The Synthesis, X-ray Structure Analysis, and Photophysical Characterization of 4-[(E)-2-(4-Cyanophenyl)diazenyl]-morpholine
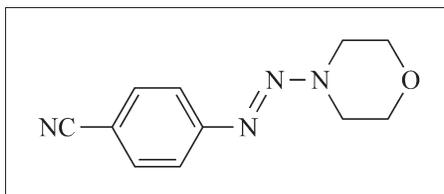
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A novel triazene, 4-[(E)-2-(4-cyanophenyl)diazenyl]-morpholine (**1**) was prepared via a diazonium ion coupling reaction between 4-aminobenzonitrile and morpholine. The x-ray structure of **1** was determined and evidenced π delocalization in the triazene subunit. The room temperature absorption spectrum of **1** in acetonitrile was dominated by an intense triazene-centered π→π* transition at 325 nm. Compound **1** was observed to be luminescent, with an emission maximum at 434 nm in room temperature acetonitrile solution. The emission spectrum of **1** in propionitrile glass at 77K exhibited a narrowed emission band with a maximum at 449 nm. Broad emission from 400–700 nm with poorly resolved vibrational structure was observed from solid **1** at room temperature.

INTRODUCTION

Triazenes are a diverse class of compounds that possess three consecutively bonded nitrogen atoms. The first nitrogen atom in a triazene is bonded to the second by a double bond, which is bonded to the third by a single bond, for example, RN=N—NR'R''. The classic synthesis of triazenes involves the coupling of an amine to an aryl diazonium ion [1,2]. A recent and versatile synthetic procedure yields triazenes from the reaction of organic azides with N-heterocyclic carbenes [3].

Triazenes have been utilized in a variety of research areas. In organic synthesis, they have been used as protecting groups for aromatic amines, as linkers in solid-phase peptide synthesis and as synthons for novel heterocyclic compounds [4–6]. Triazenes have also been investigated as antitumor agents and incorporated into novel conductive aromatic polymers [7,8]. More recently, triazenes have been employed as easily prepared and handled equivalents for the *in situ* generation of reactive diazonium ions, which can participate in palladium-catalyzed reactions that form conjugated materials [9].

Our research utilizes triazenes as diazonium ion equivalents to prepare luminescent stilbenoid metal-organic materials via the method of Sengupta et al [10]. Compound **1** (Scheme 1) is a logical synthon for our research, because it is easily prepared from economical and readily available reagents. It also has a versatile nitrile group, which can be transformed into other functional groups or act as a metal ligand. In this work, we present the synthesis of **1** and its crystal structure. The photophysical characterization of **1**, the first for a triazene prepared from morpholine, is also detailed.

RESULTS AND DISCUSSION

Compound **1** was prepared in good yield (64%). It exhibited the predicted spectroscopic characteristics, except for the ^{13}C-NMR spectrum. The expected resonances for the aromatic ring and the nitrile substituent were observed, as well as three broad singlets at 45.1, 51.3, and 66.4 ppm for the morpholine ring. The assignment of these singlets to the carbons of the morpholine ring was supported by the HMQC NMR spectrum of **1**, which showed a connection between the broad carbon resonances and the morpholine protons. Three signals were observed instead of the expected two because the partial π character of the N—N single bond inhibited its rotation, which resulted in the magnetic nonequivalence of the morpholine carbons [11,12]. The identity of **1** was corroborated by an elemental analysis that yielded acceptable values and a EI-HR-MS that had an [M+H]$^+$ peak at m/z = 217.1081, which was ∼ 1.5 ppm less than the calculated value.
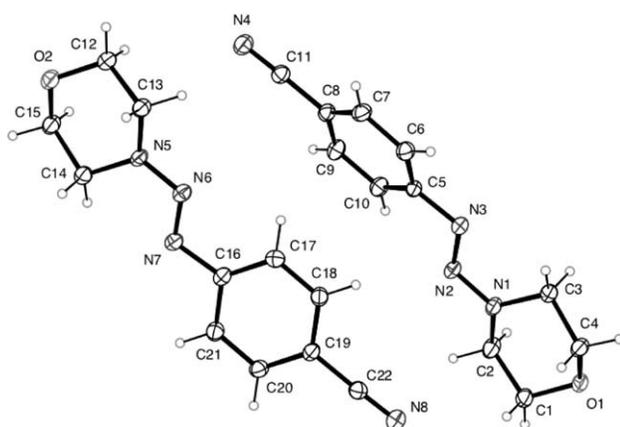
Compound **1** was recrystallized from petroleum ether to yield yellow needles that were suitable for X-ray

