COMMUNICATION

Reaction of 2-alkylamino-1-azaazulenes with *N*-phenylbenzylideneamine *N*-oxide; one pot synthesis of the 12*H*-11,12,13-triazaazuleno[2,1-*b*]fluorene ring system

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2-Alkylamino-1-azaazulenes react with *N*-phenylbenzylideneamine *N*-oxide to give pentacyclic 12-alkyl-5-phenyl-12*H*-11,12,13-triazaazuleno[2,1-*b*]fluorene-2-carbaldehydes, novel pericyclic 22π aromatic heterocycles, in one pot.

The chemistry of fuzed azaazulenes is of interest because of their physical and chemical properties,[1–7] in comparison with those of azulenes. Cycloaddition is an excellent and versatile methodology for the formation of fused heterocycles. Recently, we reported the cycloaddition reaction of 2-amino-1-azaazulenes with heterocumulenes, such as ketenes[8] and aryl isocyanates,[9] giving new fused heterocycles. It is well known that nitrones undergo 1,3-dipolar cycloadditions with a variety of dipolarophiles to give mainly isoxazoline derivatives.[10,11] The reaction of 1-azaazulenes with nitrones is expected to give rise to a novel cycloaddition, being different from that of other heterocycles. Here we report the interesting cycloaddition reaction of 2-alkylamino-1-azaazulenes with *N*-phenylbenzylideneamine *N*-oxide to give a novel pentacyclic compound in one pot.

Treatment of 2-ethylamino-1-azaazulene **1a** with excess *N*-phenylbenzylideneamine *N*-oxide in benzene at reflux for 10 days gave the pentacyclic 12-ethyl-5-phenyl-12*H*-11,12,13-triazaazuleno[2,1-*b*]fluorene-2-carbaldehyde **4a** (19%) in one pot together with 3-benzoyl-2-ethylamino-1-azaazulene **2a** (55%) and 2-{*N*-ethyl-*N*-[2-ethylamino-1-azaazulen-3-yl-(phenyl)methyl]amino}-1-azaazulene **3a** (13%) (Scheme 1). Preferential formation of **4a** (45%) was achieved by treating **1a** with *N*-phenylbenzylideneamine *N*-oxide in boiling xylene for 4 days, which also gave reduced amounts of **2a** (29%) and **3a** (11%). Similar treatment of **1b** with *N*-phenylbenzylideneamine *N*-oxide in boiling xylene for 10 days gave **2b** (10%), **3b** (32%) and **4b** (26%).

The structures of these compounds were deduced from inspection of their spectroscopic data and elemental analyses. From inspection of its mass spectrum [*m*/*z* 432 (M^+)] and elemental analysis, it was shown that **3a** has the molecular formula $C_{29}H_{28}N_4$, suggesting that **3a** has two 2-ethylamino-1-azaazulene moieties; inspection of its ^{1}H NMR spectrum agreed with this supposition. It was shown that **3a** has a methine and an amino group from its ^{1}H NMR spectrum (δ_H 6.27) and IR spectrum (ν_{max} 3404 cm^{-1}), respectively. From these results, we assigned the structure. In the ^{1}H and ^{13}C NMR spectra of **4a**, a formyl signal is seen at δ_H 10.07 and δ_C 192.52. In its ^{1}H NMR spectrum, five protons of a seven-membered ring are seen at δ_H 7.60–8.80, with only a small divergence in their coupling constants (*J* 9.8–10.4); the results suggested that **4a** would have aromatic character. The UV–VIS absorption spectrum of **4a** has a characteristic strong band at 541 nm (log ε 4.01), suggesting that **4a** has a highly conjugated structure. The structure of **4a** was finally determined by an X-ray structural determination.† An ORTEP drawing[12] of **4a** is shown in Fig. 1. In the X-ray structure, bond alternation cannot be seen, and the divergence of the bond lengths is small. Furthermore, the bond lengths in the benzene ring are rather perturbed (1.375–1.427 Å). All the results show that **4a** is a novel pericyclic 22π aromatic heterocycle.

