Reactions of 2-Hydrazino-1-azaazulenes with Diphenylcyclopropenone

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The reaction of ethyl 2-hydrazino-1-azaazulene-3-carboxylate with diphenylcyclopropenone (DPP) gave ethyl (*Z*)-2-[*N'*-(3-amino-2,3-diphenylpropenoyl)hydrazino]-1-azaazulene-3-carboxylate, ethyl 8,9-diphenyl-1,2,9b-triazaindeno[1,7,6-*bcd*]azulene-3-carboxylate, ethyl (*E*)-3-(1,2-diphenylethyl)-1,2,3a-triazacyclopent[*a*]-azulene-9-carboxylate, and ethyl 2-amino-1-azaazulene-3-carboxylate (**8a**), together with the products of **8a** with DPP. However, the reaction of 2-hydrazino-1-azaazulene with DPP gave 4*H*-2,3-diphenyl-1,4a-diazabenz-[*a*]azulen-4-one, (*Z*)-3-[(1-azaazulen-2-yl)amino]-2,3-diphenylpropenamide, 3,4-diphenyl-3,4-dihydro-2*H*-1,4a-diazabenz[*a*]azulen-2-one and 2-amino-1-azaazulene. The structures of the obtained products were determined by inspections of their physical and spectral data, as well as single-crystal X-ray structure analyses of some of these compounds. The reaction mechanisms are discussed.

Cycloaddition reactions of diphenylcyclopropenone (DPP) with heterocycles are interesting for the construction of novel heterocycles;[1—10] we have also reported on the cycloaddition of 2-amino-1-azaazulenes with DPP, which proceeded like amino-substituted heterocycles with DPP[5] and afforded novel heterocycles.[11] Recently, Toda et al. reported on a reinvestigation of the reactions of DPP with phenylhydrazine, which afforded the hydrazones (acidic conditions) or pyrazolone derivatives and/or aminocinnamohydrazides (basic conditions).[12] Cycloaddition reactions of azaazulenes have received attention, and we have reported that the reactions of 2-hydrazino-1-azaazulenes with dimethyl acetylenedicarboxylate gave cycloadducts and the hydrazone derivatives.[13] Therefore, we were promoted to investigate the reaction of 2-hydrazino-1-azaazulenes with DPP, leading to interesting results, in which novel cyclizations were observed.

Reactions of 2-Hydrazino-1-azaazulenes with DPP. The treatment of ethyl 2-hydrazino-1-azaazulene-3-carboxylate[14] (**1a**) with DPP in refluxing xylene for 2 h gave a complex mixture; ethyl (*Z*)-2-[*N'*-(3-amino-2,3-diphenylpropenoyl)hydrazino]-1-azaazulene-3-carboxylate (**2**), ethyl 8,9-diphenyl-1,2,9b-triazaindeno[1,7,6-*bcd*]azulene-3-carboxylate (**3**), ethyl (*E*)-3-(2,3-diphenylethyl)-1,2-3a-triazacyclopent[*a*]azulene-9-carboxylate (**4**), ethyl 2-[*N'*-(phenyloxalyl)hydrazino]-1-azaazulene-3-carboxylate (**5**), ethyl (*E*)-2-(2,3-diphenylpropenamido)-1-azaazulene-3-carboxylate[11] (**6**), ethyl (*Z*)-2-(2,3-diphenylpropenamido)-1-azaazulene-3-carboxylate[11] (**7**), and ethyl 2-amino-1-azaazulene-3-carboxylate (**8a**)[15] were isolated from the mixture, in 23, 14, 3, 2, 8, 3, and 20% yields, respectively. When the reaction was carried out in refluxing acetonitrile for 4 h, **2** (28%), **3** (21%), **4** (2%), **5** (2%), **6** (1%), **7** (2), and **8a** (39%) were obtained (Chart 1). It is considered that **5** was a secondary product which would be produced under a post-treatment. Indeed, **2** was converted to **5** by contact with silica gel in 42% yield. The reaction could proceed by the hydration of **2** and a successive oxidative cleavage. compounds **6** and **7** would be produced from **8a**.[11]

The structures of these compounds were deduced on the basis of their spectral data as well as elemental analyses; the structures of **2**, **3**, **4**, and **5** were confirmed by X-ray structural analyses (see below). From a consideration of the ^{1}H and ^{13}C NMR spectra of **2**, it is suggested that **2** has an ordinary 1-azaazulene skeleton. The ^{1}H and ^{13}C NMR spectra of **3** showed that **3** had four seven-membered ring protons; this indicated that cyclization occurred at the seven-membered ring. In the ^{1}H NMR spectrum of **4**, one vinyl proton was seen at δ=7.49, and seven-membered ring protons at δ=6.86 (t, J=9.8 Hz, H-6), 7.12 (d, J=9.2 Hz, H-4), 7.2—7.4 (H-5 and 7, superposed with phenyl protons), and 9.18 (d, J=11.6 Hz, H-8). These results suggested that **4** has a heptafulvene-like skeleton. In the ^{1}H NMR spectrum of **5**, deshielded *o*-phenyl protons were seen at δ=8.33 (d, J=7.3 Hz) together with other phenyl protons (δ=7.45 and 7.61) and protons of the 1-azaazulene ring. The ^{13}C NMR spectrum of **5** showed three carbonyl carbons

