

FORMATIONS OF 1,1'-BIAZAZULANONES THROUGH [8+2]-TYPE CYCLO-
ADDITION REACTIONS OF TROPONE AZINE WITH HETEROCUMULENES

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Abstract — Reaction of *N*-aryl-2,4,6-cycloheptatrien-1-imine with hydrazine afforded tropone azine, which reacted with chloroketenes to give 1,1'-biazaazulanones via [8+2]-type cycloadducts followed by elimination of hydrochloride. The similar reaction using phenyl isocyanate afforded a [8+2]-type 1:2 cycloadduct, while the reaction with phenyl isothiocyanate yielded only a 1:1 cycloadduct. ^{15}N and ^{13}C nmr spectra on C=N bond of tropone azine showed a minor contribution of a dipolar structure compared with the case of *N*-aryl-2,4,6-cycloheptatrien-1-imines.

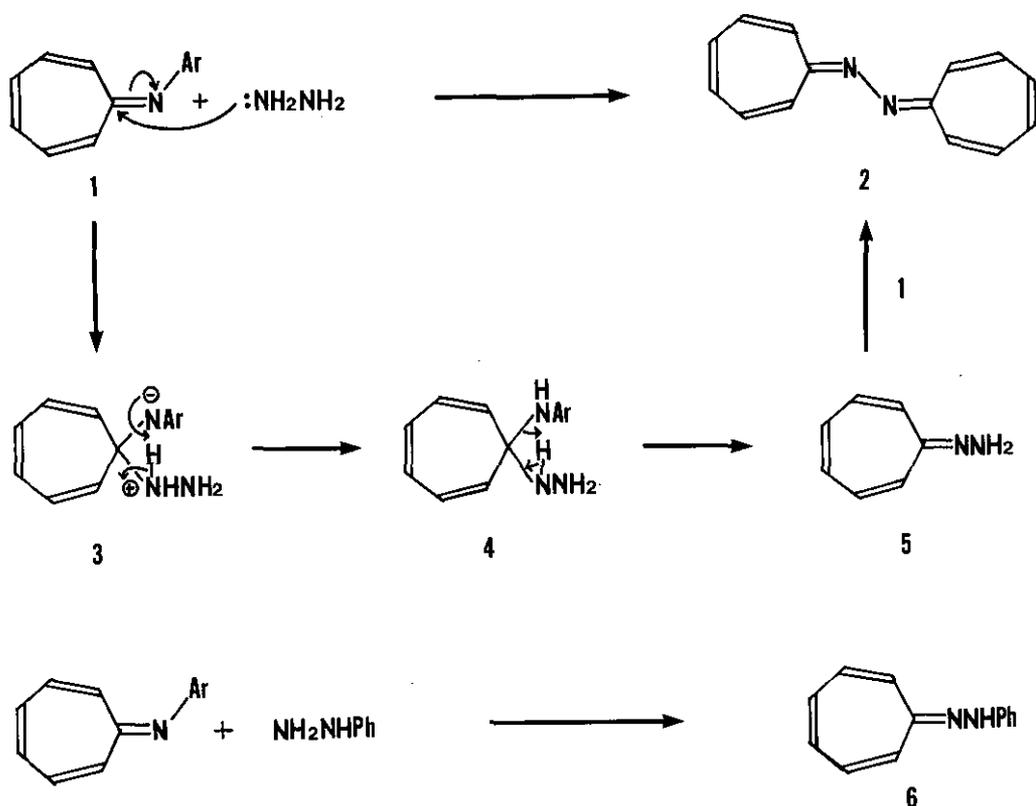
Cyclic cross conjugated systems such as pentafulvalene or heptafulvalenes have drawn attention in view of preparative and theoretical aspects of the electrocyclic reaction.¹ But the researches on the addition reactions of these compounds seem to be a few² probably because of their instabilities and low reactivities.^{1,2}

2,4,6-Cycloheptatrien-1-imines are known to react with heterocumulenes and active acetylenes to give [8+4]- or [8+2]-type cycloadducts.³ The reactivity of 2,4,6-cycloheptatrien-1-imines is partially attributed to a dipolar structure, which has a negative charge at 8-position similar to 2,4,6-cycloheptatrien-1-one. However, in the addition reactions the behaviors of 2,4,6-cycloheptatrien-1-imines are different from that of 2,4,6-cycloheptatrien-1-one, which mainly gives [4+2]-type cycloadducts.⁴

