Syntheses and Cycloadditions of Ethyl 2-(Benzylidene)hydrazino-1-azaazulene-3-carboxylates with Dimethyl Acetylenedicarboxylate

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Syntheses and cycloadditions of ethyl 2-(benzylidene)hydrazino-1-azaazulene-3-carboxylates were investigated. Condensations of ethyl 2-hydrazino-1-azaazulene-3-carboxylate with benzaldehyde and *p*-methoxybenzaldehyde gave corresponding hydrazones in good yields. Reactions of ethyl 2-(benzylidene)hydrazino-1-azaazulene-3-carboxylate (**2a**) and ethyl 2-(*p*-methoxybenzylidene)hydrazino-1-azaazulene-3-carboxylate with dimethyl acetylenedicarboxylate gave novel 1 : 2-adducts, 4a,11,11a-triazaindeno[5,6-*a*]azulene derivatives and 2-methoxycarbonylimino-1-(2-pyrrolylmethyl)-1-azaazulene derivatives as major products. Reaction of **2a** with electron deficient olefins (tetracyanoethylene, *N*-methylmaleimide) gave no cycloadduct but a cyclization product of **2a**, 3-phenyl-1,2,3a-triazacyclopent[*a*]azulene-9-carboxylate. The structures of the obtained compounds were analyzed 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 showed interesting features and gave a wide variety of heterocycle-annulated azaazulenes.[1—8] It is well known that hydrazones behave like azomethine imine and proceed on dipolar cycloadditions to give heterocycles.[9—12] In spite of the potentiality of the 1-azaazulen-2-ylhydrazones for leading to novel heterocycles, studies had not been done. Now we have synthesized 2-(benzylidene)hydrazino-1-azaazulenes, which would be considered as extended azomethine imine, by condensation of ethyl 2-hydrazino-1-azaazulene-3-carboxylate with benzaldehydes and *p*-methoxybenzaldehyde, and studied the reactions of the hydrazones with dimethyl acetylenedicarboxylate (DMAD) and electron-deficient olefins (Chart 1).

Ethyl 2-hydrazino-1-azaazulene-3-carboxylate (**1**) was synthesized in a 99% yield by the treatment of ethyl 2-chloro-1-azaazulene-3-carboxylate with 80% hydrazine hydrate in refluxing ethanol for 1 h. The treatment of **1** with benzaldehyde and *p*-methoxybenzaldehyde in refluxing ethanol for 1 h gave ethyl 2-(benzylidene)hydrazino-1-azaazulene-3-carboxylate (**2a**) and ethyl 2-(*p*-methoxybenzylidene)hydrazino-1-azaazulene-3-carboxylate (**2b**) in 90.5% and 74% yields, respectively.

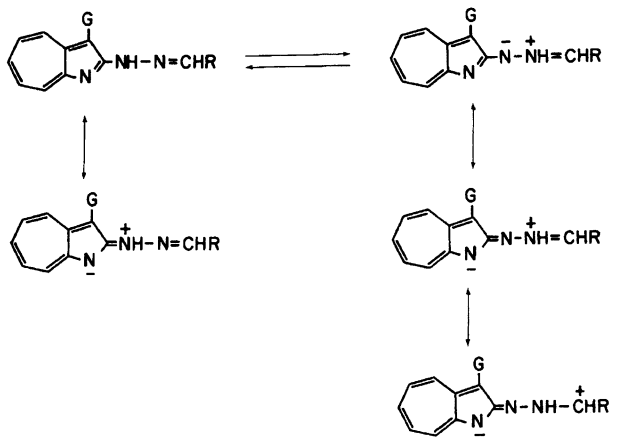


Chart 1.

Reactions of 2a and 2b with DMAD. The reaction of **2a** with DMAD gave a complex mixture, and the seven compounds **3a**, **4**, **5a**, **6a**, **7a**, **8**, and **9a** were isolated from the mixture (Chart 2). The reaction conditions and the results are listed in Table 1. The compound **7a** was converted to **6a** and **9a** with heating and/or contact with silica gel.

The slightly unstable compound **3a** was a 1 : 1-adduct and assigned as 11-ethyl 4,5-dimethyl 3-phenyl-1,2,5a-triazacyclohept[*a*]azulene-4,5,11-tricarboxylate on the basis of its spectral data as well as high-resolution mass spectral data. In its ^{1}H NMR spectrum, H-6 and H-10 protons were seen at δ=8.89 (d, J=11.0 Hz) and 9.37 (d, J=9.2 Hz), respectively, and the remaining seven-membered ring protons at δ=7.10—7.40. The coupling constants of H-6 and H-10 showed the presence of bond alternation of a seven-membered ring. It is considered therefore that the structure of **3a** was a 1,2-fuzed 1-azaazulene rather than a 2-substituted 1-azaazulene.

