Synthesis and some reactions of 1,2-diamino-1,3-diaza- and 1,2-diamino-1-azaazulenium salts

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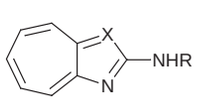
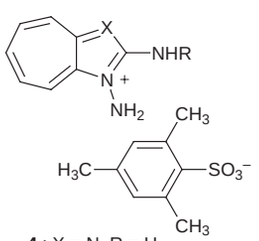
Amination of azaazulenes **1**–**3** with *O*-mesitylsulfonylhydroxylamine occurs at N-1 and gives the corresponding azaazulenium salts **4**–**6**. The treatment of the salts **4** and **6** with potassium carbonate gives 1-amino-2-imino-1,2-dihydro-1,3-diaza- and 1-azaazulenes. The structure of 1-amino-2-ethylimino-1,2-dihydro-1-azaazulene (**10**) was characterized by X-ray crystal structure analysis. Reaction of the salt **4** with acetic anhydride gave 2-methyl-1,3,3a,9-tetraazacyclopent[*a*]azulene. The reaction of the salts **4** and **5** with diethyl ethoxymethylenedicarboxylate (DEEM) in the presence of potassium carbonate in acetonitrile gave 1,3,3a,9-tetraaza- (**19**) and 1,3,3a-triazacyclopent[*a*]azulene derivatives (**21**) as major products, whereas the reaction in ethanol gave 1,2a,3-triaza- (**17**) and 2a,3-diazabenz[*cd*]-azulene derivatives (**22**), respectively. Similar treatment of **6** with DEEM gave diethyl (2-ethylimino-1,2-dihydro-1-azaazulen-1-yl)aminomethylenemalonate **23**, which converted to 2a,3-diazabenz[*cd*]azulene derivative (**24**). The salts **4**–**6** reacted with active methylene compounds such as diethyl acetonedicarboxylate, diethyl oxalacetate and ethyl pyruvate, at the *N*-amino group followed by a cyclization at the C-8 position on the azaazulene ring to give 1,2a,3-triaza- (**25**, **28**, **29**) and 2a,3-diazabenz[*cd*]azulene derivatives (**26**, **27**, **30**). Cycloaddition of the salts **4**–**6** with acetylenic esters in the presence of potassium carbonate proceeded regioselectively and gave 1,2a,3-triaza- (**32**–**35**) or 2a,3-diazabenz[*cd*]azulene derivatives (**31**, **36**, **37**, **39**–**41**).

Introduction

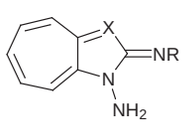
Heterocyclic *N*-aminides are highly useful synthetic intermediates for the preparation of fused nitrogen-bridgehead heterocycles.[1] Recently, we reported the synthesis and reactions of 2-methoxy-1-azaazulenium-*N*-aminide,[2] where some interesting fused heterocycles were obtained. It is known that 1-amino-2-imino-1,2-dihydropyridine,[3–6] generated from the 1,2-diaminopyridinium salt with base, reacts with a variety of α,β-unsaturated compounds to give [1,2,4]triazolo[1,5-*a*]pyridine derivatives.[6] As a continuation of our studies on the preparation of new fused non-alternant heterocycles, we are interested in the synthesis of 1,2-diaminoazaazulenium salts, which should be a good source of fused heterocycles. In this paper we report on the synthesis and some reactions of 1-amino-2-imino-1,2-dihydro-1,3-diazaazulene, 1-amino-2-imino-1,2-dihydro-1-azaazulene and 1-amino-2-ethylimino-1,2-dihydro-1-azaazulene derived from their corresponding salts. One of the structures, 1-amino-2-ethylimino-1,2-dihydro-1-azaazulene, was confirmed by X-ray crystal structure analysis.



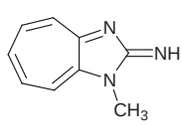
1 : X = N, R = H
2 : X = CH, R = H
3 : X = CH, R = Et
12 : X = CCO_2Et, R = $COCH_3$



4 : X = N, R = H
5 : X = CH, R = H
6 : X = CH, R = Et
13 : X = CCO_2Et, R = $COCH_3$



7 : X = N, R = H
9 : X = CH, R = H
10 : X = CH, R = Et
16 : X = CO_2Et, R = $COCH_3$



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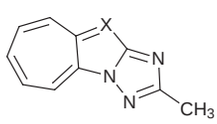


11 : X = N
14 : X = CCO_2Et
15 : X = CH

Results and discussion

The desired 1,2-diamino-1,3-diaza- (**4**) and 1,2-diamino-1-aza- (**5**) and 1-amino-2-ethylamino-1-azaazulenium salts (**6**) were obtained in good yields by treatment of the corresponding azaazulenes **1**–**3** with *O*-mesitylsulfonylhydroxylamine (MSH) in dichloromethane. In the ^{1}H NMR spectra of the salts **4**–**6**, two different amino protons were observed at around δ 6.3 (2H, br s) and 8.6–9.6 (2H, br). In addition 1H singlets at δ 6.6–6.9, assignable to H-3, were seen in the ^{1}H NMR spectra of **5** and **6**. These indicate that the amination occurred at N-1.

Treatment of the salt **4** with potassium carbonate in ethanol gave slightly unstable yellow crystals **7**. In the ^{1}H NMR spectrum of **7**, a 2H singlet, assignable to amino protons, was observed at δ 4.55. This is compatible with the observation that the amino protons of 1-amino-1-azaazulen-2(1*H*)-one were

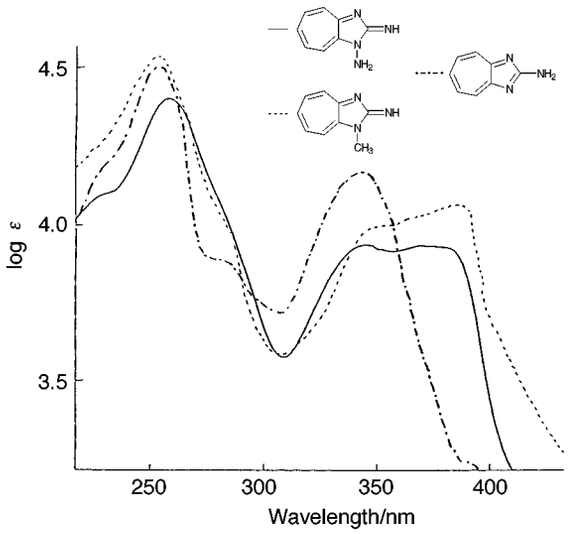


Fig. 1 Electronic absorption spectra of 1-amino-2-imino-1,2-dihydro-1,3-diazaazulene **7**, 2-imino-1-methyl-1,2-dihydro-1,3-diazaazulene **8** and 2-amino-1,3-diazaazulene.

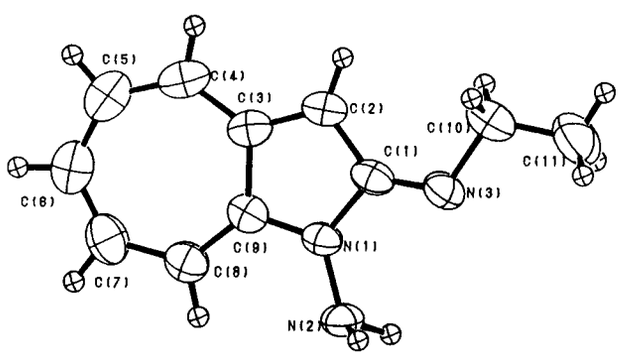


Fig. 2 An ORTEP drawing of **10** with thermal ellipsoid plot (50% probability). Selective bond lengths (Å); N(1)–N(2) 1.407(4), N(1)–C(1) 1.407(4), N(1)–C(9) 1.365(4), N(3)–C(1) 1.283(4), N(3)–C(10) 1.407(4), C(1)–C(2) 1.441(5), C(2)–C(3) 1.363(4), C(3)–C(4) 1.415(5), C(3)–C(9) 1.468(5), C(4)–C(5) 1.357(5), C(5)–C(6) 1.414(6), C(6)–C(7) 1.363(6), C(7)–C(8) 1.414(5), C(8)–C(9) 1.371(4).

seen at δ 4.54.[2] The electronic spectrum of **7** resembles that of 2-imino-1-methyl-1,2-dihydro-1,3-diazaazulene **8**[7] (Fig. 1). Therefore we assigned the structure of **7** to 1-amino-2-imino-1,2-dihydro-1,3-diazaazulene not 2-amino-1,3-diazaazulenium 1-aminide. Similar treatment of **5** afforded compound **9**, but was rather unstable and was not isolated. When 1-amino-2-ethylamino-1-azaazulenenium salt **6** was treated with potassium carbonate in acetonitrile for 2 days at room temperature, 1-amino-2-ethylimino-1,2-dihydro-1-azaazulene (**10**) was obtained in 89% yield as stable crystals. The structure of **10** was confirmed by X-ray crystal structure analysis. There are two independent molecules in a unit cell of **10**, but they have essentially the same geometry. Therefore an ORTEP drawing[8] of only one conformer is shown in Fig. 2.

To complement the synthesis, the structures of 1-amino-2-imino-1,2-dihydro-1,3-diazaazulene (**7**) and 1-amino-2-imino-1,2-dihydro-1-azaazulene (**9**) were studied by MO calculations using PM3.[9,10] The calculated bond lengths and charges on the heavy atoms of **7** and **9** are presented in Fig. 3. In Fig. 4, the HOMO and the LUMO and their energy levels are presented.