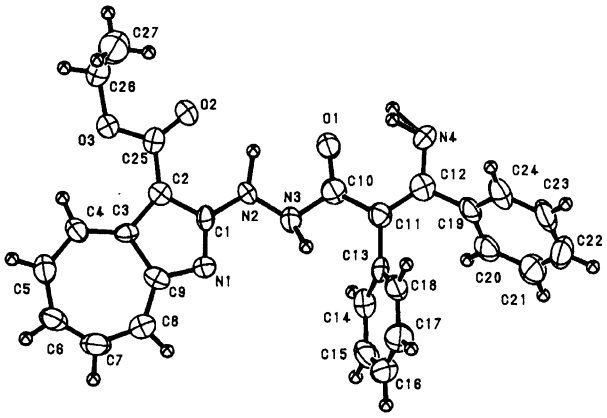


Fig. 1. ORTEP drawing of **2** showing 50% probability of thermal ellipsoids.

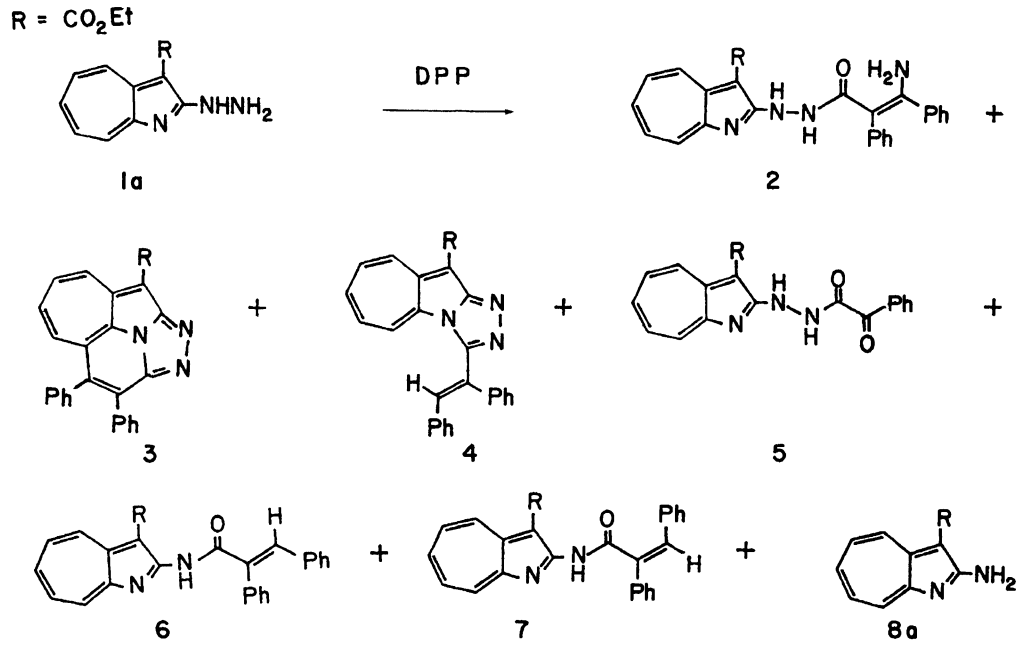
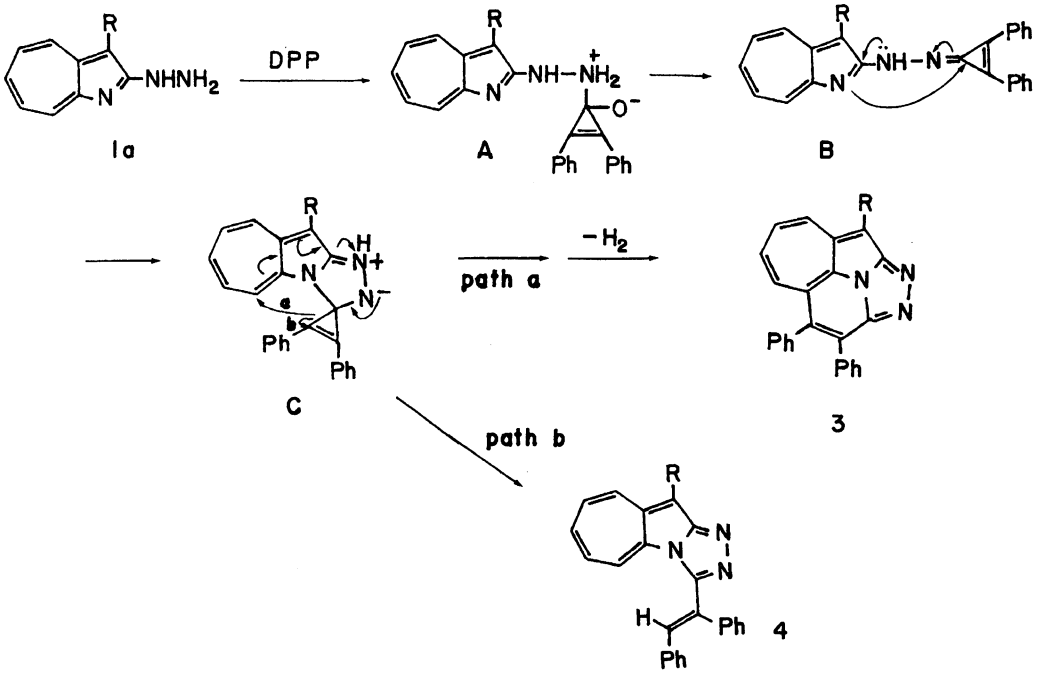


