawing[5] of **2** is shown in Fig. 1. In the IR spectrum of **2**, the amino group absorption appears at ν 3284 and 3156 cm^{-1}. Its mass spectrum shows the peaks at *m/z* 161 and 160, arising from the *N*-amino-2-methoxy-1-azaazulenium ion and 2-methoxy-1-azaazulenium *N*-imide, respectively. The X-ray structure of **2** shows that the electron-deficient benzene ring of mesitylenesulfonate lies over the pyrrole moiety of the 1-azaazulene ring and the bond-alternation of the seven-membered ring is rather small [1.38–1.40 Å, except C(6)–C(7)]; this suggests that the cation is spread mainly over the seven-membered ring moiety which has a tropylium cation character with the electron density on the pyrrole moiety being relatively high. This result is in agreement with evidence from the ^{1}H NMR spectrum, in which the protons of the seven-membered ring resonate at rather lowfield (δ 8.24–8.92).

The salt **2** was stable as a solution in ethanol in the absence of a base or an ion-exchange resin. Addition of aq. sodium hydroxide to an ethanolic solution of **2**, however, caused its colour to change from yellow into green, although no distinct product was isolated. The treatment of **2** with potassium carbonate in ethanol followed by water gave 1-amino-1-azaazulen-2(1*H*)-one[6] **3** (66%). Expecting to isolate the 2-methoxy-1-azaazulenium *N*-imide **A**, **2** was treated with an Amberlite IRA-410 ion-exchange resin in acetonitrile; no change occurred and none of the expected *N*-imide was obtained. Treatment of **2** with a wet Amberlite IRA-410 ion-exchange resin in acetonitrile, gave none of the expected compound **A**, instead **3** was obtained in 81% yield. The results show that the C-2 position of the *N*-imide **A** has a high reactivity towards nucleophiles.

With a view to constructing a series of stable extended betaines and subsequent cyclization of these, acylation of **2** was attempted. Treatment of **2** with benzoyl chloride or other acyl chlorides gave complex mixtures, no distinct products being isolated. Earlier work with pyridinium *N*-imides has shown that treatment of *N*-aminopyridinium salts with ethyl cyanoacetate under basic conditions leads to acylation;[7] we therefore treated **2** with ethyl cyanoacetate in the presence of potassium carbonate in acetonitrile. However, in marked contrast to the reaction of pyridinium *N*-imide,[7] the reaction failed to give an *N*-acyl derivative, instead giving rise to ethyl (1-amino-1,2-dihydro-1-azaazulen-2-ylidene)cyanoacetate **4** (92%), the IR spectrum of which showed absorption for an amino group (ν 3364 and 3300 cm^{-1}), a conjugated cyano group (ν 2184 cm^{-1}) and an ethyl ester group (ν 1668 cm^{-1}). The inherent aromaticity of **4** was evidenced by the appearance in its ^{1}H NMR spectrum of signals for the seven-membered ring protons in the aromatic region with but a small difference in the coupling constants (J 9.8–10.4). No methoxy group signal was observed, indicating that the substitution had occurred at the C-2 position. The structure of **4** was finally determined by X-ray crystal structure analysis from which it was deduced that the ester group and the

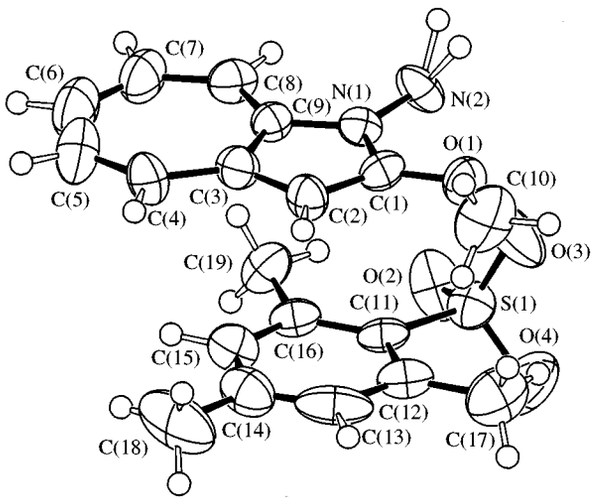
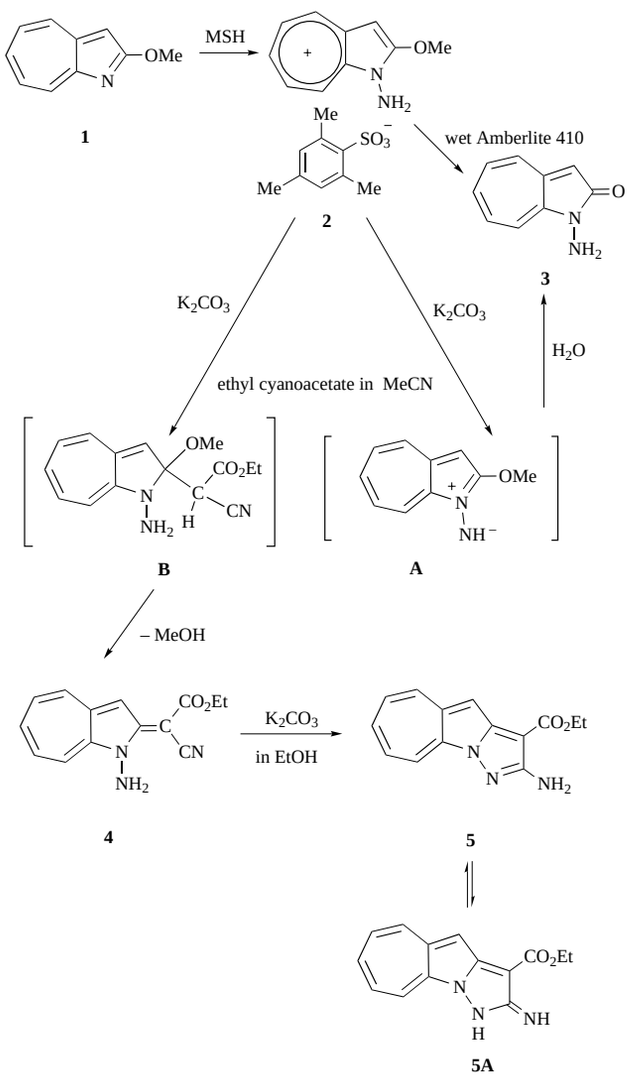