Compound **4** was identical with 9-ethyl 1,2,3-trimethyl 3a-azacyclopent[*a*]azulene-1,2,3,9-tetracarboxylate[1] form the inspection of its spectral data and elemental analysis. In its ^{1}H NMR spectrum, H-4 and H-8 protons were seen at δ=8.53 (d, J=11.0 Hz) and 9.94 (d, J=9.2 Hz), respectively, and the remaining seven-membered ring protons at δ=7.20—7.50.

The chemical shifts of ^{1}H NMR spectra of **3a** and **4** suggested that the nature of these compounds are essentially aromatic. Furthermore, from the consideration of the presence of bond alternation in these compounds, it is suggested that these compounds have the nature of perturbed 1-azaazulenes and not peripheral conjugation.

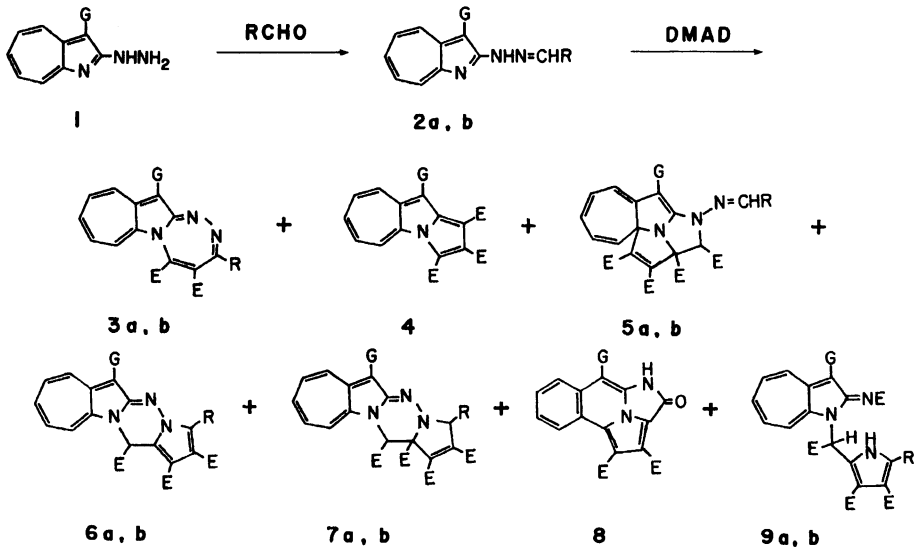


Chart 2.

Table 1. Reaction of **2a** and **2b** with DMAD

Entry	2	Conditions	Time	Products/%						
			h	**3**	**4**	**5**	**6**	**7**	**8**	**9**
1	**2a**	Benzene reflux	6	6	2	8	13	38	8	9
2	**2a**	MeCN reflux	20	—	1	10	13	10	10	11
3	**2a**	Xylene reflux	3	2	3	2	19	11	6	5
4	**2b**	MeCN reflux	2	—	5	4	6	—	4	5

The compound **5a** was a 1:2-adduct from its elemental analysis and assigned as 5-ethyl 1,2,2a,3-tetramethyl 4-benzylideneamino-2a,3-dihydro-4*H*-4,10b-diazapentaleno[1,6-*aj*]azulene-1,2,2a,3,5-pentacarboxylate from the inspection of its ^{1}H NMR spectrum, which coincided with the 2a,3-dihydro-4*H*-4,10b-diazapentaleno-[1,6-*aj*]azulene system.[1)]

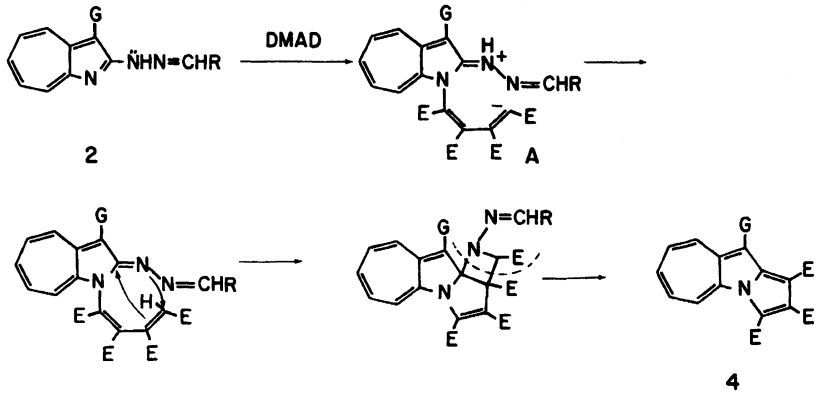
The structures of **7a**, **8**, and **9** were confirmed by the X-ray analyses (see below), and assigned as 10-ethyl 2,3,3a,4-tetramethyl 3a,4-dihydro-1-phenyl-4a,11,11a-triaza-1*H*-indeno[5,6-*a*]azulene-2,3,3a,4,10-pentacarboxylate, 5-ethyl 2,3-dimethyl 3,4-dihydro-2-oxo-4,9b-diazapentaleno[1,6-*ab*]naphthalene-1,2,5-tricarboxylate, and ethyl 2-methoxycarbonylimino-1-[methoxycarbonyl-[3,4-bis(methoxycarbonyl)-5-phenylpyrrol-2-yl]methyl]-1-aza-1,2-dihydroazulene-3-carboxylate, respectively.