Chart 1.



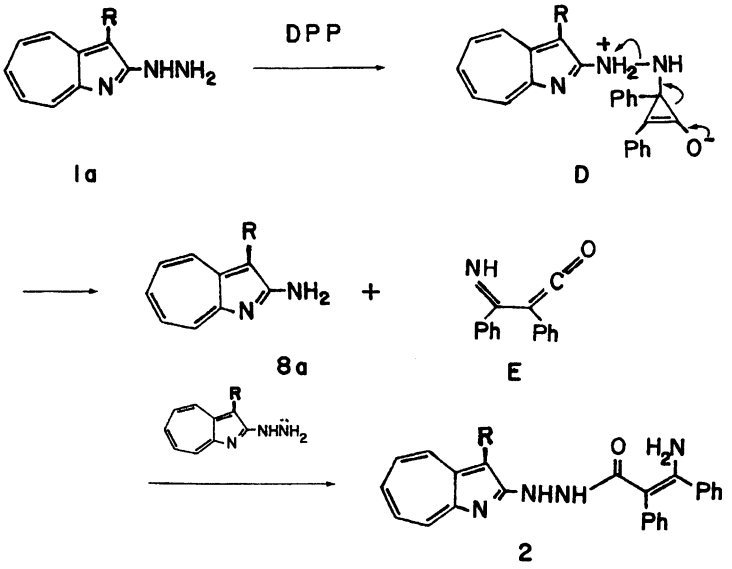
Scheme 1.

(δ=163.44, 168.39 and 203.00), carbons of one ethyl group, and appropriate aromatic carbons.

One reasonable mechanism for the formation of **3** and **4** is shown in Scheme 1. The reaction of **1a** with DPP produced the hydrazone **B** via intermediate **A**; then **B** cyclized to produce the spiro compound **C**. A rearrangement of **C** and successive dehydrogenation furnished **3** (path a). A ring-cleavage of **C** readily led to **4** (path b).

A plausible mechanism for the formation of **2** and **8a** is shown in Scheme 2. The reaction of **1a** with DPP could afford intermediate **D**. The cleavage of **D** gave **8a** and the iminoketene intermediate **E**. The addition of **1** to **E** furnished **2**. Although Toda showed another mechanism for the formation of aminocinnamohydrazides and the amines (in this case, correspond to **2** and **8a**),[12] we prefer the iminoketene formation mechanism, which was presented by Kascheres on the reactions of DPP with "pyridinium *N*-imines".[6]

The reaction of **1b** with DPP showed a rather different feature compared to that for **1a**. Thus, the treatment of **1b** with DPP in refluxing acetonitrile for 3 h gave 4*H*-2,3-diphenyl-1,4a-diazabenz[*a*]-azulen-4-one (**9**), (*Z*)-3-[(1-azaazulen-2-yl)amino]-2,3-di-



Scheme 2.

phenylpropenamide (**10**), 3,4-diphenyl-3,4-dihydro-2*H*-1,4a-diazabenz[*a*]azulen-2-one[11] (**11**), and 2-amino-1-azaazulene[16] (**8b**) in 11, 9, 4, and 16% yields, respectively, along with 27% of the recovered **1b** (Chart 2).

The structures of these compounds were deduced on the basis of their spectral data as well as elemental analyses, and the structure of **10** was confirmed by an X-ray structural analysis (see below). Compound **9** was $C_{24}H_{16}N_2O$ from an elemental analysis, and its mass spectrum (M^+, m/z 348). The structure of **9** was deduced by comparing its spectral data with those of the 4*H*-1,4a-diazabenz[*a*]azulen-4-one system.[17] In the ^{1}H NMR spectra of **9**, a proton resonating at δ=9.81—9.87 was seen, which would be deshielded by the carbonyl group on C-4. Furthermore, cyclization of **10** easily gave rise to **9** by heating or treating with silica gel; this supported the consideration of the structure of **9**. Thus, the treatment of **10** in refluxing xylene for 4 h gave **9** in 80% yield, and the treatment of **10** with silica gel in chloroform for 12 d at room temperature gave **9** (16%) and a recovery of **10** (80%).