We found a high yield formation of tropone azine (8,8'-bi-2,4,6-cycloheptatrien-1-imine) in the reaction of *N*-aryl-2,4,6-cycloheptatrien-1-imine with hydrazine.⁵ Tropone azine is considered to be a homolog of both 2,4,6-cycloheptatrien-1-imine and heptafulvalene. As a result, tropone azine is expected to react as 8π - and 16π -components in the cycloaddition reactions. As a series of our researches on the addition reactions of tropone compounds,^{4a,6} we studied reactions of tropone azine with cumulenes to give 1,1'-biaza-

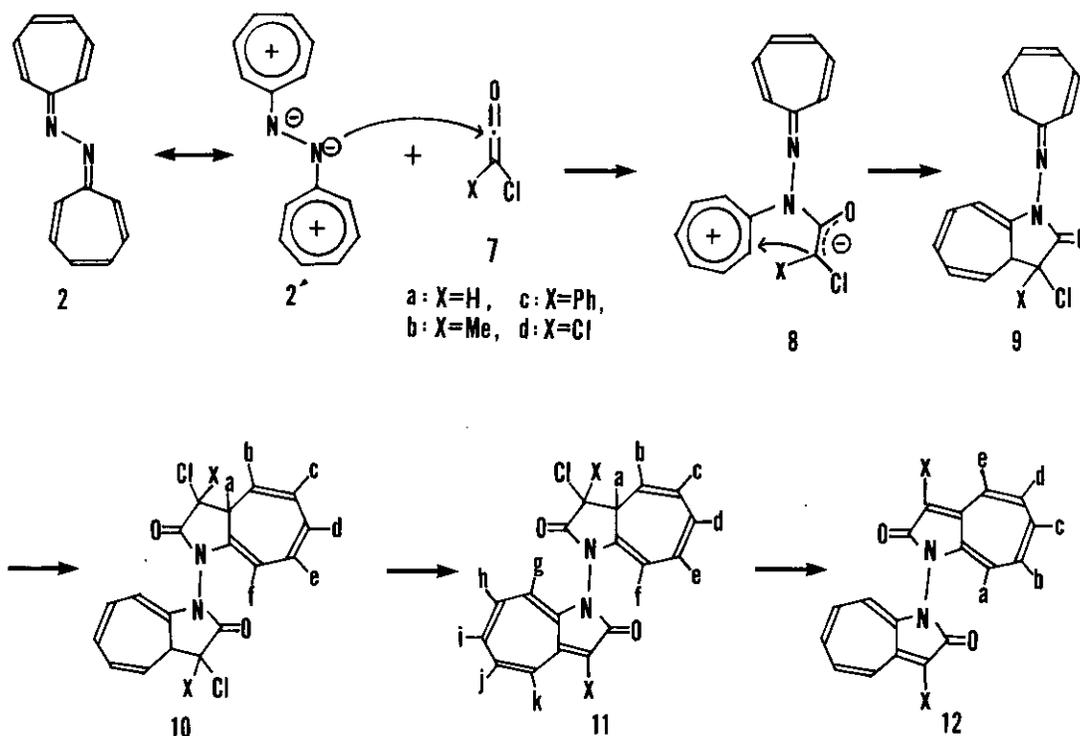
azulanones (1,1'-bi-1-azaazulen-2(1*H*)-one) and 1,1'-biimidazolidin-2-ones.⁷

The reaction of *N*-aryl-2,4,6-cycloheptatrien-1-imine (1) with hydrazine at room temperature for 4 h afforded 84% yield of tropone azine (2) whose structure was confirmed by the coincidence of its melting point and spectral properties to those of the authentic sample.⁵ The formation of 2 was considered to proceed through an intermediate (4), which then eliminated aniline derivative to form tropone hydrazone (5). The successive reaction of 5 with 1 afforded 2. The formation of phenylhydrazone (6) in the reaction of 1 with phenylhydrazine supported the existence of the intermediate (5) in the above reaction.



Reaction of 2 and chloroketene (7a) in the presence of excess amount of triethylamine afforded 1,1'-biazaazulanone (12a) in 7% yield. The similar reactions using chloromethyl- (7b), chlorophenyl- (7c) and dichloroketenes (7d) gave 1,1'-biazaazulanones (12b-d) in 59, 86, and 80% yields, respectively. On the other hand, in the short period reaction of 2 with 7b another type of products (10b and 11b) were afforded in 9 and 38% yields, respectively, as well as a 22% yield of 12b.

