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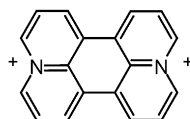
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ABSTRACT

The 3a,9a-diazaperylenium dication (1) was synthesized for the first time in two steps from *p*-phenylene diamine. Ab initio calculations show a twisted ground state with a 6.4° tilt between the two quinolizinium building blocks. Dication 1 is photoluminescent in fluid solutions of H_2O, CH_3CN, and CH_3NO_2, but not in rigid matrices of the same solvents. This phenomenon has been attributed to a geometric relaxation of the tilted ground state into an emitting planar lowest singlet excited state.

Several symmetric diaza analogues of small fused polyaromatic systems are known. Notable examples include 1,10-phenanthroline, a common chelating agent, 2,6-diazaanthracene,[1] which has been involved recently in directed self-assembly of chiral macrocyclic tetranuclear Pd and Pt molecular squares,[2] 2,7-diazapyrene,[3] whose diquaternized dicationic derivative is water soluble and has been used as a sensitizer for photooxidations,[4] and as a DNA intercalator,[5] and also 2,9-diazaperopyrene, whose *N*,*N*′-dimethyl dicationic derivative also interacts and binds nucleic acid components and catalyzes the photocleavage of single stranded oligonucleotides.[6] The monoquaternized derivative of 2,7-diazapyrene has been used also as a fluorescent dopant of sol-gel type materials for sensing O_2.[7]

Similarly, derivatives of 3,9-diazaperylene have been known since the 1980s.[8] A five-step synthesis and the photophysics of 1,7-diazaperylene were reported in the 1990s,[9] and a two-step synthesis of 1,12-diazaperylene from isoquinoline was described in 2001.[10] The 3a,9a-diazaperylenium dication (1), an isomer of the *N*,*N*′-diprotonated forms of 3,9-, 1,7-, and 1,12-diazaperylene, has not been known.[11]

1
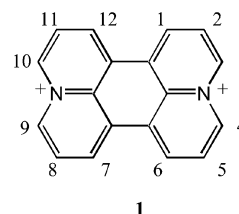
In contrast, the quinolizinium building block of **1** has been known since 1954,[12] and has been the subject of numerous spectroscopic,[13] crystallographic,[14] chemical,[15] theoretical,[16]

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(2) (a) Stang, P. J.; Olenyuk, B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 732−736. (b) Olenyuk, B.; Whiteford J.; Stang, P. J. *J. Am. Chem. Soc.* **1996**, *118*, 8221−8230.

(3) (a) Sotiriou-Leventis, C.; Mao, Z. *J. Heterocycl. Chem.* **2000**, *37*, 1665−1667. (b) Sotiriou-Leventis, C.; Mao, Z.; Rawashdeh, A.-M. M. *J. Org. Chem.* **2000**, *65*, 6017−6023.

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and biochemical studies.[17] Meanwhile, recently we developed a one-step synthesis of 1,2,3,4,5,6,7,8,9,10,11,12-dodecahydro-3a,9a-diazaperylene, **2**, from *p*-phenylene diamine, **3**, and 1-bromo-3-chloropropane.[18] With the ready availability of **2**, it was decided to attempt the synthesis of **1** itself. This paper comprises the first report on the synthesis and spectroscopic properties of **1**.

Oxidation of the *N,N′*-diprotonated form of **2**, **2**-2H⁺, was carried out with HgO in acetic acid in analogy to Hünig's method for the synthesis of the *N,N′*-dimethyl-2,7-diazapyrenium dication from *N,N′*-dimethyl-1,3,6,8-tetrahydro-2,7-diazapyrene.[19] Scheme 1 summarizes the synthesis of **1** from

Scheme 1. Synthesis of the 3a,9a-Diazaperylenium Dication (**1**)
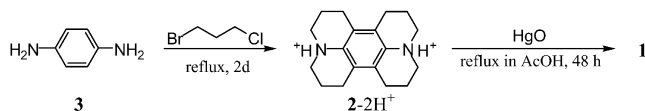
3 via **2**-2H⁺. The yield of the first step (88%) was reported before.[18] The yield of the second step was 15%.

The crude product from the HgO reaction is a practically clean mixture of **1** and **4** in a 1:3 molar ratio by NMR.
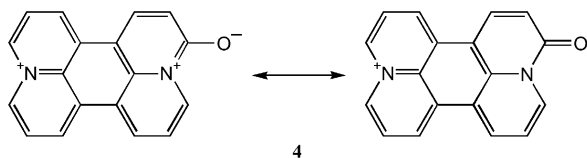
Compounds **1** and **4** were separated on alumina pretreated with HCl.[20] The ¹H-NMR spectra of **1** and **4** are compared in Figure 1. The loss of symmetry in **4** is evident. Chemical

