Retraction

After the online publication of this Communication (March 30, 2007), it has been brought to the authors' attention that the ^{13}C NMR spectra of the assumed azepinoazepine synthesized are essentially identical to those of the viologen structure.[1] ^{1}H NMR spectra also support this finding, although they were measured in different solvents and at different field strengths.[2] The authors therefore retract this Communication and apologize for any inconvenience.

[1] W. W. Porter III, T. P. Vaid, *J. Org. Chem.* **2005**, *70*, 5028.
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Ring Expansion of a 4,4′-Bipyridyl Derivative into π-Conjugated Azepinoazepines

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Nitrogen Heterocycles

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Ring Expansion of a 4,4′-Bipyridyl Derivative into π-Conjugated Azepinoazepines**

Isao Yamaguchi, Saori Tsutsui, and Moriyuki Sato*

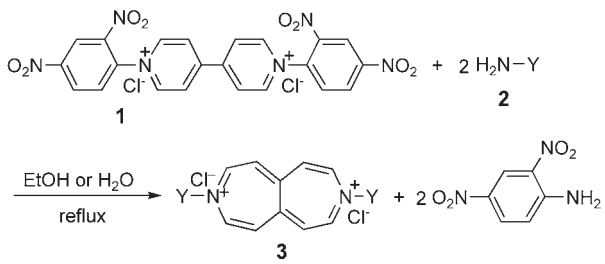
Azepine derivatives fused with aromatic rings represent an important class of compounds as they display potential or proven pharmacologic activity.[1] A large number of reports on synthetic approaches towards these compounds have been published.[2] Metal-complex-catalyzed intramolecular cyclization reactions are useful for the synthesis of azepine derivatives fused with aromatic rings such as benzene, imidazole, and pyridine rings.[3] However, these cyclization reactions sometimes cause undesirable side reactions. Ring-expansion reactions are also utilized for the preparation of azepine derivatives, and they proceed without side reactions.[4] It has been reported that the photolysis of diazidonaphthalenes causes ring expansion to yield azepinoazepines.[4d] These azepinoazepines are not fully unsaturated, and attempts to convert them into fully unsaturated diazaheptalene have been unsuccessful. Fully unsaturated azepinoazepine should show interesting optical and electrochemical properties as a result of its π-conjugated electron system. To the best of our knowledge, there has been only one report on the azepinoazepines[4d] and fully unsaturated azepinoazepines have not been prepared so far.

Recently, we reported the ring expansion of the pyridyl group of *N*-(2,4-dinitrophenyl)pyridinium chloride into diaza[12]annulene by reaction with an amine.[5] According to this reaction, the reaction of 1,1′-bis(2,4-dinitrophenyl)-4,4′-bipyridinium dichloride (**1**) with an amine may provide a diaza[12]annulene dimer. However, we found that the reaction yields unexpected products, namely N-substituted azepinoazepines. These products are a new type of azepine derivative with an expanded π-conjugation system.

Organic reactions in aqueous media have received considerable attention because of their potential advantages with regard to costs, safety, and environmental concerns.[6] In contrast to many reports on organic reactions in mixtures of water and organic solvents, organic syntheses in water, except for simple hydrolysis reactions, are limited as a result of the poor solubility of organic reactants in water. Compound **1** and certain amines used as starting materials in this work are soluble in water, and the previously reported reaction of water-soluble *N*-(2,4-dinitorophenyl)pyridinium chloride with amines proceeds smoothly in water to provide N-substituted diaza[12]annulene through ring expansion of the pyridyl group. These results urged us to carry out the reaction of **1** with amines in water.

Herein, we report the results of the reaction of **1** with various amines **2** in ethanol and water, as well as the structures and optical and electrochemical properties of the obtained azepinoazepines **3**. A plausible reaction pathway is also proposed.

Reaction of **1** with substituted amines **2** (1:2) in refluxing EtOH (Scheme 1) gave rise to N-substituted azepinoazepine dichlorides **3**. Use of water-soluble amines **2a**–**2d** under aqueous conditions also yielded the azepinoazepines **3a**–**3d**. The results of these reactions are summarized in Table 1. The obtained azepinoazepines **3** were soluble in water and in organic solvents such as methanol, *N*,*N*-dimethylformamide, and dimethyl sulfoxide. Their structures were determined by FAB mass spectrometry, ^{1}H and ^{13}C NMR spectroscopy, and elemental analysis.