From an inspection of the structure of **10**, it seems that DPP formally inserted to the N–N bond of the hydrazine moiety. One reasonable mechanism for the formation of **10** and **9** is shown in Scheme 3. An attack of the hydrazine **1b** to DPP gave the dipolar interme-

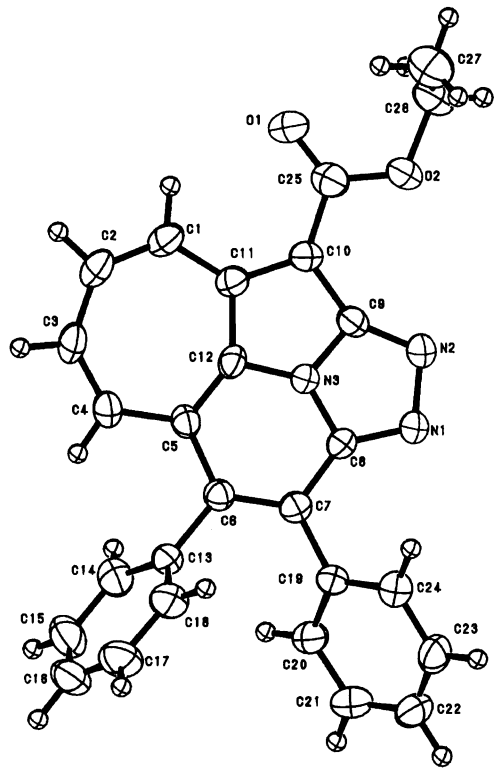


Fig. 2. ORTEP drawing of **3** showing 50% probability of thermal ellipsoids.

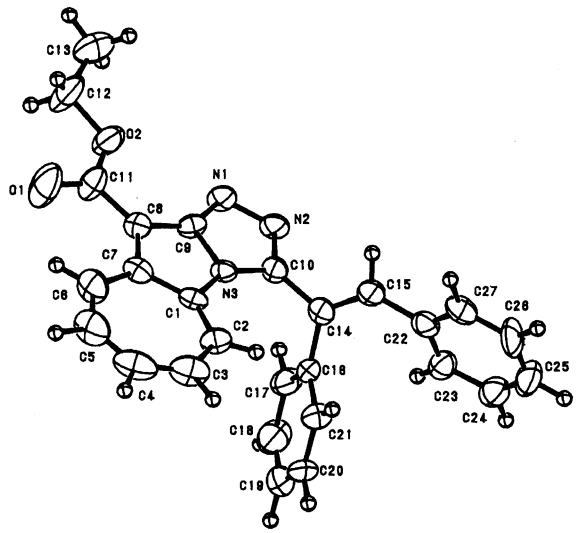


Fig. 3. ORTEP drawing of **4** showing 50% probability of thermal ellipsoids.

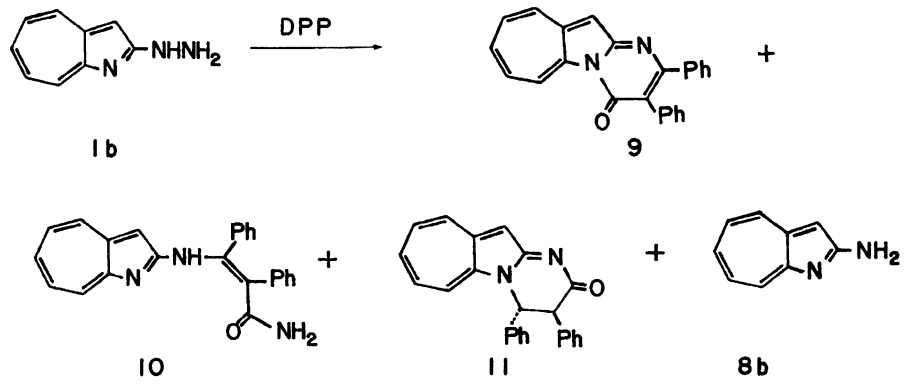
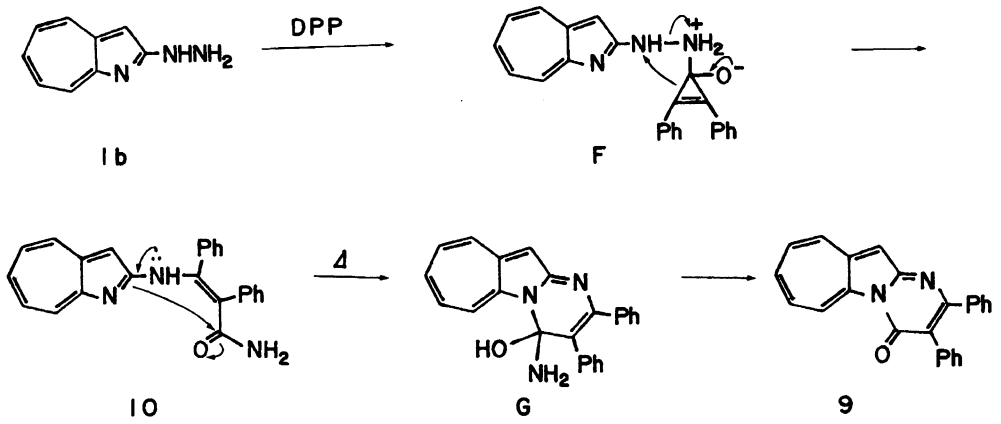


Chart 2.