shift assignment in the case of **4** was carried out with ¹H− ¹H COSY and HETCOR experiments (see the Supporting Information).
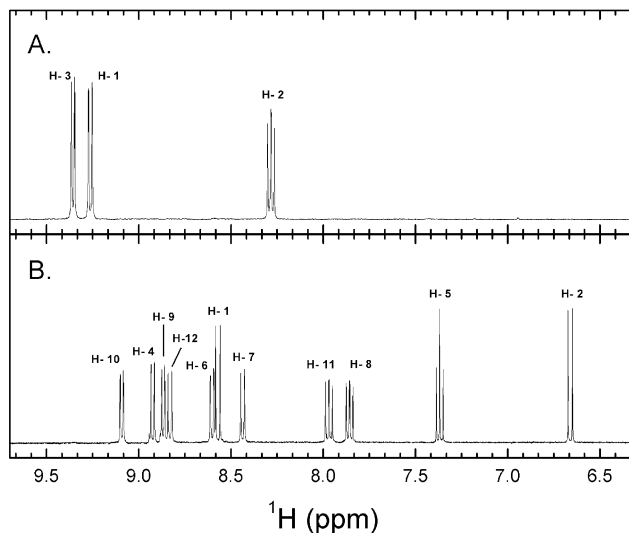
Figure 1. ¹H NMR spectra (400 MHz) of **1** (A) and **4** (B) in DMSO-d_6.

Alternatively, preparation of **1** by oxidation of **2**-2H⁺ with Pd/C in refluxing ethanol, acetic acid, or a high temperature (290 °C) melt[21] was unsuccessful. In some instances, traces of **1** were detected by emission; nevertheless it could not be extracted quantitatively. Similarly, oxidation with MnO_2[3a] was also unsuccessful.

The perchlorate salt of **1** is soluble to a variable degree in several polar solvents ranging from water to acetonitrile, nitromethane, and DMSO. Dilute solutions of **1** are yellowish, but depending on the angle of observation they may appear blue due to the strong photoluminescence. Spectroscopic data for **1** in several solvents are summarized in Table 1. Typical absorption, emission, and excitation spectra in CH_3CN are shown in Figure 2. The absorption spectrum is somewhat different from that of perylene (or other diazaperylene derivatives) in that it shows an additional vibrationally resolved absorption feature in the near-UV (345, 359, and 375 nm). The absorption and excitation spectra overlap. The blue emission is attributed to $S_1 \rightarrow S_0$ fluorescence. Both absorption and emission spectra are structured allowing determination of the Stokes shifts, which are consistently rather large (17−20 nm) for a rigid system, and probably indicate a structural reorganization between the ground and the lowest excited state beyond the usual bond elongation upon photoexcitation. (By comparison, the Stokes shift we observed for perylene in cyclohexane was 12 nm.) Time-resolved fluorescence spectroscopy gives monoexponential decays and the emission lifetimes (Table 1) are close to those

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Table 1. Spectroscopic Data for **1**

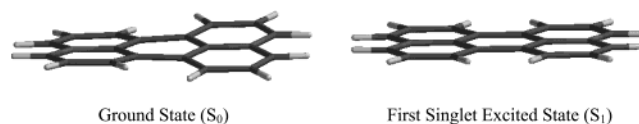| solvent =	absorption max, nm (log ϵ)[a]				emission max, nm[b]			
	H₂O	CH₃CN	CH₃NO₂	DMSO	H₂O[c] (6.8[e])	CH₃CN[c] (7.4[e])	CH₃NO₂[c] (6.2[e])	DMSO[d] (4.4[e])
	224 (4.18)	223 (4.17)			441	442	441	443
	244 (4.32)	245 (4.30)			465	466	468	471
	343 (3.84)	346 (3.79)	345 (3.91)	347 (3.90)	495 (sh)	498 (sh)	499 (sh)	502
	357 (3.96)	358 (3.95)	359 (4.03)	362 (3.97)				
	374 (3.87)	374 (3.85)	376 (3.92)	385 (sh)				
	394 (4.03)	395 (4.02)	397 (4.04)	406 (4.04)				
	422 (4.06)	422 (4.05)	424 (4.10)	432 (4.08)				

[a] For comparison, the corresponding data for perylene in cyclohexane are the following: 218 (4.32), 251 (4.38), 386 (3.85), 408 (4.18), and 434 nm (4.29). [b] For comparison, the emission maxima of perylene in cyclohexane are at 446.5, 473.5, and 504.8 nm. [c] At room temperature. No emission at 77 K. [d] In frozen matrix at 77 K. No emission at room temperature. [e] Emission (fluorescence) lifetimes (τ_r, in ns).

of perylene (measured 5.6 ± 0.3 ns in CH₃CN and 5.5±0.4 ns in cyclohexane) and of 1,7-diazaperylene (e.g., 5.1 ns in ethanol).[9b] The emission quantum yield (Φ) of **1** was determined in CH₃CN and was found equal to 0.75 ± 0.01. (By comparison, the literature reported fluorescence quantum yield of perylene is 0.92−0.94.[9b,22]) It is noted that the ratio (0.76) of the radiative lifetimes of **1** (see Table 1) and perylene in CH₃CN is approximately equal to the quantum yield ratio (0.81), indicating the excited states of the two compounds have about equal natural lifetimes (τ_o). Further analysis based on the fact that $\Phi = \tau_o/\tau_r$ shows that the rate constant for the nonradiative decay of **1** is ∼3 times higher than the nonradiative decay of perylene (4.5×10^7 s^{-1} vs 1.3×10^7 s^{-1}, respectively). That indicates that the first excited state of **1** has additional modes of deactivation available.