Fig. 1 An ORTEP drawing of **2** with thermal ellipsoid plot (50% probability). Selective bond lengths (Å); N(1)–C(1) 1.375(9), N(1)–C(9) 1.362(9), N(1)–N(2) 1.414(8), C(1)–C(2) 1.38(1), C(2)–C(3) 1.40(1), C(3)–C(9) 1.45(1), C(3)–C(4) 1.40(1), C(4)–C(5) 1.38(1), C(5)–C(6) 1.40(1), C(6)–C(7) 1.34(1), C(7)–C(8) 1.40(1), C(8)–C(9) 1.38(1).



Scheme 1

amino group were *trans* orientated. Since there were two independent molecules in a unit cell of **4** which had essentially the same geometry, an ORTEP drawing[5] of only one isomer is shown in Fig. 2. The bond alternation of the 1-azaazulene ring is clearly seen (1.363–1.415 Å), suggesting that **4** is an extended heptafulvene, for which the resonance contribution of the tropylium cation form would be quite small.

Formation of **4** may be interpreted as follows: the acidity of the amino proton of **2** would be decreased since the positive charge is spread over a seven-membered ring and the electron-withdrawing ability of N-1 is decreased. Therefore, the base attacks the acidic proton of ethyl cyanoacetate rather than the amino proton of **2**, to give, preferentially, the carbanion. Addition of the carbanion to the C-2 position of **2** would lead to the intermediate **B**, from which successive elimination of methanol would give **4**. In the methanol-elimination stage, the favourable *anti*-orientation of the ester group with respect to the amino group may be attributed to steric repulsion between the ester and the amino groups.

Interestingly, when the reaction was performed in ethanol, the cyclization product, ethyl 2-amino-3,3a-diazacyclopent[*a*]-azulene-1-carboxylate **5**, was obtained in an 18% yield together with **4** (31%); it is expected that the cyclization of **4** would be facilitated by treatment with strong base in ethanol. We therefore treated **4** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a strong base having no nucleophilicity; the cyclization product **5**, however, was obtained in a yield of only 7%. Formation of **5** in high yield (83%) was achieved by the treatment of **4** with potassium carbonate in ethanol at ambient temperature for 18 h. The structure of **5** was deduced from inspection of the spectroscopic data as well as elemental analysis. Thus, in its ^{1}H NMR spectrum, a 1H singlet (at δ 6.92) was assigned to H-9 whilst amino protons [at δ 5.42 (2H, br)] and seven-membered ring protons [at δ 6.92 (1H, s), 7.14–7.37 (3H, m), 7.95 (1H, d, *J* 8.0) and 8.09 (1H, d, *J* 8.5)] were present along with ethyl ester signals. In the IR spectrum, the cyano group absorption disappeared, and an amino absorption appeared (ν 3414, 3395, 3240 and 3174 cm^{-1}). Inspection of the IR data suggests that **5** exists as a tautomeric mixture with the imino form **5A**.

Employing conditions where the base attacks only the amino proton of **2** and in the absence of nucleophiles, 1-azaazulene *N*-imide **A** was expected to be formed and then to react further. Thus, **2** was treated with diethyl ethoxymethylenemalonate (DEEM), having no acidic hydrogen, in the presence of potassium carbonate in ethanol to yield in a one-pot reaction ethyl 2-ethoxy-2a,3-diazabenz[*cd*] azulene-5-carboxylate **6a** (26%). In the reaction, the methoxy group was replaced by the ethoxy group after attack of ethoxide on the reactive C-2 of **A** or **C**. Performed in acetonitrile, the reaction gave ethyl 2-methoxy-2a,3-diazabenz[*cd*]azulene-5-carboxylate **6b** (48%), ethyl 3,3a-diazacyclopent[*a*]azulene-1-carboxylate **7** (2%) and diethyl (2-oxo-1,2-dihydro-1-azaazulen-1-yl)aminomethylenemalonate **8** (9%), the cyclization predominantly proceeding at the C-8 position of the 1-azaazulene ring. The structures of these compounds (except **7**) were deduced from inspection of the spectroscopic data as well as elemental analysis; compound **7** was identified on the basis of its spectral properties by analogy with those of **10a** and **10b**. In the ^{1}H NMR spectrum of **6a**, the signals of the seven-membered ring protons appear at rather highfield (δ 5.6–7.6) together with two 1H singlets, assignable to H-10 and H-4, at δ 5.76 and 7.76; the large range for the coupling constants of the seven-membered ring protons (*J* 8.5–12.8 Hz) show the presence of bond alternation. This observation suggests that the contribution of the azaindolizine moiety is larger than that of the azaazulene moiety in the resonance form and this implies that **6a** and **6b** have inherently a butadiene-bridged azaindolizine character. In the ^{1}H NMR spectrum of **7**, the seven-membered ring protons appear in the aromatic region [δ 7.08–7.32 (m, H-5, 6, 7), 7.93 (d, *J* 11.0, H-8) and 8.27 (d, *J* 8.5, H-4)], and two 1H singlets, assignable to H-9 and H-2, appear at δ 7.06 and 8.42. In its IR spectrum, an ester carbonyl signal is seen at 1687 cm^{-1}. In the ^{1}H NMR spectrum of **8**, there are two ethyl ester groups [δ 1.26 (3H, t, *J* 7.0), 1.38 (3H, t, *J* 7.0), 4.19 (2H, q, *J* 7.0), 4.32 (2H, q, *J* 7.0)], one vinylic proton at δ 6.97 (d, *J* 10.4) coupled with an amino proton at δ 10.40