Determination of the bond lengths of **10** by X-ray analysis and those of **7** and **9** by MO calculation revealed large bond alternations in the seven-membered ring. This result shows that they have inherently hydrazine-substituted extended heptafulvene character.

To seek the formation of a stable 2-aminoazaazulenium *N*-imide, we tried to acetylate the salt **4**. Thus when salt **4** was

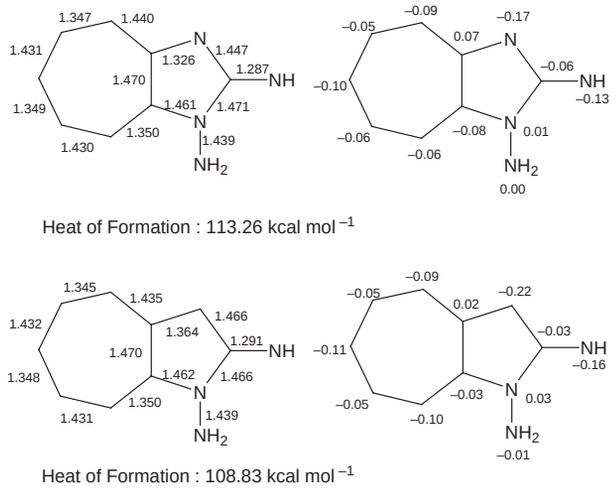


Fig. 3 Bond lengths and atomic charges for optimized structures of the 1-amino-2-imino-1,2-dihydro-1,3-diazaazulene **7** (upper) and 1-amino-2-imino-1,2-dihydro-1-azaazulene **9** (lower) obtained from the PM3 MO calculation.

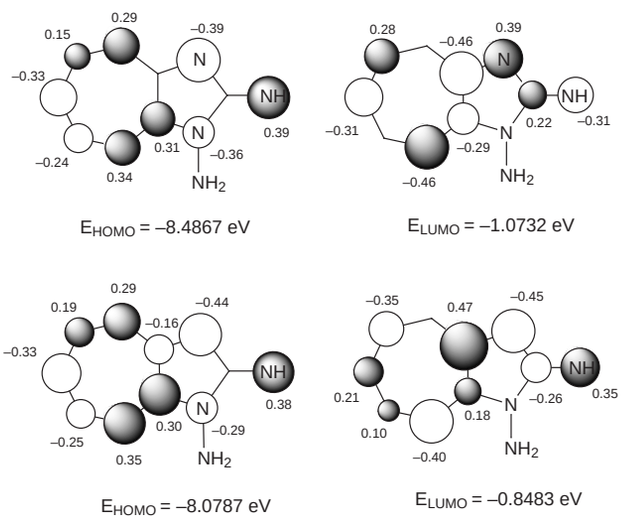
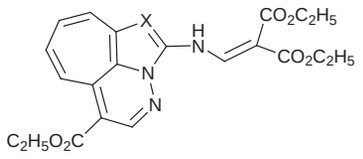


Fig. 4 HOMO and LUMO of the 1-amino-2-imino-1,2-dihydro-1,3-diazaazulene **7** (upper) and 1-amino-2-imino-1,2-dihydro-1-azaazulene **9** (lower) with the orbital energies and the renormalized PM3 MO coefficients.

heated with acetic anhydride in the presence of sodium acetate for one day, cyclization occurred and 2-methyl-1,3,3a,9-tetraazacyclopent[*a*]azulene (**11**) was obtained in 83% yield; however, an *N*-acetyl compound was not isolated. This result suggests that acetylation occurred on an amino group, and successive condensation with another amino group produced the cyclization product **11**. So we next performed the reaction of ethyl 2-acetylamino-1-azaazulene-3-carboxylate (**12**) with MSH and obtained 1-amino-1-azaazulenium salt **13** in 32% yield. Cyclization of **13** was achieved by treatment with polyphosphoric acid and ethyl 2-methyl-1,3,3a-triazacyclopent[*a*]azulene-9-carboxylate (**14**) and 2-methyl-1,3,3a-triazacyclopent[*a*]azulene (**15**) were isolated in 44 and 21% yield, respectively. Treatment of **13** with sodium hydrogen carbonate gave ethyl 2-acetylimino-1-amino-1,2-dihydro-1-azaazulene-3-carboxylate (**16**) (44%) and **14** (12%).

It is known that heterocyclic *N*-imides react with diethyl ethoxymethylenemalonate (DEEM) to give *N′*-substituted *N*-imides, which cyclize to pyrazolo[1,5-*a*]pyridine,[11,12] and that 1-amino-2-imino-1,2-dihydropyridine generated from 1,2-diaminopyridinium salt reacts with DEEM to give [1,2,4]-triazolo[1,5-*a*]pyridine derivatives.[6] In our study of the reaction of 2-methoxy-1-azaazulene *N*-imide with DEEM, cyclization occurred in a one-pot reaction and two kinds of cycloproducts,



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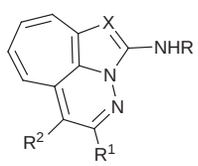
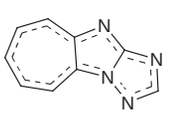
22 : X = CH

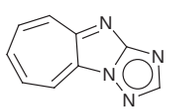


18 : X = N, R = H, R^1 = H, R^2 = CO_2Et
24 : X = CH, R = H, R^1 = H, R^2 = CO_2Et
25 : X = N, R = H, R^1 = CH_2CO_2Et, R^2 = CO_2Et
26 : X = CH, R = H, R^1 = CH_2CO_2Et, R^2 = CO_2Et
27 : X = CH, R = Et, R^1 = CH_2CO_2Et, R^2 = CO_2Et
28 : X = N, R = H, R^1 = R^2 = CO_2Et
29 : X = N, R = R^2 = H, R^1 = CO_2Et
30 : X = CH, R = Et, R^1 = R^2 = CO_2Et
31 : X = CH, R = H, R^1 = R^2 = CO_2Me
33 : X = N, R = R^1 = H, R^2 = CO_2Me
36 : X = CH, R = H, R^1 = R^2 = CO_2Me
37 : X = CH, R = R^1 = H, R^2 = CO_2Et
39 : X = CH, R = Et, R^1 = R^2 = CO_2Me
40 : X = CH, R = Et, R^1 = H, R^2 = CO_2Me

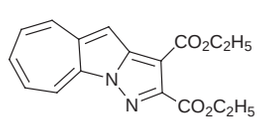
19 : X = N
21 : X = CH



19A



19B



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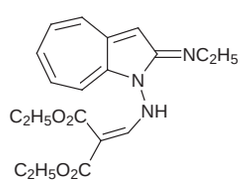

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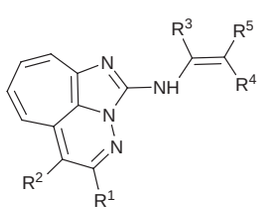
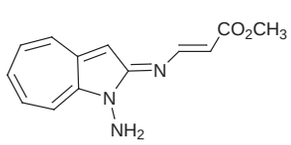


32 : R^1 = R^2 = R^3 = R^4 = CO_2Et, R^5 = H
34 : R^1 = R^3 = R^5 = H, R^2 = R^4 = CO_2Me
35 : R^1 = R^3 = R^4 = H, R^2 = R^5 = CO_2Me



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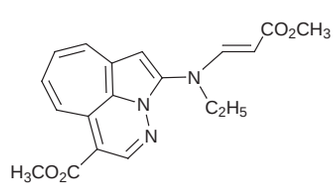

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3,3a-diazacyclopent[*a*]azulene and 2a,3-diazabenz[*cd*]azulene derivatives, were obtained.[2] Therefore, it was expected that the reaction of 1,2-diaminoazaazulenium salts with DEEM would afford different types of cycloadducts compared with those obtained from 1,2-diaminopyridinium salt. Thus we treated the salt **4** with DEEM in the presence of potassium carbonate in acetonitrile and obtained diethyl (5-ethoxycarbonyl-1,2a,3-triazabenz[*cd*]azulen-2-yl)aminomethylenemalonate (**17**) (7%), ethyl 2-amino-1,2a,3-triazabenz[*cd*]azulene-5-carboxylate (**18**) (8%) and 1,3,3a,9-tetraazacyclopent[*a*]azulene (**19**) (47%). When the reaction was performed in ethanol, the yields had apparently changed and **17** (63%) was obtained as a major product along with **18** (4%) and **19** (29%).

Compound **18** was identical to the product from the reaction of **4** with ethyl propiolate (see below). The structure of **19** was deduced by X-ray crystal structure analysis. An ORTEP drawing[8] of **19** is shown in Fig. 5. The bond lengths of the seven-membered ring of **19** were determined to be approximately 1.357–1.403 and those of the tetraazapentalene moiety approximately 1.320–1.369 Å. Although bond-alternation of the ring is observed, the divergence is rather smaller than that seen in diethyl 3,3a-diazacyclopent[*a*]azulene-1,2-dicarboxylate (**20**).[2] This suggests that **19** has the pericyclic conjugation form **A** as well as the triazole-fused heptafulvene **B**.