Compound **6a** was $C_{29}H_{25}N_3O_8$ from the elemental analysis, and in its ^{1}H NMR spectrum three methyl esters at δ=3.64, 3.76, and 3.90 and one methine proton at δ=6.70 were observed. Therefore, it is considered that methyl formate was eliminated from **7a**. Seven-membered ring protons were seen at δ=6.93 (dd, J=10.4 and 9.2 Hz), 6.95 (d, J=9.2 Hz), 7.18 (dd, J=11.6 and 9.2 Hz), 7.19 (dd, J=10.4 and 9.2 Hz), and 8.70 (d, J=11.6 Hz), and this result showed that **6a** had 1,2-fuzed 1-azaazulene nuclei. Therefore, **6a** was assigned as 10-ethyl 2,3,4-trimethyl 1-phenyl-4a,11,11a-triaza-4*H*-indeno[5,6-*a*]azulene-2,3,4,10-tetracarboxylate. The ^{13}C NMR spectrum of **6a** showed four carbonyl carbons, one ethyl and three methyl carbons, one methine carbons, and appropriate aromatic carbons, and these results substantiated the structure.

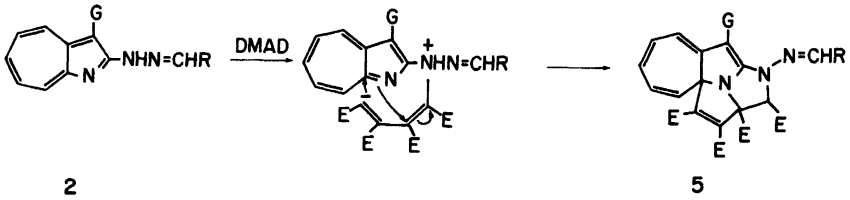
In a similar manner, **2b** was reacted with DMAD, and the results are listed in Table 1.

Formations of **4** and **5** were similar to the reaction of 2-(substituted amino)-1-azaazulenes with DMAD,[1)] and this suggested that the reaction mechanisms were the same. In this case, (benzylidene)hydrazino group of **2** behaved as *N*-substituted amino group. Plausible mechanisms for the formations of **4** and **5** are drawn in Schemes 1 and 2, respectively.

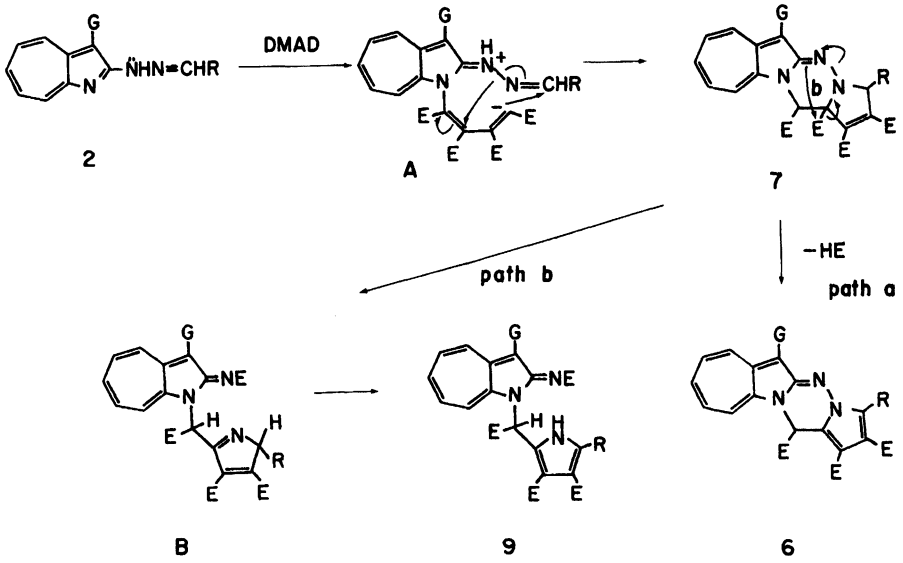
Plausible mechanisms for the formation of **7**, **6**, and **9** are shown in Scheme 3. Attacks of DMAD occurred at *N*-1 on **2a** producing dipolar species **A**, which is the same as an intermediate in the formation of **4**. Cyclization of dipolar intermediate **A** gave **7** (path a). Elimination of methyl formate from **7** afforded **6**. Rearrangement of **7** produced the ring-cleaved intermediate **B**, and successive proton migration furnishes **9** (path b).



