A Convenient Synthesis and Spectroscopic Characterization of N,N'-Bis(2-propenyl)-2,7-diazapyrenium Quaternary Salts

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N,N'-Bis(2-propenyl)-2,7-diazapyrenium salts are synthesized in good yield from the reaction of 1,4,5,8-naphthalenetetracarboxylic dianhydride with allylamine, followed by LiAlH₄ reduction and subsequent oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). The nature of the counteranion depends on the solvent system used for recrystallization of the crude product from the final DDQ-oxidation step. X-ray analysis shows that if recrystallization is carried out in boiling CH₃OH/H₂O (1:1, v/v), the counteranion in the resulting deep-red crystals is always the alkoxy anion of 2-cyano-5,6-dichloro-3-hydroxy-1,4-benzoquinone, whether the final DDQ oxidation ends with addition of HClO₄ or HCl; on the other hand, if recrystallization is carried out with anhydrous acetonitrile, the product is N,N'-bis(2-propenyl)-2,7-diazapyrenium diperchlorate or dichloride depending on whether the DDQ oxidation is followed by addition of concd HClO₄ or concd HCl, respectively. Importantly, if the DDQ oxidation is quenched with HBr, Br⁻ is oxidized to Br₂ by unreacted DDQ, and the resulting product is N,N'-bis(2,3-dibromopropyl)-2,7-diazapyrenium dibromide. Comparative absorption and time-resolved emission studies provide evidence for possible dimerization of N,N'-bis(2-propenyl)-2,7-diazapyrenium diperchlorate in CH₃CN.

Introduction

2,7-Diazapyrenium dications combine luminescence properties similar to those of pyrene, redox properties and photoactivity similar to those encountered in viologens, and intercalation properties similar to those of pyrene, redox properties and oxygen. The same authors proposed that the corresponding luminescent material has shown sensitivity to bond to the framework of silica aerogels, and the et al. have proposed 2,7-diazapyrenium dications as attractive subunits for incorporation into macrocyclic structures to make photo- and electroactive receptors. N. D. Lilienthal et al. have demonstrated that N,N'-dimethyl-2,7-diazapyrenium dication can function as a redox-dependent receptor for aromatic carboxylates; it was proposed further that, due to water solubility, that dication could be potentially useful for electrochemical sensors for nonactivated aromatics in water. More recently, Leventis et al. published that N-(3-trimethoxysilylpropyl)-2,7-diazapyrenium bromide (1) can covalently bond to the framework of silica aerogels, and the derived luminescent material has shown sensitivity to oxygen. The same authors proposed that the corresponding dicaticonic salt, namely, N,N'-bis(3-trimethoxysilylpropyl)-2,7-diazapyrenium dibromide (2), having two possible points of attachment onto a sol–gel framework, would be expected to retain an alignment imposed by an externally applied force field during gelation.

On the basis of reports for the synthesis of analogous systems, an attractive method for the synthesis of 2 would be through addition of trimethoxysilane to N,N'-bis(2-propenyl)-2,7-diazapyrenium bromide using Speir’s catalyst (H₂PtCl₆). The synthesis of N,N'-bis(2-propenyl)-2,7-diazapyrenium dication can potentially be carried out by diquat-ernization of 2,7-diazapyrene. However, traditional methods for the synthesis of 2,7-diazapyrene involve oxidation

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of 1,3,6,8-tetrahydro-N,N′-dimethyl-2,7-diazapyrene with either Se or 10% Pd/C in high-temperature melts.\(^\text{16,17}\) Both methods are cumbersome, but the selenium method can be hazardous.\(^\text{16}\) For the synthesis of N,N′-dimethyl-2,7-diazapyrenium dication, the above procedures have been circumvented by a direct but low-yield (20%) oxidation of 1,3,6,8-tetrahydro-N,N′-dimethyl-2,7-diazapyrene with mercuric acetate in boiling glacial acetic acid.\(^\text{16,18}\) The latter method, however, lacks generality. For instance, the oxidation of 1,3,6,8-tetrahydro-N,N′-bis(2-propenyl)-2,7-diazapyrene (5) cannot be carried out in the presence of mercuric acetate because the latter could be added across the double bonds of the allyl groups.