Reactions of the salts **5** and **6** with DEEM in the presence of potassium carbonate are essentially comparable with those of the 1,2-diamino-1,3-diazaazulenium salt **4**. Thus, on treatment

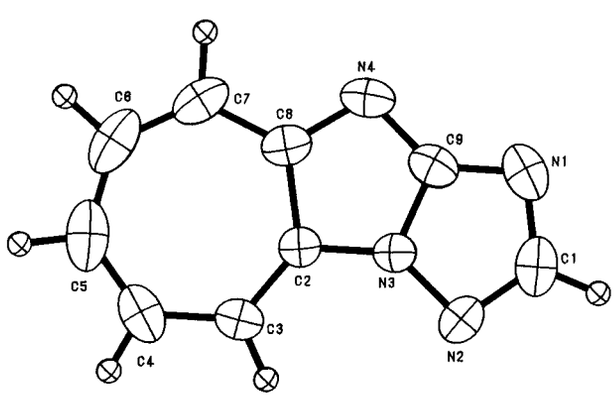

Fig. 5 An ORTEP drawing of **19** with thermal ellipsoid plot (50% probability). Selective bond lengths (Å); N(1)–C(1) 1.358(3), N(1)–C(9) 1.327(3), C(1)–N(2) 1.320(3), N(2)–N(3) 1.366(2), N(3)–C(9) 1.358(3), N(3)–C(2) 1.369(2), C(2)–C(3) 1.360 (3), C(3)–C(4) 1.403(3), C(4)–C(5) 1.371(4), C(5)–C(6) 1.401(4), C(6)–C(7) 1.357(4), C(7)–C(8) 1.394(3), C(8)–C(2) 1.468(3), C(8)–N(4) 1.349(3), N(4)–C(9) 1.359(3).

of 1,2-diamino-1,2-dihydro-1-azaazulene generated from **5** with DEEM in acetonitrile, 1,3,3a-triazacyclopent[*a*]azulene (**21**) was obtained as a single product (96%). On the other hand, when the reaction was performed in ethanol, diethyl (5-ethoxycarbonyl-2a,3-diazabenz[*cd*]azulen-2-yl)aminomethylenemalonate (**22**) (12%) was obtained together with **21** (50%).

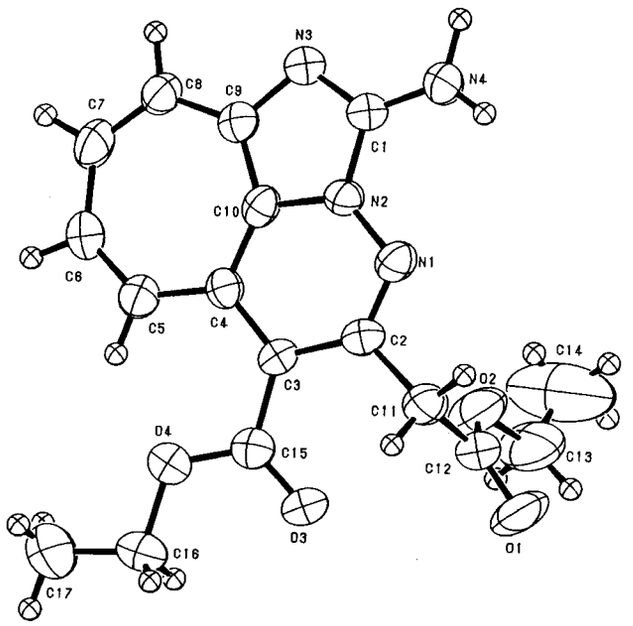

Fig. 6 An ORTEP drawing of **25** with thermal ellipsoid plot (50% probability). Since C(14) showed disorder, the calculation was performed based on the one specified point. Selective bond lengths (Å); N(1)–N(2) 1.382(6), N(1)–C(2) 1.308(7), N(2)–C(1) 1.364(7), N(2)–C(10) 1.387(7), N(3)–C(1) 1.319(7), N(3)–C(9) 1.382(7), N(4)–C(1) 1.342(7), C(2)–C(3) 1.447(8), C(3)–C(4) 1.431(7), C(4)–C(5) 1.452(8), C(5)–C(6) 1.372(8), C(6)–C(7) 1.427(9), C(7)–C(8) 1.337(8), C(8)–C(9) 1.415(8), C(9)–C(10) 1.396(7).

Reaction of the salt **6** with DEEM in the presence of potassium carbonate and silica gel in ethanol yielded diethyl (2-ethylimino-1,2-dihydro-1-azaazulen-1-yl)aminomethylenemalonate (**23**) in 92% yield, which converted to ethyl 2-ethylamino-2a,3-diazabenz[*cd*]azulene-5-carboxylate (**24**).

Next we examined the reaction of 1-amino-2-imino-1,2-dihydro-1,3-diazaazulene (**7**) from the salt **4** with diethyl acetonedicarboxylate (DAD), which has three active sites, the active methylene moiety, a ketonic carbonyl group and the ester carbonyl groups. Thus we treated salt **4** with diethyl acetonedicarboxylate in the presence of potassium carbonate and obtained ethyl (2-amino-5-ethoxycarbonyl-1,2a,3-triazabenz-[*cd*]azulen-4-yl)acetate (**25**) in a 59% yield. The structure of **25** was deduced by X-ray crystal structure analysis. An ORTEP drawing[8] of **25** is shown in Fig. 6. This result suggests that initially a condensation of the carbonyl group of diethyl acetonedicarboxylate with the amino group at N-1 on the 1-azaazulene ring occurred and a successive attack of a carbanion, derived from the active methylene moiety, to C-8 leads to **25**. The reactions of **5** and **6** with diethyl acetonedicarboxylate proceeded similarly and gave **26** (30%) and **27** (36%), respectively.

To further investigate this consideration, we performed the reactions of **4** with some active methylene compounds, such as diethyl oxalacetate and ethyl pyruvate. Thus the treatment of **4** with diethyl oxalacetate in the presence of potassium carbonate gave diethyl 2-amino-1,2a,3-triazabenz[*cd*]azulene-4,5-dicarboxylate (**28**) (25%), and the treatment with ethyl pyruvate gave ethyl 2-amino-1,2a,3-triazabenz[*cd*]azulene-4-carboxylate (**29**) (25%). Similar treatment of **6** with diethyl oxalacetate gave diethyl 2-ethylamino-1,2a,3-triazabenz[*cd*]azulene-4,5-dicarboxylate (**30**) (30%) together with **10** (45%). The results support the theory that the reaction proceeds in a similar manner to the reaction of diethyl acetonedicarboxylate.

It is known that heterocyclic *N*-aminides perform a 1,3-dipolar cycloaddition with acetylenic esters,[1,2,13] however 1-amino-2-imino-1,2-dihydropyridine generated from 1,2-diaminopyridinium salt reacted with an activated acetylene to give [1,2,4]triazolo[1,5-*a*]pyridine derivatives.[6] Since 1-amino-2-imino-1,2-dihydro-1,3-diazaazulene (**7**) is predicted to have the character of an aminoheptafulvene, its reaction with a dipolarophile would be particularly interesting, where an extended dipolar cycloaddition or a sequence reaction of Michael addition–cyclization–elimination could occur. Thus the salt **4** was treated with dimethyl acetylenedicarboxylate (DMAD) in the presence of potassium carbonate in acetonitrile, and dimethyl 2-amino-1,3,3a-triazabenz[*cd*]-azulene-4,5-dicarboxylate (**31**) was isolated in 25% yield. Similar treatment of **4** with diethyl acetylenedicarboxylate gave **28** (26%) together with diethyl (4,5-diethoxycarbonyl-1,2a,3-triazabenz[*cd*]azulen-2-yl)aminofumarate (**32**) (7%). In these reactions, 1,3,3a,9-tetraaza- (**19**) and 1,3,3a-triazacyclopent-[*a*]azulene derivatives (**21**), were not detected. The results show that an extended dipolar cycloaddition is preferred. As expected, a dipolar cycloaddition with unsymmetrically substituted acetylenic ester was regioselective. Thus, methyl propiolate, following the same procedure as for DMAD, gave the methyl 2-amino-1,2a,3-triazabenz[*cd*]azulene-5-carboxylate (**33**) (43%) together with methyl (*Z*)-3-(5-methoxycarbonyl-1,2a,3-triazabenz[*cd*]azulen-2-yl)aminoacrylate (**34**) (14%) and methyl (*E*)-3-(5-methoxycarbonyl-1,2a,3-triazabenz[*cd*]azulen-2-yl)aminoacrylate (**35**) (1%). Similar treatment of ethyl propiolate gave ethyl 2-amino-1,2a,3-triazabenz[*cd*]azulene-5-carboxylate (**18**) (26%). The ^{1}H NMR spectrum of **18** shows the H-6 proton resonates at a lower field δ 7.71 (d, *J* 12.2), which could be attributed to the anisotropic effect of the ester group situated at C-5, this compares with δ 5.31 (d, *J* 12.2) for ethyl 2-amino-1,2a,3-triazabenz[*cd*]azulene-4-carboxylate (**29**). This result supports the structural assignment. In a similar manner, **5** reacted with DMAD and MP to give **36** and **37** along with **38**, respectively, and we also treated **6** with DMAD and MP in the presence of potassium carbonate and obtained **39** (37%) and **40** (38%) along with **41** (7%).