Scheme 1.



Scheme 2.



Scheme 3.

Single-Crystal X-Ray Structure Analysis of 7a, 8, and 9a. ORTEP drawings[13] of compounds **7a** and **9a** and a PLUTO drawing[14] of **8** are shown in Figs. 1, 2, and 3, respectively. The numberings given in Figs. 1, 2, and 3 are arbitrary, and are not consistent with those of the IUPAC nomencleature. Crystal data are shown in Table 2.[15] Selected bond distances of compounds **7a** and **9a** are listed in Table 3.[15]

From the consultation of the bond distances, bond alternations of seven-membered rings of **7a** and **9a** (1.35—1.46 Å) are observed. This result agrees with the consideration that large divergences of the coupling constants ($\Delta J=2.4$ Hz) are observed in the ^{1}H NMR spectra of seven-membered protons of **7a** and **9a** and the fact suggests the presence of bond alternation.

Since the crystal of **8** adopted enantiomeric twins, structure analysis was insufficient and the final *R*-value was not good. Consequently, only the structural form for **8** was presumed and detailed interpretation was not desirable.

Cyclization of 2a. When **2a** was treated with tetracyanoethylene (TCNE) in refluxing *t*-butylbenzene for 1 h, no cycloadduct was obtained. Instead, the cyclization product of **2a**, ethyl 3-phenyl 1,2,3a-triazacyclopent[*a*]azulene-9-carboxylate (**10**), was obtained in a 38% yield. The structure of **10** was deduced from

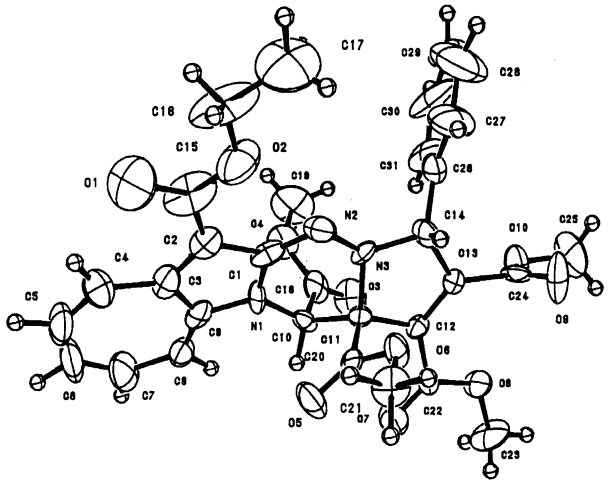


Fig. 1. ORTEP drawing of **7a**.

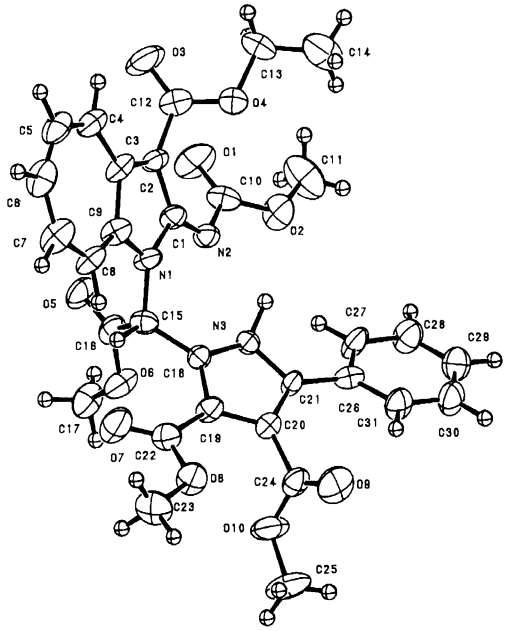


Fig. 2. ORTEP drawing of **9a**.

the inspections of its spectral data as well as elemental analysis. Treatment of **2a** with *N*-methylmaleimide in refluxing xylene for 48 h also gave **10** in a 6% yield. When no electron-deficient olefins were present, treatment of **2a** in refluxing *t*-butylbenzene even for 48 h gave only a trace of **10** along with 99% of recovered **2a**. Therefore, it is considered that the olefins catalyzed the cyclization of **2a**. Plausible mechanism is shown in Scheme 4. First a Michael addition of **2a** with TCNE produces the dipolar species **C**, successive cyclization and aromatization affords **10**.

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.