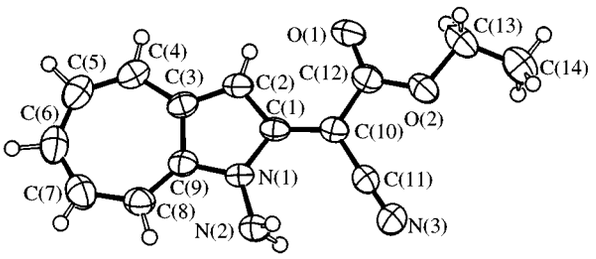
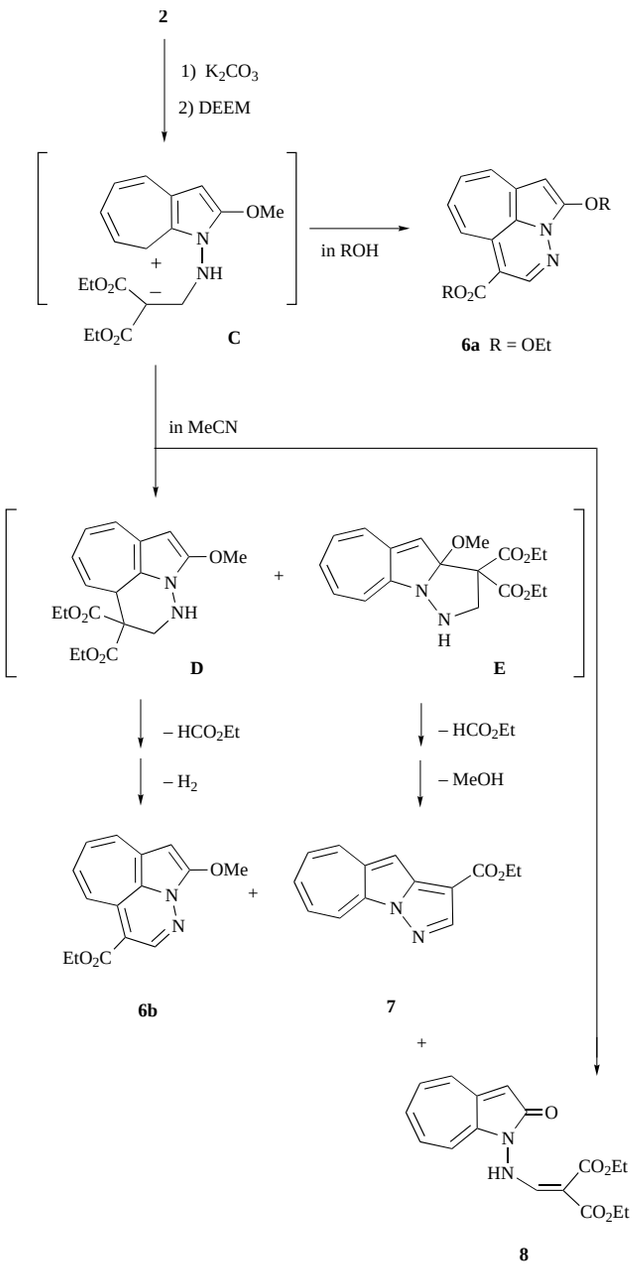


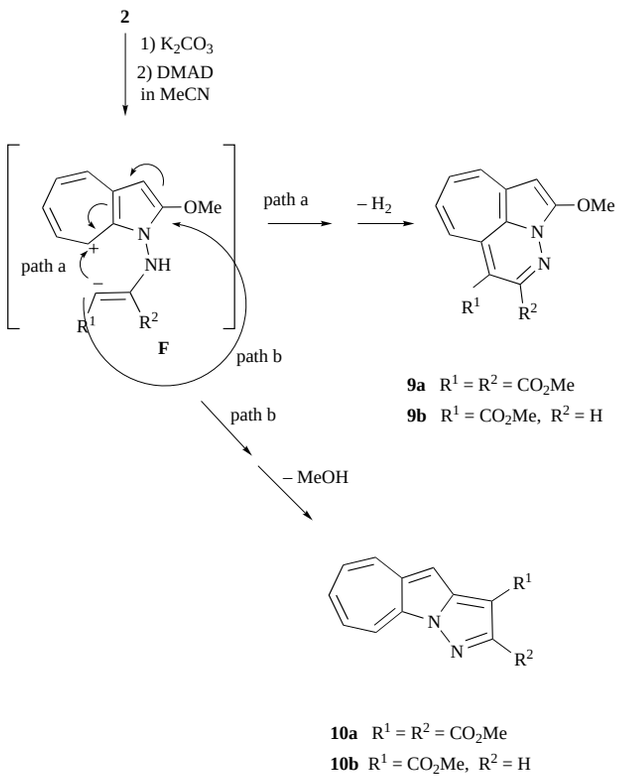
Fig. 2 An ORTEP drawing of **4** with thermal ellipsoid plot (50% probability). Selective bond lengths (Å); N(1)–C(1) 1.392(3), N(1)–C(9) 1.375(3), N(1)–N(2) 1.397(3), C(1)–C(2) 1.409(4), C(2)–C(3) 1.369(4), C(3)–C(9) 1.450(4), C(3)–C(4) 1.421(4), C(4)–C(5) 1.363(4), C(5)–C(6) 1.400(5), C(6)–C(7) 1.358(5), C(7)–C(8) 1.410(4), C(8)–C(9) 1.364(4), C(1)–C(10) 1.401(4), C(10)–C(11) 1.420(4), C(10)–C(12) 1.458(4), C(12)–O(1) 1.210(4), C(11)–N(3) 1.149(3).



