Cycloaddition Reactions of 2-Acetylamino-, 2-Alkylamino-, 8-Ethylamino-, and 8-Acetylamino-1-azaazulenes with Dimethyl Acetylenedicarboxylate

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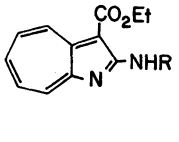
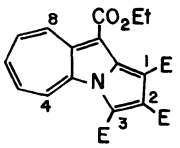
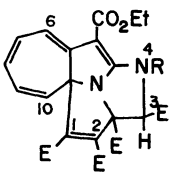
The reactions of 2- and 8-(substituted amino)-1-azaazulenes with dimethyl acetylenedicarboxylate (DMAD) were investigated. Treatment of ethyl 2-acetylamino-1-azaazulene-3-carboxylate with DMAD in refluxing acetonitrile gave 9-ethyl 1,2,3-trimethyl 3a-azacyclopent[*a*]azulene-1,2,3,9-tetracarboxylate, 5-ethyl 1,2,2a,3-tetramethyl 4-acetyl-2a,3-dihydro-4*H*-4,10b-diazapentaleno[1,6-*aj*]azulene-1,2,2a,3,5-pentacarboxylate (**3a**), and dimethyl (10-ethoxycarbonyl-4-methoxycarbonyl-2,4a-dihydro-2-oxo-2*H*-1,4a-diazabenz[*a*]azulen-3-yl)maleate. Compound **3a** thermally rearranged to 9-ethyl 2,3,10,11-tetramethyl 1-acetyl-2,3,4,4a-tetrahydro-1*H*-1,4-diaza-3,4a-ethenofluorene-2,3,9,10,11-pentacarboxylate. The reaction of ethyl 2-alkylamino-1-azaazulene-3-carboxylate with DMAD gave the corresponding 4-alkyl-2a,3-dihydro-4*H*-4,10b-diazapentaleno[1,6-*aj*]azulene derivatives, and the etheno-bridged 1-azaheptalene derivative. The reaction of 8-ethylamino-3-phenyl-1-azaazulene with DMAD gave trimethyl 1-phenyl-2a-azabenz[*cd*]azulene-3,4,5-tricarboxylate, tetramethyl 6-ethyl-1-phenyl-4a,5-dihydro-6*H*-2a,6-diazapentaleno[1,6-*cd*]azulene-3,4,4a,5-tetracarboxylate, tetramethyl 3-phenyl-9b-azaindeno[1,6,7-*bcd*]azulene-1,2,8,9-tetracarboxylate, and dimethyl [8-phenyl-1,2,3-tris(methoxycarbonyl)-8*H*-3a-azacyclopent[1,2-*a*]inden-8-yl]maleate. However, the reaction of 8-acetylamino-3-phenyl-1-azaazulene with DMAD gave dimethyl-1-phenyl-2a,5-diazabenz[*cd*]azulene-3,4-dicarboxylate, trimethyl 3-phenyl-8,9b-diazaindeno[1,6,7-*bcd*]azulene-1,2,9-tricarboxylate, dimethyl 3-phenyl-8,9b-diazaindeno[1,6,7-*bcd*]azulene-1,2-dicarboxylate, tetramethyl 6-acetyl-1-phenyl-4a,5-dihydro-6*H*-2a,6-diazapentaleno[1,6,7-*cd*]azulene-3,4,4a,5-tetracarboxylate. The structures of the obtained compounds were determined by inspections of their physical and spectral data, and by single-crystal X-ray analyses of some of these compounds. The reaction mechanisms of these reactions are discussed.

Cycloaddition reactions of azaazulenes with acetylenic esters have received attention,[1-7] and it is known that the reactions showed various features which depended upon the nature of the substituents and/or the reaction conditions. Participation of the substituents was especially remarkable on the reactions of 2-amino-1-azaazulenes.[1,2] It is therefore expected that the reactions of 2-(substituted amino)-1-azaazulenes with DMAD proceed novel cycloaddition reactions that are hitherto unknown. We then carried out the reaction of ethyl 2-acetylamino- and 2-alkylamino-1-azaazulene-3-carboxylates and 8-ethylamino- and 8-acetylamino-1-azaazulenes with dimethyl acetylenedicarboxylate (DMAD), and found that the reactions proceeded interesting cycloadditions.

Reactions of 2-(Substituted Amino)-1-azaazulenes. Treatment of ethyl 2-acetylamino-1-azaazulene-3-carboxylate with DMAD in refluxing acetonitrile for 6 h gave a complex mixture. From that mixture, three compounds, 9-ethyl 1,2,3-trimethyl 3a-azacyclopent[*a*]-azulene-1,2,3,9-tetracarboxylate (**2**) (24% yield), 5-ethyl 1,2,2a,3-tetramethyl 4-acetyl-2a,3-dihydro-4*H*-4,10b-diazapentaleno[1,6-*aj*]azulene-1,2,2a,3,5-pentacarboxylate (**3a**) (35% yield), and dimethyl (10-ethoxycarbonyl-4-methoxycarbonyl-2,4a-dihydro-2-oxo-2*H*-1,4a-diazabenz[*a*]azulen-3-yl)maleate[2] (**4**) (4% yield), were isolated



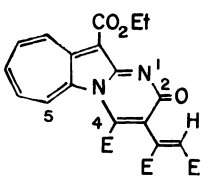


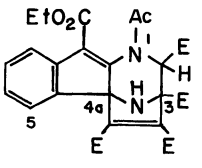


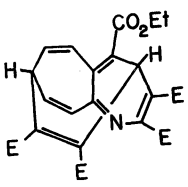
1a: R=Ac
1b: R=Et
1c: R=CH_2Ph
1d: R=$CH_2CH{=}CH_2$
1e: R=*t*-Bu

2: E=CO_2Me

3a: R=Ac, E=CO_2Me
3b: R=Et, E=CO_2Me
3c: R=CH_2Ph, E=CO_2Me
3d: R=$CH_2CH{=}CH_2$, E=CO_2Me
3e: R=*t*-Bu, E=CO_2Me







4: E=CO_2Me **5**: E=CO_2Me **6**: E=CO_2Me

by silica gel column chromatography. A prolonged reaction gave 9-ethyl 2,3,10,11-tetramethyl 1-acetyl-2,3,4,4a-tetrahydro-1*H*-1,4-dihydro-3,4a-ethenofluorene-2,3,9,10,11-pentacarboxylate (**5**) (41% yield), together with **2** (19% yield) and **4** (13% yield); compound **3a** was not obtained. Compound **5** was a thermal rearranged product of **3a**, which obtained by the treatment of **3a** in refluxing acetonitrile for 6 d, or in refluxing xylene for 2 d, in 65 and 84% yields, respectively.

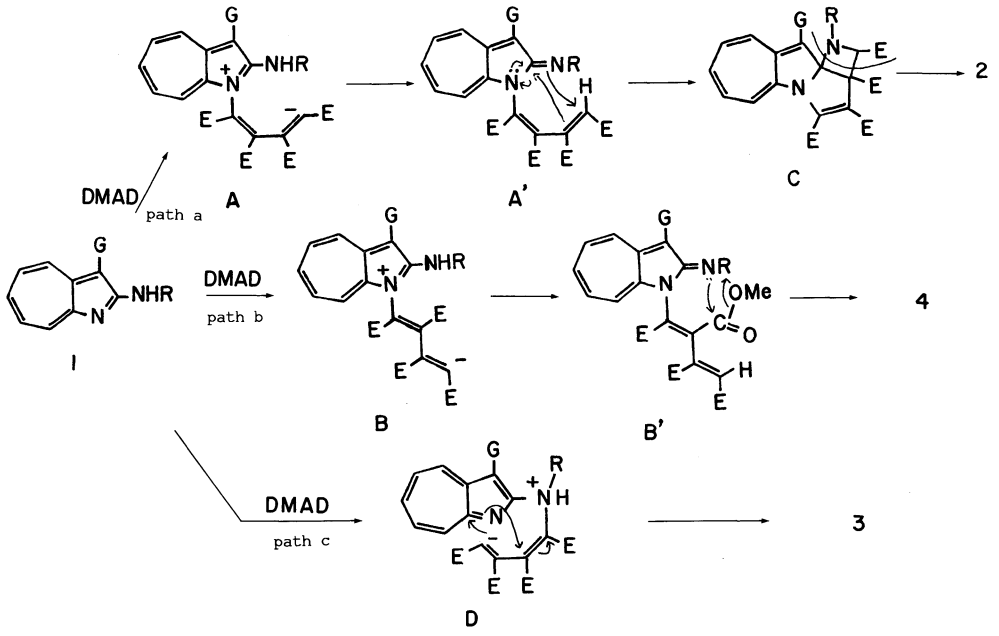
The reactions of 2-alkylamino-1-azaazulenes (**1b**—**1e**) with DMAD were slightly different. The reaction conditions and results are shown in Table 1. In these reactions (excluded the case of **1e**), compounds **3b**—**3d** and etheno-bridged 1-azaheptalene derivative **6** were obtained; compounds **2** and **5** were not obtained.