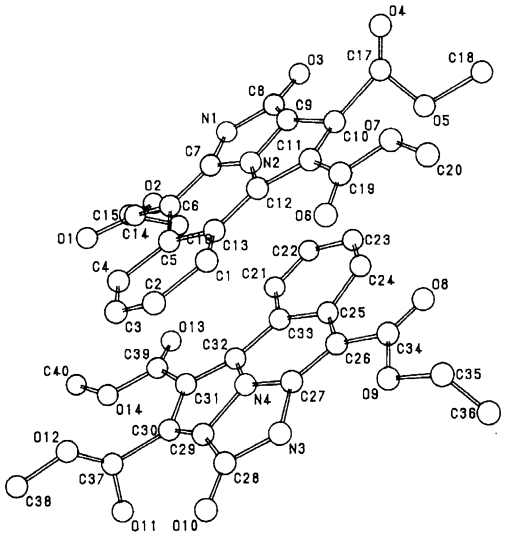


Fig. 3. PLUTO drawing of **8**. Hydrogen atoms are omitted for clarity.

IR spectra were recorded on a Hitachi 270-50 infrared spectrophotometer for Nujol mulls. Mass spectra and high-resolution mass spectra were taken with a JEOL JMS-01SG-2 spectrometer. Kieselgel 60 was used for column chromatography and Kieselgel 60G for thin-layer chromatography.

Synthesis of 1. A mixture of ethyl 2-chloro-1-azaazulene-3-carboxylate (5.00 g) and 80% hydrazine hydrate (10 ml) in ethanol (60 ml) was refluxed for 1 h and then cooled. The precipitate was collected by filtration and washed with cold ethanol to give **1** (4.85 g, 99%) as yellow needles; mp 70.0—71.0 °C; ^{1}H NMR δ=1.47 (3H, t, J=7.0 Hz), 2.5—3.8 (2H, br), 4.45 (2H, q, J=7.0 Hz), 7.52 (1H, t, J=9.8 Hz), 7.68 (1H, t, J=9.8 Hz), 7.70 (1H, dd, J=11.0 and 9.8 Hz), 8.17 (1H, d, J=9.8 Hz), 8.25 (1H, brs), and 8.89 (1H, d, J=11.0 Hz). IR 3380, 3300, 3150 (NH), and 1660 cm^{-1} (C=O). Found: C, 62.30; H, 5.62; N, 18.21%. Calcd for $C_{12}H_{13}N_3O_2$: C, 62.33; H, 5.66; N, 18.17%.

Synthesis of 2. A solution of **1** (1.70 g) and benzaldehyde (1.00 g) in ethanol (50 ml) was refluxed for 1 h and then the solvent was evaporated. Recrystallization of the residue from cyclohexane gave **2a** (2.125 g, 90.5%) as yellow needles; mp 150—151 °C; ^{1}H NMR δ=1.51 (3H, t, J=7.3 Hz), 4.50 (2H, q, J=7.3 Hz), 7.35—7.50 (3H, m), 7.57 (1H, t, J=9.8 Hz), 7.70 (1H, dd, J=10.4 and 9.8 Hz), 7.75 (1H, dd, J=10.4 and 9.8 Hz), 7.86 (2H, dd, J=7.9 and 2.0 Hz), 8.11 (1H, s), 8.41 (1H, d, J=10.4 Hz), 8.91 (1H, d, J=10.4 Hz), and 10.85 (1H, brs); IR 3200 (NH) and 1656 cm^{-1} (C=O and C=N). Found: C, 71.14; H, 5.46; N, 12.97%. Calcd for $C_{19}H_{17}N_3O_2$: C, 71.46; H, 5.37; N, 13.16%.

In a similar manner, **2b** was synthesized in a 74% yield.

2b: Yellow needles (from cyclohexane), mp 157—159 °C; ^{1}H NMR δ=1.58 (3H, t, J=7.3 Hz), 3.76 (3H, s), 4.63 (2H, q, J=7.3 Hz), 6.58 (2H, d, J=8.55 Hz), 7.79 (2H, d, J=8.55 Hz), 7.80—7.90 (2H, m), 7.95—8.05 (1H, m), 8.48 (1H, s), 9.00—9.08 (1H, m), 9.42 (1H, d, J=9.15 Hz), and 11.30 (1H, brs); IR 3256 (NH), 1696, and 1664 cm^{-1} (C=O and C=N). Found: C, 68.83; H, 5.56; N, 11.94%. Calcd for $C_{20}H_{19}N_3O_3$: C, 68.75; H, 5.48; N, 12.03%.

Reaction of 2 with DMAD. General Procedure. A solution of **2** (1.5 mmol), DMAD (4.5 mmol) in the solvent

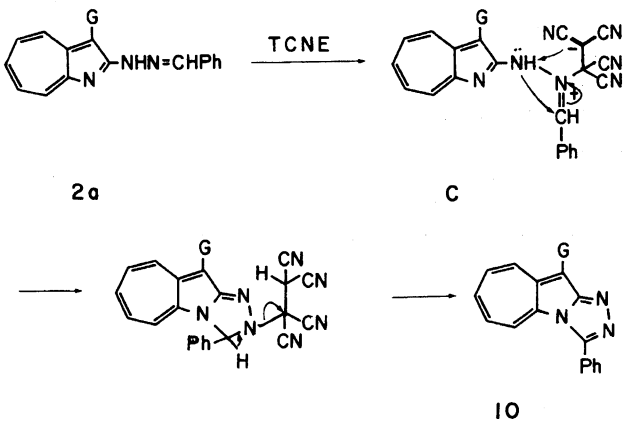
Table 2. Crystal and Structure Analyses Data of Compounds **7a**,**8**, and **9a**

