Synthesis and Spectroscopic Properties of the Elusive 3a,9a-Diazaperylenium Dication

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SUPPORTING INFORMATION

Experimental Section

Methods. Absorption spectra were obtained with a Beckman DU 640B Spectrophotometer. Emission and excitation spectra were obtained with a Perkin-Elmer LS-5 spectrophotometer with a Perkin-Elmer R100A recorder. Time-resolved emission data were obtained with a system composed of an ORIEL pulsed N_2 laser model 79111, a Spectrograph model 77480, and an InstaSpecV image intensifier/CCD detector using a Stamford Research Systems, Inc. four-channel delay/pulse generator model DG535. The same apparatus was employed in low temperature emission studies, which were conducted with a specially made Dewar. Emission quantum yields were determined using perylene in cyclohexane as an actinometer.[9b]

^{1}H and ^{13}C nmr spectra were obtained with a Varian INOVA 400 MHz nmr spectrometer, and are referenced vs. TMS. MALDI mass spectrometry was conducted using a sinapinic acid matrix (10 μg in 270 mL of 7:3 CH_3CN/H_2O) and an Applied Biosystems Model Voyager-DE PRO mass spectrometer.

SCF Hartree-Fock *ab initio* calculations for the ground and the first singlet excited state of **1** were conducted through Spartan02 v102 (by Wavefunction, Inc.) and the 6-31G** basis set.

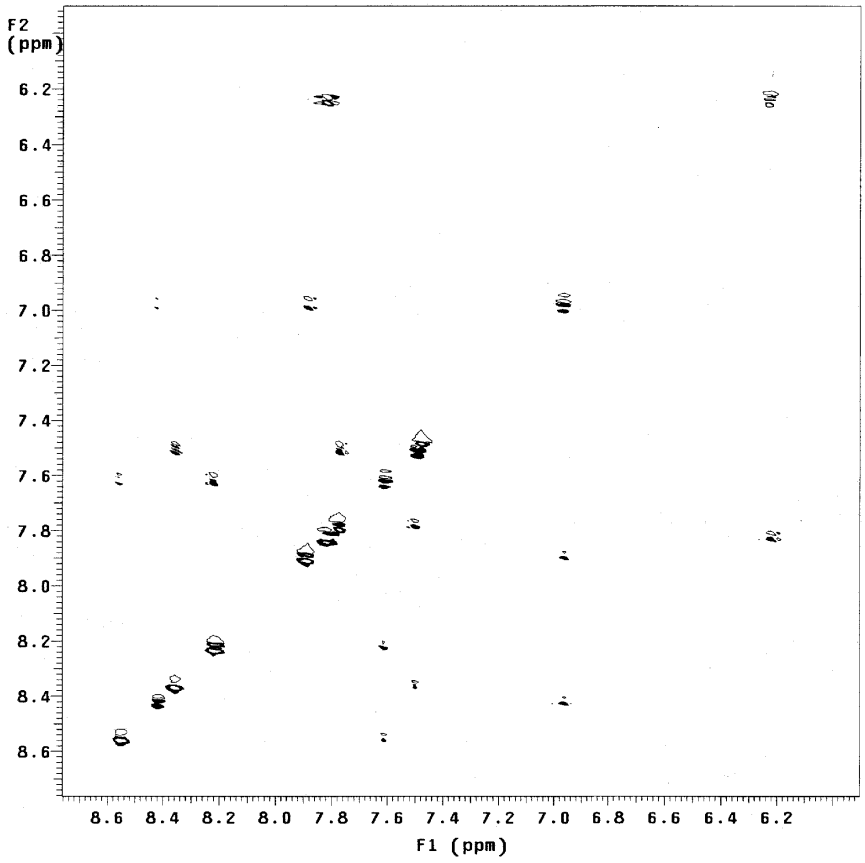
Materials. 1,2,3,4,5,6,7,8,9,10,11,12-dodecahydro-3a,9a-diazaperylene, **2**, and its diprotonated mixed bromide/chloride salt, [**2**-2H$^+$]Br$^-$Cl$^-$, were prepared as described before.[18]

3a,9a-Diazaperylenium diperchlorate (**1**).