In this paper, we report an alternative simple procedure where 5 can be oxidized directly with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) at room temperature to the N,N′-bis(2-propenyl)-2,7-diazapyrenium dication in good yield.

### Results and Discussion

Scheme 1 summarizes the route for the synthesis of various salts containing the N,N′-bis(2-propenyl)-2,7-

diazapyrenium dication. The first step involves preparation of N,N′-bis(2-propenyl)-1,4,5,8-naphthalenetetracarboxylic diimide (4) from the reaction of 1,4,5,8-naphthalenetetracarboxylic dianhydride (3) with allylamine at room temperature for 6 h. This step comprises a simplifying modification of Hüning's procedure where 1,4,5,8-naphthalenetetracarboxylic acid was converted first into the tetrakis(N-methylammonium) salt by evaporation of its solution in aqueous methylamine.\(^\text{16}\) Subsequently, that salt was heated in 1-methylpyrrolidone for 1 h at 150–203 °C to give N,N′-dimethyl-1,4,5,8-naphthalenetetracarboxylic diimide in 89% yield. Here, we found that the direct reaction of 3 with allylamine in water proceeds quantitatively to an insoluble precipitate of analytically pure 4 in excellent yield (95%). The second step involves AlCl₃-catalyzed reduction of 4 with LiAlH₄ to yield 1,3,6,8-tetrahydro-N,N′-bis(2-propenyl)-2,7-diazapyrene (5), which was isolated by Soxhlet extraction and recrystallized from CHCl₃/hexane (68%). The targeted N,N′-bis(2-propenyl)-2,7-diazapyrenium dication (in compounds 6–8) was synthesized by oxidation of 5 with DDQ in anhydrous CH₃CN at room temperature for 10 h, followed by addition of concentrated acid carrying the intended anion for the diazapyrenium salt. For example, if the reaction ends with addition of concd HClO₄, and the crude product is recrystallized from boiling anhydrous acetonitrile, pale-yellow N,N′-bis(2-propenyl)-2,7-diazapyrenium diperchlorate (7) is obtained in good yield (72%). Similarly, if the reaction ends with addition of concd HCl, yellow N,N′-bis(2-propenyl)-2,7-diazapyrenium dichloride (8) is obtained in good yield (72%).


Synthesis of 2,7-Diazapyrenium Quaternary Salts

OH/H₂O (1:1, v/v, reflux 1 h), the counterion in the recrystallization from CH₃CN, HBr, Br⁻ is normally used under powerful oxidizing agent frequently employed in synthesis of the dications (Figure 4B). The electronic absorption spectra of N,N'-bis(2-propenyl)-2,7-diazapyrenium dications 6, 7, and 8 are compared in Figure 5. The spectra of 6 and 8 are essentially identical, retaining the features expected for the N,N'-dimethyl-2,7-diazapyrenium dication. Compound 6 exhibits an additional broad maximum at 477 nm (ε 3200 M⁻¹ cm⁻¹; 1600 M⁻¹ cm⁻¹ for each red counteranion), assigned to the alkoxy anion of 2,7-diazapyrenium dication is placed between the planes of the dication (Figure 4B).