	7a	**8**	**9a**
Formula	$C_{31}H_{29}N_3O_{10}$	$C_{20}H_{16}N_2O_7$	$C_{31}H_{29}N_3O_{10}$
Formula weight	603.58	396.36	603.58
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$; Z=2	$P\bar{1}$; Z=4	$P\bar{1}$; Z=2
Lattice paramaters			
a/Å	11.194(4)	13.229(3)	10.460(4)
b/Å	14.787(5)	13.826(5)	16.432(9)
c/Å	9.859(4)	11.872(5)	9.021(5)
α/°	91.93(4)	106.54(4)	104.02(5)
β/°	109.82(3)	105.60(2)	100.94(4)
γ/°	77.75(3)	90.37(3)	91.49(4)
V/Å^3	1499(1)	1997(1)	1473(1)
D_{calcd}/g cm^{-1}	1.337	1.318	1.361
Crystal size/mm^3	0.06×0.12×0.42	0.10×0.14×0.80	0.22×0.26×0.44
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	50.0°	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: 3742, Unique: 3445	Total: 7667, Unique: 7271	Total: 6254, Unique: 5879
No. of observations[c)]	1065	1678	1607
No. of variables	397	523	397
Residuals R; R_w	0.052; 0.054	0.193; 0.265	0.058; 0.063
Max Shift/Error	0.64	0.40	0.01
$\Delta\rho$max/e$^-$ Å^{-3}	0.20	2.53	0.26

a) See Ref. 16. b) See Ref. 17. c) $I<3.00\sigma(I)$.

Table 3. Selected Bond Distances (l/Å) of **7a** and **9a**

	7a	**9a**
C(1)–C(2)	1.49(2)	1.43(1)
C(2)–C(3)	1.39(2)	1.37(1)
C(3)–C(4)	1.46(2)	1.42(1)
C(4)–C(5)	1.36(2)	1.35(1)
C(5)–C(6)	1.38(2)	1.39(1)
C(6)–C(7)	1.35(2)	1.37(1)
C(7)–C(8)	1.44(2)	1.40(1)
C(8)–C(9)	1.37(2)	1.36(1)
C(9)–C(3)	1.44(2)	1.47(1)
C(1)–N(1)	1.40(2)	1.40(1)
C(9)–N(1)	1.39(2)	1.39(1)



Scheme 4.

(50 ml) was refluxed and then the solvent was evaporated. Separation of the residue by column chromatography and preparative thin-layer chromatography gave **3**,**4**,**5**,**6**,**7**, and **8**, in the order. The reaction conditions and the results were listed in Table 1.

3a: Red brown needles, mp 218—219 °C; ^{1}H NMR δ=1.17 (3H, t, J=7.3 Hz), 3.75 (3H, s), 4.07 (3H, s), 4.26 (2H, q, J=7.3 Hz), 7.10—7.40 (3H, m), 7.45—7.53 (3H, m), 7.64—7.70 (2H, m), 8.89 (1H, d, J=11.0 Hz), and 9.37 (1H, d, J=9.2 Hz). HRMS Found: m/z 395.1631. Calcd for $C_{25}H_{21}N_3O_6$: M, 395.1633.

4: Brown needles (from cyclohexane–dichloromethane), mp 188—189 °C (lit,[1)] 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). Found: C, 60.71; H, 4.66; N, 3.42%.

5a: Yellow needles (from hexane), mp 117—118 °C (decomp); ^{1}H NMR δ=1.19 (3H, t, J=7.0 Hz), 3.67 (3H, s), 3.75 (3H, s), 3.84 (3H, s), 3.89 (3H, s), 4.00—4.20 (1H, m), 4.25—4.45 (1H, m), 5.57 (1H, d, J=11.0 Hz), 5.72 (1H, s),

6.01 (1H, dd, J=11.0 and 7.0 Hz), 6.26 (1H, dd, J=10.7 and 7.0 Hz), 6.39 (1H, dd, J=10.7 and 7.9 Hz), and 6.90 (1H, d, J=7.9 Hz), 7.35—7.50 (3H, m), 7.61—7.68 (2H, m), and 7.69 (1H, s); IR 1744, 1700, 1690, (C=O), and 1632 cm^{-1} (C=N). Found: C, 61.57; H, 4.72; N, 6.99%. Calcd for $C_{31}H_{29}N_3O_{10}$: C, 61.69; H, 4.84; N, 6.96%.