The structures of 12 were deduced on the basis of their spectral properties and were confirmed by their resemblances to those of the analogous compounds.^{7,8} Uv spectra showed characteristic patterns as azaazulanones. The absorptions at ca. 1680 cm^{-1} in the ir spectra were reasonably attributable to the carbonyl groups of azaazulanones. ^1H Nmr and ^{13}C nmr spectra were compatible to the structures of azaazulanones. The assignment of the protons on seven-membered ring moieties was decided using NOE experiment⁹ and double resonance technique.

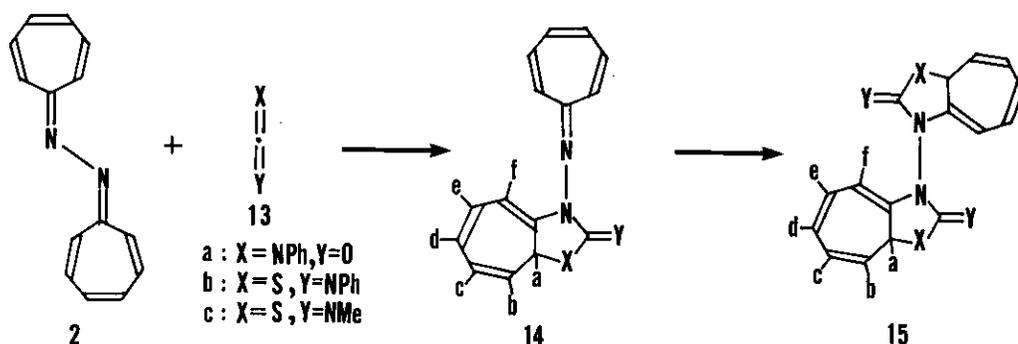


The structures of 10b and 11b were decided by their spectral properties^{10,11} and were confirmed by the formation of 1,1'-biazaazulanone (12b) through dehydrochlorination. The reaction was considered to proceed through nucleophilic attack of the nitrogen atom of 2 to the central carbon atoms of ketenes (7) to afford the intermediate (8), which then cyclized to give 1:1 adducts (9). The similar additions of ketenes with 9 yielded 1:2 adducts (10), which gave 11 and 12 through dehydrochlorination.

Reaction of 2 with phenyl isocyanate (13a) at 60°C for 16 h under a nitrogen stream gave 1:2 adduct (15a) in 64% yield. The similar reaction with phenyl isothiocyanate (13b) gave only 1:1 adduct (14b) in 78% yield. On the other hand, the reaction using methyl isothiocyanate (13c) did not afford any product under various reaction conditions.¹²

The structures of 14 and 15 were deduced on the basis of their spectral properties. ¹H Nmr and ¹³C nmr spectra indicated the existence of 1,7-disubstituted cycloheptatriene and phenyl moieties.^{3, 11} Ir spectrum of 15a showed strong absorption at 1740 cm⁻¹, which was characteristic of the carbonyl group of imidazolidin-2-one ring. The absorption due to C=N bond was observed at 1650 cm⁻¹ in the ir spectrum of 14b.

The reaction was considered to proceed through the similar reaction mechanism as the previous reactions with ketenes.



In order to investigate the reaction mechanism in detail, molecular orbital calculation by MNDO method was carried out on cumulenes (7 and 13) and 2.¹³ A large positive charge was located on the central carbon atoms of cumulenes, and the large charge separation on C=N bond of 2 supported the above mechanism. ¹⁵N and ¹³C nmr spectra of C=N bonds of 2 and 1 were measured.¹⁴ The results were summarized in Table 2. A smaller contribution of the dipolar structure in 2 compared to that of 1 explained the low reactivity of 2 in the addition reactions to chloroketene (7a) and methyl isothiocyanate (13c).