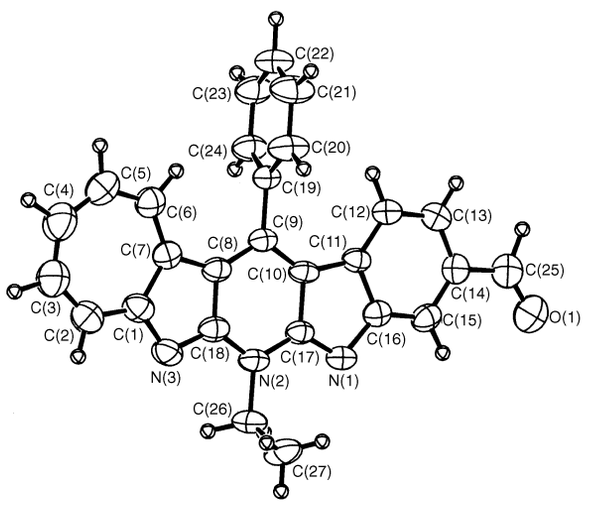
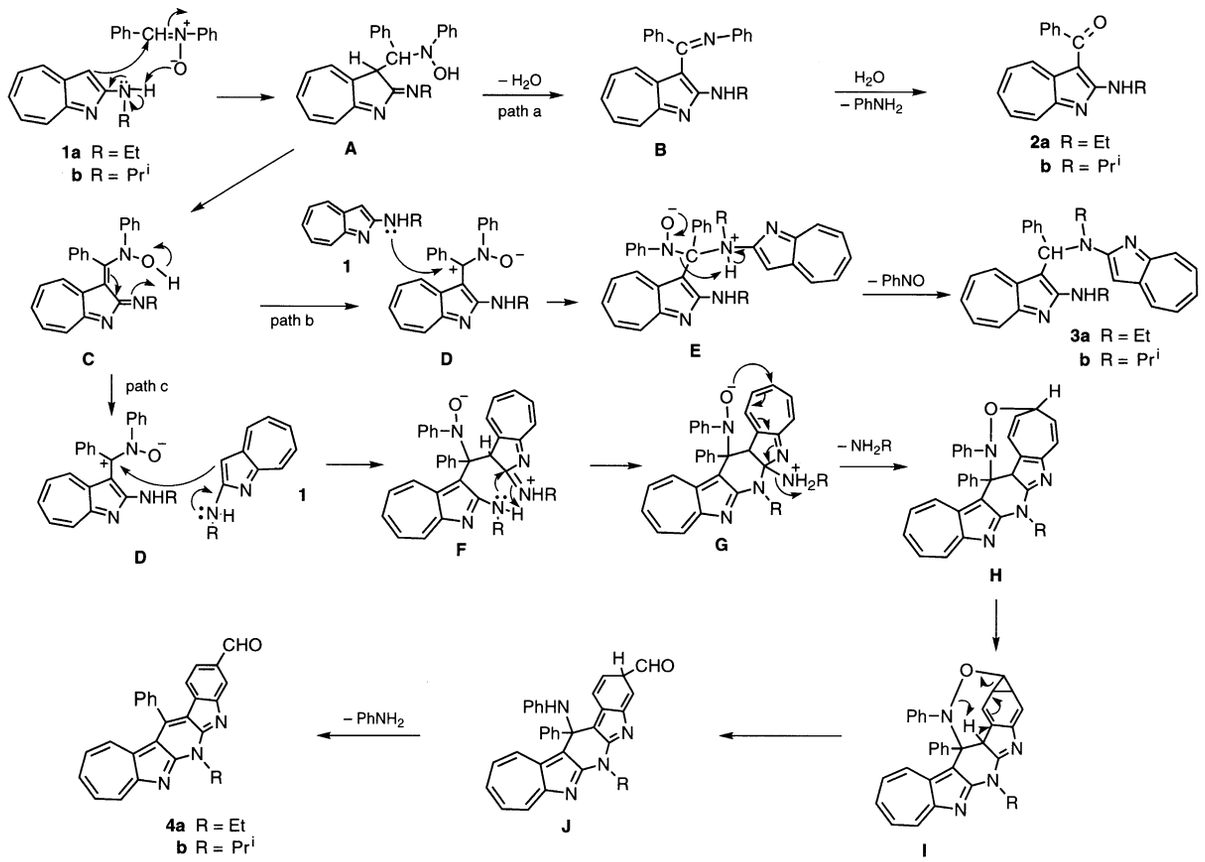