6a: Red prisms (from cyclohexane–dichloromethane), mp 177—178 °C; ^{1}H NMR δ=1.23 (3H, t, J=7.3 Hz), 3.64 (3H, s), 3.76 (3H, s), 3.90 (3H, s), 4.15—4.40 (2H, m), 6.70 (1H, s), 6.93 (1H, dd, J=10.4 and 9.2 Hz), 6.95 (1H, d, J=9.2 Hz), 7.18 (1H, dd, J=11.6 and 9.2 Hz), 7.19 (1H, dd, J=10.4 and 9.2 Hz), 7.35—7.50 (3H, m), 7.68 (2H, dd, J=7.9 and 1.8 Hz), and 8.70 (1H, d, J=11.6 Hz); ^{13}C NMR δ=14.22, 51.56, 51.98, 53.08, 53.39, 60.37, 112.63, 115.11, 127.61, 128.10, 128.80, 129.78, 130.66, 130.82, 130.97, 132.83, 134.20, 136.52, 146.68, 147.60, 148.60, 163.31, 165.84, 165.93, and 166.21; IR 1746, 1732, 1710, and 1682 cm^{-1} (C=O). Found: C, 63.41; H, 4.82; N, 7.64%. Calcd for $C_{29}H_{25}N_3O_8 \cdot H_2O$: C, 63.04; H, 4.74; N, 7.60%.

7a: Red-brown prisms (from hexane–dichloromethane), mp 198—199 °C; ^{1}H NMR δ=1.22 (3H, t, J=7.3 Hz), 3.60 (3H, s), 3.74 (3H, s), 3.76 (3H, s), 3.85 (3H, s), 4.10—4.30 (2H, m), 5.87 (1H, s), 5.95 (1H, s), 6.15 (1H, d, J=9.2 Hz), 6.45 (1H, dd, J=11.6 and 9.2 Hz), 6.80 (2H, dd, J=11.6 and 10.4 Hz), 7.20—7.40 (5H, m), and 8.06 (1H, d, J=11.6 Hz); IR 1750, 1734, 1720, and 1690 cm^{-1} (C=O). Found: C, 61.77; H, 4.85; N, 7.02%. Calcd for $C_{31}H_{29}N_3O_{10}$: C, 61.69; H, 4.84; N, 6.96%.

8: Colorless prisms (from hexane–dichloromethane), mp 252—254 °C; ^{1}H NMR δ=1.56 (3H, t, J=7.0 Hz), 4.05 (6H, s), 4.62 (2H, q, J=7.0 Hz), 7.68 (1H, dd, J=7.9 and 6.3 Hz), 7.78 (1H, dd, J=8.5 and 7.3 Hz), 8.99 (1H, d, J=7.9 Hz), 9.28 (1H, d, J=8.5 Hz), and 9.45 (1H, brs); IR 1702, 1632 cm^{-1} (C=O). Found: C, 56.16; H, 3.96; N, 6.18%. Calcd for $C_{20}H_{16}N_2O_7 \cdot 1/2\ CH_2Cl_2$: C, 56.11; H, 3.91; N, 6.38%.

9a: Yellow needles (from hexane), mp 157—158 °C; ^{1}H NMR δ=1.36 (3H, t, J=7.0 Hz), 3.72 (3H, s), 3.77 (3H, s), 3.83 (3H, s), 3.89 (3H, s), 4.20—4.50 (2H, m), 7.25—7.70 (9H, m), 8.27 (1H, d, J=9.8 Hz), 8.72 (1H, d, J=11.0 Hz), and 12.29 (1H, brs); IR 1756, 1732, 1720, 1700, and 1690 cm^{-1} (C=O). Found: C, 61.73; H, 4.78; N, 6.84%. Calcd for $C_{31}H_{29}N_3O_{10}$: C, 61.69; H, 4.84; N, 6.96%.

5b: Yellow needles (from hexane), mp 105—106 °C; ^{1}H NMR δ=1.17 (3H, t, J=7.0 Hz), 3.66 (3H, s), 3.75 (3H, s), 3.83 (3H, s), 3.84 (3H, s), 3.87 (3H, s), 3.98—4.18 (1H, m), 4.23—4.38 (1H, m), 5.54 (1H, d, J=10.4 Hz), 5.67 (1H, s), 6.00 (1H, dd, J=10.4 and 6.7 Hz), and 6.25 (1H, dd, J=11.0 and 6.7 Hz), 6.38 (1H, dd, J=11.0 and 7.3 Hz), 6.90 (2H, d, J=9.15 Hz), 6.92 (1H, d, J=7.3 Hz), 7.60 (2H, d, J=9.15 Hz), and 7.74 (1H, s); IR 1744, 1720 (SH), 1690 (C=O), and 1632 cm^{-1} (C=N). Found: C, 60.47; H, 4.78; N, 6.59%. Calcd for $C_{32}H_{31}N_3O_{11}$: C, 60.66; H, 4.93; N, 6.63%.