The structures of these products were deduced on the basis of their absorption spectral data, as well as elemental analyses and mass spectra. For example, their elemental analyses and/or mass spectra coincided with the compositions of the proposed structures. From inspections of the ^{1}H NMR and ^{13}C NMR spectra of **2**, the existence of one ethyl ester, three methyl esters, and a fuzed 1-azaazulene ring was considered. In the ^{1}H NMR spectra of **3a**—**3e**, signals of one methine proton at around δ=5.5, and in their ^{13}C NMR spectra, three sp^3 carbon signals (one methine and two quaternary carbons) are seen. The structures of compounds **3a**—**3e** were confirmed by analogy of their spectroscopic data, and by the X-ray analysis of **3c** (see below). The structure of **5** was confirmed by the X-ray analysis (see below). In the ^{1}H NMR spectrum of **6**, in addition to ester signals, one methine proton signal at δ=3.99 (s) and signals of five protons at δ=2.39 (m), 5.51 (dm, J=9.8 Hz), 5.72 (dm, J=10.4 Hz), 6.60 (d, J=9.8 Hz), and 7.41 (d, J=10.4 Hz), considered to be the cycloheptatriene structure (–CH=CH–CHR–CH=CH–), were observed. No signals due to the alkylamine moiety were observed. In its ^{13}C NMR spectrum, two sp^3 carbon signals at δ=26.87 (d) and 40.97 (d) were seen. From the results, we tentatively assigned the structure. Unfortunately, no preferable crystal for X-ray analyses was obtained, and we could not determine the definite structure of **6**.

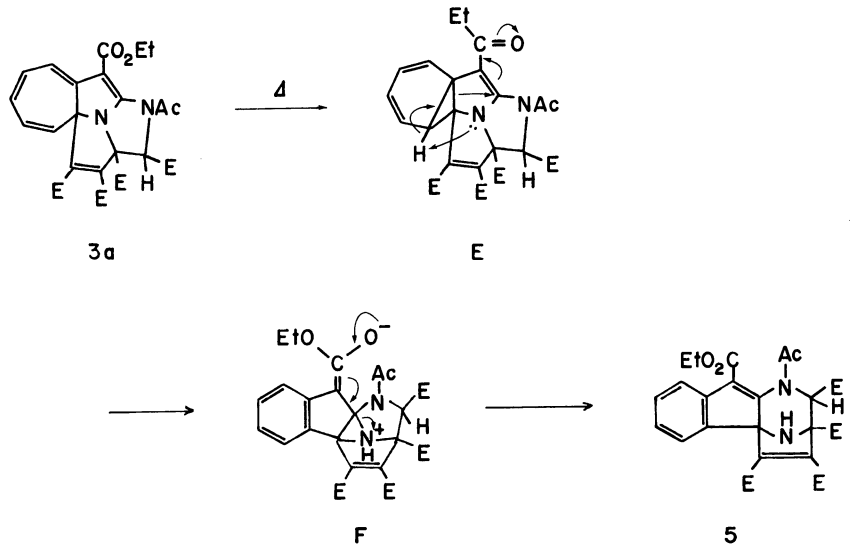
Table 1. Reaction of **1a**—**1e** with DMAD

Entry	1	Time	Products/%					
			2	3	4	5	6	1
1	**1a**	6 h	24	35	4	—	—	—
2	**1a**	18 h	18.5	30	8	17	—	—
3	**1a**	5 d	19	—	13	41	—	—
4	**1b**	6 h	—	55	—	—	16	17
5	**1c**	6 h	—	17	—	—	30	3
6	**1d**	6 h	—	28	—	—	29	7
7	**1e**	45 h	1	10	—	—	1	63

One conceivable mechanism for the reaction of **1** with DMAD is shown in Scheme 1. When attacks of DMAD occurred at N-1 on **1**, dipolar species **A** and **B** are produced. A proton shift of **A** and successive cyclization gives **C**. An elimination of $AcNCHCO_2Me$ from **C** furnishes **2** (path a). A similalr cyclization-elimination was observed on the reaction of 2-substituted benzimidazoles with DMAD.[8,9] A hydrogen shift of **B** gives **B'**. The cyclization of **B'** and a successive elimination of AcOMe furnishes **4** (path b). When attacks of DMAD occurred at the amino group, dipolar species **D** is produced. The cyclization of **D**, as shown by arrows,



Scheme 1.



Scheme 2.

furnishes **3** (path c).

A plausible mechanism for the transformation of **3a** to **5** is shown in Scheme 2. Valence tautomerization of the cycloheptatriene moiety of **3a** gives a norcaradiene intermediate (**E**), which converts into **F**, and furnishes **5**.

Single-Crystal X-Ray Structure Determination of 3c and 5. The crystals of **3c** belong to a monoclinic system with cell dimensions of a=11.85(1), b=29.98(1), c=16.562 (7) Å, β=93.48 (6)°, and V=5875 (7) Å^3. The space group is $P2_1/c$ and Z=4. The empirical formula is $C_{31}H_{30}N_2O_{10}$, the moleculalr weight is 590.59, and the caluculated density is 1.168 g cm^{-3}. Three-dimensional X-ray data were collected by the use of graphite-monochromated Mo $K\alpha$ radiation (λ=0.71069 Å) on a Rigaku AFC5S diffractometer up to a maximum 2θ of 55.0°. The intensity data of 12600 independent reflections were collected and 3799 with $|F_o|>3\sigma|F_o|$ were used in the present X-ray analysis. The structure was solved by the direct method (MITHRIL).[10] The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was converged to a conventional R factor of 0.055. All of the calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation.[11,12] A PLUTO drawing[13] of **3c** is shown in Fig. 1.

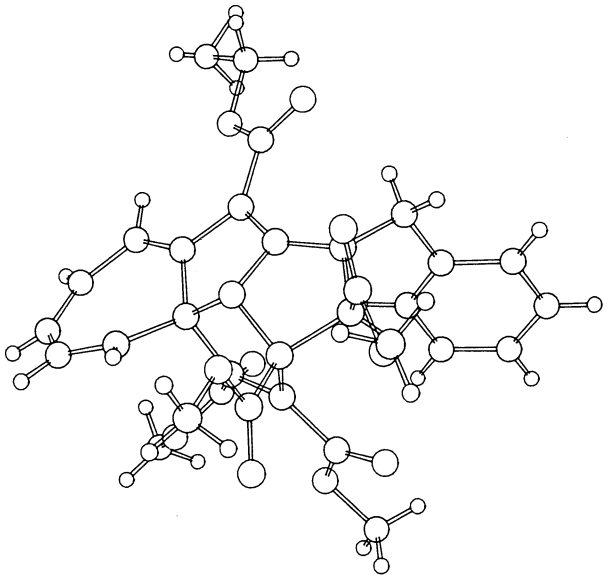


Fig. 1. PLUTO drawing of **3c**.

The crystals of **5** belong to a monoclinic system with cell dimensions of a=9.424 (2), b=11.377 (3), c=24.181 (7) Å, β=93.55 (2)°, and V=2587.9 (12) Å^3. The space group is $P2_1/c$ and Z=4. The empirical formula is $C_{26}H_{26}N_2O_{11}$, the molecular weight is 542.51, and the caluculated density is 1.39 g cm^{-3}. Three-dimensional X-ray data were collected by the use of graphite-monochromated Mo $K\alpha$ radiation (λ=0.71073 Å) on a Syntex R3 automatic four-circle diffractometer up to a maximum 2θ of 50°. The intensity data of 4827 independent reflections were collected; 3653 with $|F_o|>3\sigma|F_o|$ were used in the present X-ray analysis. The structure was solved by the direct method (MULTAN 78). All non-hydrogen atoms were located on the initial E synthesis. The remaining hydrogens were located by a difference Fourier map, and were included in additional calculations. Block-diagonal least-squares refinements with anisotropic 39 non-hydrogen atoms and 26 isotropic hydrogens converged to a conventional R factor of 0.057. All of the calculations were carried out on a HITAC M-680H computer of Hiroshima University using a structure analysis program system (UNICS3).[12,14] An ORTEP drawing[15] of **5** is shown in Fig. 2.

Reactions of 8-Ethylamino- and 8-Acetylamino-1-azaazulenes with DMAD. A treatment of 8-ethyl-

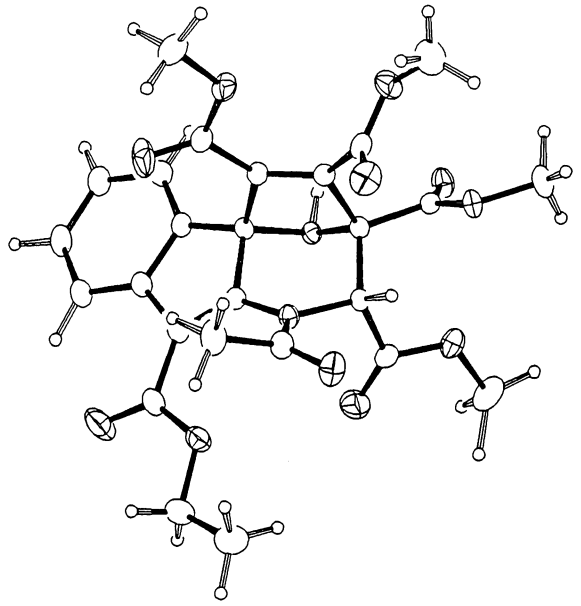
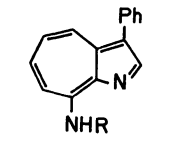
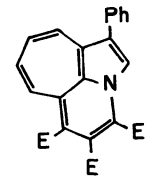


Fig. 2. ORTEP drawing of **5**.

