REACTION OF 2-CHLORO-1-AZAAZULENE WITH DIPHENYLCYCLOPROPENONE; DIMERIZATION OF THE CYCLOADDUCT ATTENDED BY *cine*-SUBSTITUTION AND REARRANGEMENT

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Abstract — 2-Chloro-1-azaazulene reacted with diphenylcyclopropenone to give 3,4-diphenyl-2a,5-dihydro-2*H*-2a-azabenz[*cd*]azulene-2,5-dione and 6-[(3,4-diphenyl-5-oxo-2a,5-dihydro-2*H*-2a-azabenz[*cd*]azulen-2-ylidene)-methyl]-3,4-diphenyl-2a,5-dihydro-2a-azaacenaphtylen-5-one; the latter would be produced *via* cycloaddition and a successive *cine*-substitution followed by rearrangement.

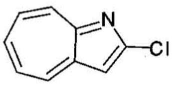
INTRODUCTION

The chemistry of azaazulenes is of interest for their physical and chemical properties as well as physiological properties,[1] in comparison with those of azulenes. Cycloadditions of diphenylcyclopropenone (DPP) with heterocycles are interesting for the synthetic viewpoint that the reaction gave a some variety of fused heterocycles;[2–8] we reported the cycloadditions of 2-amino- and 2-hydrazino-1-azaazulenes with DPP,[9—11] where variable cycloadducts were obtained being dependent on the nature of substituents on the 1-azaazulenes. To expand the reaction, we examined the reaction of 2-chloro-1-azaazulene (**1**) with DPP, and found that the reaction proceeded a different pathway from that of 2-amino-1-azaazuzlenes with DPP and gave an interesting dimer of 1 : 1-adduct.

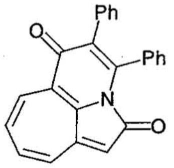
RESULTS AND DISCUSSION

The treatment of 2-chloro-1-azaazulene (**1**) with 1.5 equivalent molar of DPP in acetonitrile under reflux for 3 h gave two kinds of cycloadducts (**2**) (4%) and (**3**) (19%) along with recovered **1** (58%). The reaction at higher temperature did not improve the results; when the reaction was performed in refluxing *tert*-butylbenzene for 1 h, the reaction showed a complex feature and the compound (**3**) was isolated in 19% yield together with recovered **1** (55%). The compound (**2**) was analyzed as $C_{24}H_{15}NO_2$ from its MS spectrum and elemental analysis; the compound (**2**) would be a hydrolyzed product of the 1 : 1-adduct of **1** with DPP. In the IR spectrum of **2**, two carbonyl peaks appeared at 1744 and 1629 cm^{-1}. In its ^1H

NMR spectrum, a 1H singlet appeared at δ 5.82, and four seven-membered protons were seen at δ 6.84, (1H, dd, J 11.0, 8.3), 6.93 (1H, dd, J 11.6, 8.3), 7.20 (1H, d, J 11.0), and 7.87 (1H, d, J 11.6). From the results, the compound (**2**) was deduced as 3,4-diphenyl-2a,5-dihydro-2*H*-2a-azabenz[*cd*]azulene-2,5-dione. The compound (**3**) was analyzed as $C_{48}H_{30}N_2O_2$ from its MS spectrum and elemental analysis. Its ^{1}H NMR spectrum showed rather complex feature and the IR spectrum showed the signals at 1632 and 1606 cm^{-1} assignable to carbonyl group; the structure could not be deduced from the spectral analysis. Eventually, the structure of **3** was determined as 6-[(3,4-diphenyl-5-oxo-2a,5-dihydro-2*H*-2a-azabenz[*cd*]azulen-2-ylidene)methyl]-3,4-diphenyl-2a,5-dihydro-2a-azaacenaphtylen-5-one by X-Ray structure analysis. The ORTEP drawing[12] of **3** is shown in Figure 1.