Scheme 2

(d, *J* 10.4), and protons assignable to 1-azaazulen-2(1*H*)-one ring protons [δ 6.06 (1H, s), 6.96–7.16 (3H, m), 7.50 (1H, d, *J* 11.0) and 7.95 (1H, d, *J* 11.0)]. In its IR spectrum, an NH signal at 3248 cm^{-1} and a broad carbonyl signal at 1698 cm^{-1} are seen. This spectral evidence allowed structure assignment.

Since it is known that 1,3-dipolar cycloadditions of heterocyclic *N*-imides with acetylenic esters proceed easily,[1,8] we extended the reaction to the *N*-imide **A**, expecting extended dipolar cycloaddition to occur. Thus, treatment of **2** with dimethyl acetylenedicarboxylate (DMAD) in the presence of potassium carbonate in acetonitrile gave dimethyl 2-methoxy-2a,3-diazabenz[*cd*]azulene-4,5-dicarboxylate **9a** (33%) and dimethyl 3,3a-diazacyclopent[*a*]azulene-1,2-dicarboxylate **10a** (55%) along with dimethyl fumarate. Similar treatment of **2** with methyl propiolate gave methyl 2-methoxy-2a,3-diazabenz[*cd*]azulene-5-carboxylate **9b** (18%) and methyl 3,3a-diazacyclopent[*a*]azulene-1-carboxylate **10b** (24%). This suggests that the reaction proceeded regioselectively *via* a dipolar intermediate.



Scheme 3

The spectral data of **9** and **10** are comparable with those of **5** and **6**. In contrast to the reaction of DEEM, cyclization of acetylenic esters occurred predominantly from N-1 to the C-2 position of **A**. The results are explicable as follows; the large malonate anion moiety of **C** would preferentially attack the less hindered C-8, whereas the more reactive vinyl anion moiety of **F** would easily attack C-2, a more hindered but reactive site.

An ORTEP drawing[5] of **10a** is shown in Fig. 3. An inspection of the bond lengths shows that the pyrazole moiety has reasonable values,[9] whereas the seven-membered ring shows a wide range of values (1.351–1.434 Å). This suggests that compound **10a** exists as a perturbed heptafulvene with a pyrazole moiety rather than the pericyclic 14π conjugated compound. This agrees with the conclusion drawn from the ^{1}H NMR evidence, in which the seven-membered ring protons appear in the aromatic region (δ 7.07–8.33) with a considerable range for the coupling constants (*J* 8.5–11.0 Hz).

Experimental

All reactions were carried out under an argon atmosphere. Melting points were measured using a Yanagimoto micro-melting apparatus and are uncorrected. ^{1}H NMR spectra (250 MHz) were recorded on Hitachi R-250H spectrometer using deuteriochloroform as a solvent with tetramethylsilane as an

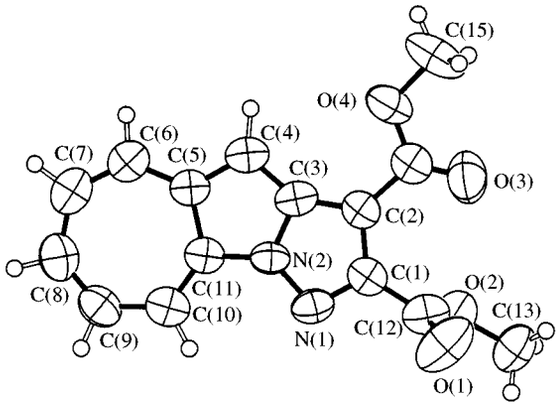


Fig. 3 An ORTEP drawing of **10a** with thermal ellipsoid plot (50% probability). Selective bond lengths (Å); N(1)–C(1) 1.319(7), N(2)–C(3) 1.377(7), N(1)–N(2) 1.358(6), N(2)–C(11) 1.392(7), C(1)–C(2) 1.417(8), C(2)–C(3) 1.387(8), C(3)–C(4) 1.392(8), C(4)–C(5) 1.400(7), C(5)–C(6) 1.407(8), C(5)–C(11) 1.463(8), C(6)–C(7) 1.369(8), C(7)–C(8) 1.427(9), C(8)–C(9) 1.350(8), C(9)–C(10) 1.433(8), C(10)–C(11) 1.342(7).

internal standard unless otherwise stated; *J* values are recorded in Hz. Electronic spectra were taken with Hitachi 220A spectrophotometer using ethanol as a solvent. IR spectra were recorded for KBr pellets on a Hitachi 270-50 infrared spectrophotometer and Nicolet FT-IR Impact 410 unless otherwise stated. Kieselgel 60 was used for column chromatography.