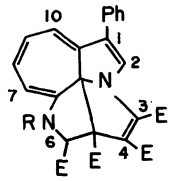
amino-3-phenyl-1-azaazulene (**7a**) with DMAD in refluxing acetonitrile for 1 h gave trimethyl 1-phenyl-2a-azabenz[*cd*]azulene-3,4,5-tricarboxylate (**8**) (12% yield), tetramethyl 6-ethyl-1-phenyl-4a,5-dihydro-6*H*-2a,6-diazapentaleno[1,6-*cd*]azulene-3,4,4a-5-tetracarboxylate (**9a**) (25% yield), tetramethyl 3-phenyl-9b-azaindeno-[1,6,7-*bcd*]azulene-1,2,8,9-tetracarboxylate (**10**) (5% yield), and dimethyl [8-phenyl-1,2,3-tris(methoxycarbonyl)-8*H*-3a-azacyclopent[1,2-*a*]inden-8-yl]maleate (**11**) (4% yield). It is considered that compound **10** would be a product from **8** and DMAD. A reaction of **8** with DMAD was therefore carried out, affording **10** (28% yield) and pentamethyl 3-phenyl-2a,9a-dihydro-9b-azaindeno[1,6,7-*bcd*]azulene-1,2,8,9,9a-pentacarboxylate (**12**) (23% yield). Compound **12** was converted to **10**, by heating in acetonitrile for 4 h, in 45% yield.



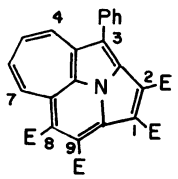
7a: R=Et
7b: R=Ac



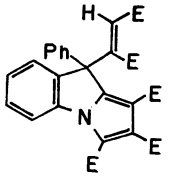
8: E=CO_2Me



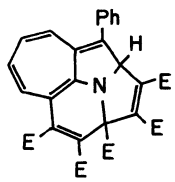
9a: R=Et, E=CO_2Me
9b: R=Ac, E=CO_2Me



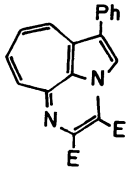
10: E=CO_2Me



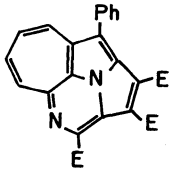
11: E=CO_2Me



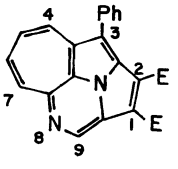
12: E=CO_2Me



13: E=CO_2Me



14: E=CO_2Me



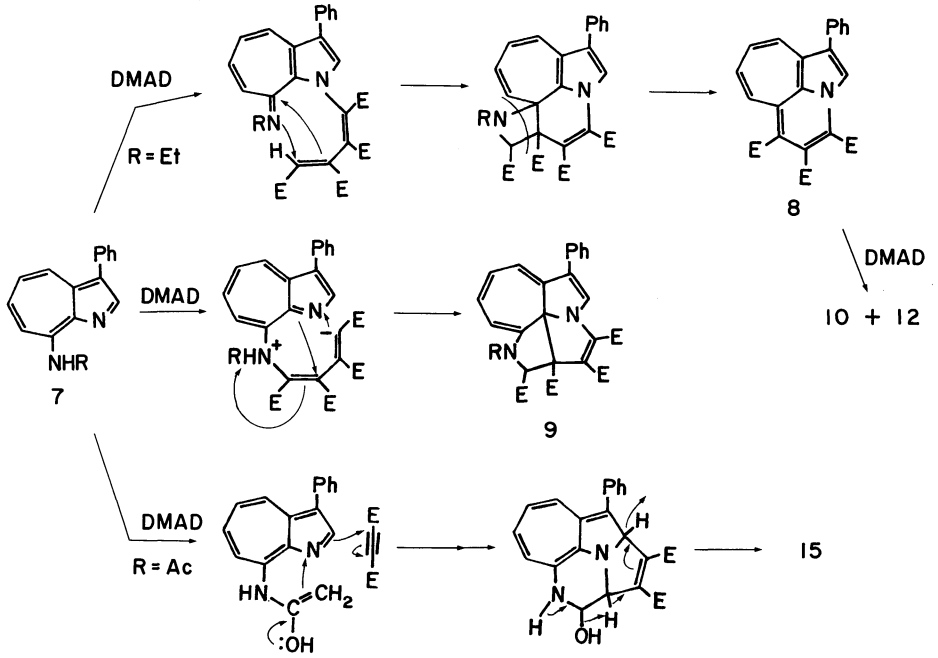
15: E=CO_2Me

These structures were deduced by elemental analyses and spectral inspections, as well as chemical reactions. In the ^1H NMR spectrum of **8**, three methyl ester signals were observed. The signals of the seven-membered ring protons are comparable to those of 2a,5-diazabenz[*cd*]-azulene system.[16,17] In the ^1H NMR spectrum of **10**, in addition to four ester methyl signals and phenyl protons, seven-membered ring protons are seen at δ=6.43 (dd, J=11.3 and 8.5 Hz), 6.77 (dd, J=12.2 and 8.5 Hz), 7.21 (d, J=12.2 Hz); the remaining one proton overlaps with phenyl signals. The structure of **10** was confirmed by the X-ray analysis (see below). In the ^1H NMR spectrum of **12**, one methine proton is seen at δ=4.13 (s) and seven-membered ring protons are seen at δ=6.33 (dd, J=11.0 and 8.6 Hz), 6.77 (dd, J=12.2 and 8.6 Hz), 6.96 (d, J=11.0 Hz), and 7.98 (d, J=12.2 Hz), together with five methyl ester and phenyl signals. The fact that the cycloaddition of **8** with DMAD afforded **12** and a successive elimination of methyl formate from **12** gave **10**, supported the structures of **8** and **12**. In the ^1H NMR spectrum of **9a**, seven-membered ring protons are seen at δ=5.48 (d, J=12.2 Hz), 5.68 (dd, J=11.6 and 7.9 Hz), 6.25 (dd, J=11.6 and 7.9 Hz), and 6.59 (d, J=11.0 Hz); this suggests the existence of the cycloheptatriene structure. From observations of its ^1H NMR (δ=4.75) and ^{13}C NMR spectra (δ=56.57 (d), 72.57 (s), and 74.14 (s)), one methine and two quaternary carbons were found. Based on an analogy of a spectral inspection of the **3a**—**3e** case, we determined the structure. The structure of **11** was determined by X-ray analysis (see below).

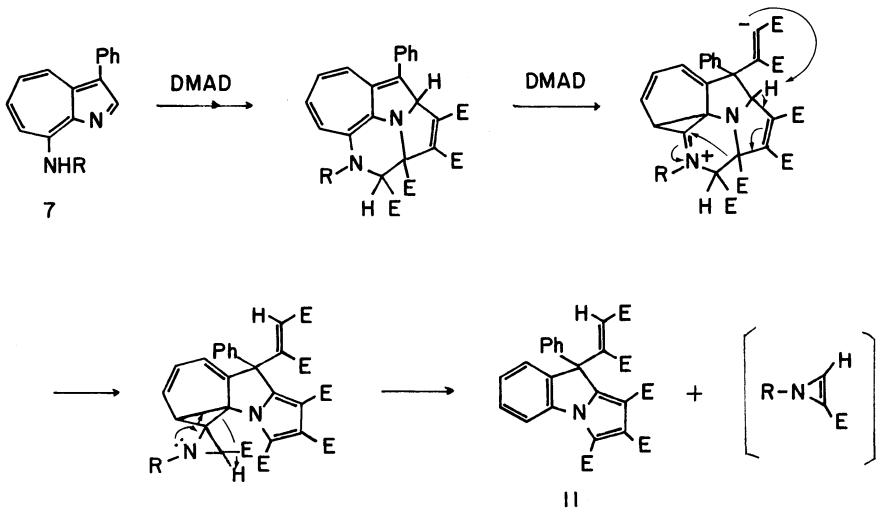
A treatment of 8-acetylamino-3-phenyl-1-azaazulene (**7b**) with DMAD in refluxing acetonitrile for 3 h gave dimethyl 1-phenyl-2a,5-diazabenz[*cd*]azulene-3,4-dicarboxylate[16] (**13**) (2% yield), trimethyl 3-phenyl-8,9b-diazaindeno[1,6,7-*bcd*]azulene-1,2,9-tricarboxylate **14** (14% yield), dimethyl 3-phenyl-8,9b-diazaindeno[1,6,7-*bcd*]azulene-1,2-dicarboxylate (**15**) (4% yield), and **9b** (10% yield). Compound **13** reacted with DMAD in refluxing acetonitrile for 24 h and gave **14** in 36% yield. The structure of **15** was determined by X-ray analysis. The structure of **14** was deduced from a spectral inspection, as well as the chemical behavior where **14** was derived from **13**, and on an analogy regarding spectral behavior to that of **15**.

