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Novel Photochromic Spiroheterocyclic Molecules via Oxidation of 1,8-Diaminonaphthalene

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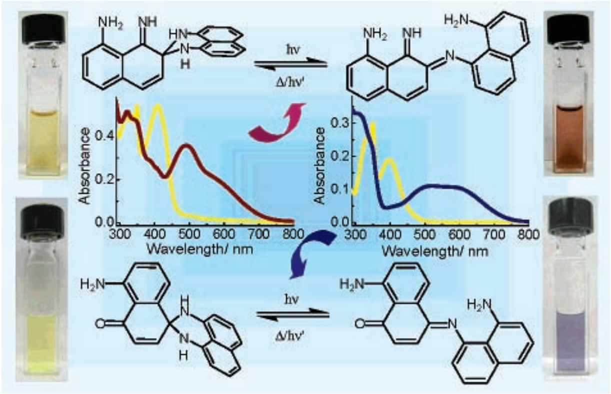
ABSTRACT



Novel spiroheterocyclic molecules, namely, 2,3-dihydro-2-spiro-7′-[8′-imino-7′,8′-dihydronaphthalen-1′-amine]perimidine, PNI, and 2,3-dihydro-2-spiro-4′-[8′-aminonaphthalen-1′(4*H*)-one]perimidine, PNO-*p*, were obtained by oxidation of 1,8-diaminonaphthalene using manganese dioxide. These molecules exhibit thermally reversible photochromism with good photofatigue resistance, and their photogenerated forms possess broad absorption in the visible region.

Photomodulation of the chemical structure of organic molecules forms the basis of a host of light-driven molecular devices and switches wherein photochromic materials form a vital entity.[1] The superior photochromic properties of spiroheterocyclic molecules such as spiropyrans, spirooxazines, and chromenes have attracted intense research that has identified their wide application prospects in the area of photonic materials.[1a,b,f,2]

Photochromism in these systems involves a photoinduced C−X (X = O, N,or S) bond cleavage at the spiro junction that leads to an extended π-conjugation between two aromatic units that are orthogonally oriented in the initial spiro form. During the course of our studies, we observed that oxidation of 1,8-diaminonaphthalene using manganese dioxide yields novel spiroheterocyclic photochromic molecules. These molecules exhibit thermally and photochemically reversible photochromism and possess good photofatigue resistance. The photogenerated forms of these molecules exhibit broad absorption in the visible spectrum which is a

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(1) (a) *Photochromism-Molecules and Systems*; Dürr, H., Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, 1990. (b) *Organic Photochromic and Thermochromic Compounds*; Crano, J. C., Guglielmetti, R. J., Eds.; Plenum Press: New York, 1999; Vols.1 and 2. (c) *Molecular Switches*; Ferringa, B. L., Ed.; Wiley-VCH: Weinheim, 2001. (d) *Photochromism: Memories and Switches*, Special issue, *Chem. Rev.* **2000**, *100*, 1683−1890. (e) *Molecular Machines*, Special issue, *Acc. Chem. Res.* **2001**, *34*, 409−522. (f) Bousas-Laurent, H.; Dürr, H. *Pure Appl. Chem.* **2001**, *73*, 639. (g) *Photoreactive Materials for Ultrahigh-Density Optical Memory*; Irie, M., Ed.; Elsevier: Amsterdam, 1994. (h) Myles, A. J.; Branda, N. R. *Adv. Funct. Mater.* **2002**, *12*, 167.