Scheme 1

1
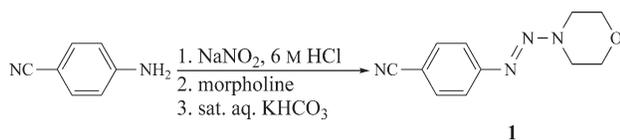
analysis. The *ORTEP* representation of **1** is shown in Figure 1. The asymmetric unit consisted of two independent molecules of **1** whose bond lengths and angles were essentially identical, with the largest difference between them being the magnitude of the torsion angle between the N=N double bond and the plane of the phenyl ring, 26.42(16)° for one and 6.88(16)° for the other. The N−N double bond was found to adopt an (*E*)-configuration with a N(3)−N(2)−N(1) bond angle of 114.72(10)°, which deviated from the optimal trigonal planar geometry by approximately 6°. The N(2)−N(3) group participated in π delocalization with the morpholine nitrogen N(1) that was evidenced by N(1)−N(2) and N(2)−N(3) bond lengths of 1.3320(13) and 1.2748(14) Å, respectively. These values are between literature value of 1.222 Å for a N=N double bond and 1.420 Å for a N(sp^2)−N(sp^3) single bond [13]. The bond angles of the morpholine nitrogen N(1) varied from 114.73(10) to 122.63(10)°, which indicated some degree of sp^2 hybridization of N(1) and its participation in π delocalization with N(2)−N(3). The morpholine ring adopted a chair-like conformation with the N(2)−N(3) group in an equatorial position on N(1). The structure of **1** was similar to the structures of related triazenes [14,15].

While the photophysical characteristics of molecules containing a N−N double bond (azo compounds) have been extensively documented, information regarding the photophysical properties of triazenes is limited [16]. The experimental photophysical data for compound **1** are

Table 1

Photophysical data for compound **1**.

Medium/Temperature	$\lambda_{max,abs}$ nm $(\varepsilon)^a$	$\lambda_{max,em}$ nm $(\lambda_{exc}$ nm)
CH$_3$CN solution/r.t.	230 (9,200)	434 (300)
	325 (20,100)	
CH$_3$CH$_2$CN glass/77 K		449 (300)
solid state/r.t.		469 (350)
		569
		613

^{a} Extinction coefficient units M^{-1}cm^{-1}.

listed in Table 1. The room temperature electronic absorption and emission spectra of **1** in room temperature acetonitrile solution are presented in Figure 2.

The absorption spectrum of **1** in room temperature acetonitrile was dominated by an intense absorption band at 325 nm, which was assigned to a π→π* transition that arose from the triazene subunit. A less intense absorption band at 230 nm was assigned to a π→π* transition in the phenyl ring. Excitation of a dilute (2.0 × 10^{-5}M) acetonitrile solution of **1** at room temperature yielded an emission spectrum with a band that had a maximum at 434 nm. The excitation of a dilute (2.0 × 10^{-5}M) solution of **1** in propionitrile at 77 K yielded a slightly red-shifted, narrower emission band with a maximum at 449 nm. Solid **1** at room temperature yielded weak, broad emission from 400–700 nm with poorly resolved fine structure that had maxima at 469, 569, and 613 nm. All observed emission was assigned to a π*→π transition centered on the triazene moiety. The observed absorption and emission properties of **1** agreed with those found in the literature for similar compounds [17,18].

Figure 1. *ORTEP* view of **1**. Ellipsoids are represented at the 50% probability level.
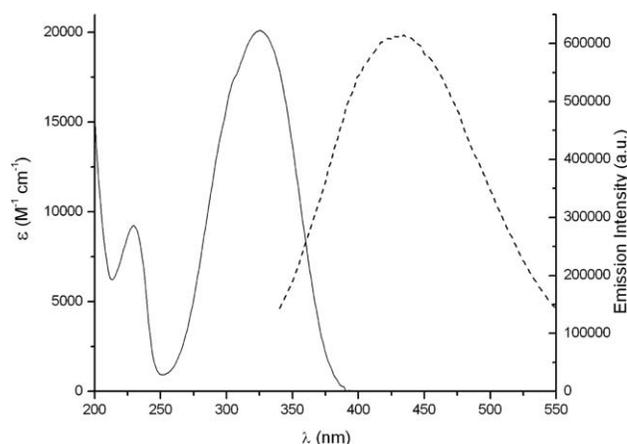
Figure 2. Room temperature electronic absorption and emission spectra of compound **1** in acetonitrile solution. (—) absorption spectrum; (- - -) emission; spectrum (λ_{exc} = 300 nm).