Plausible mechanisms for the reaction of **7** with DMAD are shown in Schemes 3 and 4.

Single-Crystal X-Ray Structure Determination of 10, 11 and 15. ORTEP drawings of compounds **10**, **11**, and



Scheme 3.



Scheme 4.

15 are shown in Figs. 3, 4, and 5, respectively. The numberings given in Figs. 3, 4, and 5 are arbitrary, and are not consistent with those of the IUPAC nomencleature. Crystal data are shown in Table 2.[12] Selected bond distances, angles, and torsion angles of compounds **10** and **15** are listed in Tables 3, 4, and 5. These results show that the ring systems of **10** and **15** are nearly planar. The C–C bond lengths of the cyclazine moieties of **10** and **15** are at around 1.40 Å, whereas those of the seven-membered rings show a bond-alternation: The C(4)–C(5) bonds are 1.35 and 1.347 Å, the C(5)–C(6) bonds are 1.42 and 1.443 Å, the C(6)–C(7) bonds are 1.34 and 1.350 Å, and the C(7)–C(8) bonds are 1.46 and 1.449 Å, respectively. These facts show that compounds **10** and **15** have butadiene-bridged cycl[3.2.2]-azine structures. We stated early that cyclohepta[*ef*]-cycl[3.2.2]azine (9b-azaindeno[1,6,7-*bcd*]azulene) systems, like **10** and **15**, have butadiene-bridged cycl[3.2.2]azine properties: Resonance form **G**, from a consideration of ^{1}H NMR studies, where large divergencies of the coupling constants ($J_{4,5} \approx J_{5,6} \approx J_{6,7} =$ 3.4—3.7 Hz) were observed.[17] On the other hand, Noguchi et. al. claimed that the systems receive a major contribution of resonance form **H** from considerations of

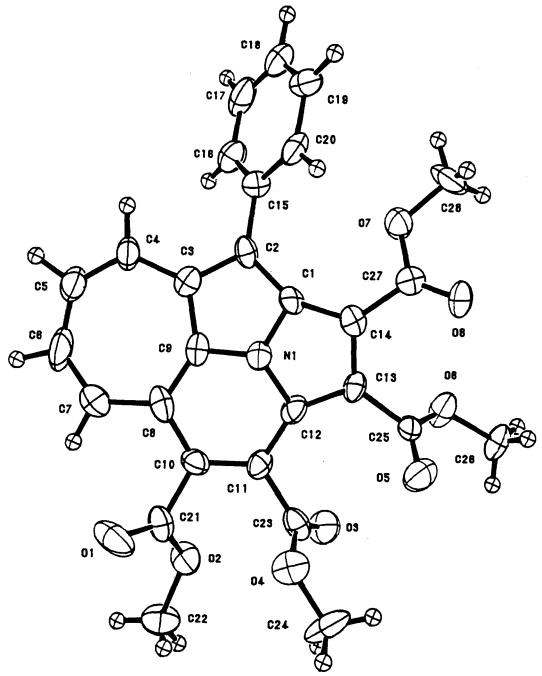


Fig. 3. ORTEP drawing of **10**.

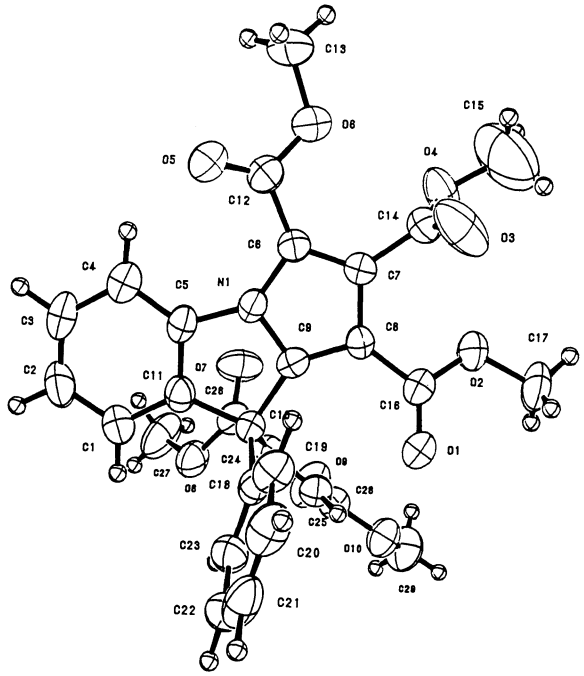


Fig. 4. ORTEP drawing of **11**.

Table 2. Crystal and Structure Analyses Data of Compounds **10**, **11**, and **15**

	10	**11**	**15**
Formula	$C_{28}H_{21}NO_8$	$C_{29}H_{25}NO_{10}$	$C_{23}H_{16}N_2O_4$
Formula weight	499.48	547.53	384.39
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$; Z=4	$P2_1/c$; Z=4	$P2_1/c$; Z=4
Lattice parameters			
a/Å	14.56(1)	17.060(4)	20.998(5)
b/Å	8.106(3)	9.670(2)	12.093(6)
c/Å	20.514(3)	17.051(3)	7.359(3)
β/°	96.01(3)	109.17(2)	109.17(2)
V/Å^3	2407(2)	2657(1)	1841(1)
D_{calcd}/g cm^{-3}	1.378	1.398	1.387
Crystal size/mm^3	0.40×0.12×0.64	0.42×0.46×0.62	0.04×0.18×0.80
Diffractometer	Rigaku AFC5S	Rigaku AFC5S	Rigaku AFC5S
Radiation	Mo $K\alpha$ (λ=0.71069 Å)	Mo $K\alpha$ (λ=0.71069 Å)	Mo $K\alpha$ (λ=0.71069 Å)
Monochrometer	Graphite	Graphite	Graphite
Scan type	ω–2θ	ω–2θ	ω–2θ
2θ Max	55.0°	55.0°	55.0°
Computer program	TEXSAN System[a)]	TEXSAN System[a)]	TEXSAN System[a)]
Structure solution	Direct method; MITHRIL[b)]	Direct method; MITHRIL[b)]	Direct method; MITHRIL[b)]
Hydrogen atom treatment	Calculated, not refined	Calculated, not refined	Calculated, not refined
Refinement	Full-matrix, anisotropic	Full-matrix, anisotropic	Full-matrix, anisotropic
Least-squares weight	$4F_o^2/\sigma(F_o^2)$	$4F_o^2/\sigma(F_o^2)$	$4F_o^2/\sigma(F_o^2)$
No. of measurement ref.	Total: 5225, Unique: 4997	Total: 6694, Unique: 6483	Total: 4572, Unique: 4458
No. of observations[c)]	1021	2632	1196
No. of variables	334	280	262
Residuals R; R_w	0.056; 0.061	0.071; 0.089	0.054; 0.057
Max Shift/Error	0.10	1.91	0.01
$\Delta\rho_{max}$/e$^-$ Å^{-3}	0.27	1.30	0.21

a) See Ref. 11. b) See Ref. 10. c) $I<3.00\sigma(I)$.

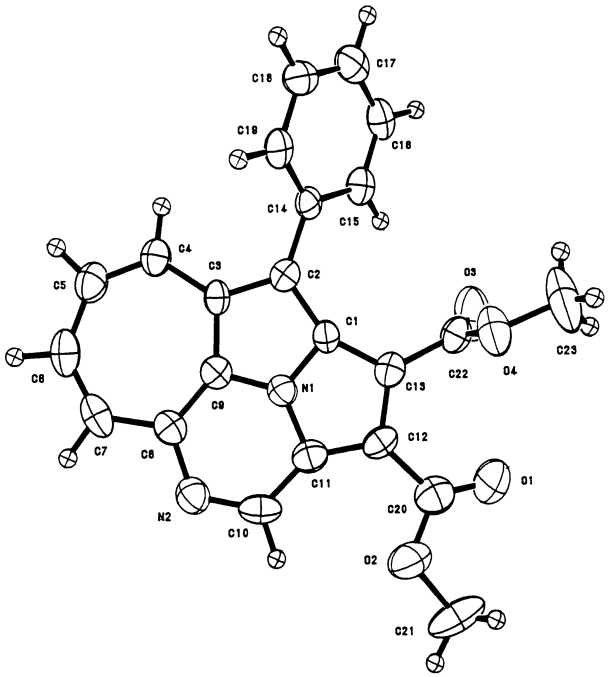


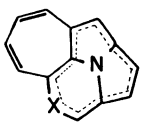
Fig. 5. ORTEP drawing of **15**.