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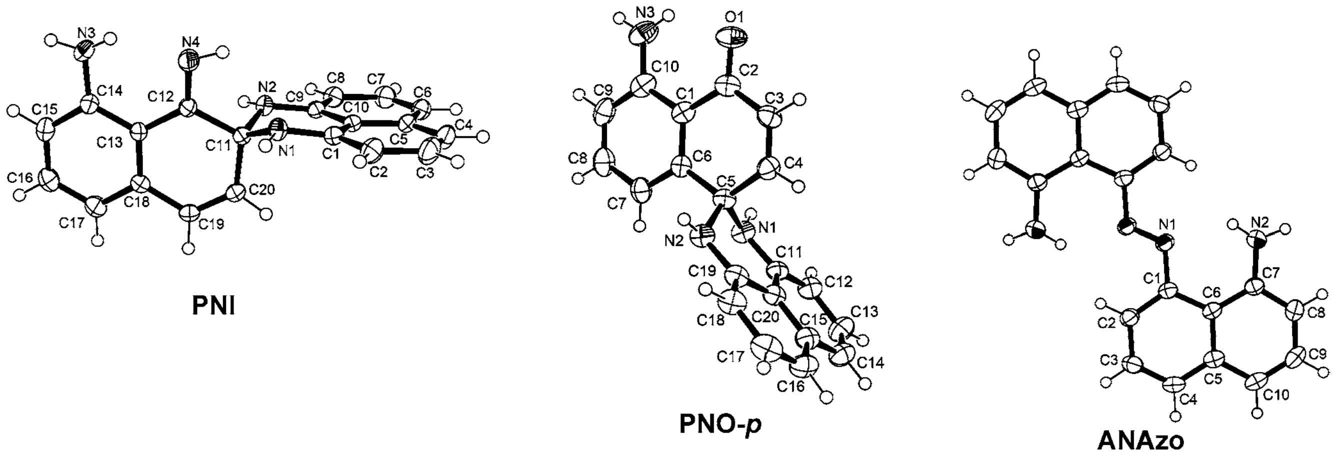
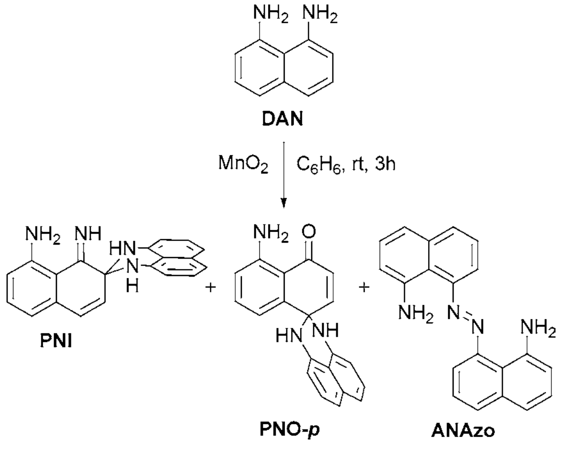


Figure 1. ORTEP diagrams of the oxidation products of 1,8-diaminonaphthalene.

prerequisite of materials used in photochromic opthalmic lenses. In most cases, neutrality of the activated color, characterized by the broadness of the visible light absorption, has been accomplished by mixing several photochromic molecules possessing absorption over different parts of the visible region.[1b,3,4] In this paper we describe the preparation and photochromic properties of the newly obtained spiroheterocyclic molecules that are expected to form potential candidates in generating photochromic materials.

1,8-Diaminonaphthalene, **DAN**, was oxidized in the presence of manganese dioxide as shown in Scheme 1. The reaction yielded two spiroheterocyclic products, 2,3-dihydro-2-spiro-7′-[8′-imino-7′,8′-dihydronaphthalen-1′- amine]perimidine, **PNI**, and 2,3-dihydro-2-spiro-4′- [8′- aminonaphthalen-1′(4*H*)-one] perimidine, **PNO-*p***, along with (*E*)-8-((8′-aminonaphthalen-1-yl)diazenyl)naphthalen-1-amine, **ANAzo**.

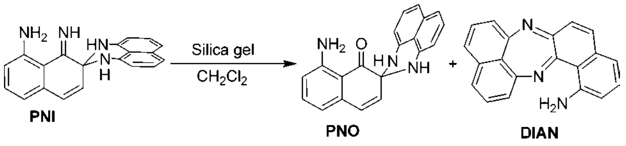
Scheme 1



The structures of these products were unequivocally elucidated using ^{1}H NMR, single-crystal X-ray diffraction, and elemental analyses. Figure 1 shows the ORTEP diagram of the products obtained. Using a high dilution (×25 times) reaction condition, in which a benzene solution of **DAN** was slowly added (over 50 h) to a suspension of manganese dioxide in benzene, we observed the formation of an intermediate product, 8-amino-1-iminonaphthalen-2(1*H*)-one.[5] The formation of the spiroheterocyclic product, **PNI**, hence became conceivable to result from the condensation of **DAN** with this intermediate.