To confirm that the reaction proceeded *via* the 1-amino-2-imino-1,2-dihydro-1-azaazulene form, compound **10** was treated with DMAD and MP. In the reaction of **10** with DMAD, **39** was obtained in 27% yield, and the reaction of **10** with MP gave **40** (31%) and **41** (15%). This result supports the theory that the reaction of the azaazulenium salts formed 1-amino-2-imino-1,2-dihydro-1-azaazulenes (**7**, **9** and **10**) at first in the presence of potassium carbonate, and then the 1-azaazulenes (**7**, **9** and **10**) reacted with the reagents.

Experimental

Melting points were measured using Yanagimoto micro-melting apparatus and are uncorrected. ^{1}H NMR spectra (250 MHz) and ^{13}C NMR spectra (62.87 MHz) were recorded on a Hitachi R-250H spectrometer using deuteriochloroform as a solvent with tetramethylsilane as an internal standard unless otherwise stated; *J* values are recorded in Hz. Electronic spectra were recorded with a Hitachi 220A spectrophotometer using ethanol as a solvent. IR spectra were recorded for KBr pellets on a Nicolet FT-IR Impact 410. Mass spectra were recorded on a LC-MS Waters Integrity System. Kieselgel 60 was used for column chromatography.

Synthesis of 1,2-diamino-1,3-diazaazulenium salt 4

To a solution of 2-amino-1,3-diazaazulene (**1**) (0.147 g, 1.00 mmol) in dichloromethane (30 ml) in an ice–water bath was added dropwise over a period of 5 min the solution of *O*-mesitylsulfonylhydroxylamine (MSH) (0.267 g, 1.00 mmol) in dichloromethane (4 ml). After being stirred overnight at room temperature, the resulting precipitates were collected by filtration and rinsed with dichloromethane, and then dried to give 1,2-diamino-1,3-diazaazulenium salt (**4**) (0.342 g, 95%), which was recrystallized from methanol to give colorless microneedles, mp 147–148 °C; δ_H (DMSO-d_6) 2.17 (3H, s), 2.48 (6H,

s), 6.32 (2H, br s), 6.73 (2H, s), 8.10–8.50 (5H, m) and 8.60–9.65 (2H, br); ν_{max}/cm^{-1} 3361, 3323, 3260 and 3148 (NH); λ_{max}/nm (log ε) 224 (4.30), 258 (4.41), 342 (3.95), 370 (3.91) and 418 (1.71, sh) (Found: C, 54.4; H, 5.7; N, 14.9. Calc. for $C_{17}H_{20}N_4O_3S\cdot H_2O$: C, 54.0; H, 5.9; N, 14.8%).

In a similar manner, we synthesized 1,2-diamino-1-aza-azulenium salt (**5**) (52%) and 1,2-diamino-1-azaazulenium salt (**6**) (89%).

1,2-Diamino-1-azaazulenium salt (**5**): yellow micro-needles (from methanol), mp 172–174 °C; δ_H (DMSO-d_6) 2.16 (3H, s), 2.50 (6H, s), 6.24 (2H, br s), 6.62 (1H, s), 6.74 (2H, s), 7.56–7.79 (3H, m), 8.01 (1H, d, *J* 9.2), 8.14–8.19 (1H, m) and 8.80 (2H, br); ν_{max}/cm^{-1} 3298, 3217, 3180 and 3119 (NH); λ_{max}/nm (log ε) 268 (4.45), 304 (4.11, sh), 414 (3.93), 460 (3.46, sh) and 498 (2.45, sh) (Found: C, 59.9; H, 5.9; N, 11.6. Calc. for $C_{18}H_{21}N_3O_3S$: C, 60.1; H, 5.9; N, 11.7%).

1,2-Diamino-1-azaazulenium salt (**6**): yellow micro-needles (from methanol), mp 202–204.5 °C; δ_H (DMSO-d_6) 1.25 (3H, t, *J* 7.0), 2.16 (3H, s), 2.48 (6H, s), 3.49 (2H, qd, *J* 7.0 and 6.1), 6.29 (2H, br s), 6.73 (2H, s), 6.88 (1H, s), 7.67 (1H, t, *J* 9.8), 7.71 (1H, dd, *J* 9.8 and 9.2), 7.79 (1H, dd, *J* 11.0 and 9.8), 8.01 (1H, d, *J* 9.2), 8.14 (1H, d, *J* 11.0) and 8.95 (1H, br t, *J* 6.1); ν_{max}/cm^{-1} 3380, 3164, 3134 and 3103 (NH) (Found: C, 61.7; H, 6.7; N, 10.9. Calc. for $C_{20}H_{25}N_3O_3S$: C, 62.0; H, 6.5; N, 10.8%).

Reaction of 1,2-diamino-1,3-diazaazulenium salt 4 with potassium carbonate

A mixture of **4** (0.360 g, 1.00 mmol) and potassium carbonate (0.691 g, 5.00 mmol) in ethanol (100 ml) was stirred for 3 days at room temperature. The solution turned yellow. The mixture was filtered and evaporation of the filtrate gave 1-amino-2-imino-1,2-dihydro-1,3-diazaazulene (**7**) as a yellow solid (0.150 g, 94%), which was recrystallized from hexane–dichloromethane to give unstable yellow micro-needles, mp 122–125 °C; δ_H 4.55 (2H, br s), 7.00 (1H, tm, *J* 10.4) and 7.20–7.60 (5H, m); ν_{max}/cm^{-1} 3290, 3253, 3250 and 3080 (NH); λ_{max}/nm (log ε) 258 (4.40), 344 (3.94), 370 (3.94) and 406 (3.27, sh); *m*/*z* (rel. intensity) 160 (M$^+$, 100%), 145 (66) and 145 (15) (Found: C, 56.6; H, 5.3; N, 32.8. Calc. for $C_8H_8N_4\cdot 1/2\ H_2O$: C, 56.8; H, 5.4; N, 33.1%).

Reaction of 1-amino-2-ethylamino-1-azaazulenium salt 6 with potassium carbonate

A mixture of 1-amino-2-ethylamino-1-azaazulenium salt (**6**) (1.94 g, 5.00 mmol) and potassium carbonate (1.40 g, 10.13 mmol) in acetonitrile (200 ml) was stirred for 2 days at room temperature. The solution turned orange. The mixture was evaporated. To the residue, hexane was added, and the mixture filtered. Evaporation of the filtrate gave 1-amino-2-ethylimino-1,2-dihydro-1-azaazulene (**10**) as orange needles (0.833 g, 89%), which were recrystallized from hexane to give red prisms, mp 223–225 °C (decomp.); δ_H 1.25 (3H, t, *J* 7.3), 3.40 (2H, td, *J* 7.0 and 6.1), 4.31 (2H, s), 5.98 (1H, s), 6.35–6.40 (1H, m), 6.68 (1H, dd, *J* 11.0 and 8.6), 6.75–6.90 (2H, m) and 6.97 (1H, d, *J* 11.0); δ_C 16.90, 44.69, 97.23, 106.72, 124.10, 125.84, 131.18, 132.10, 141.95, 148.02 and 159.16; ν_{max}/cm^{-1} 3281 and 3164 (NH); λ_{max}/nm (log ε) 240 (4.09), 272 (4.41), 298 (4.18), 425 (4.05) and 450 (3.79, sh); *m*/*z* (rel. intensity) 187 (M$^+$, 59%), 171 (87), 157 (12), 144 (68), 129 (20), 210 and 102 (100) (Found: C, 70.5; H, 7.1; N, 22.3. Calc. for $C_{11}H_{13}N_3$: C, 70.6; H, 7.0; N, 22.4%).

Reaction of 1,2-diamino-1,3-diazaazulenium salt 4 with acetic anhydride–sodium acetate

A mixture of **4** (0.360 g, 1.00 mmol), acetic anhydride (10 ml) and sodium acetate (0.100 g) was refluxed for 1 day. Water was added to the mixture, and neutralized with sodium hydrogen carbonate, then extracted with chloroform. The extract was dried over sodium sulfate and evaporated. The residue was chromatographed with chloroform–ethyl acetate (1 : 1) to give 2-methyl-1,3,3a,9-tetraazacyclopent[*a*]azulene (**11**) (0.152 g, 83%).

Compound **11**: orange needles (from ethyl acetate), mp 171–172 °C; δ_H 2.71 (3H, s), 7.95–8.13 (3H, m) and 8.60–8.72 (2H, m); δ_C 16.05, 120.66, 129.57, 132.71, 135.24, 135.91, 136.34, 137.62, 162.67 and 171.00; λ_{max}/nm (log ε) 236 (4.14), 290 (4.54), 294 (4.52, sh), 326 (3.65, sh), 372 (3.28, sh) and 416 (3.13); *m*/*z* (rel. intensity) 184 (M$^+$, 100%), 156 (12), 115 (15) and 103 (15) (Found: C, 59.9; H, 4.9; N, 27.9. Calc. for $C_{10}H_8N_4\cdot H_2O$: C, 59.4; H, 5.0; N, 27.7%).

Synthesis of 2-acetylamino-3-ethoxycarbonyl-1-amino-1-aza-azulenium salt 13

To a solution of ethyl 2-acetylamino-1-azaazulene-3-carboxylate (**12**) (0.293 g, 1.13 mmol) in dichloromethane (2.5 ml) in an ice–water bath was added dropwise over a period of 5 min a solution of MSH (0.864 g, 4.02 mmol) in dichloromethane (2 ml) and stirred for 0.5 h. After being stirred for 1 h at room temperature, diethyl ether (10 ml) was added to the mixture. The resulted precipitates were collected by filtration and rinsed with dichloromethane, and then dried to give 2-acetylamino-3-ethoxycarbonyl-1,2-diamino-1-azaazulenium salt (**13**) (0.172 g, 32%). The combined filtrate was evaporated, and the residue was dissolved in water. The solution was neutralized with sodium hydrogen carbonate, then the mixture was extracted with chloroform. The extract was dried over sodium sulfate and was evaporated. Chromatography of the residue with chloroform gave recovered **12** (0.072 g, 25%).