Table 3. Selected Bond Distances (l/Å) and Angles (ϕ/°) of **10**

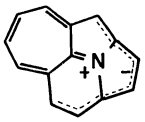
C(1)–C(2)	1.43(1)	C(1)–N(1)–C(9)	115(1)
C(2)–C(3)	1.41(1)	C(1)–N(1)–C(12)	115(1)
C(3)–C(4)	1.43(1)	C(9)–N(1)–C(12)	130(1)
C(4)–C(5)	1.35(2)	C(1)–C(2)–C(3)	108(1)
C(5)–C(6)	1.42(2)	C(3)–C(4)–C(5)	127(1)
C(6)–C(7)	1.34(2)	C(4)–C(5)–C(6)	130(1)
C(7)–C(8)	1.46(2)	C(5)–C(6)–C(7)	134(1)
C(8)–C(9)	1.39(2)	C(6)–C(7)–C(8)	127(1)
C(9)–C(3)	1.46(2)	C(7)–C(8)–C(9)	121(1)
C(8)–C(10)	1.43(2)	C(8)–C(9)–C(3)	138(1)
C(10)–C(11)	1.40(1)	C(8)–C(10)–C(11)	123(1)
C(11)–C(12)	1.39(1)	C(10)–C(11)–C(12)	120(1)
C(12)–C(13)	1.41(1)	C(12)–C(13)–C(14)	109(1)
C(13)–C(14)	1.41(2)	C(13)–C(14)–C(1)	109(1)
C(14)–C(1)	1.42(1)	C(2)–C(3)–C(9)	108(1)
C(1)–N(1)	1.37(1)	C(9)–C(8)–C(10)	116(1)
C(9)–N(1)	1.34(1)		
C(12)–N(1)	1.38(1)		

Table 4. Selected Bond Distances (l/Å) and Angles (ϕ/°) of **15**

C(1)–C(2)	1.438(8)	C(1)–N(1)–C(9)	115.2(5)
C(2)–C(3)	1.412(7)	C(1)–N(1)–C(11)	116.2(5)
C(3)–C(4)	1.436(8)	C(9)–N(1)–C(11)	128.5(6)
C(4)–C(5)	1.347(8)	C(1)–C(2)–C(3)	106.9(5)
C(5)–C(6)	1.443(9)	C(3)–C(4)–C(5)	126.7(6)
C(6)–C(7)	1.350(9)	C(4)–C(5)–C(6)	131.0(6)
C(7)–C(8)	1.449(8)	C(5)–C(6)–C(7)	132.1(6)
C(8)–C(9)	1.383(8)	C(6)–C(7)–C(8)	127.0(6)
C(9)–C(3)	1.437(8)	C(7)–C(8)–C(9)	121.3(6)
C(8)–N(2)	1.366(7)	C(8)–C(9)–C(3)	139.8(6)
N(2)–C(10)	1.343(8)	C(8)–N(2)–C(10)	120.4(5)
C(10)–C(11)	1.402(8)	N(2)–C(10)–C(11)	123.2(6)
C(11)–C(12)	1.415(8)	C(11)–C(12)–C(13)	109.1(6)
C(12)–C(13)	1.408(8)	C(12)–C(13)–C(1)	108.4(5)
C(13)–C(1)	1.417(7)	C(2)–C(3)–C(9)	108.3(5)
C(1)–N(1)	1.358(7)	C(9)–C(8)–N(2)	120.3(6)
C(9)–N(1)	1.345(7)		
C(11)–N(1)	1.372(1)		



G



H

UV and ^{1}H NMR spectra and HMO calculation.[18] The present studies of X-ray analyses are consist with our consideration. By consulting the bond order of Noguchi's HMO calculation as well as the ^{1}H NMR spectra,[18] it seems that the data are compatible with the results of the present X-ray analyses, rather than their conclusion.

Experimental

Melting points 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. IR spectra were recorded on a Hitachi 270-50 infrared spectrophotometer for Nujol mulls, unless otherwise stated. Mass spectra were determined with a JEOL JMS-01SG-2 spectro-

Table 5. Selected Torsion Angles (ϕ/°) of **10** and **15**

10		**15**	
C(3)–C(4)–C(5)–C(6)	−3(3)	C(3)–C(4)–C(5)–C(6)	0(1)
C(2)–C(1)–N(1)–C(9)	−2(2)	C(2)–C(1)–N(1)–C(9)	1.8(7)
C(1)–C(2)–C(3)–C(9)	−2(2)	C(1)–C(2)–C(3)–C(9)	1.4(7)
C(5)–C(6)–C(7)–C(8)	−5(4)	C(5)–C(6)–C(7)–C(8)	0(1)
C(6)–C(7)–C(8)–C(9)	0(3)	C(6)–C(7)–C(8)–C(9)	−1(1)
C(8)–C(10)–C(11)–C(12)	3(2)	C(8)–N(2)–C(10)–C(11)	−2(1)
C(8)–C(9)–N(1)–C(12)	4(2)	C(8)–C(9)–N(1)–C(11)	−1.9(9)
C(9)–N(1)–C(12)–C(11)	−2(2)	C(9)–N(1)–C(11)–C(10)	1.6(9)
C(12)–N(1)–C(1)–C(14)	1(1)	C(11)–N(1)–C(1)–C(13)	0.5(7)
C(9)–C(8)–C(10)–C(11)	−1(2)	C(9)–C(8)–N(2)–C(10)	1.3(9)

meter (70 eV). High-resolution mass spectra were obtained on the same instrument. Kieselgel 60 was used for column chromatography.

Synthesis of 1a. A mixture of ethyl 2-amino-1-azaazulene-3-carboxylate[1] (2.01 g) and acetic anhydride (20 ml) was heated for 2 h at 80°C. Water (200 ml) was added to the mixture, which was then neutralized with sodium hydrogencarbonate. The precipitate was collected by filtration and dried to give **1a** (2.2 g, 92%), which was recrystallized from cyclohexane–dichloromethane to give yellow needles; mp 127—128°C; ^{1}H NMR δ=1.52 (3H, t, J=7.3 Hz), 2.59 (3H, s), 4.52 (2H, q, J=7.3 Hz), 7.80—8.00 (3H, m), 8.65 (1H, d, J=9.8 Hz), 9.15—9.22 (1H, m), and 10.50 (1H, brs, exchangeable with D_2O); IR 3272 (NH), 1696, and 1658 cm^{-1} (C=O). Found: C, 65.20; H, 5.43; N, 10.82%. Calcd for $C_{14}H_{14}N_2O_3$: C, 65.11; H, 5.46; N, 10.85%.

Synthesis of 1b—1e. A solution of ethyl 2-chloro-1-azaazulene-3-carboxylate (1.00 g) and 70% ethylamine (0.50 g) in ethanol (30 ml) was refluxed for 2 h, then evaporated. Water (100 ml) was added to the residue, the mixture was then neutralized with sodium hydrogencarbonate and extracted with chloroform. The extract was dried (Na_2SO_4) and evaporated. Chromatography of the residue with benzene gave **1a** as yellow oil (1.04 g, 99%); ^{1}H NMR δ=1.37 (3H, t, J=7.3 Hz), 1.47 (3H, t, J=7.0 Hz), 3.78 (2H, qd, J=7.3 and 5.5 Hz), 4.44 (2H, q, J=7.0 Hz), 7.40 (1H, t, J=10.4 Hz), 7.51 (1H, brt, J=5.5 Hz, exchangeable with D_2O), 7.59 (1H, t, J=10.4 Hz), 7.63 (1H, t, J=10.4 Hz), 8.10 (1H, d, J=10.4 Hz), and 8.75 (1H, d, J=10.4 Hz); IR (neat) 3364 (NH) and 1670 cm^{-1} (C=O). Picrate of **1b**: Yellow needles (from ethanol), mp 201—203°C. Found: C, 50.65; H, 4.09; N, 14.58%. Calcd for $C_{20}H_{19}N_5O_9$: C, 50.74; H, 4.05; N, 14.79%.

In a similar manner, we synthesized **1c** (92%), **1d** (98%), and **1e** (94%).

1c: Yellow needles (from cyclohexane), mp 88—89°C; ^{1}H NMR δ=1.45 (3H, t, J=7.0 Hz), 4.43 (2H, q, J=7.0 Hz), 4.99 (2H, d, J=6.7 Hz), 7.27—7.50 (6H, m), 7.62 (1H, t, J=9.8 Hz), 7.66 (1H, t, J=9.8 Hz), 7.82 (1H, brt, J=6.7 Hz, exchangeable with D_2O), 8.14 (1H, d, J=9.8 Hz), and 8.81 (1H, d, J=9.8 Hz); IR 3345 (NH) and1662 cm^{-1} (C=O). Found: C, 74.51; H, 5.96; N, 9.08%. Calcd for $C_{19}H_{18}N_2O_2$: C, 74.49; H, 5.92; N, 9.14%.