Scheme 3.

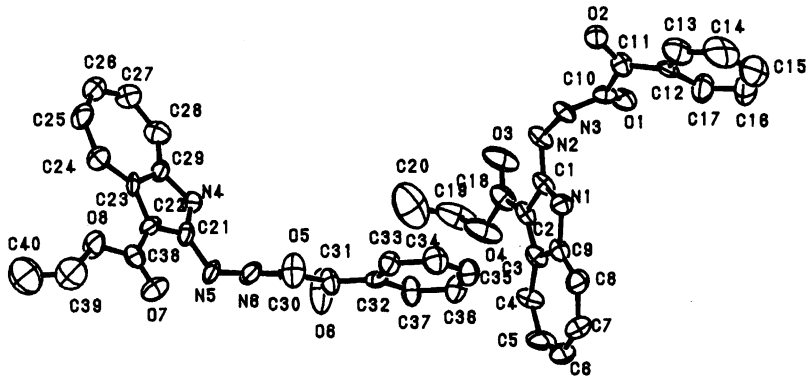


Fig. 4. ORTEP drawing of **5** showing 50% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity.

diate **F**, and a successive bond migration-bond cleavage upon **F** furnished **10**. It is considered that the absence of an electron-withdrawing group on the 1-azaazulene ring suppressed the formation of the hydrazone by dehydration, and permitted the insertion of DPP to the N–N bond. Cyclization of **10** gave intermediate **G**, and a successive elimination of ammonia from **G** afforded **9**. Although the counterpart of **8b** was not obtained, it is considered that **8b** is formed by a dissociation of the adduct of **1b** and DPP; this process would be the same as in the case of **1a** with DPP. Compound **11** could be formed by the reaction of **8b** with DPP.[11]

Single-Crystal X-Ray Structure Analysis of 2, 3, 4, 5 and 10.

ORTEP drawings[18] of compounds 2, 3, 4, 5, and 10 are shown in Figs. 1, 2, 3, 4, and 5, respectively. The numberings given in Figs. 1, 2, 3, 4, and 5 are arbitrary, and are not consistent with those of the IUPAC nomecleature. The crystal data are shown in Table 1.[19] Selected bond distances of compounds **2**, **3**, **4**, **5**, and **10** (concerning the 1-azaazulene moiety) are listed in Table 2.[19] The alphabetical symbols of the bond distances are given for a comparison to 1-azaazulene, as shown in Fig. 6. The crystal structure of **5** contained two crystallographically independent molecules per asymmetric

Table 1. Crystal and Structure Analyses Data of Compounds **2**, **3**, **4**, **5**, and **10**

	2	**3**	**4**	**5**	**10**
Formula	$C_{27}H_{24}N_4O_3$	$C_{27}H_{19}N_3O_2$	$C_{27}H_{21}N_3O_2$	$C_{20}H_{17}N_3O_4$	$C_{24}H_{19}N_3O$
Formula weight	452.51	417.47	419.48	363.37	365.43
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$C2/c$; $Z=8$	$P2_1$; $Z=4$	$P\bar{1}$; $Z=2$	$P\bar{1}$; $Z=4$	$P2_1/c$; $Z=4$
Lattice paramaters					
a/Å	25.36(3)	12.954(2)	9.977(7)	11.51(1)	11.103(3)
b/Å	11.668(6)	9.214(2)	12.615(6)	15.38(1)	8.952(2)
c/Å	17.41(2)	18.011(3)	9.82(1)	10.41(1)	19.423(3)
α/°			110.47(6)	99.13(9)	
β/°	116.62(5)	104.85(1)	104.86(7)	99.76(9)	99.32(2)
γ/°			98.77(5)	93.4(1)	
V/Å^3	4604(5)	2078.0(6)	1078(2)	1787(4)	1905.1(6)
D_{calcd}/g cm^{-1}	1.305	1.334	1.292	1.351	1.274
Crystal size/mm^3	0.06×0.10×1.00	0.22×0.40×0.86	0.04×0.16×0.64	0.26×0.34×0.66	0.20×0.54×0.68
Diffractometer	Rigaku AFC5S	Rigaku AFC5S	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)	Mo $K\alpha$ (λ=0.71069 Å)	Mo $K\alpha$ (λ=0.71069 Å)
Monochrometer	Graphite	Graphite	Graphite	Graphite	Graphite
Scan type	ω–2θ	ω–2θ	ω–2θ	ω–2θ	ω–2θ
2θ Max	55.0°	55.0°	55.0°	55.0°	55.0°
Computer program	TEXSAN System[a]	TEXSAN System[a]	TEXSAN System[a]	TEXSAN System[a]	TEXSAN System[a]
Structure solution	Direct method; MITHRIL[b]	Direct method; MITHRIL[b]	Direct method; MITHRIL[b]	Direct method; MITHRIL[b]	Direct method; MITHRIL[b]
Hydrogen atom treatment	Calculated, not refined	Calculated, not refined	Calculated, not refined	Calculated, not refined	Calculated, not refined
Refinement	Full-matrix, anisotropic	Full-matrix, anisotropic	Full-matrix, anisotropic	Full-matrix, anisotropic	Full-matrix, anisotropic
Least-squares weight	$4F_o^2/\sigma^2(F_o^2)$	$F_o^2/\sigma^2(F_o^2)$	$4F_o^2/\sigma^2(F_o^2)$	$F_o^2/\sigma^2(F_o^2)$	$4F_o^2/\sigma^2(F_o^2)$
No. of measurement ref.	Total: 4986, Unique: 4858	Total: 5277, Unique: 5962	Total: 5233, Unique: 4945	Total: 7104, Unique: 6695	Total: 4897, Unique: 4663
No. of observations[c]	1049	2210	1173	1598	1871
No. of variables	340	289	289	487	329
Residuals R; R_w	0.058; 0.061	0.050; 0.054	0.056; 0.058	0.060; 0.061	0.046; 0.048
Max shift/error	0.00	0.00	0.01	0.07	0.18
$\Delta\rho$ max/e$^-$ Å^{-3}	0.19	0.18	0.20	0.26	0.16