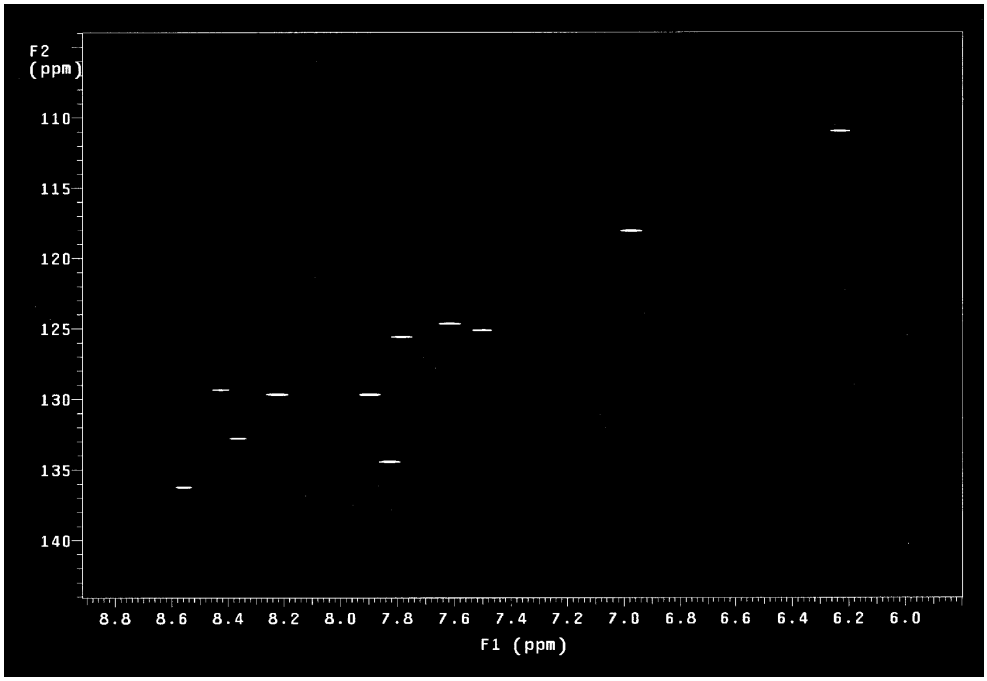
Solid [**2**-$2H^+$]Br^-Cl^- (0.99 g, 2.57 mmol) was added quickly to a solution of HgO (8.14 g, 37.6 mmol, Fisher) in acetic acid (200 mL, Fisher) at room temperature The resulting solution turned dark blue immediately producing orange emission under UV light. That emission turns quickly to blue (*ca.* within 15 min at room temperature) and the reaction mixture was refluxed under unhydrous conditions for 48 h. At the end of the period the flask was allowed to cool to room temperature and the reaction mixture was filtered and the precipitates (that include elemental Hg) were washed with CH_3CO_2H. The filtrate was concentrated to ~30 mL, and diethyl ether was added to induce precipitation. The solid was collected, dried, weighted (5.8 g) and subjected to soxhlet extraction with water for 24 h. After evaporation of the solvent ^{1}H nmr shows that the crude product (0.71 g) is a practically clean mixture of **1** and **4** in a 1:3 molar ratio. The two compounds were separated by column chromatography on acidic alumina (prepared by stirring neutral alumina with a 0.3 mol/L HCl solution, in a 1:2 w/w adsorbent-to-acid ratio).[20] A minor green-emitting impurity is eluted first with CH_3CN. Subsequently, a 9:1 v/v mixture of CH_3CN/CH_3OH elutes **4**, and a 6:4 v/v mixture of CH_3CN/CH_3OH elutes **1**. The chromatographic solvent was removed under reduced pressure. The product was dissolved in 5 mL water and a 2 mL solution containing 2 g of $NaClO_4$ was added. The resultant solution was cooled overnight in the refrigerator. The precipitate was collected, redissolved in CH_3NO_2, filtered and precipitated with ether to yield analytically pure **1**. (Note that an analogous procedure involving a saturated aqueous solution of NH_4BF_4 rather than the $NaClO_4$ solution does not induce a quantitative precipitation of the tetrafluoroborate salt of **1**.) Received 0.18 g (15 %), mp>300 ^{o}C; ^{1}H nmr (400 MHz, DMSO-d_6): δ 9.36 (d, 2H, 3-H, $J_{2,3}$=6.41 Hz), 9.26 (d, 2H, 1-H, $J_{1,2}$=7.87 Hz), 8.28 (dd, 2H, 2-H, $J_{2,3}$=6.77, $J_{1,2}$=7.88 Hz); ^{1}H nmr (400 MHz, D_2O): δ 8.99 (d, 2H, 3-H, $J_{2,3}$=6.59 Hz), 8.96 (d, 2H, 1-H, $J_{1,2}$=8.06 Hz), 7.99 (dd, 2H, 2-H, $J_{2,3}$=6.77, $J_{1,2}$=8.06 Hz); ^{13}C nmr (100 MHz, DMSO-d_6): δ 138.4 (d, 3-C, $J_{H\text{-}C}$=18.5 Hz), 138.0 (s, 12d-C), 133.0 (d, 2-C, $J_{H\text{-}C}$=12.9 Hz), 127.4 (s, 12c-C), 124.4 (d, 1-C, $J_{H\text{-}C}$=23.6 Hz); ms: (MALDI) 256.1051 (M^+), (theoretical ionic mass: 256.0995). Anal. Calcd. For $C_{18}H_{12}N_2O_8Cl_2$ (455.2074): C, 47.49; H, 2.66; N, 6.15. Found: C, 47.20; H, 2.75; N, 6.22.