1d: Yellow needles (from cyclohexane), mp 68—69°C; ^{1}H NMR δ=1.47 (3H, t, J=7.0 Hz), 4.35—4.55 (5H, m), 5.20 (1H, dd, J=9.8 and 1.2 Hz), 5.33 (1H, dd, J=17.1 and 1.2 Hz), 5.9—6.2 (1H, m), 7.42 (1H, t, J=9.8 Hz), 7.60 (1H, dd, J=10.4 and 9.8 Hz), 7.64 (1H, t, J=9.8 Hz), 8.11 (1H, d, J=9.8 Hz), and 8.78 (1H, d, J=10.4 Hz); IR 3345 (NH), 1662, and 1650 cm^{-1} (C=O). Found: C, 70.20; H, 6.21; N, 11.07%. Calcd for $C_{15}H_{16}N_2O_2$: C, 70.29; H, 6.29; N, 10.93%.

1e: Yellow needles (from hexane), mp 84—86°C; ^{1}H NMR δ=1.47 (3H, t, J=7.3 Hz), 1.62 (9H, s), 4.44 (2H, q, J=7.3 Hz), 7.36 (1H, t, J=10.4 Hz), 7.56 (1H, t, J=10.4 Hz), 7.60 (1H, t, J=10.4 Hz), 7.81 (1H, brs, exchangeable with D_2O), 8.07 (1H, d, J=10.4 Hz), and 8.73 (1H, d, J=10.4 Hz); IR 3340 (NH) and 1652 cm^{-1} (C=O). Found: C, 70.68; H, 7.31; N, 10.07%. Calcd for $C_{16}H_{20}N_2O_2$: C, 70.29; H, 6.29; N, 10.93%.

Reaction of 1 with DMAD. General Procedure: A solution of **1a** (0.452 g) and DMAD (1.00 g) in dry acetonitrile (30 ml) was refluxed for 6 h and evaporated. The residue was chromatographed. Elution with chloroform gave **2** (0.171 g, 24%) and **3a** (0.366 g, 35%), successively. Elution with chloroform–ethyl acetate (1 : 1) gave **4** (0.03 g, 4%) as red needles (from cyclohexane), mp 192—194°C (lit,[2] mp 192°C).

2: Brown needles (from cyclohexane), mp 189—190°C; ^{1}H NMR δ=1.38 (3H, t, J=7.3 Hz), 3.87 (3H, s), 3.93 (3H, s), 4.00 (3H, s), 4.44 (2H, q, J=7.3 Hz), 7.20—7.50 (3H, m), 8.53 (1H, d, J=11.0 Hz), and 9.94 (1H, d, J=9.2 Hz); ^{13}C NMR δ=14.23 (q), 51.70 (q), 52.29 (q), 52.73 (q), 61.20 (t), 93.60 (s), 106.01 (s), 114.20 (s), 127.17 (d), 129.76 (d), 131.03 (d), 133.50 (d), 134.77 (s), 137.06 (d), 139.65 (s), 141.85 (s), 143.51 (s), 160.39 (s), 162.97 (s), 164.05 (s), and 165.14 (s); MS m/z (rel intensity) 413 (100, M$^+$), 382 (16), 368 (7), 322 (5), 193 (6), and 92 (8). Found: C, 61.00; H, 4.47; N, 3.36%. Calcd for $C_{21}H_{19}NO_8$: C, 61.02; H, 4.63; N, 3.39%.

3a: Yellow prisms (from cyclohexane), mp 136—138°C; ^{1}H NMR δ=1.34 (3H, t, J=7.0 Hz), 2.26 (3H, s), 3.65 (3H, s), 3.79 (3H, s), 3.81 (6H, s), 4.25 (1H, dq, J=11.6 and 7.0 Hz), 4.34 (1H, dq, J=11.6 and 7.0 Hz), 5.68 (1H, d, J=11.0 Hz), 5.82 (1H, s), 6.14 (1H, dd, J=11.0 and 6.7 Hz), 6.29 (1H, dd, J=11.0 and 6.7 Hz), 6.36 (1H, dd, J=11.0 and 7.3 Hz), and 7.03 (1H, d, J=7.3 Hz); ^{13}C NMR δ=14.18 (q), 24.72 (q), 52.73 (q), 52.86 (q), 53.19 (q), 53.85 (q), 60.66 (t), 68.75 (d), 76.78 (s), 81.41 (s), 96.10 (s), 115.49 (d), 118.26 (d), 125.15 (s), 126.80 (d), 127.63 (d), 129.14 (d), 135.40 (s), 147.72 (s), 158.41 (s), 161.07 (s), 162.70 (s), 163.09 (s), 166.73 (s), 167.00 (s), and 169.52 (s); IR 1772, 1752, 1732, 1696, 1634 (C=O), and 1604 cm^{-1} (C=N). Found: C, 57.52; H, 4.85; N, 5.21%. Calcd for $C_{26}H_{26}N_2O_{11}$: C, 57.56; H, 4.83; N, 5.16%.

Similarly, **1b—1e** were reacted with DMAD. The reaction conditions and the results are summarized in Table 1.

3b: Orange prisms (from cyclohexane), mp 149—150°C; ^{1}H NMR δ=1.10 (3H, t, J=7.0 Hz), 1.32 (3H, t, J=7.3 Hz), 3.49 (1H, dq, J=15.9 and 7.0 Hz), 3.64 (3H, s), 3.78 (3H, s), 3.80 (3H, s), 3.83 (3H, s), 4.18 (1H, dq, J=15.9 and 7.0 Hz), 4.22 (2H, d, J=7.3 Hz), 5.41 (1H, d, J=11.0 Hz), 5.59 (1H, s), 5.90 (1H, dd, J=11.0 and 6.7 Hz), 6.21 (1H, dd, J=11.0 and 6.7 Hz), 6.36 (1H, dd, J=11.0 and 7.9 Hz), and 6.92 (1H, d, J=7.9 Hz); ^{13}C NMR δ=12.17 (q), 14.53 (q), 43.33 (t), 52.60 (q), 57.72 (q), 53.12 (q), 53.57 (q), 59.34 (t), 71.60 (d), 78.13 (s), 80.19 (s), 83.71 (s), 111.96 (d), 115.51 (d), 123.30 (d), 124.61 (s), 127.63 (d), 127.89 (d), 130.34 (d), 137.80 (s), 149.32 (s), 161.91 (s), 163.69 (s), 164.04 (s), 167.29 (s), 167.54 (s), and 169.95 (s); IR 1768, 1756, 1728, 1716, 1678 (C=O), and 1625 cm^{-1} (C=N). Found: C, 59.48; H, 5.41; N, 4.62%. Calcd for $C_{26}H_{26}N_2O_{11}$: C, 59.54; H, 5.38; N, 4.58%.

3c: Orange prisms (from cyclohexane), mp 142—144°C; ^{1}H NMR δ=1.28 (3H, t, J=7.3 Hz), 3.50 (3H, s), 3.68 (3H, s), 3.74 (6H, s), 4.20 (1H, dq, J=11.0 and 7.3 Hz), 4.25 (1H, dq, J=11.0 and 7.3 Hz), 4.37 (1H, d, J=15.3 Hz), 5.29 (1H, s), 5.50 (1H, d, J=11.0 Hz), 5.89 (1H, d, J=15.3 Hz), 5.99 (1H, dd, J=11.0 and 6.7 Hz), 6.23 (1H, dd, J=11.0 and 6.7 Hz), 6.39 (1H, dd, J=11.0 and 7.9 Hz), 6.98 (1H, d, J=7.9 Hz), 7.14—7.18 (2H, m), and 7.24—7.31 (3H, m); ^{13}C NMR δ=14.46 (q), 51.53 (t), 52.27 (q), 53.08 (q), 53.51 (q), 59.60 (t), 69.98 (d), 78.05 (s), 80.33 (s), 84.05 (s), 112.41 (d), 116.01 (d), 123.65 (d), 124.93 (s), 127.99 (d), 128.04 (d), 128.31 (d×2), 128.80 (d×2), 130.40 (d), 135.50 (s), 137.92 (s), 150.66 (s), 161.03 (s), 163.87 (s), 164.33 (s), 167.24 (s), 167.23 (s), and 161.47 (s), IR 1772, 1746, 1728, 1670 (C=O), and 1592 cm^{-1} (C=N). Found: C, 63.19; H, 5.05; N, 4.78%. Calcd for $C_{31}H_{30}N_2O_{10}$: C, 63.05; H, 5.12; N, 4.74%.