a) See Ref. 20. b) See Ref. 21. c) $I>3.00\sigma$ (I).

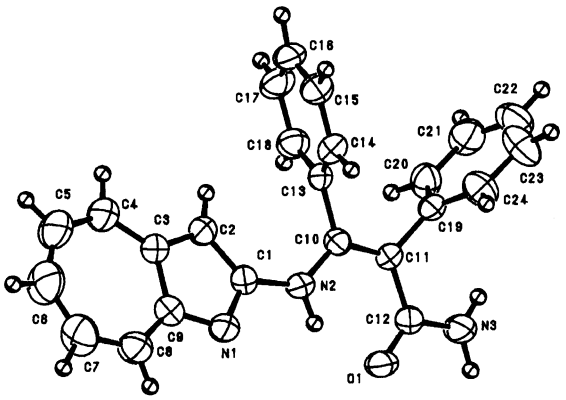


Fig. 5. ORTEP drawing of **10** showing 50% probability of thermal ellipsoids.

unit; the values for only one isomer are given in Table 2.

From consulting of the bond distances, in contrast with 1-azaazulenes **2** and **10**, a distinct bond alternation of the seven-membered ring of **3** (1.35—1.44 Å) can be observed; it is considered that **3** would be a butadiene bridged cyclazine, as shown in similar systems.[22—24] A small bond alternation is seen on **4**, suggesting that **4** has a contribution due to the heptafulvene moiety. This result agreed with a conclusion based on the NMR spectra.

Experimental

Melting points are uncorrected. ^{1}H (250 MHz) and ^{13}C (62.87 MHz) NMR specra 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. Mass spectra were taken with a JEOL JMS-01SG-2 spectrometer. Kieselgel 60 was used for column chromatography and Kieselgel 60 G for preparative thin-layer chromatography.

Reaction of 1a with DPP. a) A mixture of **1a**[14] (0.500 g, 2.16 mmol) and DPP (0.446 g, 2.23 mmol) in dry xylene (50 ml) was refluxed for 2 h; the solvent was then evaporated. Chloroform (10 ml) was added to the residue

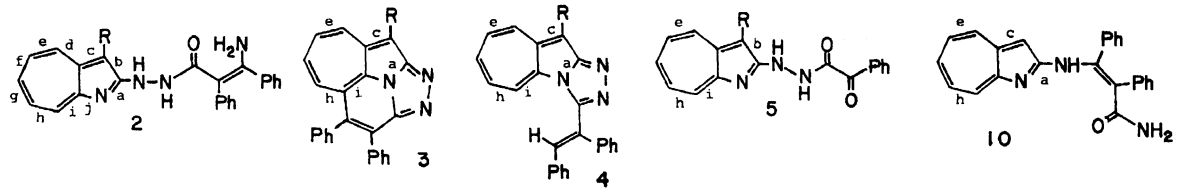


Fig. 6. Compounds **2**, **3**, **4**, **5**, and **10** with the alphabethical symbols of the bond lengths.