Characterization of **4**: mp>300 ^{o}C; uv-vis (CH_3CN): λ_{max}, nm (log ε) 246 (4.04), 291 (3.63), 351 (3.73), 385 (sh), 402 (3.83), 465 (sh), 484 (3.66), 541 (3.69); ^{1}H nmr (400 MHz, DMSO-d_6): δ 9.08 (d, 1H, 10-H, $J_{10\text{-}11}$=6.77 Hz), 8.91 (d, 1H, 4-H, $J_{4,5}$=7.15), 8.86 (d, 1H, 9-H, $J_{8,9}$=6.60 Hz), 8.82 (d, 1H, 12-H, $J_{11\text{-}12}$=7.50 Hz), 8.60 (d, 1H, 6-H, $J_{5,6}$=7.51 Hz), 8.56 (d, 1H, 1-H, $J_{1,2}$=9.89 Hz), 8.43 (d, 1H, 7-H, $J_{7,8}$=7.88 Hz), 7.96 (dd, 1H, 11-H, $J_{10\text{-}11}$=6.60 Hz, $J_{11\text{-}12}$=8.05 Hz), 7.85 (dd, 1H, 8-H, $J_{7,8}$=6.59 Hz, $J_{8,9}$=8.06 Hz), 7.36 (t, 1H, 5-H, $J_{4,5}$=7.33 Hz, $J_{5,6}$=7.33 Hz), 6.65 (d, 1H, 2-H, $J_{1,2}$=9.71 Hz); ^{1}H nmr (400 MHz, D_2O): δ 8.56 (d, 1H, 10-H, $J_{10\text{-}11}$=6.59 Hz), 8.37 (d, 1H, 4-H, $J_{4,5}$=6.59), 8.36 (d, 1H, 9-H, $J_{8,9}$=6.96 Hz), 8.17 (d, 1H, 12-H, $J_{11\text{-}12}$=8.05 Hz), 7.83 (d, 1H, 6-H, $J_{5,6}$=7.14 Hz), 7.73 (d, 1H, 1-H, $J_{1,2}$=9.52 Hz), 7.71 (d, 1H, 7-H, $J_{7,8}$=6.74 Hz), 7.63 (dd, 1H, 11-H, $J_{10\text{-}11}$=6.59 Hz, $J_{11\text{-}12}$=8.06 Hz), 7.51 (dd, 1H, 8-H, $J_{7,8}$=6.59 Hz, $J_{8,9}$=8.06 Hz), 6.96 (t, 1H, 5-H, $J_{4,5}$=7.33 Hz, $J_{5,6}$=7.32 Hz), 6.20 (d, 1H, 2-H, $J_{1,2}$=9.52 Hz); ^{13}C nmr (100 MHz, D_2O): δ 157.5 (amide C=O), 137.4, 137.0, 136.3, 134.3, 132.9, 130.8, 129.7, 129.4, 129.1, 125.62, 125.58, 125.2, 124.8, 118.1, 111.0, 105.9; ms: (MALDI) 271.1011 (M^{+}), (theoretical ionic mass: 271.0866).