Table 1. Values of Net Atomic Charges on Central Carbon Atoms of Cumulenes

Cumulene	Charge	Cumulene	Charge
7a	+0.290	13a	+0.408
7b	+0.311	13b	+0.287
7c	+0.311	13c	+0.286
7d	+0.322		

Table 2. ^{13}C and ^{15}N Nmr Chemical Shifts and Net Atomic Charges on C=N Bonds of Tropone Azine (2) and *N*-Aryl-2,4,6-cycloheptatrien-1-imines (1)

cycloheptatrien- 1-imines	chemical shift / ppm		net atomic charge	
	^{13}C	^{15}N	C	N
Ar=C ₆ H ₄ (<i>p</i> -OMe)	163.34	310.0	+0.145	-0.261
Ar=C ₆ H ₄ (<i>p</i> -Me)	162.82	312.3	+0.143	-0.262
Ar=C ₆ H ₄ (<i>p</i> -Cl)	163.65	306.6	+0.153	-0.269
Ar=C ₆ H ₄ (<i>p</i> -Br)	163.47	-	+0.152	-0.269
tropone azine	160.06	338.1	+0.108	-0.218

EXPERIMENTAL

Melting points were recorded on a Yanagimoto Micro Melting Point Apparatus and were uncorrected. Nmr spectra were measured with a Varian XL-200 spectrometer. Ir and uv spectra were measured with JASCO FT/IR-5300 and Hitachi 220A spectrophotometers, respectively. Mass spectra were measured with Hitachi M-2000S spectrometer. Wakogel C-200 and Wakogel B-5F were used for column and thin-layer chromatography, respectively. ^{15}N Nmr Spectral Measurements of 2,4,6-Cycloheptatrien-1-imines. Enriched nitromethane (δ 380.23 ppm) was used as an external standard. The sample solutions contained 2,4,6-cycloheptatrien-1-imines (5.6 mmol) and chromium (III) acetate (0.34 mmol) as a relaxation reagent in deuterium chloroform (2.2 ml). Puls width, puls interval, and data acquisition time were 20 μs , 5.0 s, and 0.533 s, respectively. The accumulations from 13000 to 16000 times were made to obtain the spectra.

Synthesis of Tropone Azine (2). A mixture of 1 (1.0 mmol) and hydrazine monohydrate (200 mg, 4.0 mmol) in ethanol (3.0 ml) was stirred at room temperature for 4 h. After evaporation of the solvent the residue was poured into water, extracted with dichloromethane, and dried over anhydrous sodium sulfate. After removing the solvent, the residue was separated with column chromatography on silica gel to give 2 (90 mg, 84%, hexane-ethyl acetate 4:6) and aniline derivative (100 %, hexane-ethyl acetate 1:1).

Reaction of 1 with Phenylhydrazine. A mixture of 1 (1.7 mmol) and phenylhydrazine (200 mg, 1.8 mmol) in dichloromethane (5.0 ml) was heated at 48°C for 24 h. The reaction mixture was separated with column chromatography on silica gel to give 6 (45 mg, 23%, hexane-ethyl acetate 3:1), aniline derivative (41%, hexane-ethyl acetate 4:2), recovered 1 (50%, hexane-ethyl acetate, 8:1) and recovered phenylhydrazine (150 mg, 76%, hexane-ethyl acetate 4:6).

Reaction of 2 with Chloroacetone (7a). To a solution of 2 (210 mg, 1.0 mmol) and triethyl amine (1.0 g, 10 mmol) in dichloromethane (5.0 ml) was added chloroacetyl chloride (950 mg, 8.0 mmol) at room temperature under a nitrogen stream. After the addition completed,

the mixture was refluxed for 20 h, poured into water, extracted with dichloromethane, and dried over anhydrous sodium sulfate. After removing the solvent, the residue was separated with column chromatography on silica gel to give an oily mixture containing 12a (64 mg, ethyl acetate-dichloromethane 9:1), which was purified with thin layer chromatography on silica gel using ethyl acetate as a developing solvent to give pure 12a (21 mg, 7%, R_f =0.56).

12a: oil. Hrms: m/z 288.0918. Calcd for $C_{18}H_{12}N_2O_2$: m/z 288.0898. Ms m/z (rel. intensity) : 288 (M^+ , 72), 256 (24), 244 (29), 167 (23), 149 (100). Ir (oil): 1680, 1600 1540, 1490 cm^{-1} . Uv (MeOH): 263 (log ϵ , 4.61), 386 (4.14), 404 nm (4.17). 1H Nmr ($CDCl_3$) δ 6.24 (s, H_f), 6.50 (dd, H_a), 6.88-7.05 (m, H_b and H_c), 7.13 (dd, H_d), 7.56 (d, H_e). Coupling constants in Hz: J_{ab} =8.5, J_{ac} =1.2, J_{bd} =1.6, J_{cd} =9.1, J_{de} =11.2. ^{13}C Nmr ($CDCl_3$) δ 102.6, 112.0, 130.2, 130.6, 131.5, 133.0, 142.9, 145.9, 165.3.