Scheme 1. Reaction of 1,1′-bis(2,4-dinitrophenyl)-4,4′-bipyridinium dichloride (**1**) with amines **2**. See Table 1 for Y groups.

Figure 1 depicts the ^{1}H NMR spectra of **3d**–**3g** in D_2O. Peaks at approximately $\delta = 9.3$ and 8.7 ppm are assigned to H^a and H^b of the azepinoazepine ring, respectively. The observation of the two signals of the azepinoazepine ring suggests that π electrons are delocalized along the azepinoazepine ring, as shown in Figure 1. ^{13}C NMR spectroscopy data also support this view, showing three signals attributed to the azepinoazepine ring.[7] The ^{1}H NMR peak positions of the azepinoazepine ring of **3a**–**3h** are essentially the same, independent of the structure of the N substituents. The difference in the chemical shifts between the two halophenyl hydrogen atoms H^c and H^d of **3d**, **3f**, and **3g** are $\delta = 0.38$, 0.11, and 0.57 ppm, respectively, whereas the two signals of chlorophenyl hydrogen atoms of **3e** are located at essentially the same position. These data suggest that the azepinoazepine

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

Table 1: Reaction of 1,1′-bis(2,4-dinitrophenyl)-4,4′-bipyridinium dichloride **1** with amines **2**.[a]

Entry	Y (amine)	**2**	Solvent	Product	Yield [%][b]
1	C_6H_5	**2a**	EtOH	**3a**	91
2			H_2O		75
3	4-$MeOC_6H_4$	**2b**	EtOH	**3b**	90
4			H_2O		69
5	2,5-$Me_2C_6H_3$	**2c**	EtOH	**3c**	84
6			H_2O		45
7	4-FC_6H_4	**2d**	EtOH	**3d**	91
8			H_2O		71
9	4-ClC_6H_4	**2e**	EtOH	**3e**	78
10	4-BrC_6H_4	**2f**	EtOH	**3f**	88
11	4-IC_6H_4	**2g**	EtOH	**3g**	84
12	*p*-terphenyl	**2h**	EtOH	**3h**	95
13	*n*-hexyl	**2i**	EtOH	**3i**	38

[a] A solution of **1** and **2** in 1:2 molar ratio in either ethanol (entries 1, 3, 5, 7, and 9–13) or water (entries 2, 4, 6, and 8) was heated at reflux for 12 h under nitrogen (see Scheme 1 for details). [b] Yield of isolated product.

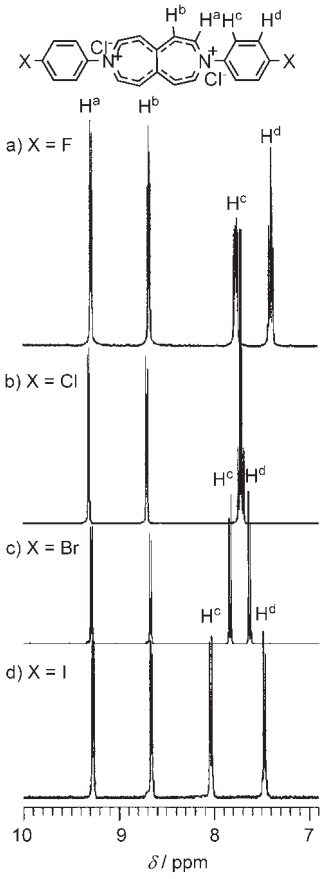


Figure 1. ^{1}H NMR spectra of **3d**–**3g** in D_2O.

ring has an electron-withdrawing property similar to that of the chloro group.

The absorption peaks of **3** are influenced by the structures of the N substituents, as summarized in Table 2. Azepinoazepine dichloride **3h** with *p*-terphenyl substituents shows absorptions at longer wavelengths as compared to the other azepinoazepines, and the absorptions of **3i** with non-aromatic substituents lie at the shortest wavelength among the azepinoazepine dichlorides. These data suggest that the π-conjugation system is expanded from the azepinoazepine ring to the aromatic N substituents. The observation of the absorption of **3b** at a wavelength longer than that of **3c** is explained by the steric effect of the methyl group at the 2-position of the 2,5-dimethylphenyl ring that may hinder the expansion of the π-conjugation system.