The synthesis of **1** was attractive for its operational simplicity, good yield and its use of inexpensive starting materials. Determination of the x-ray structure of **1** revealed two independent molecules in the asymmetric unit as well as π delocalization of the nitrogen atoms that comprise the triazene moiety. Compound **1** was found to be luminescent both at room temperature and at 77 K. The presented characterization of the photophysical properties of **1** was the first noted for a triazene synthesized from morpholine.

EXPERIMENTAL

The synthetic procedure was carried out using standard techniques. Solvents and reagents were used as received. ^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL ECX 300 MHz spectrometer using TMS as the internal standard. The IR spectrum was recorded as a KBr disk on a JASCO 460 FT-IR. Elemental analysis was done by M-H-W Laboratories of Tucson, Arizona. Mass spectrometry was provided by the Washington University Mass Spectrometry Resource with support from the NIH National Center for Research Resources (Grant No. P41RR0954).

Emission and absorption spectra were recorded at room temperature and at 77 K in spectrophotometric grade acetonitrile and propionitrile (99% purity) utilizing a HoribaJobinYvon FluoroMax-4 fluorometer and a Hewlett Packard 8453 diode array spectrometer. All solutions were deoxygenated with argon before luminescence measurements. All emission spectra were corrected for detector response utilizing a correction curve supplied by the fluorometer manufacturer.

4-[(E)-2-(4-cyanophenyl)diazenyl]-morpholine (1). 1.00 g (8.7 mmol) of 4-aminobenzonitrile was added to 4 mL of 6M HCl and heated on a hot water bath to yield a white suspension, which was cooled to 0°C. This suspension was maintained at 0°C, and a solution of 0.61 g (8.9 mmol) of NaNO$_2$ in 2 mL of H$_2$O was added dropwise with stirring over 10 min. A clear orange-brown solution resulted. To this stirred solution, 0.81 mL (0.81 g, 9.3 mmol) of morpholine was added dropwise over 10 min; a yellow-orange solid formed. The mixture was allowed to reach room temperature, and then brought to pH = 8 with saturated aqueous KHCO$_3$. The yellow-orange solid was collected using suction filtration, washed well with H$_2$O and dried in air. The crude product was recrystallized from petroleum ether to give yellow needles, 1.17 g (64%), mp 81.5–82.0°C; IR (KBr): 3062, 2915, 2220 (C≡N), 1597 (C=C), 1494 (N=N) cm^{-1}; ^{1}H-NMR (deuteriochloroform): δ 3.87 (br. s, 8H), 7.49 (d, 2H, ^3J = 8.6 Hz), 7.61 (d, 2H, ^3J = 8.9 Hz); ^{13}C NMR (deuteriochloroform): δ 45.1, 51.3, 66.4, 108.9, 119.4, 121.3, 133.2, 153.5; 196.3; EI-HR-MS: m/z for [M+H]$^+$ = 217.1081, Calcd. m/z for [M+H]$^+$ = 217.1089. *Anal.* Calcd. for C$_{11}$H$_{12}$N$_4$O: C, 61.25; H, 5.88, N, 26.16. Found: C, 61.13; H, 5.61; N, 25.93.

A pale yellow lath fragment of **1** (0.40 mm × 0.33 mm × 0.05 mm) was used for data collection at T = 90 K on a Nonius KappaCCD diffractometer equipped with an Oxford Cryosystems Cryostream chiller and graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). A total of 24,607 measured reflections with θ_{max} = 27.1° yielded 4,727 unique data. The structure was solved by direct methods, and structure refinement was carried out using SHELXL-97 [19]. All hydrogen atoms were visible in difference maps, but were placed in calculated positions in the refinement.

Single-crystal X-ray diffraction data for **1**.C$_{11}$H$_{12}$N$_4$O, FW = 216.25, triclinic, $P\bar{1}$, a = 9.2329(15) Å, b = 10.438(2) Å, c = 11.853(2) Å, α = 87.977(8)°, β = 70.664(10)°, γ = 83.027(12)°, V = 1069.9(3) Å^3, Z = 4, ρ_{calc} = 1.343 Mg/m^3, μ = 0.09 mm^{-1}, $F(000)$ = 456, R$_{int}$ = 0.024 for 3,445 observed reflections with $I > 2\sigma I$), R_1/wR_2 = 0.042/0.119, Goodness-of-fit on F^2 = 1.03, 289 parameters.

CCDC 756812 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccd.cam.ac.uk/data_request/cif.

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