Preparation of *N*-amino-2-methoxy-1-azaazulenium salt 2

To the solution of 2-methoxy-1-azaazulene (0.160 g, 1.00 mmol) in dichloromethane (3 ml) in an ice–water bath was added dropwise over a period of 10 min a solution of *O*-mesitylenesulfonylhydroxylamine (0.430 g, 2.00 mmol) in dichloromethane (1.5 ml). After the mixture had been stirred for 1 h at room temperature, the resulting precipitate was filtered off, dried and recrystallized from methanol–ethyl acetate to give *N*-amino-2-methoxy-1-azaazulenium salt **2** (0.333 g, 89%) as yellow prisms, mp 147–148 °C; δ_H([$^2H_6$]-DMSO) 2.15 (3H, s), 2.48 (6H, s), 3.40 (2H, br), 4.39 (3H, s), 6.72 (2H, s), 7.28 (1H, s), 8.28–8.40 (3H, m), 8.92 (1H, d, *J* 9.8) and 8.98 (1H, d, *J* 11.0); ν_{max}/cm^{-1} 3284 and 3156 (NH); λ_{max}/nm (log ε) 272 (4.57), 318 (3.59, sh) and 416 (3.60); (EtOH + 1 drop of 1 M aq. NaOH) 266 (4.54), 410 (3.87), 600 (2.83) and 640 (2.79); *m/z* (rel. intensity) 161 (14), 160 (45), 145 (42), 131 (50), 104 (62), 78 (50), 77 (100) and 76 (52) (Found: C, 60.4; H, 6.1; N, 7.1. Calc. for $C_{19}H_{22}N_2O_4S$: C, 60.9; H, 5.9; N, 7.5%).

Reaction of 2 with a wet Amberlite IRA-410 ion-exchange resin

A mixture of **2** (0.375 g, 1.00 mmol) and Amberlite IRA-410 ion-exchange resin (1.00 g) swelled with water in acetonitrile (20 ml) was stirred for 1 day at room temperature. The mixture was filtered and the filtrate was evaporated. The residue was chromatographed with chloroform to give 1-amino-1-azaazulen-2(1*H*)-one **3** (0.129 g, 81%) as yellow needles, mp 161–162 °C (lit.,[7] mp 160 °C); δ_H 4.54 (2H, br s), 6.09 (1H, s), 6.94–7.27 (3H, m), 7.57 (1H, d, *J* 9.2) and 7.55 (1H, d, *J* 11.0); ν_{max}/cm^{-1} 3279, 3188 (NH) and 1714 (C=O); λ_{max}/nm (log ε) 268 (4.47), 412 (3.81), 460 (3.21, sh) and 492 (2.59, sh) (Found: C, 67.8; H, 5.1; N, 17.3. Calc. for $C_9H_8N_2O$: C, 67.5; H, 5.0; N, 17.5%).

Reaction of 2 with water

A mixture of **2** (0.060 g, 0.16 mmol) and potassium carbonate (0.130 g, 1.00 mmol) in ethanol (10 ml) was stirred for 1 h at room temperature after which it was diluted with water (0.5 ml). Stirring was continued for 30 min after which the mixture was evaporated. The residue was washed with chloroform and filtered and the filtrate was evaporated. The residue was chromatographed with chloroform to give **3** (0.017 g, 66%).

Reaction of 2 with ethyl cyanoacetate

(a) A mixture of **2** (0.375 g, 1.00 mmol) and potassium carbonate (0.650 g, 5.00 mmol) in dry acetonitrile (30 ml) was stirred at room temperature for 1 h after which it was treated with ethyl cyanoacetate (0.170 g, 1.50 mmol). Stirring was continued for 24 h after which the mixture was filtered and the residue was washed with dichloromethane. The combined filtrates were evaporated and the residue was chromatographed with chloroform to give ethyl (1-amino-1,2-dihydro-1-azaazulen-2-ylidene)-cyanoacetate **4** (0.118 g, 92%); red needles (from hexane–dichloromethane), mp 181–182 °C; δ_H 1.36 (3H, t, *J* 7.0), 4.28 (2H, q, *J* 7.0), 5.00 (2H, br), 7.11–7.39 (4H, m), 7.62 (1H, d, *J* 10.4) and 7.87 (1H, d, *J* 9.8); ν_{max}/cm^{-1} 3363, 3292 (NH), 2182 (CN) and 1668 (C=O); λ_{max}/nm (log ε) 272 (4.33), 352 (4.06), 484 (4.32) and 556 (3.76, sh) (Found: C, 66.0; H, 5.2; N, 16.3. Calc. for $C_{14}H_{13}N_3O_2$: C, 65.9; H, 5.1; N, 16.5%).