Reaction of 2 with chloromethylketene (7b). To a solution of 2 (100 mg, 0.5 mmol) and triethylamine (510 mg, 5.0 mmol) in chloroform (2.5 ml) slowly added a solution of 2-chloropropionyl chloride (250 mg, 2.0 mmol) in chloroform (2.5 ml) at room temperature under a nitrogen stream. After the addition completed, the mixture was refluxed for 96 h. After the usual workup, the mixture was separated with column chromatography on silica gel to give orange crystals 12b (110 mg, 59%, hexane-ethyl acetate 2:8 as a eluent).

12b: mp 259-261°C (from ethyl acetate). Hrms: m/z 316.1199. Calcd for $C_{20}H_{16}N_2O_2$: m/z 316.1210. Ms m/z (rel. intensity) : 316 (M^+ , 81), 278 (8), 201 (8), 159 ($M^+/2+1$, 91), 158 ($M^+/2$, 100). Ir (KBr): 1680, 1600, 1550, 1500 cm^{-1} . Uv (MeOH): 270 (log ϵ , 4.61), 386 (4.07), 407 nm (4.06). 1H Nmr ($CDCl_3$) δ 2.20 (s, 6H, Me), 6.30 (dd, H_a), 6.70-6.90 (m, H_b and H_c), 7.00 (dd, H_d), 7.54 (d, H_e). Coupling constants in Hz: J_{ab} =8.0, J_{ac} =1.9, J_{bd} =2.0, J_{cd} =9.0, J_{de} =11.6. ^{13}C Nmr ($CDCl_3$) δ 110.0, 111.1, 127.6, 129.5, 130.7, 131.2, 140.3, 142.3, 165.6.

Reaction of 2 with chlorophenylketene (7c). To a solution of 2 (210 mg, 1.0 mmol) and triethylamine (1.0 g, 10 mmol) in dichloromethane (5.0 ml) was added a solution of chlorophenylacetyl chloride (760 mg, 4.0 mmol) in dichloromethane (3.0 ml) at room temperature under a nitrogen stream. After the addition completed, the mixture was stirred at room temperature for 24 h. After the usual workup, the mixture was separated with column chromatography on silica gel to give red crystals 12c (380 mg, 86%, dichloromethane as a eluent).

12c: mp >300°C (from ethyl acetate). Hrms: m/z 363.1143. Calcd for $C_{24}H_{15}N_2O_2$: m/z 363.1133. Ms m/z (rel. intensity) : 440 (M^+ , 100), 352 (19), 204 (56), 174 (19), 149 (54). Ir (KBr): 1690, 1590, 1540, 1510 cm^{-1} . Uv (MeOH): 244 (log ϵ , 4.63), 281 (4.62), 413 nm (4.36). 1H Nmr ($CDCl_3$) δ 6.58 (dd, H_a), 6.84-7.02 (m, H_b and H_c), 7.08 (ddd, H_d), 7.36-7.82 (m, 10H, Ph), 7.94 (d, H_e). Coupling constants in Hz: J_{ab} =8.8, J_{ac} =1.9, J_{bd} =3.1, J_{cd} =8.6, J_{de} =

11.2. ^{13}C Nmr (CDCl_3) δ 111.7, 127.8, 128.4, 128.6, 129.0, 130.9, 131.3, 131.5, 132.8, 139.8, 142.2.

Reaction of 2 with dichloroketene (7d). To a solution of 2 (210 mg, 1.0 mmol) and triethylamine (1.0 g, 10 mmol) in dichloromethane (5.0 ml) was slowly added a solution of dichloroacetyl chloride (590 mg, 4.0 mmol) in dichloromethane (5.0 ml) at room temperature under a nitrogen stream. After the addition completed, the mixture was stirred at room temperature for 24 h. After the usual workup, the mixture was separated with column chromatography on silica gel to give yellow crystals 12d (287 mg, 80%, ethyl acetate as a eluent).