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gregates occupy a near energy continuum in shallow potential wells, thus explaining the broadening of the absorption features of the diazapyrenium moiety in 7. By providing the energy to promote a molecule to the excited state, the stabilizing interactions in the aggregates should disappear, producing identical excited states from all three compounds 6, 7, and 8. Indeed, that is confirmed by the emission spectra of 6, 7, and 8, which are identical, with identical excited-state lifetimes, ~10 ns (Figure 6, inset). Having two positive charges each, the N,N′-bis(2-propenyl)-2,7-diazapyrenium moieties experience strong electrostatic repulsions. Therefore, it is rather difficult to explain aggregation by simple π-system interactions (i.e., attractive forces between induced dipoles and quadrupoles). It is speculated thereof that dimerization in solution is mediated by a negatively charged ClO4− held between two diazapyrenium moieties. There are indications that ClO4− promotes electrostatic aggregate formation. However, due to the larger size of the alkoxy anion of 10 and the smaller size of Cl− in comparison with ClO4−, similar aggregates in solutions of 6 are weak, while aggregates of 8 would require closer proximity of the diazapyrenium moieties, thus becoming unstable due to strong electrostatic repulsions. The X-ray data of 6 and 7 (Figures 2 and 4B) show that ClO4− can be accommodated between the 2,7-diazapyrenium dications, while anions of 10 are not, thus supporting this hypothesis.

Conclusions

We have described a new three-step facile route to the \( N,N'^\text{-bis(2-propenyl)-2,7-diazapyrenium dication} \), from commercially available \( 1,4,5,8\text{-naphthalenetetra-carboxylic dianhydride} \). Our method is general and can be used for the synthesis of any \( N,N'^\text{-dialkyl-2,7-diazapyrenium dication} \), without having to synthesize first the \( 2,7\text{-diazapyrene} \). Unexpectedly, it was discovered that \( N,N'^\text{-bis(2-propenyl)-2,7-diazapyrenium dication} \) shows a special affinity toward the alkoxy anion of \( 2\text{-cyano-5,6-dichloro-3-hydroxy-1,4-benzoquinone} \), which is produced from unreacted DDQ and water during recrystallization. It was found further that if the DDQ oxidation is quenched with HBr, Br\(^{-}\) is oxidized to Br\(_2\) by the DDQ excess, and the resulting product is

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**Figure 3.** ORTEP plot of \( N,N'^\text{-bis(2-propenyl)-2,7-diazapyrenium diperchlorate (7)} \). Thermal ellipsoids are drawn at the 50% probability level.

**Figure 4.** Packing diagram for \( N,N'^\text{-bis(2-propenyl)-2,7-diazapyrenium diperchlorate (7)} \). (A, top) projection down the c axis; (B, bottom) projection down the a axis.
chased from Aldrich or Fisher and used as received unless otherwise stated.

**N,N'-Bis(2-propenyl)-1,4,5,8-naphthalenetetracarboxylic Diimide (4).** Naphthalenetetracarboxylic dianhydride (3), (12.5 g, 46.6 mmol) was dissolved in a stirred aqueous solution of allylamine (500 mL, 40% v/v) under nitrogen. The solution was stirred at room temperature for 6 h under nitrogen. During this time, analytically pure diimide 4 precipitated as an off-white product, which was filtered, washed with distilled water, and dried under vacuum: yield 15.3 g (95%); mp ~266 °C; 1H NMR (TFA/CDCl3, 500 MHz) δ 3.57 (4H, d, Jab = 5.8 Hz, Hå), 4.01 (2H, dd, Jcd = 0.98, Jbd = 10.3 Hz, Hbd), 4.11 (2H, dd, Jcd = 0.98, Jbd = 17.2 Hz, Hbd), 4.74 (2H, ddt, Jab = 5.8 Hz, Jbc = 10.3 Hz, Jbd = 17.2 Hz, Hbd), 7.52 (4H, s, ArH); 13C NMR (TFA/CDCl3, 125 MHz) 44.1, 119.0, 126.9, 127.2, 130.3, 132.7, 164.7 (NC=O). Anal. Calcd for C58H32N8O6: C, 69.36; H, 4.07; N, 8.09. Found: C, 69.10; H, 4.08; N, 8.07.