(b) A mixture of **2** (0.375 g, 1.00 mmol) and potassium carbonate (0.650 g, 5.00 mmol) in abs. ethanol (30 ml) was stirred at room temperature for 1 h after which it was treated with ethyl cyanoacetate (1.20 g, 1.00 mmol). Stirring was continued for 24 h after which the mixture was filtered and the residue was washed with dichloromethane. The combined filtrates were evaporated and the residue was chromatographed with chloroform to give **4** (0.080 g, 31%) and ethyl 2-amino-3,3a-diazacyclopent[*a*]azulene-1-carboxylate **5** (0.047 g, 18%); green micro-needles (from hexane–dichloromethane), mp 150–151 °C; δ_H 1.43 (3H, t, *J* 7.0), 4.37 (2H, q, *J* 7.0), 5.42 (2H, br), 6.92 (1H, s), 7.14–7.37 (3H, m), 7.95 (1H, d, *J* 8.0) and 8.09 (1H, d, *J* 8.5); ν_{max}/cm^{-1} 3411, 3395, 3259, 3173 (NH) and 1676 (C=O); λ_{max}/nm (log ε) 268 (4.21), 332 (4.54), 370 (4.19, sh), 424 (3.63, sh) and 522 (3.32); *m/z* (rel. intensity) 256 (M^+ + 1, 57), 255 (M^+, 79), 208 (62), 207 (100), 183 (17), 155 (23) and 127 (16) (Found: C, 65.5; H, 5.2; N, 16.1. Calc. for $C_{14}H_{13}N_3O_2$: C, 65.9; H, 5.1; N, 16.5%).

Cyclization of ethyl (1-amino-1,2-dihydro-1-azaazulen-2-ylidene)cyanoacetate 4

A mixture of **4** (0.096 g, 0.376 mmol) and potassium carbonate (0.260 g, 1.88 mmol) in abs. ethanol (20 ml) was stirred at room temperature for 17 h after which it was filtered. The residue was washed with dichloromethane and the combined filtrates were evaporated. The residue was chromatographed with chloroform to give ethyl 2-amino-3,3a-diazacyclopent[*a*]azulene-1-carboxylate **5** (0.080 g, 83%).

Reaction of 2 with diethyl ethoxymethylenemalonate

(a) A mixture of **2** (0.375 g, 1.00 mmol) and potassium carbonate (0.650 g, 5.00 mmol) in abs. ethanol (20 ml) was stirred for 1 h at room temperature after which it was treated with diethyl ethoxymethylenemalonate (0.250 g, 1.15 mmol). Stirring was continued for 24 h after which the mixture was filtered and the residue was washed with dichloromethane. The combined filtrates were evaporated and the residue was chromatographed with chloroform to give ethyl 2-ethoxy-2a,3-diazabenz[*cd*]-azulene-5-carboxylate **6a** (0.075 g, 26%) as dark green needles (from hexane–dichloromethane), mp 111–112 °C; δ_H 1.29 (3H, t, *J* 7.0), 1.50 (3H, t, *J* 7.0), 4.19 (2H, q, *J* 7.0), 4.22 (2H, q, *J* 7.0), 5.67 (1H, dd, *J* 11.0, 8.5), 5.76 (1H, s), 6.23 (1H, dd, *J* 12.8, 8.5), 6.61 (1H, d, *J* 11.0), 7.61 (1H, d, *J* 12.8) and 7.76 (1H, s); ν_{max}/cm^{-1} 1667 (C=O); λ_{max}/nm (log ε) 240 (4.43), 260 (4.44), 286 (4.23, sh), 362 (3.30, sh), 406 (4.30), 476 (2.94, sh), 520 (3.01), 564 (3.17), 616 (3.21), 680 (3.07) and 756 (2.60); *m/z* (rel. intensity) 285 (M^+ + 1, 49), 284 (M^+, 58), 256 (74), 255 (86), 228 (64), 227 (100) and 126 (39) (Found: C, 67.8; H, 5.8; N, 9.8. Calc. for $C_{16}H_{16}N_2O_3$: C, 67.6; H, 5.7; N, 9.9%).

(b) A mixture of **2** (0.375 g, 1.00 mmol), potassium carbonate (0.650 g, 5.00 mmol) and diethyl ethoxymethylenemalonate (1.10 g, 5.08 mmol) in dry acetonitrile (20 ml) was stirred at room temperature for 2 days after which it was filtered. The residue was washed with dichloromethane and the combined

filtrates were evaporated. The residue was chromatographed with chloroform to give an identified brown oily compound (0.070 g), ethyl 2-methoxy-2a,3-diazabenz[*cd*]azulene-5-carboxylate **6b** (0.135 g, 48%), ethyl 3,3a-diazacyclopent[*a*]azulene-1-carboxylate **7** (0.004 g, 2%) and diethyl (2-oxo-1,2-dihydro-1-azaazulen-1-yl)aminomethylenemalonate **8** (0.030 g, 9%), successively.

Compound **6b**: dark green needles (from hexane–dichloromethane), mp 162–163 °C; δ_H 1.30 (3H, t, *J* 7.3), 3.99 (3H, s), 4.19 (2H, q, *J* 7.3), 5.68 (1H, dd, *J* 10.4, 8.5), 5.78 (1H, s), 6.24 (1H, dd, *J* 12.8, 8.5), 6.62 (1H, d, *J* 10.4), 7.62 (1H, d, *J* 12.8) and 7.74 (1H, s); ν_{max}/cm^{-1} 1673 (C=O); λ_{max}/nm (log ε) 240 (4.39), 260 (4.41), 284 (4.21, sh), 362 (3.89, sh), 384 (4.06, sh), 406 (4.29), 480 (2.75, sh), 520 (2.99), 562 (3.16), 616 (3.20), 678 (3.05) and 756 (2.58); *m/z* (rel. intensity) 270 (M^+, 35), 255 (26), 227 (65) and 126 (100) (Found: C, 66.5; H, 5.5; N, 10.0. Calc. for $C_{15}H_{14}N_2O_3$: C, 66.7; H, 5.2; N, 10.4%).