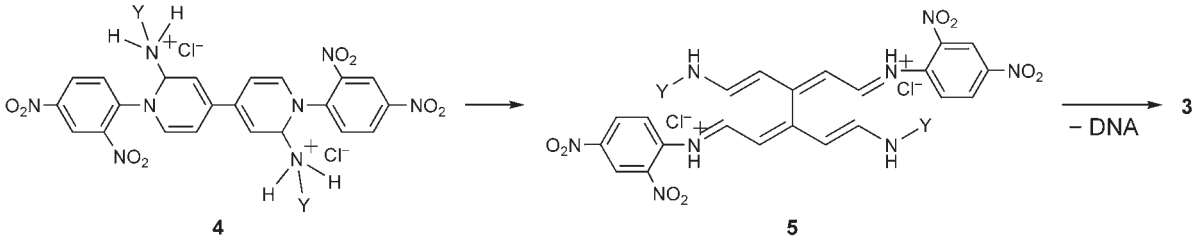
Table 2: Absorption and electrochemical data for azepinoazepines **3**.

Entry	**3**	λ_{max}[a] [nm] ($\log\varepsilon$)	$E_{pc}(1), E_{pc}(2)$ [V][b]	$E_{pa}(1), E_{pa}(2)$ [V][b]
1	**3a**	245 (4.11), 320 (4.49)	−1.53	−0.48, 0
2	**3b**	253 (4.26), 380 (4.67)	−1.51	−0.84, −0.45
3	**3c**	255 (4.05), 268 (4.07), 299 (3.97)	−1.84	−0.92, −0.44
4	**3d**	255 (4.02), 299 (4.09), 321 (4.08)	−1.48	−0.57, −0.05
5	**3e**	259 (4.12), 290 (4.13), 326 (4.16)	−1.23, −1.74	−1.10, −0.61
6	**3f**	254 (4.05), 329 (4.19)	−1.17, −1.73	−1.11, −0.13
7	**3g**	240 (4.07), 342 (4.27)	−1.06, −1.88	−0.15
8	**3h**	289 (4.35), 385 (3.99)	−1.47	−0.88, −0.31
9	**3i**	261 (≈3.8)	−2.02	−1.75, −1.19

[a] Absorption in ethanol. [b] Film cast on a Pt plate, measured in a CH_2Cl_2 solution of $(Et_4N)BF_4$ (0.1 M). The sweep rate was 50 mVs^{-1}. E_{pc} = Peak cathode potential versus Ag^+/Ag. E_{pa} = Peak anode potential versus Ag^+/Ag.

Cyclic voltammetry measurements suggested that the film of the azepinoazepines cast on a Pt plate underwent two-step electrochemical reduction of the azepinoazepine ring in a dichloromethane solution containing 0.1M $(NEt_4)BF_4$. The electrochemical data also are summarized in Table 2. Azepinoazepines **3e**–**3g** with N-halophenyl substituents showed two reduction peaks, which were coupled with anodic peaks $E_{pa}(1)$ and $E_{pa}(2)$. Although the peaks attributed to the two-step electrochemical reduction of the other azepinoazepines **3a**–**3d**, **3h**, and **3i** were duplicated, the two anodic peaks were separately observed. The reduction potential was dependent on the N substituent; product **3i** with its electron-donating *n*-hexyl substituents (Table 2, entry 9) showed a peak at higher reduction potential as compared to **3d**–**3g**, which have electron-withdrawing substituents (entries 4–7). The yellow film of the azepinoazepines changed to green after the electrochemical reduction and returned to yellow after crossing the $E_{pa}(2)$ peak.

Scheme 2 shows a plausible reaction mechanism for formation of the N-substituted azepinoazepine dichlorides. The nucleophilic addition of an amine to the pyridinium rings of **1** occurs first to provide the intermediate **4**. Subsequently, ring opening of the dihydropyridyl rings of **4** gives an



Scheme 2. Possible reaction mechanism for the formation of N-substituted azepinoazepine dichlorides **3**.

intermediate **5**, which undergoes cyclization by elimination of 2,4-dinitroaniline (DNA) to provide **3**.