12d: mp $>300^\circ\text{C}$ (from dichloromethane). Hrms: m/z 356.0084. Calcd for $\text{C}_{18}\text{H}_{10}\text{N}_2\text{O}_2\text{Cl}_2$: m/z 356.0118. Ms m/z (rel. intensity) : 356 (M^+ , 27), 256 (32), 236 (100), 194 (40), 180 ($\text{M}^+/2$, 26). Ir (KBr): 1710, 1600, 1540, 1490 cm^{-1} . Uv (MeOH): 231 (log ϵ , 4.43), 274 (4.74), 391 (4.31), 412 nm (4.32). ^1H Nmr (CDCl_3) δ 6.54 (dd, H_a), 6.95–7.15 (m, H_b and H_c), 7.25 (ddm, H_d), 7.70 (d, H_e). Coupling constants in Hz: J_{ab} = 7.5, J_{ac} = 2.6, J_{cd} = 9.1, J_{de} = 11.2. ^{13}C Nmr (CDCl_3) δ 112.4, 117.9, 127.3, 131.3, 131.8, 133.7, 139.5, 141.0.

Short Period Reaction of 2 with 7b. To a solution of 2 (210 mg, 1.0 mmol) and triethylamine (1.0 g, 10 mmol) in dichloromethane (5 ml) was added a solution of 2-chloropropionyl chloride (510 mg, 4.0 mmol) in dichloromethane (3 ml) at room temperature under a nitrogen stream. After the addition completed, the mixture was heated at 40°C for 21 h. After the usual workup, the mixture was separated with column chromatography on silica gel to give crystals of 11b (130 mg, 38%, hexane-ethyl acetate 6:4) and 12b (72 mg, 22%, hexane-ethyl acetate 3:7), and a mixture containing 10b (71 mg, hexane-ethyl acetate 7:3), which was further purified with thin layer chromatography on silica gel using hexane-ethyl acetate 2:1 as a developing solvent to give an oil 10b (35 mg, 9%, R_f = 0.74).

10b: oil. Hrms: m/z 388.0720. Calcd for $\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_2\text{Cl}_2$: m/z 388.0696. Ms m/z (rel. intensity): 388 (M^+ , 54), 317 (M^+-Cl_2 , 50), 263 (36), 194 ($\text{M}^+/2$, 85), 159 ($\text{M}^+/2-\text{Cl}$, 90), 130 (100). Ir (oil): 1760, 1600, 1550, 1460 cm^{-1} . Uv (MeOH): 262 nm (log ϵ , 3.97). ^1H Nmr (CDCl_3) δ 2.02 (s, 6H, Me), 3.37 (dm, H_a), 5.31 (dd, H_b), 5.78 (d, H_f), 6.26 (ddm, H_c), 6.42 (dd, H_d), 6.58 (dd, H_e). Coupling constants in Hz: J_{ab} = 4.8, J_{bc} = 9.8, J_{cd} = 6.2, J_{de} = 10.6, J_{ef} = 6.2. ^{13}C Nmr (CDCl_3) δ 22.4, 49.2, 99.3, 117.1, 127.1, 127.9, 128.7.

11b: mp $218-220^\circ\text{C}$ (from benzene). Hrms: m/z 352.0977. Calcd for $\text{C}_{20}\text{H}_{17}\text{N}_2\text{O}_2\text{Cl}$: m/z 352.0977. Ms m/z (rel. intensity) : 352 (M^+ , 81), 317 (M^+-Cl , 256 (81), 192 ($\text{M}^+-\text{azaazulanone}$ moiety, 100), 175 (97). Ir (KBr): 1760, 1690, 1600, 1550 cm^{-1} . Uv (MeOH): 265 (log ϵ , 4.59), 385 (3.91), 407 nm (3.91). ^1H Nmr (CDCl_3) δ 3.12 (s, 6H, Me), 3.44 (dm, H_a), 5.28 (d, H_f), 5.40 (dd, H_b), 6.30 (ddm, H_c), 6.36–6.50 (m, H_d and H_e), 6.74 (d, H_g), 6.78–8.10 (m, H_h , H_i , and H_j), 8.40 (d, H_k). Coupling constants in Hz: J_{ab} = 4.5, J_{bc} = 9.7, J_{cd} = 5.5, J_{ef} = 4.2, J_{gh} = 8.6, J_{jk} = 11.1. ^{13}C Nmr (CDCl_3) δ 7.9, 22.6, 49.4, 64.1, 99.8, 109.5, 111.5, 117.4, 127.0, 127.6,

127.7, 128.4, 128.7, 129.7, 130.8, 131.3, 139.4, 140.1, 163.2, 169.5.