Compound **7**: dark violet needles; δ_H 1.42 (3H, t, *J* 7.0), 4.38 (2H, q, *J* 7.0), 7.06 (1H, s), 7.08–7.32 (3H, m), 7.93 (1H, d, *J* 11.0), 8.27 (1H, d, *J* 8.5) and 8.42 (1H, s); ν_{max}/cm^{-1} 1687 (C=O).

Compound **8**: yellow oil; δ_H 1.26 (3H, t, *J* 7.0), 1.38 (3H, t, *J* 7.0), 4.19 (2H, q, *J* 7.0), 4.32 (2H, q, *J* 7.0), 6.06 (1H, s), 6.97 (1H, d, *J* 10.4), 6.96–7.16 (3H, m), 7.50 (1H, d, *J* 11.0), 7.95 (1H, d, *J* 11.0) and 10.40 (1H, d, *J* 10.4); ν_{max}/cm^{-1} 3248 (NH), 1698 and 1658 (sh) (C=O); λ_{max}/nm (log ε) 258 (4.33), 276 (4.39), 390 (3.74), 406 (3.77), 458 (3.09, sh) and 492 (2.47, sh); *m/z* (rel. intensity) 330 (M^+, 8), 257 (4), 171 (29), 145 (100), 144 (64), 117 (37) and 90 (23) (Found: C, 61.8; H, 5.9; N, 8.2. Calc. for $C_{17}H_{18}N_2O_5$: C, 61.8; H, 5.5; N, 8.5%).

Reaction of 2 with dimethyl acetylenedicarboxylate

A mixture of **2** (0.375 g, 1.00 mmol), potassium carbonate (0.650 g, 5.00 mmol) and dimethyl acetylenedicarboxylate (0.440 g, 3.09 mmol) in dry acetonitrile (20 ml) was stirred for 24 h at room temperature. The mixture was filtered and the residue was washed with dichloromethane. The combined filtrate was evaporated. The residue was chromatographed with chloroform to give a mixture of dimethyl 2-methoxy-2a,3-diazabenz[*cd*]azulene-4,5-dicarboxylate **9a** and dimethyl 3,3a-diazacyclopent[*a*]azulene-1,2-dicarboxylate **10a** (0.261 g, **9a**:**10a** = 38:62 from ^{1}H NMR). The mixture was chromatographed repeatedly with benzene–chloroform to give pure **9a** (0.054 g, 17%) and **10a** (0.126 g, 44%), together with dimethyl fumarate (0.076 g).

Compound **9a**: dark green needles (from hexane–dichloromethane), mp 186–187 °C; δ_H 3.66 (3H, s), 3.81 (3H, s), 3.96 (3H, s), 5.65 (1H, dd, *J* 11.0, 8.5), 5.79 (1H, s), 6.16 (1H, dd, *J* 12.8, 8.5), 6.56 (1H, d, *J* 11.0) and 7.07 (1H, d, *J* 12.8); ν_{max}/cm^{-1} 1731 and 1684 (C=O); λ_{max}/nm (log ε) 238 (4.40), 262 (4.38), 288 (4.20), 318 (3.62, sh), 362 (3.91, sh), 404 (4.19), 480 (2.67, sh), 520 (2.90, sh), 566 (3.03), 618 (3.05), 676 (2.90) and 756 (2.29, sh); *m/z* (rel. intensity) 314 (M^+, 36), 299 (100), 271 (17), 153 (31) and 126 (76) (Found: C, 60.8; H, 4.8; N, 8.4. Calc. for $C_{16}H_{14}N_2O_5$: C, 61.1; H, 4.5; N, 8.9%).

Compound **10a**: dark violet needles (from hexane–dichloromethane), mp 146–147 °C; δ_H 3.88 (3H, s), 4.01 (3H, s), 7.01 (1H, s), 7.07–7.36 (3H, m), 7.89 (1H, d, *J* 11.0), 8.33 (1H, d, *J* 8.5) and 8.42 (1H, s); ν_{max}/cm^{-1} 1737 and 1705 (C=O); λ_{max}/nm (log ε) 252 (4.29), 302 (4.60), 318 (4.41), 376 (3.72, sh), 396 (3.92), 420 (3.93), 480 (3.33, sh), 522 (3.41), 558 (3.37), 616 (3.12, sh) and 680 (2.56, sh); *m/z* (rel. intensity) 284, (M^+, 72), 253 (100), 181 (54), 165 (36), 140 (76) and 113 (19) (Found: C, 63.5; H, 4.7; N, 9.8. Calc. for $C_{15}H_{12}N_2O_4$: C, 63.4; H, 4.3; N, 9.9%).

Reaction of 2 with methyl propiolate

A mixture of **2** (0.375 g, 1.00 mmol), potassium carbonate (0.650 g, 5.00 mmol) and dimethyl propiolate (0.420 g, 5.00 mmol) in dry acetonitrile (20 ml) was stirred at room temperature for 24 h after which it was filtered. The residue was washed with dichloromethane and the combined filtrates were evaporated. The residue was chromatographed with chloroform to give methyl 2-methoxy-2a,3-diazabenz[*cd*]azulene-5-carboxylate **9b** (0.046 g, 18%) and methyl 3,3a-diazacyclopent[*a*]-azulene-1-carboxylate **10b** (0.056 g, 24%).