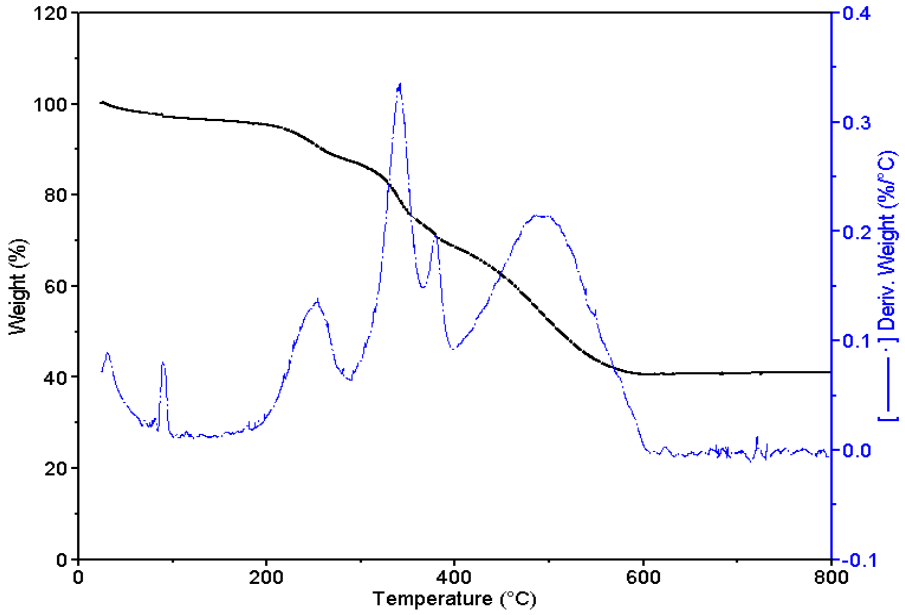
^{1}H-^{1}H COSY of 4 in D_2O at 400 MHz



^{13}C-^{1}H HETCOR of 4 in D_2O

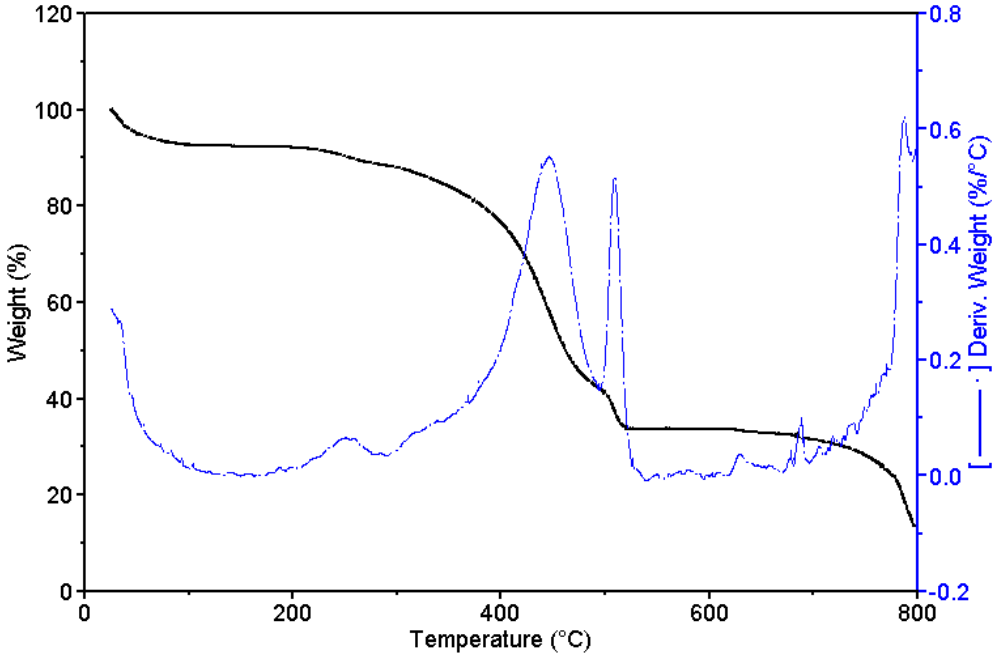


TGA Data for 1



Heating rate 10 ^{O}C, Range: 25 ^{O}C to 800 ^{O}C.
Instrumentation: TA Instruments. TGA 2950.

TGA Data for 4



Heating rate 10 ^{O}C, Range: 25 ^{O}C to 800 ^{O}C.
Instrumentation: TA Instruments. TGA 2950