Compound **13**: yellow micro-needles (ethanol), mp 113.5–114.5 °C; δ_H (DMSO-d_6) 1.42 (3H, t, *J* 7.0), 2.16 (3H, s), 2.23 (3H, s), 2.50 (6H, s), 4.47 (2H, q, *J* 7.0), 6.70 (2H, s), 8.15 (1H, dd, *J* 11.0 and 10.4), 8.18 (1H, dd, *J* 10.4 and 9.2), 8.31 (1H, dd, *J* 11.0 and 9.2), 8.33 (1H, d, *J* 11.0), 8.83 (1H, br), 9.27 (1H, d, *J* 11.0), 9.61 (1H, br) and 11.81 (1H, br); ν_{max}/cm^{-1} 3425, 3343, 3260 (NH), 1713 and 1699 (C=O) (Found: C, 58.1; H, 5.9; N, 8.8. Calc. for $C_{23}H_{27}N_3O_6S$: C, 58.3; H, 5.8; N, 8.9%).

Reaction of 2-acetylamino-3-ethoxycarbonyl-1-amino-1-aza-azulenium salt 13 with polyphosphoric acid

A mixture of **13** (0.320 g, 0.67 mmol) and polyphosphoric acid (5 ml) was heated for 4 h at 115 °C. To the mixture, water was added, neutralized with sodium hydrogen carbonate, and extracted with chloroform. The extract was dried over sodium sulfate and was evaporated. The residue was chromatographed with ethyl acetate–chloroform (1 : 1) to give ethyl 2-methyl-1,3,3a-triazacyclopent[*a*]azulene-9-carboxylate (**14**) (0.076 g, 44%) and 2-methyl-1,3,3a-triazacyclopenta[*a*]azulene (**15**) (0.026 g, 21%).

Compound **14**: reddish violet prisms (from ethyl acetate), mp 154–154.5 °C; δ_H 1.51 (3H, t, *J* 7.3), 2.73 (3H, s), 4.58 (2H, q, *J* 7.3), 7.72–7.79 (3H, m), 8.61 (1H, d, *J* 7.9) and 9.59–9.65 (1H, m); ν_{max}/cm^{-1} 1675 (C=O); *m*/*z* (rel. intensity) 255 (M$^+$, 10%), 210 (14), 183 (100), 141 (13) and 114 (23) (Found: C, 65.7; H, 5.4; N, 16.5. Calc. for $C_{14}H_{13}N_3O_2$: C, 65.9; H, 5.1; N, 16.5%).

Compound **15**: violet needles (from hexane–dichloromethane), mp 115–116 °C; δ_H 2.68 (3H, s), 7.20–7.45 (4H, m), 8.04 (1H, d, *J* 11.0) and 8.23 (1H, d, *J* 7.9) (Found: C, 70.9; H, 5.0; N, 22.6. Calc. for $C_{11}H_9N_3\cdot 1/5\ H_2O$: C, 70.7; H, 5.1; N, 22.5%).

Reaction of 13 with sodium hydrogen carbonate

The solution of **13** (0.086 g, 0.18 mmol) in water (20 ml) was adjusted to pH 10 by addition of sodium hydrogen carbonate, then the mixture was extracted with chloroform. The extract was dried over sodium sulfate and was evaporated. The residue was chromatographed with ethyl acetate to give ethyl 2-acetyl-

Table 1 Conditions and yields for the reactions of **4**–**6** with DEEM, active methylene compounds and acetylenic esters

Substrate	Reagent	Solvent	Time/days	Products (Yield, %)		
4	DEEM	MeCN	2	**17** (7)	**18** (8)	**19** (47)
4	DEEM	EtOH	3	**17** (63)	**18** (4)	**19** (29)
5	DEEM	MeCN	7	**21** (96)		
5	DEEM	EtOH	7	**21** (50)	**22** (12)	
6	DEEM	EtOH	5	**23** (92)		
4	DAD	MeCN	2	**25** (59)		
5	DAD	MeCN	2	**26** (30)		
6	DAD	MeCN	4	**27** (36)		
4	Diethyl oxalacetate	MeCN	3	**28** (25)		
6	Diethyl oxalacetate	EtOH	4	**30** (30)	**10** (45)	
4	Ethyl pyruvate	MeCN	2	**29** (25)		
4	DMAD	MeCN	2	**31** (25)		
4	DEAD	MeCN	2	**32** (7)	**28** (26)	
4	MP	MeCN	5	**33** (43)	**34** (14)	**35** (1)
5	DMAD	MeCN	2	**36** (5)		
5	MP	MeCN	6	**38** (57)	**37** (10)	
6	DMAD	EtOH	4	**39** (37)		
6	MP	MeCN	4	**40** (38)	**41** (7)	

imino-1-amino-1,2-dihydro-1-azaazulene-3-carboxylate (**16**) (0.022 g, 44%) and ethyl 2-methyl-1,3,3a-triazacyclopent[*a*]-azulene-9-carboxylate (**14**) (0.005 g, 12%).

Compound **16**: yellow needles (from hexane–ethanol), mp 115.5–116 °C; δ_H (DMSO-d_6) 1.38 (3H, t, *J* 7.3), 1.97 (3H, s), 4.41 (2H, q, *J* 7.3), 7.76–7.97 (5H, m), 8.24 (2H, br) and 8.95 (1H, d, *J* 10.4); ν_{max}/cm^{-1} 3365, 3290, 3223 (NH), 1675 and 1658 (C=O and C=N) (Found: C, 57.4; H, 5.9; N, 14.2. Calc. for $C_{14}H_{15}N_3O_3 \cdot H_2O$: C, 57.7; H, 5.9; N, 14.2%).

Reaction of the salts 4, 5 and 6 with diethyl ethoxymethylenemalonate, diethyl acetonedicarboxylate, diethyl oxalacetate, ethyl pyruvate and acetylenic esters—a typical procedure

A mixture of **4** (0.360 g, 1.00 mmol), diethyl ethoxymethylenemalonate (DEEM) (0.650 g, 3.00 mmol) and potassium carbonate (0.691 g, 5.00 mmol) in acetonitrile (150 ml) was stirred for 7 h at room temperature, then silica gel (5.00 g) was added to the mixture and the stirring was continued for 2 days. The mixture was filtered and the residue was washed with ethyl acetate. The combined filtrate was evaporated. The residue was chromatographed with chloroform to give diethyl (5-ethoxycarbonyl-1,2a,3-triazabenz[*cd*]azulen-2-yl)aminomethylenemalonate (**17**) (0.028 g, 7%) and ethyl 2-amino-1,2a,3-triazabenz[*cd*]azulene-5-carboxylate (**18**) (0.022 g, 8%). Elution from ethyl acetate–chloroform (1:1) gave 1,3,3a,9-tetraazacyclopent[*a*]azulene (**19**) (0.080 g, 47%).

Compound **17**: dark green needles (from hexane–dichloromethane), mp 154–156 °C; δ_H 1.28 (3H, t, *J* 7.3), 1.31 (3H, t, *J* 7.3), 1.38 (3H, t, *J* 7.0), 4.21 (2H, q, *J* 7.3), 4.24 (2H, q, *J* 7.3), 4.35 (2H, q, *J* 7.0), 6.02 (1H, dd, *J* 11.0 and 9.2), 6.46 (1H, dd, *J* 12.2 and 9.2), 6.90 (1H, d, *J* 11.0), 7.75 (1H, d, *J* 12.8), 7.83 (1H, s), 8.77 (1H, d, *J* 12.8) and 11.37 (1H, br d, *J* 12.8); δ_C 14.22, 14.28, 14.34, 60.22, 60.47, 61.02, 98.75, 126.88, 128.47, 128.56, 137.13, 137.28, 137.36, 138.26, 140.24, 140.43, 147.53, 152.97, 163.72, 164.31 and 167.94; ν_{max}/cm^{-1} 1733, 1695 and 1662 (C=O); *m*/*z* (rel. intensity) 426 (M^+, 2%), 380 (24), 281 (11), 207 (29), 149 (49), 97 (77) and 71 (100) (Found: C, 59.3; H, 5.3; N, 13.0. Calc. for $C_{21}H_{22}N_4O_6$: C, 59.2; H,5.2; N, 13.1%).

Compound **18**: brown needles (from hexane–dichloromethane) mp 184–186 °C; δ_H 1.30 (3H, t, *J* 7.0), 4.19 (2H, q, *J* 7.0), 4.84 (2H, br s), 5.96 (1H, dd, *J* 10.4 and 9.2), 6.42 (1H, dd, *J* 12.2 and 9.2), 6.82 (1H, d, *J* 10.4), 7.63 (1H, s) and 7.71 (1H, d, *J* 12.2); ν_{max}/cm^{-1} 3294, 3215 (NH) and 1672 (C=O); *m*/*z* (rel. intensity) 256 (M^+, 100%), 228 (81), 211 (31), 184 (28), 156 (12) and 129 (12) (Found: C, 60.7; H, 4.9; N, 21.7. Calc. for $C_{13}H_{12}N_4O_2$: C, 60.9; H, 4.7; N, 21.9%).