3d: Orange prisms (from cyclohexane), mp 161—162°C; ^{1}H NMR δ=1.31 (3H, t, J=7.3 Hz), 3.65 (3H, s), 3.78 (3H, s), 3.81 (3H, s), 3.82 (3H, s), 4.00 (1H, dd, J=15.6 and 6.1 Hz), 4.22

(2H, q, J=7.3 Hz), 4.93 (1H, dd, J=15.6 Hz), 5.11 (1H, d, J=17.5 Hz), 5.18 (1H, d, J=11.6 Hz), 5.41 (1H, d, J=11.0 Hz), 5.54 (1H, s), 5.71 (1H, dddd, J=17.5, 11.6, 6.1, and 5.2 Hz), 5.97 (1H, dd, J=11.0 and 6.7 Hz), 6.22 (1H, dd, J=11.0 and 6.7 Hz), 6.37 (1H, dd, J=11.0 and 7.9 Hz), 6.92 (1H, d, J=7.9 Hz); ^{13}C NMR δ=14.46 (q) 50.39 (t), 52.49 (q), 52.70 (q), 53.01 (q), 53.54 (q), 59.41 (q), 71.23 (d), 77.94 (s), 80.11 (s), 84.15 (s), 112.19 (d), 115.39 (d), 118.60 (t), 123.40 (d), 124.78 (s), 127.88 (d), 130.31 (d), 130.89 (d), 137.65 (s), 149.40 (s), 161.63 (s), 163.64 (s), 164.02 (s), 167.26 (s×2) and 169.89 (s); IR 1770, 1732, 1716, 1678 (C=O), and 1620 cm^{-1} (C=N). Found: C, 60.13; H, 5.24; N, 5.22%. Calcd for $C_{27}H_{28}N_2O_{10}$: C, 60.00; H, 5.22; N, 5.18%.

3e: Orange prisms (from cyclohexane), mp 135—136.5°C; ^{1}H NMR δ=1.32 (3H, t, J=7.0 Hz), 1.48 (9H, s), 3.63 (3H, s), 3.79 (3H, s), 3.80 (3H, s), 3.83 (3H, s), 4.15 (1H, dq, J=11.0 and 7.0 Hz), 4.27 (1H, dq, J=11.0 and 7.0 Hz), 5.33 (1H, d, J=11.0 Hz), 5.94 (1H, dd, J=11.0 and 6.7 Hz), 6.01 (1H, s), 6.22 (1H, dd, J=11.0 and 6.7 Hz), 6.36 (1H, dd, J=11.0 and 7.9 Hz), and 6.82 (1H, d, J=7.9 Hz); ^{13}C NMRδ=14.45 (q), 29.08 (q×3), 52.53 (q), 52.65 (q), 53.05 (q), 53.57 (q), 58.95 (s), 59.51 (q), 70.03 (d), 77.28 (s), 79.12 (s), 85.56 (s), 110.49 (d), 115.15 (d), 122.75 (d), 124.29 (s), 127.95 (d), 130.24 (d), 138.58 (s), 149.34 (s), 162.30 (s), 163.83 (s), 165.29 (s), 167.35 (s), 167.46 (s), and 169.89 (s); IR 1768, 1738, 1718, 1688 (C=O), and 1630 cm^{-1} (C=N). Found: C, 60.27; H, 5.84; N, 4.99%. Calcd for $C_{28}H_{32}N_2O_{10}$: C, 60.42; H, 5.80; N, 5.03%.

5: Colorless prisms (from cyclohexane), mp 176—177°C; ^{1}H NMR δ=1.36 (3H, t, J=7.0 Hz), 2.13 (3H, s), 3.55 (3H, s), 3.73 (3H, s), 3.83 (3H, s), 3.87 (3H, s), 4.03 (1H, s, exchengeable with D_2O), 4.33 (1H, dq, J=11.0 and 7.0 Hz), 4.40 (1H, dq, J=11.0 and 7.0 Hz), 5.62 (1H, s), 7.27 (1H, dd, J=7.9 and 7.3 Hz), 7.43 (1H, dd, J=7.9 and 7.3 Hz), 7.45 (1H, d, J=7.3 Hz), and 7.97 (1H, d, J=7.3 Hz); ^{13}C NMR δ=14.13 (q), 21.14 (q), 52.50 (q), 52.86 (q), 52.96 (q), 53.23 (q), 56.35 (d), 60.94 (t), 74.71 (s), 75.68 (s), 115.83 (s), 121.10 (s), 123.26 (d), 123.35 (d), 126.62 (d), 129.96 (d), 135.48 (s), 140.43 (s), 143.85 (s), 146.58, 161.67 (s), 161.96 (s), 162.32 (s), 166.89 (s), 168.23 (s), and 171.16 (s); IR 3284 (NH), 1766, 1738, 1726, 1710, 1690 (C=O), and 1640 cm^{-1} (C=O). Found: C, 57.54; H, 4.81; N, 5.20%. Calcd for $C_{26}H_{26}N_2O_{11}$: C, 57.56; H, 4.83; N, 5.16%.

6: Yellow prisms (from cyclohexane), mp 261—262°C; ^{1}H NMR δ=1.37 (3H, t, J=6.7 Hz), 2.39 (1H, m), 3.89 (3H, s), 3.91 (3H, s), 3.94 (3H, s), 3.99 (1H, s), 4.04 (3H, s), 4.35 (1H, dd, J=11.0 and 6.7 Hz), 4.46 (1H, dd, J=11.0 and 6.7 Hz), 5.51 (1H, dm, J=9.8 Hz), 5.72 (1H, dm, J=10.4 Hz), 6.60 (1H, d, J=9.8 Hz), and 7.41 (1H, d, J=10.4 Hz); ^{13}C NMR δ=14.29 (q), 26.87 (d), 40.96 (d), 52.79 (q), 52.98 (q), 53.03 (q), 53.21 (q), 60.84 (t), 107.63 (s), 115.19 (s), 116.46 (d), 122.29 (d), 124.97 (d), 125.28 (s), 127.75 (s), 129.06 (d), 129.29 (s), 131.16 (s), 132.25 (s), 162.45 (s), 163.87 (s), 164.08 (s), 164.58 (s), and 165.55 (s); IR 1740, 1730, and 1696 cm^{-1} (C=O); MS m/z (rel intensity) 485 (M^+; 19), 484 (78), 453 (33), 452 (41), 439 (28), 438 (22), 437 (33), 425 (39), 424 (26), 423 (100), 412 (51), 393 (24), 366 (23), 365 (46), 352 (20), 308 (23), 294 (33), 236 (29), 235 (20), 206 (21), 205 (20), 193 (30), 180 (23), 179 (42), 178 (46), 177 (32), 165 (20), and 59 (30). Found: C, 59.10; H, 4.46; N, 2.76%. Calcd for $C_{24}H_{23}NO_{10}$: C, 59.38; H, 4.77; N, 2.89%.

Thermal Rearrangement of 3a. a) A solution of **3a** (0.100 g) in dry acetonitrile (20 ml) was refluxed for 6 d and then evaporated. The residue was chromatographed with benzene–chloroform (1:1) to give a pale-yellow powder (0.095 g), which was recrystallized from hexane–dichloromethane to give **5** (0.065 g, 65%).

b) A solution of **3a** (0.080 g) in dry xylene (10 ml) was refluxed for 48 h and then evaporated. The residue was chromatographed with benzene–chloroform (1:1) to give **5** (0.067 g, 84%).

Synthesis of 7a. A mixture of 8-chloro-3-phenyl-1-azaazulene[19] (2.00 g) and 70% ethylamine (2.50 g) in ethanol (50 ml) was heated for 0.5 h, and then evaporated. The residue was dissolved to water, neutralized with sodium hydrogencarbonate, and extracted with chloroform. The extract was dried (Na_2SO_4) and evaporated. Chromatography of the residue with chloroform gave **7a** (1.833 g, 88.5%), which was recrystallized from cyclohexane to give yellow needles: Mp 105—106°C; ^{1}H NMR δ=1.45 (3H, t, J=7.3 Hz), 3.62 (2H, q, J=7.3 Hz), 4.0—6.0 (1H, br), 7.01 (1H, dd, J=10.4 and 9.2 Hz), 7.11 (1H, d, J=11.6 Hz), 7.30—7.62 (5H, m), 7.66 (1H, dd, J=11.6 and 9.2 Hz), 8.13 (1H, s), and 8.32 (1H, d, J=10.4 Hz); IR 3185 cm^{-1} (NH). Found: C, 82.31; H, 6.43; N, 11.21%. Calcd for $C_{17}H_{16}N_2$: C, 82.23; H, 6.50; N, 11.28%.

Synthesis of 7b. To the solution of 8-Amino-3-phenyl-1-azaazulene[19] (0.230 g) in acetic anhydride (10 ml) concd sulfuric acid (3 drops) was added; the mixture was allowed to stand for 3 d at room temperature. After adding water to the mixture, it was then neutralized with soidum hydrogencarbonate, and extracted with chloroform. The extract was dried (Na_2SO_4) and evaporated. Chromatography of the residue with chloroform gave **7b** (0.195 g, 71%), which was recrystallized from cyclohexane to give red needles: Mp 160—161°C (lit,[19] mp 160—161°C); ^{1}H NMR δ=2.45 (3H, s, Me), 7.30—8.65 (6H, m, H-5 and phenyl), 7.95 (1H, d, J=10.4 Hz, H-6), 8.47 (1H, s, H-2), 8.64 (1H, d, J=10.4 Hz, H-7), 9.34 (1H, d, J=11.6 Hz, H-4), and 10.0—10.9 Hz (1H, br); IR 3276 (NH), 1700, and 1688 cm^{-1} (C=O). Found: C, 77.90; H, 5.43; N, 10.51%. Calcd for $C_{17}H_{14}N_2O$: C, 77.84; H, 5.38; N, 10.68%.