6b: Red needles (from hexane), mp 187—188 °C; ^{1}H NMR δ=1.45 (3H, t, J=7.0 Hz), 3.64 (3H, s), 3.77 (3H, s), 3.84 (3H, s), 3.90 (3H, s), 4.20—4.40 (2H, m), 6.68 (1H, s), 6.90—7.00 (4H, m), 7.12—7.63 (2H, m), 7.63 (2H, d, J=8.55 Hz), and 8.69 (1H, d, J=11.0 Hz); IR 1758, 1726, 1698, and 1672 cm^{-1} (C=O). Found: C, 62.61; H, 4.80; N, 7.54%. Calcd for $C_{30}H_{27}N_3O_9$: C, 62.82; H, 4.75; N, 7.33%.

7b: Red-brown prisms (from hexane), mp 203—204 °C; ^{1}H NMR δ=1.24 (3H, t, J=7.0 Hz), 3.63 (3H, s), 3.73 (3H, s), 3.76 (3H, s), 3.78 (3H, s), 3.86 (3H, s), 4.15—4.30 (2H, m), 5.84 (1H, s), 5.94 (1H, s), 6.15 (1H, d, J=9.2 Hz), 6.45 (1H, dd, J=10.4 and 7.3 Hz), 6.75—6.90 (2H, m), 6.84 (2H, d, J=8.5 Hz), 7.19 (2H, d, J=8.5 Hz), and 8.06 (1H, d, J=12.2 Hz); IR 1744, 1735, 1698 cm^{-1} (C=O). Found: C, 60.77; H, 4.85; N, 6.90%. Calcd for $C_{32}H_{31}N_3O_{11}$: C, 60.66; H, 4.93; N, 6.63%.

9b: Yellow needles (from hexane–dichloromethane), mp 202—204 °C; ^{1}H NMR δ=1.39 (3H, t, J=7.0 Hz), 3.72 (3H, s), 3.77 (3H, s), 3.82 (3H, s), 3.83 (3H, s), 3.88 (3H, s), 4.25—4.45 (2H, m), 6.94 (2H, d, J=8.55 Hz), 7.40—7.70 (6H, m), 8.27 (1H, d, J=9.8 Hz), 8.72 (1H, d, J=11.0 Hz), and 12.15 (1H, brs); IR 1746, 1715, 1704, and 1698 cm^{-1} (C=O). Found: C, 60.43; H, 4.81; N, 6.74%. Calcd for $C_{32}H_{31}N_3O_{11}$: C, 60.66; H, 4.93; N, 6.63%.

Thermolysis of 7a. a) A solution of **7a** (0.080 g) in xylene (20 ml) was refluxed for 24 h and evaporated. The residue was chromatographed to give **6a** (0.051 g, 64%) and **9a** (0.007 g, 9%), successively.

b) A mixture of **7a** (0.150 g) and silica gel (5.0 g) in acetonitrile (30 ml) was refluxed for 60 h, then filtered. The silica gel was washed with ethyl acetate. The combined filtrate was evaporated. Chromatography of the residue gave **6a** (0.026 g, 18%), **7a** (0.037 g, 25%), and **9a** (0.052 g, 35%), successively.

Cyclization of 2a. A mixture of **2a** (0.320 g) and TCNE (0.280 g) in *t*-butylbenzene (30 ml) was refluxed for 1 h, and then the solvent was evaporated. Chromatography of the residue with chloroform gave **2a** (0.036 g, 11%) and **10** (0.123 g, 39%), successively.

10: Red-brown needles (from hexane), mp 196—197 °C; ^{1}H NMR δ=1.52 (3H, t, J=7.3 Hz), 4.57 (2H, q, J=7.3 Hz), 7.09—7.13 (1H, m), 7.38—7.48 (2H, m), 7.59—7.63 (3H, m), 7.80—7.86 (2H, m), 7.97 (1H, d, J=9.2 Hz), and 9.21—9.27 (1H, m); IR 1676 cm^{-1} (C=O). MS m/z 317 (M^+). Found: C, 68.08; H, 5.14; N, 12.77%. Calcd for $C_{19}H_{15}N_3O_2 \cdot H_2O$: C, 68.04; H, 5.11; N, 12.53%. b) A mixture of **2a** (0.300 g), *N*-methylmaleimide (0.135 g), and 5% Pd–C (0.500 g) in xylene was refluxed for 48 h, and then the solvent was evaporated. Chromatography of the residue gave **2a** (0.239 g, 80%) and **10** (0.019 g, 6%). c) A solution of **2a** (0.200 g) in *t*-butylbenzene was refluxed for 1 h and evaporated. Chromatography of the residue gave **2a** (0.197 g, 99%) and **10** (0.001 g, 0.5%).

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