1



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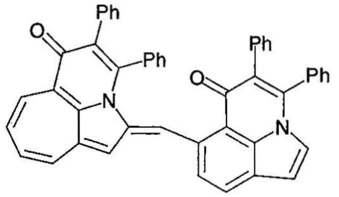

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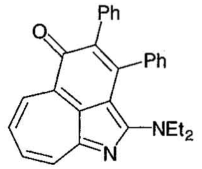

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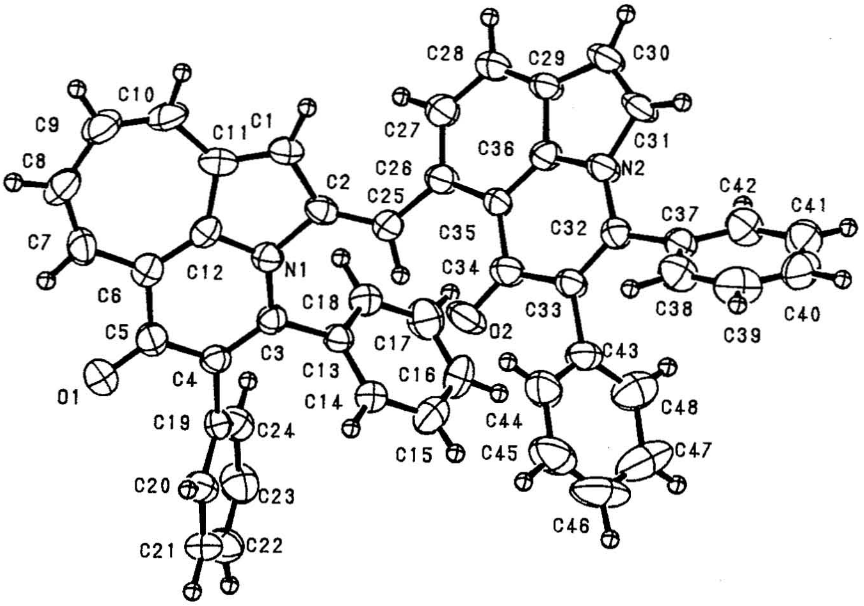
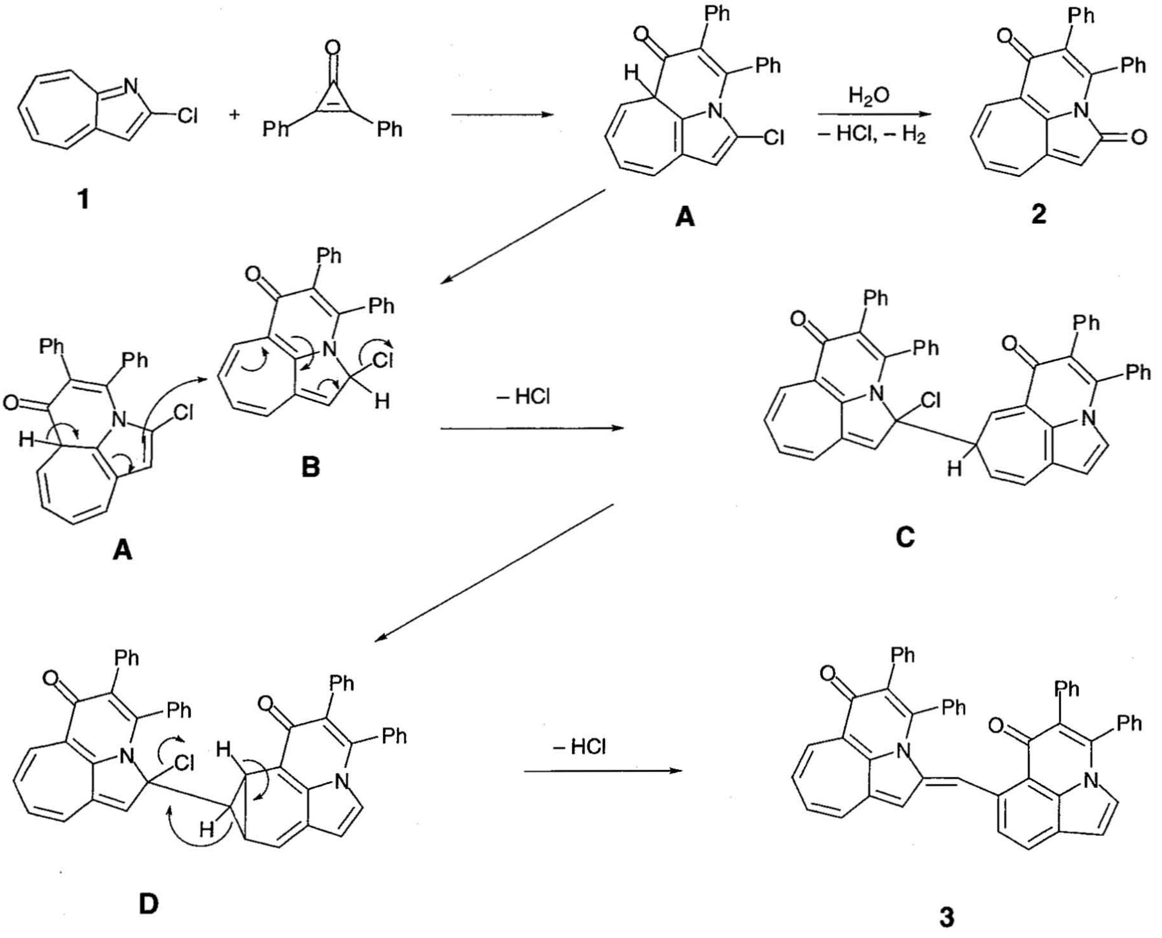