1,3,6,8-Tetrahydro-2,7-bis(2-propenyl)-2,7-diazapyrene (5). Tetrahydrofuran (250 mL, dried over LiAlH4) was added to a three-neck round-bottom flask, equipped with a reflux condenser and a magnetic stirring bar. To this flask, cooled in ice, was slowly added AlCl3 (12.2 g, 0.092 mol) under nitrogen. After AlCl3 had been dissolved, LiAlH4 (10.4 g, 0.273 mol) was slowly added into the stirred solution at 0 °C. To the resulting suspension was also added at 0 °C diimide (12.5 g, 0.036 mol), and the reaction mixture turned immediately to red and changed to green after ~10 min. The resulting mixture was stirred at room temperature for 1 h and then refluxed for 3.5 h under nitrogen. At the end of the reaction time, the reaction mixture was cooled to room temperature and poured over ice (~400 g), and the solid was filtered, washed with distilled water, and dried under vacuum (45 °C) overnight. The dry solid was subjected to Soxhlet extraction with CHCl3 (~300 mL). The chloroform solution was concentrated to ~50 mL, and hexane (50 mL) was added. The precipitated product was filtered, washed with a small amount of CHCl3/hexane (1:1), and dried under vacuum overnight: yield 7.05 g (68%); mp ~163 °C dec; 1H NMR (CDCl3, 400 MHz) δ 3.26 (4H, d, Jab = 6.6 Hz, Hå), 3.95 (8H, s, ring CH2), 5.20–5.27 (4H, m, Hå and Hbd), 6.00 (2H, ddt, Jcd = 5.8 Hz, Jbc = 10.3 Hz, Jbd = 17.0 Hz, Hbd), 7.12 (4H, s, ArH); 13C NMR (CDCl3, 100 MHz) δ 56.2, 60.3, 60.8, 117.9, 121.6, 127.7, 131.4, 135.2; UV vis (CH3CN) λmax nm (ε, M–1 cm–1) 229 (40 000), 292 (400 g), and the solid was filtered, washed with a small amount of CHCl3/hexane (1:1), and dried under vacuum overnight.

**General Method for the Synthesis of N,N'-Bis(2-propenyl)-2,7-diazapyrenium Salts 6 and 7.** Diamine 5 (0.25 g, 0.86 mmol) was added to anhydrous acetonitrile (50 mL) in a 100 mL round-bottom flask, equipped with a magnetic stirring bar. The suspension was stirred under nitrogen and heated to ~40 °C to dissolve the starting material. At that point, heating was stopped and DDQ (0.78 g, 3.44 mmol) was added to the warm solution. The color of the solution changed immediately to red and quickly turned to dark brown. The reaction mixture was stirred for 10 h at room temperature, under nitrogen, followed by the addition of 70% perchloric acid (1.0 mL, 11.6 mmol), which changed the color of the reaction mixture to clear yellow. The reaction mixture was concentrated down to ~20 mL at room temperature under vacuum, followed by the addition of dichloromethane until a yellow precipitate was observed. The resulting crude product was filtered, washed with a small amount of dichloromethane, and dried under vacuum overnight.

**N,N'-Bis(2-propenyl)-2,7-diazapyrenium Bis(2-cyano-5,6-dichloro-3-hydroxy-1,4-benzoquinone alkoxide) (6).** The crude product from above was recrystallized twice in boiling CH3OH/H2O (1:1, v/v) to give deep-red needles: yield 0.20 g (32%); mp ~350 °C; 1H NMR (DMSO-d6, 400 MHz) δ 5.53 (2H, s, aryl), 5.93 (1H, s, ring CH), 6.93, 6.96 (2H, m, ArH), 7.12, 7.23, 7.72 (6H, m, ArH), 8.91 (4H, s, ArH), 10.31 (4H, s, ArH); 13C NMR (DMSO-d6, 100 MHz) δ 64.5, 87.7, 118.0, 122.9, 126.9, 130.0, 130.7, 131.4, 136.1, 141.8, 144.6, 171.0, 171.8, 174.2; UV vis (CH3CN) λmax nm (ε, M–1 cm–1) 229 (40 000), 292 (400 g), and the solid was filtered, washed with a small amount of CHCl3/hexane (1:1), and dried under vacuum overnight.