Curiously, by freezing H₂O, CH₃CN, and CH₃NO₂ solutions of **1** in liquid N₂, all photoluminescence disappears. We are inclined to associate this phenomenon with the rather large Stokes shifts mentioned above, and attribute them both
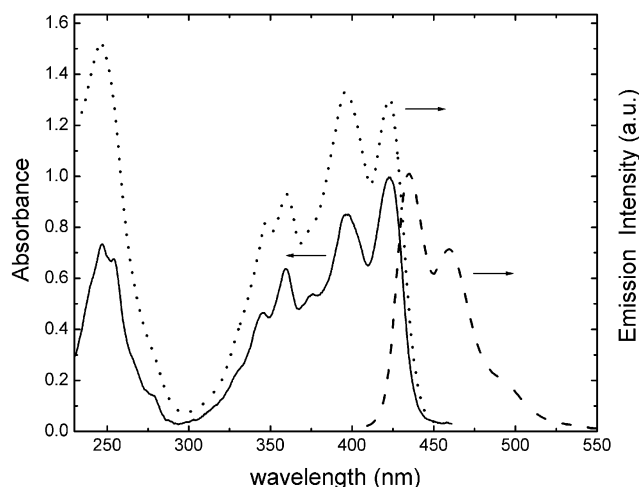

Figure 2. Absorption (—), emission (---), and excitation (•••) spectra of **1** in CH₃CN. [**1**] = 7.9×10^{-4} M. The absorption spectrum was obtained with a 0.1 cm path length quartz cell.

to a geometric relaxation upon excitation that is possible in fluid solvents but not in low-temperature rigid matrices. In analogy to the reasoning set forth for the interpretation of the identical photoemission of biphenyl and fluorene or of 2,2′-bipyridine and 4,5-diazafluorene (both pairs of molecules have geometrically different ground but identical excited states),[23] it is proposed that the geometry of **1** is twisted in the ground state and planar in the excited state. Then if that change in geometry is hindered by a rigid environment, the emitting excited state is not formed and photoemission is not observed.

A twisted ground-state geometry for **1** is not unreasonable. Reportedly, the two naphthalene rings of perylene form a dihedral angle of ca. 11°.[24] Perylene is twisted out of planarity by the steric repulsions between the bay-area H-atoms.[9b,24] The same forces are still present in **1**. An ab initio calculation (using the 6-31G** basis set) yielded a 6.39° tilt (6.26° with the 6-311+G** basis set) between the two quinolizinium rings. An ab initio calculation for the lowest singlet excited state, using configurational interactions with the 6-31G** basis set, yielded a planar geometry (0.04° tilt). (A similar calculation with the 6-311+G** basis set would be prohibitively long and was not attempted.) The results from the ab initio calculations for the S₀ and the S₁ states of **1** are shown in Scheme 2.

Scheme 2. Optimized Geometry of **1**, via HF−SCF Calculations with the 6-31G** Basis Set

Ground State (S₀)   First Singlet Excited State (S₁)

It should be noted here that in DMSO, **1** does not emit at room temperature, but it does emit at 77 K, and yields an

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(24) Shilstone, G. N.; Zannoni, C.; Verachini, C. A. *Liq. Cryst.* **1989**, *6*, 303−317.

identical spectrum to the one exhibited by **1** at room temperature in all the other solvents considered (Table 1). It is speculated that the excited state of **1** in fluid DMSO remains tilted, while at 77 K the system is forced planar and hence it becomes emissive. Certainly, these phenomena may not be unique to DMSO and further theoretical and experimental work is warranted.

In contrast to **1**, solutions of byproduct **4** are red and only weakly photoluminescent. The red-shifted absorption spectrum is a phenomenon that has been observed with 2,8-dimethoxy- and 2,8-dipentyloxy-1,7-diazaperylene as well.[9b] A broad emission at 555 nm prevails only at very low concentrations ($\sim 10^{-5}$ M). As the concentration increases (e.g., 10^{-4} M), a new broad band at $\sim$630 nm becomes dominant at the expense of the 555-nm emission, indicating formation of an eximer.

In summary, we have reported the synthesis and spectroscopic properties of **1**. It is expected that because of the sensitivity of the photoluminescence on the surrounding matrix, **1** may find an application as a fluorescent probe or,

in analogy to its quinolizinium building block, as a DNA binder with possible antileukemic action.[17]

Potential Hazard: Perchlorate salts may be explosive when heated.

Supporting Information Available: An Experimental Section giving preparation, separation, and characterization of **1** and **4**; ^{1}H-^{1}H COSY and HETCOR NMR data for **4**; TGA data for **1** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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