Reaction of 7a with DMAD. A mixture of **7a** (0.160 g), and DMAD (0.280 g) in dry acetonitrile (30 ml) was refluxed for 1 h and evaporated. The residue was chromatographed with chloroform to give **8** (0.042 g, 16%), **9a** (0.045 g, 13%), **10** (0.015 g, 5%), **11** (0.011 g, 3%), and **12** (0.010 g, 3%), successively.

8: Blue prisms (from hexane–dichloromethane), mp 166—168°C; ^{1}H NMR δ=3.70, 3.77, 3.81 (each 3H, s, OMe), 5.26 (1H, dd, J=11.0 and 7.9 Hz, H-8), 5.71 (1H, dd, J=12.2 and 7.9 Hz, H-7), 6.22 (1H, d, J=12.2 Hz, H-9), 6.31 (1H, d, J=11.0 Hz, H-6), 7.25—7.43 (5H, m, H-phenyl), 7.90 (1H, s, H-2); ^{13}C NMR δ=51.73 (q), 52.37 (q), 52.47 (q), 110.25 (s), 117.32 (d), 121.45 (s), 123.63 (d), 127.43 (s and d), 128.30 (s and d), 128.53 (d×2), 128.99 (s), 129.09 (d×2), 132.94 (s), 133.62 (d), 136.89 (d), 142.52 (s), 143.05 (s), 161.55 (s), 165.75 (s), and 166.43 (s); IR 1738, 1720 and 1710 cm^{-1} (C=O). Found: C, 68.98; H, 4.77; N, 3.36%. Calcd for $C_{24}H_{19}NO_6$: C, 69.06; H, 4.59; N, 3.36%.

9a: Yellow needles (from hexane–dichloromethane), mp 187—188°C; ^{1}H NMR δ=1.10 (3H, t, J=7.0 Hz, Me), 3.14 (1H, dd, J=13.7 and 7.0 Hz, OC$\underline{H}_2$Me), 3.23 (1H, dd, J=13.7 and 7.0 Hz, OC$\underline{H}_2$Me), 3.68, 3.76, 3.83, 3.88 (each 3H, s, OMe), 4.75 (1H, s, H-10), 5.48 (1H, d, J=12.2 Hz, H-8), 5.68 (1H, dd, J=11.6 and 7.9 Hz, H-6), 6.25 (1H, dd, J=12.2 Hz, and 7.9 Hz, H-7), 6.59 (1H, d, J=11.6 Hz, H-5), 6.65 (1H, s, H-3), and 7.20—7.50 (5H, m, H-phenyl); ^{13}C NMR δ=15.25 (q), 40.71 (t), 52.31 (q), 52.49 (q), 52.90 (q), 53.04 (q), 56.57 (d), 72.57 (s),

74.12 (s), 117.82 (d), 118.98 (d), 119.26 (s), 120.97 (s), 124.01 (d), 125.07 (s), 125.74 (d), 126.25 (d), 128.15 (d×2), 128.89 (d×2), 129.76 (d), 130.53 (s), 134.32 (s), 150.43 (s), 162.41 (s), 163.21 (s), 168.43 (s), and 169.09 (s); IR 1754, 1744, and 1720 cm^{-1} (C=O). Found: C, 65.63; H, 5.42; N, 5.31%. Calcd for $C_{29}H_{28}N_2O_8$:C, 65.39; H, 5.30; N, 5.26%.

10: Red-violet needles (from hexane–dichloromethane), mp 172—173°C; ^1H NMR δ=3.62 (3H, s, OMe), 4.03 (9H, s, OMe), 6.43 (1H, dd, J=11.3 and 8.5 Hz, H-6), 6.77 (1H, dd, J=12.2 and 8.5 Hz, H-5), 7.21 (1H, d, J=12.2 Hz, H-4), and 7.45—7.62 (6H, m, H-7 and phenyl); IR 1738, and 1712 cm^{-1} (C=O). Found: C, 67.03; H, 4.37; N, 3.09%; HRMS m/z 499.1264. Calcd for $C_{28}H_{21}NO_8$: C, 67.31; H, 4.23; N, 2.80%; M, 499.1266.

11: Colorless prisms (from hexane–dichloromethane), mp 121—122°C; ^1H NMR δ=3.38, 3.64, 3.71, 3.92, 3.95 (each 3H, s, OMe), 6.36 (1H, s), 7.20—7.50 (8H, m), 8.55 (1H, d, J=8.6 Hz); IR 1732 and 1720 cm^{-1} (C=O). Found: C, 63.52; H, 4.53; N, 2.48%. Calcd for $C_{29}H_{25}NO_{10}$: C, 63.62; H, 4.60; N, 2.56%.

12: Red prisms (from hexane–dichloromethane), mp 193—194°C; ^1H NMR δ=1.73 (3H, t, J=7.3 Hz), 3.57 (6H, brs), 3.65, 3.84 (each 3H, s), 3.6—4.0 (2H, m), 4.88 (1H, s), 4.89 (1H, s), 5.76 (1H, dd, J=11.6 and 8.5 Hz), 5.88 (1H, dd, J=11.6 and 8.5 Hz), 6.12 (1H, d, J=11.6 Hz), 6.64 (1H, d, J=11.6 Hz), and 7.27—7.45 (5H, m); IR 1740, 1730, and 1710 cm^{-1} (C=O). Found: C, 63.38; H, 4.49; N, 2.45%. Calcd for $C_{30}H_{25}NO_{10}\cdot 0.5H_2O$: C, 63.38; H, 4.61; N, 2.46%.

Reaction of 8 with DMAD. A solution of **8** (0.070 g) and DMAD (0.072 g) in acetonitrile (20 ml) was refluxed for 4 h; the solvent was then evaporated. The residue was chromatographed with chloroform to give **8** (0.017 g, 24%), **10** (0.024 g, 28%), and **12** (0.022 g, 23%), successively.

Conversion of 12 to 10. A solution of **12** (0.005 g) in xylene (10 ml) was refluxed for 22 h; the solvent was then evaporated. The residue was chromatographed with chloroform to give **10** (0.002 g, 45%) and **12** (0.001 g, 20%), successively.

Reaction of 7b with DMAD. A mixture of **7b** (0.400 g) and DMAD (0.870 g) in dry acetonitrile (30 ml) was refluxed for 5 h, and then evaporated. The residue was chromatographed with benzene–chloroform (1 : 1) to give **13**[16] (0.009 g, 2%), **14** (0.095 g, 14%), **15** (0.026 g, 4%), and **9b** (0.080 g, 10%).

14: Violet needles (from hexane–dichloromethane), mp 228—230°C; ^1H NMR δ=3.66, 4.14, 4.15 (each 3H, s), 6.62 (1H, dd, J=11.6 and 8.6 Hz), 7.04 (1H, dd, J=12.2 and 8.55 Hz), and 7.20—7.65 (7H, m); IR 1750, 1740, 1732, and 1688 cm^{-1} (C=O). Found: C, 67.62; H, 4.15; N, 6.52%. Calcd for $C_{25}H_{18}N_2O_6$: C, 67.87; H, 4.10; N, 6.33%.

15: Red needles (from hexane–dichloromethane), mp 151—152°C; ^1H NMR δ=3.81, 4.08 (each 3H, s), 6.57 (1H, dd, J=11.6 and 8.9 Hz), 6.93 (1H, dd, J=11.9 and 8.9 Hz), 7.44 (1H, d, J=11.9 Hz), 7.50—7.75 (6H, m), and 9.50 (1H, s); IR 1734 and 1714 cm^{-1} (C=O). HRMS Found: m/z 384.1107. Calcd for $C_{23}H_{16}N_2O_4$: M, 384.1109.

9b: Yellow needles (from hexane–dichloromethane), mp 172—173°C; ^1H NMR δ=2.17 (3H, s), 3.12 (3H, s), 3.72 (3H, s), 3.80 (3H, s), 3.82 (3H, s), 3.98 (1H, s), 5.44 (1H, dd, J=11.6 and 7.3 Hz), 5.74 (1H, dd, J=12.2 Hz, and 7.3 Hz), 5.79 (1H, d, J=11.6 Hz), 6.11 (1H, d, J=12.2 Hz), 6.14 (1H, s), and 7.20—7.40 (5H, m); IR 1750, 1732, and 1688 cm^{-1} (C=O). Found: C, 63.66; H, 4.73; N, 5.18%. Calcd for $C_{29}H_{26}N_2O_9$: C, 63.73; H, 4.80; N, 5.12%.

Reaction of 13 with DMAD. A solution of **13** (0.024 g) and DMAD (0.020 g) in acetonitrile (15 ml) was refluxed for 24 h, and then evaporated. The residue was chromatographed with chloroform, giving **14** (0.012 g, 36%).

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