Table 2. Selected Bond Distances (l/Å) of **2**, **3**, **4**, **5**, and **10**

	2	3	4	5[a)]	10
a	1.34(1)	1.351(4)	1.386(8)	1.32(1)	1.353(3)
b	1.42(1)	1.448(4)	1.43(1)	1.45(1)	1.398(4)
c	1.43(1)	1.417(4)	1.40(1)	1.40(1)	1.374(4)
d	1.38(1)	1.426(4)	1.41(1)	1.44(1)	1.398(4)
e	1.40(1)	1.358(4)	1.37(1)	1.37(2)	1.367(5)
f	1.38(1)	1.425(4)	1.39(1)	1.37(2)	1.381(5)
g	1.36(1)	1.365(4)	1.35(1)	1.38(2)	1.368(5)
h	1.40(1)	1.439(4)	1.40(1)	1.38(1)	1.393(5)
i	1.38(1)	1.379(4)	1.350(9)	1.37(1)	1.377(4)
j	1.36(1)	1.351(4)	1.416(9)	1.38(1)	1.355(4)

a) The values for only one isomer of the two crystallographically indipendent molecules were used.

and collection of resulted yellow crystals by filtration gave **2** (0.229 g, 23%). The filtrate was chromatographed and gave **3** (0.130 g, 14%), **4** (0.031 g, 3.4%), **5** (0.018 g, 2%), **6**[11] (0.075 g, 8%), **7**[11] (0.024 g, 3%), and **8a**[15] (0.094 g, 20%). b) A mixture of **1a** (0.300 g, 1.30 mmol) and DPP (0.310 g, 1.50 mmol) in acetonitrile (50 ml) was refluxed for 4 h and worked up as above to give **2** (0.166 g, 28%), **3** (0.144 g, 21%), **4** (0.012 g, 2%), **5** (0.011 g, 2%), **6** (0.021 g, 4%), **7** (0.010 g, 2%), and **8a** (0.108 g, 39%).

2: Yellow needles (hexane–dichloromethane), mp 223—224 °C; ^{1}H NMR δ=1.49 (3H, t, J=7.0 Hz, CH_3), 4.47 (2H, q, J=7.0 Hz, OCH_2), 7.10—7.30 (11H, m, H-phenyl and NH), 7.50 (1H, t, J=9.8 Hz, H-6), 7.65 (2H, t, J=9.8 Hz, H-5, 7), 8.11 (1H, d, J=9.8 Hz, H-4), 8.93 (1H, d, J=9.8 Hz, H-8), and 9.25 (1H, br s, NH) (two NH protons were not observed); IR 3424, 3372, 3328, 3276 (NH), 1660 and 1640 (sh) cm^{-1} (C=O); MS m/z (rel intensity) 452 (M^+, 16), 231 (37), 222 (100), 194 (23), 185 (26), 129 (11). Found: C, 71.42; H, 5.35; N, 12.41%. Calcd for $C_{27}H_{24}N_4O_3$: C, 71.67; H, 5.34; N, 12.38%.

3: Red prisms (hexane–dichloromethane), mp 267—269 °C; ^{1}H NMR δ=1.59 (3H, t, J=7.3 Hz, CH_3), 4.67 (2H, q, J=7.3 Hz, OCH_2), 7.10—7.60 (13H, m, H-5, 6, 7, and phenyl), and 9.00 (1H, d, J=11.0 Hz, H-4); ^{13}C NMR δ=14.63 (q), 61.18 (t), 128.04 (s), 128.07 (d), 128.15 (s), 128.31 (d), 128.36 (s), 128.60 (d), 128.91 (d), 130.63 (s), 130.71 (d), 130.94 (d), 131.09 (d), 131.23 (d), 131.53 (s), 132.36 (s), 132.57 (d), 134.43 (d), 136.32 (s), 138.12 (s), 140.29 (s), 158.29 (s), and 163.86 (s); IR 1684 cm^{-1} (C=O). Found: C, 78.05; H, 4.71; N, 9.89%. Calcd for $C_{27}H_{19}N_3O_2$; C, 77.68; H, 4.59; N, 10.07%.

4: Red-brown needles (hexane–dichloromethane), mp 224—225 °C; ^{1}H NMR δ=1.53 (3H, t, J=7.0 Hz, CH_3), 4.57 (2H, q, J=7.0 Hz, OCH_2), 6.86 (1H, t, J=9.8 Hz, H-6), 7.12 (1H, d, J=9.2 Hz, H-8), 7.20—7.40 (12H, m, H-5, 7, and phenyl), 7.49 (1H, s, H-vinyl), and 9.18 (1H, d, J=11.6 Hz, H-8); ^{13}C NMR δ=14.61 (q), 60.94 (t), 123.28 (d), 127.63 (s), 128.25 (d), 128.35 (d), 128.77 (d), 129.18 (d), 129.81 (d), 129.92 (s), 130.05 (d), 130.21 (d), 133.20 (d), 134.89 (s), 135.13 (d), 135.38 (s), 135.50 (s), 135.70 (d), 136.35 (d), 147.12 (s), 148.39 (s), 159.04 (s), and 163.34 (s); IR 1700 and 1680 cm^{-1} (C=O). Found: C, 77.12; H, 5.15; N, 9.88%. Calcd for $C_{27}H_{21}N_3O_2$: C, 77.30; H, 5.04; N, 10.02%.

