

Supporting Information

A Nitric Oxide-Releasing Polydiazeniumdiolate Derived from Acetonitrile

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Experimental Section

Caution! Polydiazeniumdiolated compounds can decompose violently to generate large volumes of gas and should be handled with great care.

General Information. The apparatus used for conducting reactions with oxygen-free NO has been described in reference 2 of this paper. It was further modified by the addition of potassium hydroxide pellets to the ballast tank to ensure complete removal of nitrogen dioxide from the NO, which was used directly from the supplier tank (Matheson Gas Products, Montgomery, PA). All reagents and solvents were obtained from Aldrich Chemical Company (Milwaukee, WI). Chemiluminescence measurements of NO were performed with a Thermal Energy Analyzer model 502A (Thermedics, Inc., Woburn, MA), and nitrous oxide was measured

by GC. Elemental analysis was performed by Atlantic Microlab, Inc. (Norcross, GA).

Preparation of tris-diazeniumdiolate 1. To 100 mL of anhydrous acetonitrile was added 10 mL of a solution containing 25% sodium methoxide in methanol (43.7 mmol NaOMe) and the solution was placed in a glass Parr bottle. The reaction system was flushed with argon, pressurized with NO gas at 40 psig, and stirred at room temperature for 24 h. A light yellow solid precipitated and was isolated by filtration, washed with ether, and dried *in vacuo* to yield 3.94 g of pale yellow powder (yield 85% based on added NaOMe assuming that the entire amount was the desired product). To isolate pure **1**, 110 mg of this powder was dissolved in 1.5 mL of 0.1 M NaOH and the solution was filtered to remove a small quantity of insoluble residue. The resulting solution was diluted with methanol until turbidity persisted (ca. 0.5 mL) and placed in a refrigerator to effect a **slow** crystallization. Crystallization was terminated when the first signs of a blue coloration appeared in the solution (indicating decomposition, which began from 2-6 days after preparation, depending on the batch) and the crystalline product was isolated by filtration to yield (after vacuum drying) 25 mg of **1** as the trihydrate: mp 185 °C (detonates); ^1H NMR (300 MHz, D_2O) δ 7.61 (1H, s); ^{13}C NMR (75 MHz, D_2O) δ 99.4; IR (KBr) 3000 cm^{-1} ; UV λ_{max} (10 mM NaOH, ϵ) 264 nm ($19.5 \text{ mM}^{-1} \text{ cm}^{-1}$). Anal. Calcd for $\text{C}_1\text{H}_1\text{N}_6\text{O}_6\text{Na}_3 \cdot 3\text{H}_2\text{O}$: C, 3.80; H, 2.23; N, 26.59. Found: C, 4.05; H, 2.23; N, 26.88.