Reaction of 2 with 13a. A mixture of 2 (50 mg, 0.24 mmol) and 13a (290 mg, 2.4 mmol) in dry benzene (0.5 ml) was heated at 60°C for 16 h. The reaction mixture was separated with thin layer chromatography on silica gel using hexane-ethyl acetate 3:1 as a developing solvent to give colorless crystals 15a (69 mg, 64%, $R_f=0.57$).

15a: mp 188-189°C (from ethyl acetate). Hrms: 446.1741. Calcd for $C_{28}H_{22}N_4O_2$: m/z 446.1741. Ms m/z (rel. intensity): 446 (M^+ , 9), 265 ($M^+-C_7H_6NPh$, 18), 224 ($M^+/2+1$, 100), 223 ($M^+/2$, 100). Uv (MeOH): 247 (log ϵ , 4.55), 312 nm (3.48). Ir (KBr): 1740, 1660, 1600, 1540, 1500 cm^{-1} . 1H Nmr ($CDCl_3$) δ 4.62 (d, H_a), 5.12 (dd, H_b), 5.82 (d, H_f), 6.28 (dd, H_c), 6.45 (dd, H_d), 6.64 (dd, H_e), 7.10-7.90 (m, 10H, aromatic protons). Coupling constant in Hz; $J_{ab}=2.7$, $J_{bc}=11.0$, $J_{cd}=3.8$, $J_{de}=11.0$, $J_{ef}=6.0$.

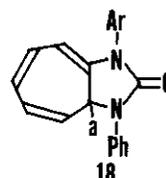
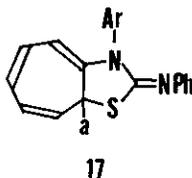
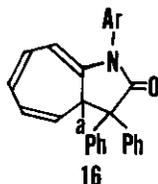
Reaction of 2 with Phenyl Isothiocyanate (13b). A mixture of 2 (210 mg, 1.0 mmol) and 13b (400 mg, 3.0 mmol) in dichloromethane (4.0 ml) was stirred at room temperature for 100 h under a nitrogen stream. The reaction mixture was separated with thin layer chromatography on silica gel using hexane-ethyl acetate 3:1 as a developing solvent to give 14b (94 mg, 78%, $R_f=0.28$), recovered 2 (130 mg, 64%, $R_f=0.41$), and recovered 13b (200 mg, 51%, $R_f=0.81$).

14b: oil. Hrms: m/z: 343.1138. Calcd for $C_{21}H_{17}N_3S$: m/z 343.1142. Ms m/z (rel. intensity): 343 (M^+ , 69), 239 ($M^+-C_7H_6N$, 44), 208 ($M^+-SCNPh$, 25), 111 (100). Uv (MeOH): 232 (log ϵ , 4.53), 316 nm (4.21). Ir (oil): 1650, 1610, 1590 cm^{-1} . 1H Nmr ($CDCl_3$) δ 4.00 (bs, H_a), 5.20 (dm, H_b), 5.58 (d, H_f), 6.20 (dd, H_c), 6.27 (dd, H_d), 6.42-7.40 (m, 12H, H_e and aromatic protons). Coupling constants in Hz; $J_{bc}=9.8$, $J_{cd}=6.4$, $J_{de}=12.8$, $J_{ef}=6.0$. ^{13}C Nmr ($CDCl_3$) δ 43.2, 99.3, 119.3, 121.6, 123.7, 124.1, 126.9, 128.9, 129.6, 129.7, 130.2, 132.4, 134.2, 134.3, 134.6, 136.7, 150.5, 151.6, 171.5.