5: Yellow prisms (ethyl acetate–chloroform), 159—160 °C; ^{1}H NMR δ=1.51 (3H, t, J=7.3 Hz, CH_3), 4.50 (2H, q, J=7.3 Hz, OCH_2), 7.45 (2H, dd, J=7.3 and 6.7 Hz, H-*m*-phenyl), 7.61 (1H, t, J=6.7 Hz, H-*p*-phenyl), 7.68 (1H, t, J=9.8 Hz, H-6), 7.71 (1H, t, J=9.8 Hz, H-7), 7.76 (1H, dd, J=10.4 and 9.8 Hz, H-5), 8.29 (1H, d, J=9.8 Hz, H-8), 8.33 (2H, d, J=7.3 Hz, H-*o*-phenyl), and 9.03 (1H, d, J=10.4 Hz, H-4) (no NH protons were observed); ^{13}C NMR δ=13.70 (q), 61.55 (t), 119.93 (s), 127.45 (d), 128.15 (d), 128.47 (d), 129.63 (d), 129.99 (d), 130.62 (d), 131.21 (d), 132.17 (d), 133.27 (d), 134.60 (s), 136.08 (s), 147.12 (s), 157.43 (s), 163.44 (s), 168.39 (s), and 203.00 (s); IR 3332, 3288 (NH), 1690, and 1668 cm^{-1} (C=O). MS m/z (rel intensity) 364 (M^++1, 2), 363 (M^+, 8), 258 (100), 212 (89), 156 (13), 105 (34). Found: C, 65.99; H, 4.96; N, 11.80%. Calcd for $C_{20}H_{17}N_3O_4$: C, 66.11; H, 4.72; N, 11.56%.

Hydrolysis of 2. After a mixture of **2** (0.085 g) and silica gel (5.0 g) in chloroform (10 ml) had been set for 2 d at room temperature, the solvent was evaporated. Chromatography of the residue with chloroform gave **5** (0.029 g, 42%).

Reaction of 1b with DPP. After a mixture of **1b**[16] (0.700 g, 4.40 mmol) and DPP (0.910 g, 5.72 mmol) in dry acetonitrile (50 ml) was refluxed for 3 h, the solvent was evaporated. Chloroform (10 ml) was added to the residue and collection of the resulting yellow crystals by filtration gave **1b** (0.187 g, 27%). The filtrate was chromatographed and yielded **9** (0.173 g, 11%), **10** (0.143 g, 9%), **11**[11] (0.066 g, 4%), and **8b**[16] (0.100 g, 16%), successively.

9: Brown needles (hexane), mp 253—254 °C; ^{1}H NMR δ=7.00 (1H, s, H-10), 7.12—7.36 (11H, m, H-6, 7, 8, and phenyl), 7.40—7.50 (2H, m, H-*o*-phenyl), 7.85 (2H, d, J=9.8 Hz, H-9), and 9.81—9.87 (1H, m, H-5); ^{13}C NMR δ=108.58 (d), 125.00 (d), 126.88 (d), 127.74 (d), 127.89 (d), 128.35 (d), 129.95 (d), 131.49 (s), 131.58 (d), 131.62 (d), 133.49 (d), 135.03 (s), 135.16 (d), 139.51 (s), 142.33 (s), 144.22 (s), 155.45 (s), 159.89 (s), and 162.04 (s); IR 1660 cm^{-1} (C=O); MS m/z (rel intensity) 348 (M^+, 100), 347 (41), 320 (28), 319 (22), 174 (11), 159 (9), 128 (7). Found: C, 83.04; H, 4.88; N, 8.04%. Calcd for $C_{24}H_{16}N_2O$: C, 82.72; H, 4.63; N, 8.04%.

10: Yellow prisms (ethyl acetate), mp 227—228 °C; ^{1}H NMR δ=5.07 (1H, s, H-1), 5.20—5.40 (1H, br, NH), 5.50—5.70 (1H, br, NH), 7.00—7.25 (10H, m, H-phenyl), 7.27 (1H, t, J=9.8 Hz, H-6), 7.39 (1H, dd, J=9.8 and 9.2

Hz, H-7), 7.51 (1H, t, J=9.8 Hz, H-5), 7.68 (1H, d, J=9.8 Hz, H-4), 8.18 (1H, d, J=9.2 Hz, H-8), and 13.11 (1H, br s, NH); IR 3476, 3312, 3275 (NH), and 1652 cm^{-1} (C=O). Found: C, 78.68; H, 5.34; N, 11.28%. Calcd for $C_{24}H_{19}N_3O$: C, 78.88; H, 5.24; N, 11.50%.

Cyclization of 10. a) After a solution of **10** (0.030 g, 0.08 mmol) in dry xylene (10 ml) was refluxed for 4 h, the solvent was evaporated. The residue was separated by preparative thin-layer chromatography with chloroform to give **9** (0.023 g, 80%).

b) A mixture of **10** (0.020 g, 0.05 mmol) and silica gel (1.5 g) in chloroform (20 ml) was set for 12 d at room temperature, then filtered. The residue was washed with ethyl acetate. The combined filtrate was evaporated and the residue was separated by preparative thin-layer chromatography with chloroform to give **9** (0.003 g, 16%) and **10** (0.016 g, 80%).

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