The product from expansion of one pyridinium ring of **1** was not obtained. On the other hand, nucleophilic addition of the NH group of the intermediate **5** to **1** followed by ring opening of the dihydropyridyl ring and elimination of 2,4-dinitroaniline may yield N-substituted diaza[13]annulenoannulene tetrachloride. However, such a product is not formed in the reaction of **1** with **2** as the lower basicity of the NH group of the intermediate **5** prevents nucleophilic addition to the pyridinium ring. These results indicate that the nucleophilic addition of an amine to the pyridyl group is a crucial step for the generation of the azepinoazepine ring.

In conclusion, N-substituted azepinoazepines were obtained in high yields by the one-pot reaction of **1** with amines. ^{1}H NMR spectra of the products revealed that the π electrons are delocalized along the azepinoazepine ring. Cyclic voltammetry analysis indicated that the azepinoazepines are electrochemically active in films, and the electrochemical reaction was accompanied by electrochromism. Polymerization of **1** with aromatic diamines could provide π-conjugated polymers with the azepinoazepine ring in the main chain. In addition, the azepinoazepines **3d–3g** with 4-halophenyl substituents could be useful starting materials for functional compounds and polymers. These topics are currently under investigation in our laboratory.

Experimental Section

Representative procedure. Preparation of **3a** in EtOH (Table 1, entry 1): 1,1′-Bis(2,4-dinitrophenyl)-4,4′-bipyridinium dichloride (**1**; 1.12 g, 2.0 mmol) and aniline (**2a**; 0.37 g, 4.0 mmol) were dissolved in dry ethanol (8 mL) under N_2. The solution was heated at reflux for 12 h under nitrogen, and then the brown precipitate from the reaction solution was separated by filtration. The precipitate was washed with acetone (150 mL) and dried under vacuum to give the title compound **3a** (0.59 g, 77%) as a brown solid. Compound **3a** was also obtained from the filtrate: Evaporation of the solvent from the filtrate gave a brown solid, which was washed with acetone (150 mL) and dried in vacuo to further afford compound **3a** (0.11 g, 14%). Total yield: 91%.

Preparation of **3a** in water (Table 1, entry 2): An aqueous solution (4 mL) of **1** (0.56 g, 1.0 mmol) and **2a** (0.19 g, 2.0 mmol) was heated at reflux for 12 h, and then the 2,4-dinitroaniline precipitated from the reaction solution was filtered. Evaporation of water gave a brown solid, which was washed with acetone (150 mL) and dried under vacuum to afford compound **3a** (0.29 g, 75%). ^{1}H NMR (400 MHz, D_2O): $\delta = 9.30$ (d, $J = 7.2$ Hz, 4H), 8.67 (d, $J = 7.2$ Hz, 4H), 7.63–7.73 ppm (m, 10H); ^{13}C{^{1}H} NMR (100 MHz, [D_6]DMSO): $\delta = 148.9$, 146.0, 142.2, 131.6, 130.2, 126.7, 124.8 ppm. FAB-MS: m/z 345 [$M-Cl^-$], 310 [$M-2Cl^-$]; elemental analysis (%) calcd for $C_{22}H_{18}N_2Cl_2 \cdot 1.5\,H_2O$: C 64.71, H 5.18, N 6.86; found: C 64.86, H 5.13, N 6.40.

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Keywords: amines · annulenes · fused-ring systems · nitrogen heterocycles · ring expansion

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[7] See Supporting Information.

Communications

Nitrogen Heterocycles

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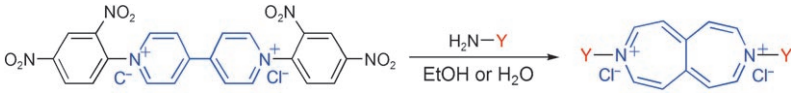
Ring Expansion of a 4,4′-Bipyridyl Derivative into π-Conjugated Azepinoazepines



Room to expand: N-substituted azepinoazepines were obtained in high yields from 1,1′-bis(2,4-dinitrophenyl)-4,4′-bipyridinium dichloride with amines. The ^{1}H NMR spectra of the products revealed that π electrons were delocalized along the azepinoazepine ring, while cyclic voltammetry analysis indicated that the azepinoazepines were electrochemically active and electrochromic as thin films.