Compound **19**: orange needles (from hexane–dichloromethane) mp 200–202 °C and 247–248 °C (polymorphism); δ_H 7.95–8.20 (3H, m), 8.48 (1H, s) and 8.68–8.78 (2H, m); δ_C 121.30, 132.46, 135.27, 136.49, 136.77, 136.89, 156.87, 160.04 and 163.22; λ_{max}/nm (log ε) 234 (4.41), 284 (4.52), 322 (3.54, sh), 366 (3.41, sh) and 416 (3.25); *m*/*z* (rel. intensity) 170 (M^+, 100%), 144 (11) and 116 (9) (Found: C, 63.5; H, 3.6; N, 32.8. Calc. for $C_9H_6N_4$: C, 63.5; H, 3.7; N, 32.9%).

In a similar manner, we treated the salts **4**–**6** with diethyl ethoxymethylenemalonate (DEEM), diethyl acetonedicarboxylate (DAD), diethyl oxalacetate, ethyl pyruvate, dimethyl acetylenedicarboxylate (DMAD), diethyl acetylenedicarboxylate (DEAD) and methyl propiolate (MP). The results are listed in Table 1.

1,3,3a-Triazacyclopent[*a*]azulene **21**: dark violet needles (from cyclohexane) mp 131–133 °C; δ_H 6.93 (1H, s), 7.18–7.46 (3H, m), 8.05 (1H, d, *J* 11.0), 8.31 (1H, dt, *J* 8.5 and 1.2) and 8.38 (1H, s); δ_C 97.78, 119.22, 127.03, 127.89, 134.78, 135.15, 142.10, 154.40, 157.57 and 160.74; λ_{max}/nm (log ε) 234 (4.17), 280 (4.52), 286 (4.53), 302 (4.19), 348 (3.45, sh), 368 (3.65), 388 (3.70), 494 (3.20), 562 (2.96, sh) and 628 (2.34, sh) (Found: C, 70.7; H, 4.2; N, 24.6. Calc. for $C_{10}H_7N_3$: C, 71.0; H, 4.2; N, 24.8%).

Diethyl (5-ethoxycarbonyl-2a,3-diazabenz[*cd*]azulen-2-yl)-aminomethylenemalonate **22**: dark green needles (from cyclohexane), mp 161–163 °C; δ_H 1.30 (3H, t, *J* 7.3), 1.34 (3H, t, *J* 7.3), 1.38 (3H, t, *J* 7.3), 4.18 (2H, q, *J* 7.3), 4.26 (2H, q, *J* 7.3), 4.34 (2H, q, *J* 7.3), 5.71 (1H, dd, *J* 10.4 and 8.5), 6.21 (1H, s), 6.25 (1H, dd, *J* 12.8 and 8.5), 6.63 (1H, d, *J* 10.4), 7.62 (1H, d, *J* 12.2), 7.89 (1H, s), 8.30 (1H, d, *J* 12.2) and 11.37 (1H, br d, *J* 12.8); ν_{max}/cm^{-1} 3245 (NH), 1686 and 1650 (C=O) (Found: C, 62.3; H, 5.6; N, 9.8. Calc. for $C_{22}H_{23}N_3O_6$: C, 62.1; H, 5.5; N, 9.9%).

Diethyl (2-ethylimino-1,2-dihydro-1-azaazulen-1-yl)amino-methylenemalonate **23**: yellow needles (from hexane–ethyl acetate), mp 154–155 °C; δ_H 1.20 (3H, t, *J* 7.3), 1.29 (3H, t, *J* 7.3), 1.36 (3H, t, *J* 7.3), 3.50 (2H, q, *J* 7.3), 4.00 (2H, q, *J* 7.3), 4.20 (2H, q, *J* 7.3), 6.38 (1H, s), 7.50–7.60 (3H, m), 7.93–7.97 (2H, m) and 8.50 (1H, s); δ_C 14.70, 14.77, 39.38, 58.94, 91.61, 121.66, 131.73, 132.74, 133.20, 134.17, 135.42, 142.93, 143.39, 155.31, 163.15, 168.46 and 171.27; ν_{max}/cm^{-1} 3350 (NH), 1699 and 1627 (C=O and C=C); *m*/*z* (rel. intensity) 357 (M^+, 2%), 355 (4), 283 (13), 281 (10), 207 (16), 149 (46), 109 (36) and 97 (100) (Found: C, 64.1; H, 6.5; N, 11.8. Calc. for $C_{19}H_{23}N_3O_4$: C, 63.9; H, 6.5; N, 11.8%).

Ethyl 2-amino-2a,3-diazabenz[*cd*]azulene-5-carboxylate **24**: green needles (from hexane), mp 99–99.5 °C; δ_H 1.29 (6H, t, *J* 7.0), 3.29 (2H, qd, *J* 7.0 and 5.5), 4.17 (2H, q, *J* 7.0), 4.47 (1H, br t, *J* 5.5), 5.68 (1H, s), 5.74 (1H, dd, *J* 11.0 and 8.6), 6.27 (1H, dd, *J* 12.8 and 8.6), 6.70 (1H, d, *J* 11.0), 7.69 (1H, d, *J* 12.8) and 7.73 (1H, s); δ_C 14.43, 14.95, 38.78, 59.18, 88.41, 94.67, 123.68,

125.42, 126.76, 134.20, 136.43, 137.62, 139.73, 146.65, 151.28 and 165.29; ν_{max}/cm^{-1} 3352 (NH) and 1667 (C=O); *m*/*z* (rel. intensity) 283 (M$^+$, 100%), 255 (48), 238 (15), 226 (57), 211 (14) and 126 (9) (Found: C, 67.9; H, 6.1; N, 14.7. Calc. for $C_{16}H_{17}N_3O_2$: C, 67.8; H, 6.1; N, 14.8%).

Ethyl 2-amino-5-ethoxycarbonyl-1,2a,3-triazabenz[*cd*]azulene-4-acetate **25**: green needles (from hexane–dichloromethane), mp 166–167 °C; δ_H 1.28 (6H, t, *J* 7.3), 3.45 (2H, s), 4.16 (2H, q, *J* 7.3), 4.18 (2H, q, *J* 7.3), 4.67 (2H, br s), 5.82 (1H, dd, *J* 11.0 and 8.5), 6.26 (1H, dd, *J* 12.2 and 8.5), 6.71 (1H, d, *J* 11.0) and 7.00 (1H, d, *J* 12.2); ν_{max}/cm^{-1} 3440, 3296 (NH), 1734, 1685 and 1644 (C=O); λ_{max}/nm (log ε) 262 (4.32), 306 (3.89, sh), 328 (3.90), 430 (4.11), 544 (2.91), 588 (3.06), 640 (3.10), 704 (2.98) and 780 (2.58, sh) (Found: C, 59.6; H, 5.3; N, 16.3. Calc. for $C_{17}H_{18}N_4O_4$: C, 59.6; H, 5.3; N, 16.4%).

Ethyl 2-amino-5-ethoxycarbonyl-2a,3-diazabenz[*cd*]azulene-4-acetate **26**: green needles (from hexane–dichloromethane), mp 156–158 °C; δ_H 1.28 (6H, t, *J* 7.3), 3.50 (2H, s), 4.16 (2H, q, *J* 7.3), 4.17 (2H, q, *J* 7.3), 4.28 (2H, br s), 5.57 (1H, dd, *J* 10.4 and 8.5), 5.72 (1H, s), 6.08 (1H, dd, *J* 12.2 and 8.5), 6.53 (1H, d, *J* 10.4) and 6.85 (1H, d, *J* 12.2); ν_{max}/cm^{-1} 3402, 3312 (NH), 1716 and 1681 (C=O); λ_{max}/nm (log ε) 268 (4.40), 298 (4.29), 394 (4.00), 422 (4.16), 530 (2.94, sh), 574 (3.07), 622 (3.11), 692 (2.96, sh) and 744 (2.65, sh) (Found: C, 63.4; H, 5.6; N, 12.0. Calc. for $C_{18}H_{19}N_3O_4$: C, 63.3; H, 5.6; N, 12.3%).

Ethyl 2-ethylamino-5-ethoxycarbonyl-2a,3-diazabenz[*cd*]-azulene-4-acetate **27**: green needles (from hexane–dichloromethane), mp 100.5–101.5 °C; δ_H 1.27 (6H, t, *J* 7.3), 3.23 (2H, qd, *J* 7.6 and 6.1), 3.48 (2H, s), 4.14 (2H, q, *J* 7.3), 4.17 (2H, q, *J* 7.30), 4.39 (1H, br t, *J* 6.1), 5.61 (1H, dd, *J* 10.4 and 8.5), 6.11 (1H, dd, *J* 12.8 and 8.5), 6.59 (1H, d, *J* 10.4) and 6.93 (1H, d, *J* 12.8); δ_C 14.19, 14.98, 38.87, 42.56, 59.73, 60.74, 88.62, 97.78, 123.04, 123.89, 127.49, 128.93, 136.25, 136.80, 139.05, 146.74, 154.43, 166.30 and 170.45; ν_{max}/cm^{-1} 3412 (NH), 1736 and 1672 (C=O); *m*/*z* (rel. intensity) 369 (M$^+$, 100%), 324 (17), 297 (16), 255 (22), 266 (25), 238 (25) and 139 (14) (Found: C, 65.2; H, 6.4; N, 11.2. Calc. for $C_{20}H_{23}N_3O_4$: C, 65.0; H, 6.3; N, 11.4%).