**Experimental Section**

**General Methods.** Elemental analyses were performed by Oneida Research Services, Inc. X-ray crystallography was performed at the University of Missouri–Columbia. Time-resolved emission data were obtained with samples in freeze-pump–thaw degassed and flame-sealed ampules using a system composed of an Oriel pulsed N2 laser model 79111 (5 ns), a Spectrograph model 77480, and an InstaSpecV image intensifier/CCD detector using a Stanford Research Systems, Inc. four-channel delay/pulse generator model DG535. Excited-state lifetimes were determined by curve fitting using the Origin 5.0 software package on a Pentium PC. Melting points were uncorrected. Starting materials and solvents were pur-
N,N'-Bis(2-propenyl)-2,7-diazapyrenium Diperchlorate (7). The crude product from above was recrystallized in boiling anhydrous acetonitrile to give pale yellow needles: yield 0.30 g (72%); mp 257 °C dec; 1H NMR (DMSO-d6, 400 MHz) δ 5.57 (2H, dd, 1Jc = 0.80 Hz, 1Jbc = 10.4 Hz, H2c), 5.60 (2H, dd, Jbc = 17.2 Hz, Jcb = 0.80 Hz, H2bc), 5.76 (4H, d, Jc = 6.4 Hz, H2c), 6.46 (4H, ddt, 1Jab = 6.4 Hz, 1Jbc = 10.4 Hz, Jcb = 17.2 Hz, H2bc), 8.92 (4H, s, ArH), 10.30 (4H, s, ArH); 13C NMR (DMSO-d6, 100 MHz) δ 64.5, 123.0, 126.3, 129.0, 130.0, 131.5, 141.9; UV-visible (CH3CN) λmax, nm (ε, M⁻¹ cm⁻¹) 217 (76 200), 231 (46 400), 263 (14 700), 351 (16 800); emission (CH3CN) λmax, nm, 337 (28 100), 375 (2600), 395 (7600), 420 (12 400); 1H NMR (CD3OD, 400 MHz) δ 5.57 (2H, dd, 1Jc = 0.80 Hz, H2c), 5.38 (2H, septet, 1Jbc = 6.6 Hz, Jcb = 17.0 Hz, H2bc), 5.47 (2H, dd, Jbc = 13.7 Hz, H2bc), 5.83 (2H, dd, Jbc = 3.9 Hz, Jcb = 9.7 Hz, H2c), 8.99 (4H, s, ArH), 10.49 (4H, s, ArH); 13C NMR (DMSO-d6, 100 MHz) peak assignment is based on HMQC and DEPT) δ 35.3 (CH, N⁺), 51.2 (CHBr), 66.2 (CH2Br), 126.6 (Ar =C), 128.8 (Ar =C), 130.3 (Ar =CH), 142.7 (Ar =CH); UV-visible (CH3CN) λmax, nm (ε, M⁻¹ cm⁻¹) 219 (16 000), 253 (31 600), 298 (2200), 310 (4900), 324 (12 500), 339 (19 000), 378 (1600), 401 (4200), 425 (7500). Anal. Calcd for C20H18N2Cl2O4: C, 49.50; H, 3.74; N, 5.77. Found: C, 49.35; H, 3.76; N, 5.66. Anal. Calcd for C20H18N2Br6: C, 31.36; H, 2.40; N, 4.26. Anal. Calcd for C20H18N2Br6: C, 31.36; H, 2.40; N, 4.26. Anal. Calcd for C20H18N2Br6: C, 31.36; H, 2.40; N, 4.26. Anal. Calcd for C20H18N2Br6: C, 31.36; H, 2.40; N, 4.26.