Compound **9b**: dark green needles (from hexane–dichloromethane), mp 186–187 °C; δ_H 3.72 (3H, s), 3.99 (3H, s), 5.70 (1H, dd, *J* 11.0, 8.5), 5.78 (1H, s), 6.25 (1H, dd, *J* 12.8, 8.5), 6.63 (1H, d, *J* 11.0), 7.61 (1H, d, *J* 12.8) and 7.73 (1H, s); ν_{max}/cm^{-1} 1686 (C=O); λ_{max}/nm (log ε) 240 (4.32), 260 (4.55), 284 (4.34, sh), 362 (4.00, sh), 384 (4.15, sh), 406 (4.38), 480 (2.87, sh), 520 (3.09), 562 (3.24), 614 (3.28), 676 (3.13) and 754 (2.67) (Found: C, 65.5; H, 5.1; N, 10.4. Calc. for $C_{14}H_{12}N_2O_3$: C, 65.6; H, 4.7; N, 10.9%).

Compound **10b**: dark violet needles (from hexane–dichloromethane), mp 160–161 °C; δ_H 3.91 (3H, s), 7.05 (1H, s), 7.07–7.31 (3H, m), 7.91 (1H, d, *J* 11.0), 8.25 (1H, d, *J* 8.5) and 8.41 (1H, s); ν_{max}/cm^{-1} 1676 (C=O); λ_{max}/nm (log ε) 252 (4.32), 266 (4.22), 278 (4.23), 304 (4.47), 318 (4.37), 376 (3.61, sh), 398 (3.81), 422 (3.80), 478 (3.31, sh), 522 (3.40), 558 (3.35), 620 (3.09, sh) and 682 (2.57, sh) (Found: C, 68.5; H, 4.8; N, 12.0. Calc. for $C_{13}H_{10}N_2O_2$: C, 69.0; H, 4.5; N, 12.4%).

X-Ray structure determinations

Crystal data for 2. Yellow prism, $C_{19}H_{22}N_2O_4S{\cdot}H_2O$, M = 392.47, orthorhombic, space group *Pbca*, a = 17.726(5), b = 17.297(3), c = 12.618(4) Å, V = 3869(3) Å^3, Z = 8, D_c = 1.347 g cm^{-3}, crystal dimensions 0.38 × 0.52 × 0.62 mm. Data were measured on a Rigaku AFC 5S radiation diffractometer with graphite-monochromated Mo-Kα radiation. A total 4952 reflections were collected using the ω–2θ scan technique to a maximum 2θ value of 55.0°. The structure was solved by direct methods and refined by a full-matrix least-squares method using TEXSAN structure analysis software,[10] with 244 variables and 1750 observed reflections [$I > 3\sigma(I)$]. The non-hydrogen atoms were refined anisotropically. The weighting scheme $\omega = 4F_o^2/\sigma^2(F_o^2)$ gave satisfactory agreement analyses. The final R and R_w values were 0.083 and 0.108. The maximum peak and the minimum peak in the final difference map were 0.57 and −0.47 e$^-$Å^{-3}.

Crystal data for 4. Orange prism, $C_{14}H_{13}N_3O_2$, M = 255.28, monoclinic, space group $P2_1/c$, a = 8.553(4), b = 11.958(5), c = 24.397(3) Å, β = 94.83(2)°, V = 2486(2) Å^3, Z = 8, D_c = 1.364 g cm^{-3}, crystal dimensions 0.24 × 0.88 × 1.00 mm. Data were measured on a Rigaku AFC 5S radiation diffractometer with graphite-monochromated Mo-Kα radiation. A total 6372 reflections (5977 unique) were collected using the ω–2θ scan technique to a maximum 2θ value of 55.0°. The structure was solved by direct methods and refined by a full-matrix least-squares method using TEXSAN structure analysis software,[10] with 447 variables and 2875 observed reflections [$I > 3\sigma(I)$]. The non-hydrogen atoms were refined anisotropically. The weighting scheme $\omega = 4F_o^2/\sigma^2(F_o^2)$ gave satisfactory agreement analyses. The final R and R_w values were 0.050 and 0.056. The maximum peak and the minimum peak in the final difference map were 0.20 and −0.27 e$^-$Å^{-3}.

Crystal data for 10a. Dark red plate, $C_{15}H_{12}N_2O_4$, M = 284.27, monoclinic, space group $P2_1/n$, a = 14.00(1), b = 7.721(7), c = 14.10(1) Å, β = 115.93(5)°, V = 1371(2) Å^3, Z = 4, D_c = 1.377 g cm^{-3}, crystal dimensions 0.08 × 0.24 × 0.80 mm. Data were measured on a Rigaku AFC 5S radiation diffractometer with graphite-monochromated Mo-Kα radiation. A total 3514 reflections (3381 unique) were collected using the ω–2θ scan technique to a maximum 2θ value of 55.0°. The structure was solved by direct methods and refined by a full-matrix least-squares method using TEXSAN structure analysis software,[10] with 190 variables and 1026 observed reflections [$I > 3\sigma(I)$]. The non-hydrogen atoms were refined anisotropically. The weighting scheme $\omega = 4F_o^2/\sigma^2(F_o^2)$ gave satisfactory

agreement analyses. The final R and R_w values were 0.063 and 0.071. The maximum peak and the minimum peak in final difference map were 0.24 and -0.21 e$^-$ Å^{-3}.

Atomic coordinates, F_o-F_c tables, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Centre and are available on request.† Any such request should be accompanied by a full bibliographic citation for this work together with the reference no. 207/120.

Acknowledgements

We thank Professor Akira Mori (Kyushu University) for measurements of mass and elemental analyses.

† For details of the scheme, see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1997, Issue 1.

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Paper 7/01793F
Received 14*th March* 1997
Accepted 1*st May* 1997