Fig. 1 An ORTEP drawing of **4a** with thermal ellipsoids (50% probability). Selective bond lengths (Å); C(1)–C(2) 1.402(6), C(2)–C(3) 1.368(7), C(3)–C(4) 1.371(8), C(4)–C(5) 1.388(7), C(5)–C(6) 1.402(7), C(6)–C(7) 1.387(6), C(7)–C(8) 1.421(5), C(8)–C(9) 1.424(5), C(9)–C(10) 1.375(5), C(10)–C(11) 1.440(6), C(11)–(12) 1.390(5), C(12)–C(13) 1.375(6), C(13)–C(14) 1.403(6), C(14)–C(15) 1.391(6), C(15)–C(16) 1.377(6), C(16)–N(1) 1.407(5), N(1)–C(17) 1.317(5), C(17)–N(2) 1.379(5), N(2)–C(18) 1.362(5), C(18)–N(3) 1.356(5), N(3)–C(1) 1.361(5), C(7)–C(1) 1.456(6), C(8)–C(18) 1.423(5), C(10)–C(17) 1.444(5), C(11)–C(16) 1.427(5), C(9)–C(19) 1.493(5), N(2)–C(26) 1.472(5).

A plausible mechanism is proposed in Scheme 1.‡ The reaction of **1** with *N*-phenylbenzylideneamine *N*-oxide gives first a hydroxylamine derivative **A**. It is plausible that the dehydration from **A** giving the imine **B** and the successive hydrolysis of **B** could furnish **2** (path a). Alternatively, dehydrogenation of **A** could produce **C**, which could easily rearrange to the nitrone **D**. Attack of the amino group of **1** at the positive carbon of the nitrone **D** then affords the adduct **E**, and successive elimination of nitrosobenzene from **E** furnishes **3** (path b). The higher steric

† However, the relatively high uncertainty on bond distances, combined with the possibility of systematic errors arising from the low proportion of observed data, means that these conclusions must be treated with some caution.

‡ We thank one of the referees for the suggestion of the possible formation of the nitrone **D**.



Scheme 1

interaction of an isopropyl group would facilitate the formation of **3**; indeed a higher yield of **3b** was observed. The formation of **4** might be initiated by the attack of C-3 of **1** on the nitrone **D**; the reaction of **D** and **1** produces **F**, and successive cyclizations give rise to **G** and then **H**. The rearrangement of **H** *via* the norcaradiene **I**, followed by the elimination of aniline from **J**, furnishes **4** (path c). From consideration of the model, it is possible that attack of the oxygen of **G** occurs at a feasible position of the seven-membered ring, where the oxygen is rather close to the C-3 position, to form **H**. It is considered that the elevated temperature facilitates the dehydrogenation of **A** and the successive cycloaddition of **D** with **1**. Indeed the yield of **4a** was enhanced to 45% in boiling xylene.

The treatment of **1a** with benzoic anhydride in boiling toluene in the presence of pyridine for 1 day gave rise to *N*-benzoylation, and yielded 2-(*N*-benzoyl-*N*-ethylamino)-1-azaazulene (78%). Therefore *C*-benzoylation, yielding **2a** preferentially by the reaction of **1a** with *N*-phenylbenzylideneamine *N*-oxide in benzene, is also meaningful. This can be understood as follows; the *N*-benzoylation occurs at the harder amino group of **1a**, whereas the *C*-benzoylation occurs at the softer, C-3 position of **1a** after treatment with 'soft' *N*-phenylbenzylideneamine *N*-oxide.

Experimental

All new compounds were characterized by their spectroscopic data as well as elemental analyses and/or mass spectra.

Reaction of 2-alkylamino-1-azaazulene 1 with *N*-phenylbenzylideneamine *N*-oxide; a typical procedure

A solution of 2-ethylamino-1-azaazulene **1a** (0.516 g, 3.00 mmol) and *N*-phenylbenzylideneamine *N*-oxide (1.773 g, 9.00 mmol) in dry benzene (60 ml) was heated under reflux for 10 days, and then the solvent was evaporated. The residue was chromatographed on a silica gel column repeatedly with chloroform to give 3-benzoyl-2-ethylamino-1-azaazulene **2a** (0.451 g, 55%), 2-{*N*-ethyl-*N*-[2-ethylamino-1-azaazulen-3-yl(phenyl)-methyl]amino}-1-azaazulene **3a** (0.170 g, 13%) and 12-ethyl-5-phenyl-12*H*-11,12,13-triazaazuleno[2,1-*b*]fluorene-2-carbaldehyde **4a** (0.111 g, 19%).