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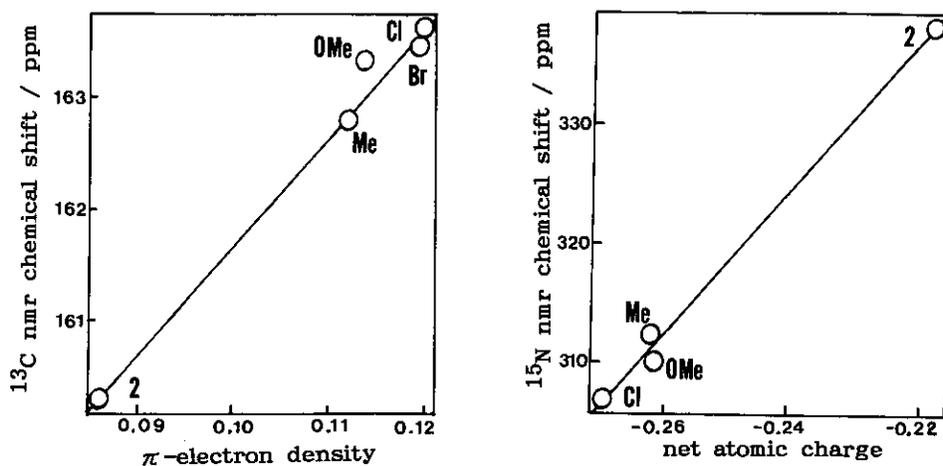
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9. Irradiation on the phenyl group of 12c caused 9–11% enhancement of the signals of the proton H_e, but the signals of H_a showed no change, suggesting H_e to be located closely to the phenyl group.
10. The location of the methine protons (H_a) at the 5-positions of five membered heterocyclic moieties of 10b, 11b, 14b, and 15a was supported by the coincidence of the chemical shifts of H_a (10b: 3.37, 11b: 3.44, 14b: 4.00, and 15a: 4.62 ppm) to those of the analogous compounds (16: 3.49–3.60, 17: 3.96–4.00, 18: 4.45–4.48 ppm).



11. ¹H Nmr and ¹³C nmr spectra of 10b and 11b indicated the existence of 1,7-disubstituted cycloheptatriene moieties. The assignment of the protons on the cycloheptatriene moieties was decided by double resonance technique in ¹H nmr spectra. The mass spectrum of 10b demonstrated that the product was a 1:2 adduct between 2 and 7b. Its ir spectrum showed the absorption due to the carbonyl group of pyrrolidine-2-one ring at 1760 cm⁻¹. Mass spectrum of 11b taughted that this was derived from the 1:2 adduct (10b), via an elimination of hydrogen chloride. Its ir spectrum showed the existence of two kinds of carbonyl groups of azaazulanone (1690 cm⁻¹) and pyrroli-

din-2-one rings (1769 cm^{-1}).

12. Reaction of 2 with *p*-toluenesulfonyl isocyanate afforded the product, which was considered to be a 1:2 adduct. But no molecular ion peak was observed in the mass spectra. Physical data of the product were as follows: colorless crystals. mp $160\text{--}163^\circ\text{C}$. Uv (MeOH): 227 ($\log \epsilon, 4.49$), 296 nm (3.86). Ir (KBr): 1770, 1670, 1600, 1550, 1370, 1320, 1170 cm^{-1} . ^1H Nmr (CDCl_3) δ 2.50 (s, Me, 6H), 4.62 (dm, H_a), 5.30 (dm, H_f), 5.51 (dd, H_b), 6.18 (ddm, H_c), 6.20–6.40 (m, H_d and H_e), 7.40–8.10 (m, aromatic protons, 8H). Coupling constants in Hz; $J_{ab} = 3.1$, $J_{bc} = 9.8$, $J_{cd} = 3.1$, $J_{ef} = 3.8$. ^{13}C Nmr (CDCl_3) δ 21.8, 56.8, 97.3, 119.0, 125.4, 127.4, 127.8, 128.2, 130.1.
13. The authors are indebted to the Computer Center of the Institute for Molecular Science for molecular orbital calculations using MOPAC program. K. Ito, K. Saito, and K. Takahashi, *Heterocycles*, 1991, 32, 1117.
14. A fairly good relation was observed between the chemical shifts of ^{15}N and ^{13}C in the nmr spectra and the electron densities on the nitrogen and the carbon atoms of the C=N bonds of 2,4,6-cycloheptatrien-1-imines as shown below. The charge effects on the chemical shifts of 2,4,6-cycloheptatrien-1-imines were calculated to be about -620 ppm per electron for ^{15}N chemical shift and -100 ppm for ^{13}C chemical shift. These values were fairly consisted with the literature values. S. Ide, K. Iwasawa, A. Yoshino, T. Yoshida, and K. Takahashi, *Magn. Reson. Chem.*, 1987, 25, 675; F. W. Wehrli and T. Wirthlin, *Interpretation of Carbon-13 NMR Spectra*, Hirokawa Publishing Co., 1980, 29.



Correlation of the electron densities with ^{13}C and ^{15}N nmr chemical shifts on C=N bonds of 1 and 2.