PNI undergoes a complete transformation into two molecules, 2,3-dihydro-2-spiro-2′-[8′-aminonaphthalen-1′(2*H*)-one]perimidine, **PNO**, and a diiminoaminonaphthalene heterocycle, **DIAN** (Scheme 2 and Figure 2), in the presence of silica gel used for column chromatography.[5]

Scheme 2



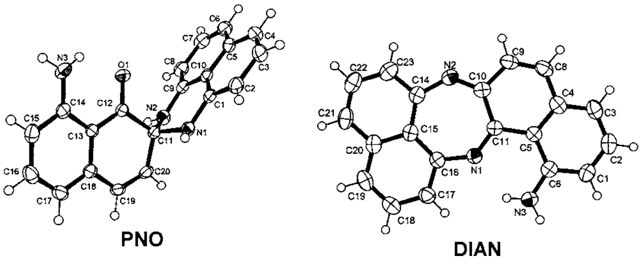


Figure 2. ORTEP diagrams of **PNO** and **DIAN**.

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(4) Salemi-Delvaux, C.; Pottier, E.; Guglielmetti, R. J.; Dubest, R.; Aubard, J. *Dyes Pigm.* **1999**, *40*, 157.

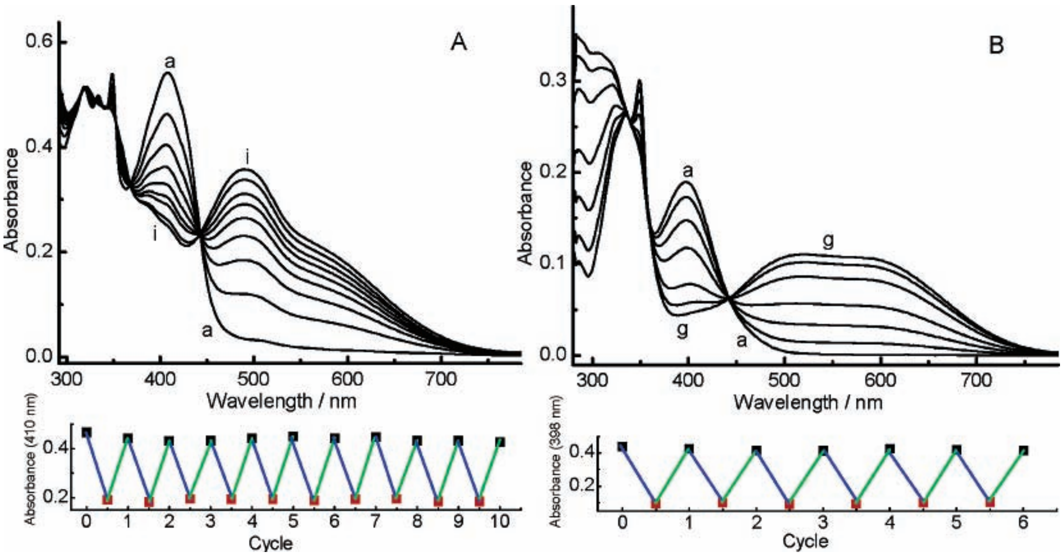


Figure 3. Absorption spectral changes upon photolysis of a toluene solution using 405 nm light at 25 °C: (A) **PNI** ($c = 2.8 \times 10^{-5}$ M), (a) 0 s, (b) 10 s, (c) 20 s, (d) 30 s, (e) 40 s, (f) 50 s, (g) 60 s, (h) 90 s, (i) 180s (PSS); (B) **PNO-*p*** ($c = 1.7 \times 10^{-5}$ M), (a) 0 s, (b) 10 s, (c) 30 s, (d) 1 min, (e) 2 min, (f) 3 min, (g) 4 min (PSS). Repeated ring close−open−close cycles of the photochromic molecules using 405 nm (blue line) and 532 nm lasers (green line) have also been shown.

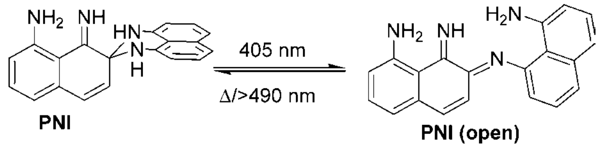
The transformation of **PNI** to **PNO** involves the hydrolysis of the imino group to a ketone moiety.[6] This solvent-independent transformation of **PNI** persisted even on degassing a dehydrated solution of **PNI** by bubbling Ar gas for at least 30 min to remove any dissolved gases, prior to the addition of silica gel. However, **PNI** is highly stable in solution, the solid state, and over surface-modified silica used in HPLC normal-phase columns.