Figure 1. An ORTEP drawing of **3** with thermal ellipsoids (50% probability).

The formation of **2** and **3** showed that the reaction occurred at N-1 position of **1** at first. The result was a contrast to the reaction of 2-dialkylamino-1-azaazulene with DPP,[11] where the reaction occurred at C-3 position at first and gave **4**. It is considered that the reactivity of C-3 position of **1** would be lower than that of 2-diethyllamino-1-azaazulene, in which C-3 carbon was contained in an enamine moiety. The results was consisted with the molecular orbital calculation by Gaussian 98 using RHF/6-31G* (Figure 2). Furthermore, 2-diethyllamino-1-azaazulene have a rather large lobe at C-3 position in its HOMO.

Plausible reaction mechanism is shown in the Scheme 1. Cycloadition of 2-chloro-1-azaazulene with DPP produced **A** at first. A hydration of **A** and a successive elimination of hydrogen chloride followed by a dehydrogenation furnished **2**. The attempt of the isolation of intermediate (**A**) was failed; the pale yellow compound turned to yellow in the silica gel chloumn. Therefore, it is thought that the elimination-addition would occure in the silica gel chloumn. A hydrogen shift of **A** led to **B**. When a *cine*-substitution of **B** with **A** occurred, the dimer (**C**) could be generated. Electrocyclic reaction of the cycloheptatriene moiety of **C** gave the norcaradiene derivative (**D**). Ring contraction of **D** attended by dehydrochrorination furnished **3**.