3-Benzoyl-2-ethylamino-1-azaazulene 2a. Orange prisms (from hexane–dichloromethane), mp 124–125 °C; δ_H 1.41 (3 H, t, *J* 7.3§), 3.83 (2 H, qd, *J* 7.3 and 6.1), 7.20–7.69 (9 H, m), 8.12 (1 H, d, *J* 10.4) and 8.30 (1 H, br s); ν_{max}/cm^{-1} 3336 (NH) and 1604 (C=O); λ_{max}(EtOH)/nm (log ε) 284 (4.43), 312 (4.25), 384 (3.86) and 456 (3.99); *m*/*z* 277 (M^+ + 1, 100), 276 (M^+, 74) and 248 (79) (Found: C, 78.3; H, 5.8; N, 10.1. Calc. for $C_{18}H_{16}N_2O$: C, 78.2; H, 5.8; N, 10.1%).

2-{*N*-Ethyl-*N*-[2-ethylamino-1-azaazulen-3-yl(phenyl)-methyl]amino}-1-azaazulene 3a. Yellow needles (from hexane), mp 90–92 °C; δ_H 0.94 (6 H, t, *J* 7.0), 3.35–3.65 (4 H, m), 6.27 (1 H, s), 7.10–7.23 (8 H, m), 7.31–7.48 (5 H, m), 7.53–7.63 (2 H, m) and 7.93 (2 H, d, *J* 9.8); ν_{max}/cm^{-1} 3404 (NH); λ_{max}(EtOH)/nm (log ε) 240 (4.29, sh), 281 (4.63), 317 (4.43), 325 (4.42, sh), 363 (3.86), 384 (3.85), 411 (3.81), 432 (3.78), 450 (3.76, sh), 482 (3.58, sh) and 510 (3.16, sh); *m*/*z* 433 (M^+ + 1, 15), 432 (M^+, 30) and 261 (100) (Found: C, 80.2; H, 6.8; N, 12.6. Calc. for $C_{29}H_{28}N_4$: C, 80.5; H, 6.5; N, 13.0%).

12-Ethyl-5-phenyl-12*H*-11,12,13-triazaazuleno[2,1-*b*]-fluorene-2-carbaldehyde 4a. Red prisms (from ethyl acetate), mp >300 °C; δ_H 1.79 (3 H, t, *J* 7.0), 5.27 (2 H, q, *J* 7.0), 6.98 (1 H, d, *J* 7.9), 7.50 (1 H, dd, *J* 7.9 and 1.5), 7.60 (1 H, t, *J* 10.4), 7.61–7.68 (2 H, m), 7.72–7.80 (3 H, m), 7.89 (1 H, t, *J* 9.8), 7.99 (1 H, d, *J* 9.8), 8.10 (1 H, ddd, *J* 10.4, 9.8 and 1.2), 8.27 (1 H, d, *J* 1.5), 8.80 (1 H, dd, *J* 10.4 and 1.2) and 10.07 (1 H, s); δ_C 13.73, 41.43, 120.46, 120.69, 121.71, 127.77, 129.57, 129.95, 130.05, 131.40, 132.20, 133.23, 135.07, 135.82, 136.06 and 192.52; ν_{max}/cm^{-1} 1634 (C=O); λ_{max}(EtOH)/nm (log ε) 258 (4.14), 293 (4.02), 280 (4.66) and 541 (4.01); *m*/*z* 401 (M^+, 49) and 373 (100) (Found: C, 79.4; H, 5.1; N, 10.1. Calc. for $C_{27}H_{19}N_3O\cdot1/2H_2O$: C, 79.0; H, 4.9; N, 10.2%).

§ *J* Values given in Hz.

X-Ray structure determination

Crystal data of 4a. Red prism, $C_{27}H_{19}N_3O$, $M = 401.47$, monoclinic, space group $P2_1/n$, $a = 13.359(8)$, $b = 10.825(6)$, $c = 14.148(3)$ Å, $\beta = 92.19(2)°$, $V = 2044.4(9)$ Å^3, $Z = 4$, $D_c = 1.304$ g cm^{-3}, crystal dimensions 0.24 × 0.28 × 0.84 mm. Data were measured on a Rigaku AFC 5S radiation diffractometer with graphite-monochromated Mo-Kα radiation. A total of 5170 reflections (4959 unique) were collected using the ω–2θ scan technique within a 2θ range of 56.0°. The structure was solved by direct methods and refined by a full-matrix least-squares method using 357 variables refined with 1793 reflections [$I > 2\sigma(I)$]. The weighting scheme $\omega = 4F_o^2/\sigma^2(F_o^2)$ gave satisfactory agreement analyses. The final refinement converged to $R = 0.060$ and $Rw = 0.054$. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/98.

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