Diethyl 2-amino-1,2a,3-triazabenz[*cd*]azulene-4,5-dicarboxylate **28**: blue–green needles (from hexane–dichloromethane), mp 200–201 °C; δ_H 1.25 (3H, t, *J* 7.0), 1.36 (3H, t, *J* 7.0), 4.14 (2H, q, *J* 7.0), 4.29 (2H, q, *J* 7.0), 4.87 (2H, br s), 5.97 (1H, dd, *J* 11.0 and 9.2), 6.41 (1H, dd, *J* 12.2 and 9.2), 6.81 (1H, d, *J* 11.0) and 7.42 (1H, d, *J* 12.2); δ_C 14.03, 14.16, 60.37, 61.96, 126.67, 128.19, 131.34, 137.25, 137.35, 138.84, 140.03, 145.40, 148.91, 155.68, 163.24 and 165.36; ν_{max}/cm^{-1} 3303, 3216 (NH), 1727 and 1700 (C=O); λ_{max}/nm (log ε) 262 (4.33), 294 (4.09, sh), 338 (4.02), 430 (4.13), 546 (2.86, sh), 592 (3.02), 596 (3.02, sh), 642 (3.09), 702 (3.00), 716 (2.98, sh) and 770 (2.68, sh); *m*/*z* (rel. intensity) 328 (M$^+$, 100%), 300 (15), 283 (13), 255 (22), 228 (31), 210 (20) and 184 (45) (Found: C, 58.4; H, 4.9; N, 17.0. Calc. for $C_{16}H_{16}N_4O_4$: C, 58.5; H, 4.9; N, 17.1%).

Ethyl 2-amino-1,2a,3-triazabenz[*cd*]azulene-4-carboxylate **29**: dark green needles (from hexane–dichloromethane), mp 230–231 °C; δ_H 1.33 (3H, t, *J* 7.3), 4.27 (2H, q, *J* 7.3), 4.56 (2H, br s), 4.92 (1H, s), 5.13 (1H, dd, *J* 11.0 and 8.5), 5.31 (1H, d, *J* 12.2), 5.59 (1H, dd, *J* 12.2 and 8.5) and 6.12 (1H, d, *J* 11.0); δ_C 14.00, 61.90, 123.37, 123.71, 124.41, 129.63, 136.95, 138.60, 139.45, 141.95, 161.48, 163.48 and 166.78; ν_{max}/cm^{-1} 3444, 3286 (NH), 1731 and 1642 (C=O); *m*/*z* (rel. intensity) 256 (M$^+$, 100%), 228 (69), 184 (34), 157 (19), 141 (16), 129 (12), 111 (31) and 97 (38) (Found: C, 60.7; H, 4.8; N, 21.9. Calc. for $C_{13}H_{12}N_4O_2$: C, 60.9; H, 4.7; N, 21.9%).

Diethyl 2-ethylamino-2a,3-diazabenz[*cd*]azulene-4,5-dicarboxylate **30**: green needles (from hexane), mp 98–99 °C; δ_H 1.25 (3H, t, *J* 7.3), 1.27 (3H, t, *J* 7.3), 1.36 (3H, t, *J* 7.3), 3.25 (2H, qd, *J* 7.3 and 6.1), 4.13 (2H, q, *J* 7.3), 4.29 (2H, q, *J* 7.3), 4.55 (1H, br t, *J* 6.1), 5.71 (1H, s), 5.76 (1H, dd, *J* 10.4 and 8.5), 6.25 (1H, dd, *J* 12.2 and 8.5), 6.69 (1H, d, *J* 10.4) and 7.39 (1H, d, *J* 12.2); ν_{max}/cm^{-1} 3403 (NH), 1736 and 1672 (C=O) (Found: C, 65.8; H, 5.6; N, 11.5. Calc. for $C_{20}H_{20}N_3O_4$: C, 65.6; H, 5.5; N, 11.5%).

Dimethyl 2-amino-1,2a,3-triazabenz[*cd*]azulene-4,5-dicarboxylate **31**: blue–green needles (from hexane–dichloromethane), mp 216–218 °C; δ_H 3.68 (3H, s), 3.85 (3H, s), 5.00 (2H, br s), 6.01 (1H, dd, *J* 11.0 and 8.5), 6.44 (1H, dd, *J* 12.2 and 8.5), 6.83 (1H, d, *J* 11.0) and 7.41 (1H, d, *J* 12.2); δ_C 51.31, 53.21, 123.74, 126.85, 128.22, 131.43, 137.41, 137.50, 138.35, 140.21, 145.40, 164.50, 171.18 and 172.52; ν_{max}/cm^{-1} 3296, 3209 (NH), 1746 and 1685 (C=O); λ_{max}/nm (log ε) 262 (3.99, sh), 340 (3.89), 374 (3.82), 526 (2.51), 572 (2.62), 622 (2.66), 682 (2.54) and 784 (2.05, sh); *m*/*z* (rel. intensity) 300 (M$^+$, 100%), 269 (44), 254 (12), 241 (13), 226 (28), 210 (16) and 183 (11) (Found: C, 55.9; H, 4.1; N, 18.7. Calc. for $C_{14}H_{12}N_4O_4$: C, 56.0; H, 4.0; N, 18.7%).

Diethyl [4,5-bis(ethoxycarbonyl)-1,2a,3-triazabenz[*cd*]azulen-2-yl]aminofumarate **32**: dark violet needles (from hexane–dichloromethane), mp 170–171 °C; δ_H 1.22 (3H, *t*, *J* 7.3), 1.32 (3H, t, *J* 7.3), 1.34 (3H, t, *J* 7.3), 1.37 (3H, t, *J* 7.3), 4.17 (2H, q, *J* 7.3), 4.20 (2H, q, *J* 7.3), 4.28 (2H, q, *J* 7.3), 4.36 (2H, q, *J* 7.3), 5.93 (1H, dd, *J* 11.0 and 8.6), 6.36 (1H, dd, *J* 12.8 and 8.6), 6.78 (1H, d, *J* 11.0), 7.07 (1H, s) and 7.12 (1H, d, *J* 12.8); ν_{max}/cm^{-1} 3440 (NH), 1741 and 1701 (C=O) (Found: C, 57.9; H, 5.4; N, 11.2. Calc. for $C_{24}H_{26}N_4O_8$: C, 57.8; H, 5.3; N, 11.2%).

Methyl 2-amino-1,2a,3-triazabenz[*cd*]azulene-5-carboxylate **33**: green needles (from hexane–dichloromethane), mp 216–219 °C and 246–247 °C (polymorphism); δ_H 3.73 (3H, s), 4.78 (2H, br s), 5.98 (1H, dd, *J* 11.0 and 9.2), 6.44 (1H, dd, *J* 12.2 and 9.2), 6.84 (1H, d, *J* 11.0), 7.62 (1H, s) and 7.72 (1H, d, *J* 12.2); ν_{max}/cm^{-1} 3407, 3293 (NH), 1691, 1662, 1646 and 1621 (C=O and C=C); *m*/*z* (rel. intensity) 242 (M$^+$, 100%), 211 (44), 183 (22) and 156 (11) (Found: C, 59.4; H, 4.2; N, 23.0. Calc. for $C_{12}H_{10}N_4O_2$: C, 59.5; H, 4.2; N, 23.1%).

Methyl (*Z*)-3-(5-methoxycarbonyl-1,2a,3-triazabenz[*cd*]azulen-2-yl)aminoacrylate **34**: brown needles (from hexane–dichloromethane), mp 184–187 °C; δ_H 3.73 (3H, s), 3.74 (3H, s), 5.14 (1H, d, *J* 8.6), 5.99 (1H, dd, *J* 11.0 and 8.5), 6.44 (1H, dd, *J* 12.2 and 8.5), 6.85 (1H, d, *J* 11.0), 7.60 (1H, dd, *J* 12.2 and 8.6), 7.72 (1H, d, *J* 12.2), 7.72 (1H, s) and 10.50 (1H, br d, 12.2); ν_{max}/cm^{-1} 3270 (NH), 1689, 1680, 1646 and 1587 (C=O and C=C); *m*/*z* (rel. intensity) 326 (M$^+$, 11%), 294 (100), 235 (8), 207 (12) and 147 (17) (Found: C, 58.6; H, 4.3; N, 16.7. Calc. for $C_{16}H_{14}N_4O_4$: C, 58.9; H, 4.3; N, 17.2%).

Methyl (*E*)-3-(5-methoxycarbonyl-1,2a,3-triazabenz[*cd*]azulen-2-yl)aminoacrylate **35**: green needles (from hexane–dichloromethane), mp 204–206 °C; δ_H 3.76 (6H, s), 6.06 (1H, dd, *J* 12.2, 9.2), 6.30 (1H, d, *J* 15.9), 6.48 (1H, dd, *J* 11.0 and 9.2), 6.89 (1H, d, *J* 11.0), 7.75 (1H, d, *J* 12.2), 7.79 (1H, s), 8.11 (1H, dd, *J* 15.9 and 12.2) and 11.14 (1H, d, *J* 12.2); ν_{max}/cm^{-1} 3437 (NH), 1722, 1681, 1623 (C=O and C=C) and 975 (*trans* CH=CH) (Found: C, 58.8; H, 4.4; N, 16.7. Calc. for $C_{16}H_{14}N_4O_4$: C, 58.9; H, 4.3; N, 17.2%).