PNI and **PNO-*p*** exhibit efficient photochromic reactions. Upon photolysis of a toluene solution of **PNI**, using 405 nm light, its absorption band centered at 410 nm decreases in intensity with a concomitant increase in that of a new band centered at 490 nm (sh 600 nm) as depicted in Figure 3A. During this change, the initial yellow solution of **PNI** turns deep brown. Similarly, photolysis of a toluene solution of **PNO-*p*** brought about a decrease in the absorbance of the band centered at 398 nm with an associated increase in that of a broad band centered at 560 nm (Figure 3B). In the case of **PNO-*p***, upon photolysis the initial yellow solution turns deep blue. It is interesting to note that the absorption bands of the activated forms of these spiroheterocycles are fairly broad covering a major portion of the visible spectra. In each case, the photogenerated species fully reverts to the initial form both thermally and photochemically using visible light. The photochromic reactions of both **PNI** and **PNO-*p*** proceed through an isosbestic point at 443 nm, which indicate a clear interconversion between two states. In toluene, at 30 °C, the lifetimes of the photoactivated colored forms of **PNI** and **PNO-*p*** were estimated to be 4.4 and 1.7 h, respectively.

Minkin et al. have studied various related spiroheterocyclic systems whose photochromic reactions have been established to involve an initial photoinduced C−N bond cleavage at the spiro junction to form a zwitter ionic state following which a proton transfer occurs to form a molecule having extended conjugation and hence deep coloration.[2,7]

The photochromic reaction in the present molecules may be described as shown in Scheme 3, where upon photolysis, the intial ring-closed spiro form transforms to a ring-opened species having an extended conjugation that results in the formation of a deep coloration. **PNI** and **PNO-*p*** undergo ring-opening reaction only in the presence of light. In the

Scheme 3



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(5) See the Supporting Information.

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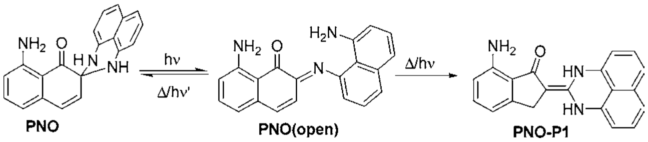
dark, even at elevated temperatures, their initial spiro forms remain unchanged. This property of the newly obtained photochromic molecules distinguishes them from related perimidine based spiroheterocyclic derivatives that undergo spontaneous formation of an equilibrium between ring-closed and ring-opened states upon dissolution in nonpolar solvents.[2,7a,b]

The composition of the closed and opened forms of these photochromic molecules in the ring-opening reaction (using 405 nm light) was estimated using ^{1}H NMR analysis. In benzene, at the photostationary state, **PNI** and **PNO-*p*** exist predominantly in the ring-opened forms with their percentages being 65 and 82%, respectively.[5] Table 1 summarizes the spectroscopic data of the current photochromic compounds. The photofatigue resistance of these derivatives was examined by carrying out a series of ring close−open−close cycles using 405 and 532 nm light (Figure 3). Even after several successive cycles involving long hours of laser irradiation (532 nm), achieving a recovery of >95% of the spiro form in each cycle, the isosbestic point remained intact. This indicates that no other photoreactions interfere with these photochromic reactions. Although **PNI** and **PNO** were structurally similar, the photoreactivity of **PNO** was varied. Upon photolysis in toluene, the yellow solution of **PNO** turned deeply colored with absorption spectral changes similar to that of **PNI**, indicating the formation of its ring-opened form.[5] Thermal and photochemical reversal of the ring-opened form also resulted in the formation of an irreversible product that was isolated and characterized to be **PNO-P1** (Scheme 4).[5] **PNO-P1** transformed thermally and photochemically to another product whose structure has yet to be characterized.

Table 1. Spectroscopic Data of the Photochromic Molecules

entry	solvent	closed form λ_{max}, nm (ϵ, M^{-1} cm^{-1})	open form λ_{max}, nm (ϵ, M^{-1} cm^{-1})	$\Phi_{(close-open)}$
PNI	toluene	410 (18 700)	490 (18 400)	0.06
PNO-p	toluene	398 (9100)	520 (6500), 595 (6200)	0.05

Scheme 4



In conclusion, we have described the photochromic properties of two novel spiroheterocyclic molecules. The efficient photochromism, good photofatigue resistance, and broad activated absorption in the visible region of these molecules are expected to make them useful in the field of photochromic materials. By judicious structural modification of these molecules their properties can be enhanced and hence these also form useful models to obtain superior photochromic materials.

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Supporting Information Available: Details of experimental procedure, structure characterization, X-ray crystal analyses data, and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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