Scheme 1

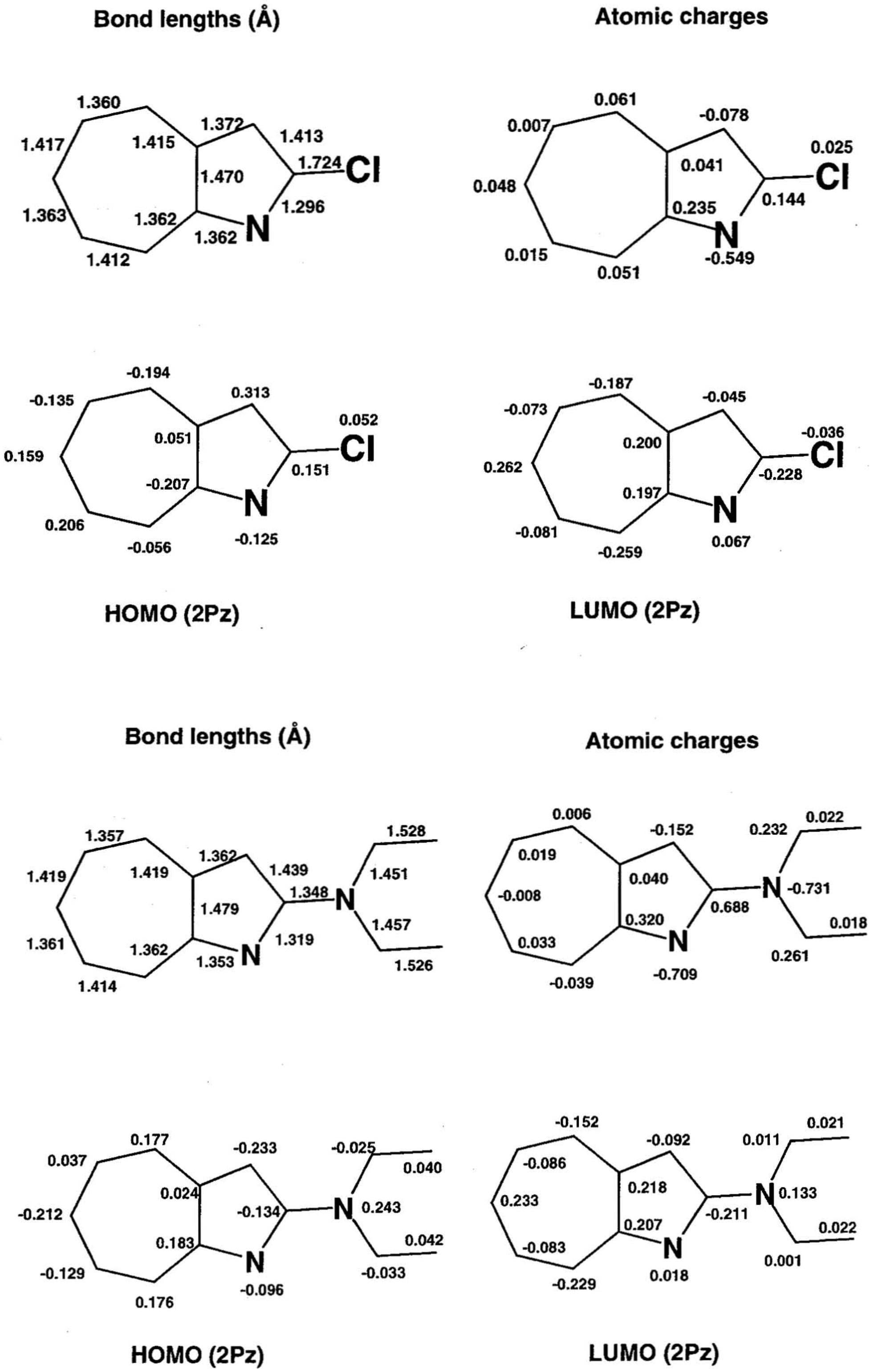


Figure 2. The molecular orbital calculation of **3** and 2-diethylamino-1-azaazulene

EXPERIMENTAL

Mps are measured using a Yanagimoto micro-melting apparatus and uncorrected. ^{1}H NMR spectra were recorded on a Bruker AVANCE 400S (400 MHz) using deuteriochloroform as a solvent with tetramethylsilane as an internal standard unless otherwise stated; *J* values are recorded in Hz. IR spectra were recorded for KBr pellets on a Nicolet FT-IR Impact 410. MS spectra were taken with on an LC-MS Waters Integrity System. Elemental analyses were taken with a Perkin Elmer 2400II. Kieselgel 60 and was used for column chromatography and Kieselgel 60G was used for thin-layer chromatography.