Dimethyl 2-amino-2a,3-diazabenz[*cd*]azulene-4,5-dicarboxylate **36**: blue–green needles (from cyclohexane–chloroform), mp 148–149 °C; δ_H 3.67 (3H, s), 3.85 (3H, s), 4.00 (2H, br s), 5.75 (1H, dd, *J* 10.4 and 8.5), 5.81 (1H, s), 6.25 (1H, dd, *J* 12.2 and 8.5), 6.65 (1H, d, *J* 10.4) and 7.41 (1H, d, *J* 12.2); ν_{max}/cm^{-1} 3447, 3349 (NH), 1739 and 1676 (C=O) (Found: C, 60.0; H, 4.5; N,13.8. Calc. for $C_{15}H_{13}N_3O_4$: C, 60.2; H, 4.4; N, 14.0%).

Methyl 2-amino-2a,3-diazabenz[*cd*]azulene-5-carboxylate **37**: green prisms (from hexane–dichloromethane), mp 105–107 °C; δ_H 3.72 (3H, s), 436 (2H, br), 5.74 (1H, dd, *J* 12.8 and 8.5), 5.78 (1H, s), 6.29 (1H, dd, *J* 11.0 and 8.5), 6.67 (1H, d, *J* 11.0), 7.68 (1H, d, *J* 12.8) and 7.77 (1H, s); ν_{max}/cm^{-1} 3396, 3304 (NH) and 1660 (C=O) (Found: C, 64.6; H, 4.7; N, 17.3. Calc. for $C_{13}H_{11}N_3O_2$: C, 64.7; H, 4.6; N, 17.4%).

Methyl 3-(1-amino-1,2-dihydro-1-azaazulen-2-ylideneamino)acrylate **38**: red prisms (from hexane–dichloromethane), mp 174–175 °C; δ_H 3.74 (3H, s), 4.70 (2H, s), 5.75 (1H, d, *J* 12.8), 6.53 (1H, s), 6.90 (1H, dd, *J* 10.4 and 9.8), 7.08 (1H, dd, *J* 10.4 and 9.8), 7.18 (1H, dd, *J* 10.4 and 9.8), 7.44 (1H, d, *J* 10.4), 7.49 (1H, d, *J* 9.8) and 8.34 (1H, d, 12.8); ν_{max}/cm^{-1} 3271, 3167

(NH), 1681, 1630 (C=O and C=C) and 970 (*trans* CH=CH) (Found: C, 64.3; H, 5.5; N, 17.3. Calc. for $C_{13}H_{13}N_3O_2$: C, 64.2; H, 5.4; N, 17.3%).

Dimethyl 2-ethylamino-2a,3-diazabenz[*cd*]azulene-4,5-dicarboxylate **39**: brown needles (from hexane–dichloromethane), mp 119.5–121 °C; δ_H 1.27 (3H, t, *J* 7.0), 3.25 (2H, qd, *J* 7.0 and 4.6), 3.66 (3H, s), 3.84 (3H, s), 4.54 (1H, br t, *J* 4.6), 5.73 (1H, s), 5.79 (1H, dd, *J* 10.4 and 8.6), 6.28 (1H, dd, *J* 12.2 and 8.6), 6.71 (1H, d, *J* 10.4), 7.39 (1H, d, *J* 12.2) and 7.71 (1H, s); ν_{max}/cm^{-1} 3396, 3379 (NH), 1753, 1743 and 1682 (C=O) (Found: C, 62.6; H, 5.3; N, 12.6. Calc. for $C_{17}H_{17}N_3O_4$: C, 62.4; H, 5.2; N, 12.8%).

Reaction of 1-amino-2-ethylimino-1,2-dihydro-1-azaazulene 10 with DMAD

A mixture of **10** (0.187 g, 1.00 mmol) and DMAD (0.426 g, 3.00 mmol) in dry acetonitrile (50 ml) was stirred for 1 day at room temperature and then the solvent was evaporated. The residue was chromatographed with benzene–chloroform (1 : 1) to give **39** (0.087 g, 27%).

In a similar manner, the reaction of **10** and methyl propiolate gave **40** (31%), **41** (17%) and recovered **10** (15%).

Compound **40**: brown needles (from hexane–dichloromethane), mp 120–121 °C; δ_H 1.29 (3H, t, *J* 7.0), 3.28 (2H, qd, *J* 7.0 and 4.6), 3.71 (3H, s), 4.49 (1H, br t, *J* 4.6), 5.69 (1H, s), 5.76 (1H, dd, *J* 10.4 and 8.5), 6.29 (1H, dd, *J* 12.8 and 8.5), 6.72 (1H, d, *J* 12.8), 7.69 (1H, d, *J* 10.4) and 7.71 (1H, s); δ_C 14.95, 38.74, 50.64, 88.47, 123.74, 125.60, 126.61, 126.70, 136.31, 136.40, 137.62, 139.82, 146.56, 151.20 and 165.66; ν_{max}/cm^{-1} 3386, 3363 (NH) 1673 and 1587 (C=O and C=C); *m*/*z* (rel. intensity) 269 (M^+, 100%), 254 (12), 240 (63) and 126 (10) (Found: C, 66.8; H, 5.7; N, 15.5. Calc. for $C_{15}H_{15}N_3O_2$: C, 66.9; H, 5.6; N, 15.6%).

Compound **41**: dark blue prisms (from hexane–dichloromethane), mp 145.5–146.5 °C; δ_H 1.16 (3H, t, *J* 7.3), 3.57 (2H, q, *J* 7.3), 3.68 (3H, s), 3.75 (3H, s), 4.92 (1H, d, *J* 13.4), 6.22 (1H, s), 6.06 (1H, dd, *J* 11.0 and 8.5), 6.23 (1H, dd, *J* 12.8 and 8.5), 6.58 (1H, d, *J* 11.0), 7.52 (1H, d, *J* 13.4), 7.75 (1H, d, *J* 12.8) and 7.83 (1H, s); ν_{max}/cm^{-1} 1705 and 1694 (C=O) (Found: C, 64.8; H, 5.4; N, 11.8. Calc. for $C_{19}H_{19}N_3O_4$: C, 64.6; H, 5.4; N, 11.9%).

X-Ray structure determinations †

Crystal data for 10. Red prisms, $C_{11}H_{13}N_3$, $M = 187.24$, monoclinic, space group $P2_1/c$, $a = 10.448(7)$, $b = 8.178(5)$, $c = 24.001(4)$ Å, $\beta = 101.14(2)°$, $V = 2012(2)$ Å^3, $Z = 8$, $D_{calcd} = 1.236$ g cm^{-3}, crystal dimensions $0.36 \times 0.46 \times 0.88$ mm. Data were measured on a Rigaku AFC 5S radiation diffractometer with graphite-monochromated Mo-Kα radiation. A total 5206 reflections (4941 unique) were collected using the ω–2θ scan technique to a maximum 2θ value of 54.9°. The structure was solved by direct methods and refined by a full-matrix least-squares method using MITHRIL,[14] using 253 variables and 2206 observed reflections ($I > 2\sigma(I)$). 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 0.064. The maximum peak and the minimum peak in the final difference map were 0.29 e Å^{-3} and −0.41 e Å^{-3}.

Crystal data for 19. Orange prisms, $C_9H_6N_4$, $M = 170.17$, monoclinic, space group $P2_1/n$, $a = 3.825(9)$, $b = 7.721(7)$, $c = 15.603(5)$ Å, $\beta = 95.58(8)°$, $V = 770(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.468$ g cm^{-3}, crystal dimensions $0.10 \times 0.24 \times 0.66$ mm. Data were measured on a Rigaku AFC 5S radiation diffractometer with graphite-monochromated Mo-Kα radiation. A total 2107 reflections (1837 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 MITHRIL,[14] using 143 variables and 1118 observed reflections ($I > 2\sigma(I)$). 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 0.043 and 0.048. The maximum peak and the minimum peak in the final difference map were 0.16 e Å^{-3} and −0.16 e Å^{-3}.

Crystal data for 25. Black prisms, $C_{17}H_{18}N_4O_4$, $M = 342.35$, monoclinic, space group $P2_1/n$, $a = 7.546(7)$, $b = 9.524(7)$, $c = 22.971(5)$ Å, $\beta = 92.22(4)°$, $V = 1650(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.378$ g cm^{-3}, crystal dimensions $0.24 \times 0.42 \times 0.64$ mm. Data were measured on a Rigaku AFC 5S radiation diffractometer with graphite-monochromated Mo-Kα radiation. A total 4315 reflections (4017 unique) were collected using the ω–2θ scan technique to a maximum 2θ value of 54.9°. All calculations were performed using TEXSAN structure analysis software.[15] The structure was solved by direct methods (SIR)[16] and refined by a full-matrix least-squares method, using 226 variables and 1817 observed reflections ($I > 2\sigma(I)$). 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 0.082 and 0.099. The maximum peak and the minimum peak in final difference map were 0.35 e Å^{-3} and −0.36 e Å^{-3}.

† CCDC reference number 207/314. See http://www.rsc.org/suppdata/p1/1999/1339 for crystallographic files in .cif format.

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