Reaction of 2-chloro-1-azaazulene (1) with diphenylcyclopropenone

A solution of 2-chloro-1-azaazulene (**1**) (0.330 g, 2.02 mmol) and DPP (0.630 g, 3.05 mmol) in dry acetonitrile (30 mL) was heated under reflux for 3 h, then the solvent was evaporated. The residue was chromatographed on silica gel column with chloroform to give recovered **1** (0.190 g, 58%), 3,4-diphenyl-2a,5-dihydro-2*H*-2a-azabenz[*cd*]azulene-2,5-dione (**2**) (0.012 g, 4%), and 6-[(3,4-diphenyl-5-oxo-2a,5-dihydro-2*H*-2a-azabenz[*cd*]azulen-2-ylidene)methyl]-3,4-diphenyl-2a,5-dihydro-2a-azaacenaphtylen-5-one (**3**) (0.128 g, 19%), successively.

Similar treattment of **1** (0.330 g, 2.02 mmol) with DPP (0.420 g, 2.04 mmol) in refluxing *tert*-butylbenzene (30 mL) for 1 h gave **1** (0.182 g, 55%) and **3** (0.130 g, 19%), and the treattment of **1** (0.330 g, 2.02 mmol) with DPP (0.630 g, 3.05 mmol) in refluxing xylene (30 mL) for 3 h gave **1** (0.182 g, 42%) and **3** (0.100 g, 15%).

2: Yellow needles (from hexane-dichloromethane), mp 185—187 ℃; δ_H 5.82 (1H, s), 6.84, (1H, dd, *J* 11.0, 8.3), 6.93 (1H, dd, *J* 11.6, 8.3), 6.97—7.07 (2H, m), 7.10—7.17 (6H, m), 7.20 (1H, d, *J* 11.0), 7.21—7.25 (2H, m), and 7.87 (1H, d, *J* 11.6); ν_{max} / cm^{-1} 1744 and 1629 (C=O); *m/z* 350 (M^+ + 1, 100), 349 (M^+, 98), 348 (97), 332 (31), 320 (92), 291 (90), 265 (24), 161 (51), and 146 (45). *Anal.* Calcd for $C_{24}H_{15}NO_2$: C, 82.50; H, 4.33; N, 4.01. Found: C, 82.61; H, 4.55; N, 4.05.

3: Violet prisms (from hexane-dichloromethane), mp 216—218 ℃; δ_H 5.80—5.90 (2H, m), 6.12—6.18 (1H, m), 6.27 (1H, s), 6.56 (1H, s), 6.74 (1H, d, *J* 3.5), 6.92—7.34 (22H, m), 7.41 (1H, d, *J* 8.0), and 7.82 (1H, d, *J* 7.9); ν_{max} / cm^{-1} 1632 and 1606 (C=O); *m/z* (rel intensity) 667 (M^+ + 1, 7), 666 (M^+, 2), 589 (11), 487 (17), 346 (36), 333 (22), 178 (100), and 149 (36). *Anal.* Calcd for $C_{48}H_{30}N_2O_2 \cdot 1/4\ CH_2Cl_2$: C, 84.23; H, 4.47; N, 4.07. Found: C, 84.56; H, 4.65; N, 4.05.

X-Ray structure determination

Crystal data of 3: Black prism, $C_{48}H_{30}N_2O_2 \cdot CH_2Cl_2$, M=751.71, monoclinic, space group P2$_1$/a, a=11.743(4), b=19.016(5), c=17.464(4) Å, β=103.02(3)°, V=3799(2) Å^3, Z=4, D_{calcd}=1.314 g/cm^3, crystal dimensions 0.30 x 0.42 x 0.88 mm. Data were measured on a Rigaku AFC 5S radiation diffractometer with graphite-monochromated Mo-Kα radiation. A total 9426 reflections (8997 unique) were collected using ω–2θ scan technique with in a 2θ range of 55.0° . The structure was solved by direct methods and refined by a full-matrix least-squares methods using 550 variables refined with 2704 reflections [$I > 3\sigma(I)$]. The weighting scheme $\omega = 4Fo^2/\sigma^2(Fo^2)$ gave satisfactory agreement analyses. The final refinement converged to R = 0.063 and Rw = 0.072.

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