3,3′-Azobis(6-amino-1,2,4,5-tetrazine): A Novel High-Nitrogen Energetic Material**

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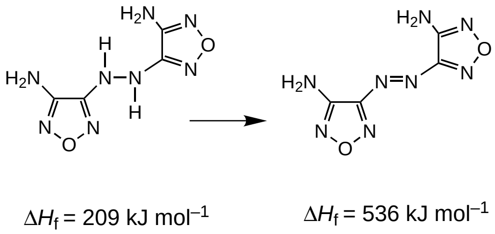
The synthesis of compounds known as high-nitrogen energetic materials has been the focus of our group for the past decade. High-nitrogen compounds form a unique class of energetic materials deriving most of their energy from their very high positive heats of formation rather than from oxidation of the carbon backbone, as with traditional energetic materials.[1] The high nitrogen content typically leads to high densities, and the low amount of hydrogen and carbon also allows for a good oxygen balance to be achieved more easily; oxygen balance is a measure of the oxygen/fuel ratio in a compound. We have demonstrated that high-nitrogen materials can show remarkable insensitivity to electrostatic discharge, friction, and impact.

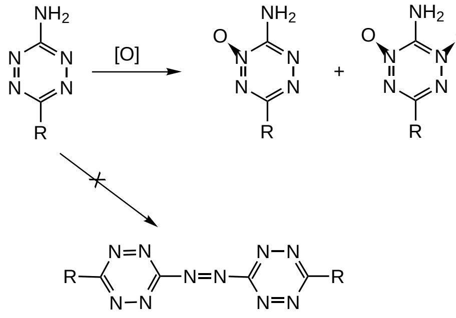
One high-nitrogen system extensively studied by our group is the 1,2,4,5-tetrazine ring. We have synthesized several energetic 1,2,4,5-tetrazines having applications as propellants, explosives, and pyrotechnic ingredients.[2] In the pursuit of new high-nitrogen materials with novel properties, we have recently been studying azo-1,2,4,5-tetrazines.

We became interested in the synthesis of azo-1,2,4,5-tetrazines from our previous studies on azo-1,2,5-oxadiazoles. We found that 327 kJ mol^{-1} of energy is gained in the transformation of 4,4′-hydrazobis-(1,2,5-oxadiazol-3-amine) to 4,4′-azobis(1,2,5-oxadiazol-3-amine) (Scheme 1). The latter material is a thermally stable, insensitive explosive.[3] Extrapolating from these data, 3,3′-azobis(6-amino-1,2,4,5-tetrazine) (**1**; see Scheme 3) would give an even higher heat of formation due to the intrinsically large heat of formation of the 1,2,4,5-tetrazine ring. Tetrazine rings linked by an azo group are practically nonexistent. The only synthesis of azo-1,2,4,5-tetrazines in the literature was reported by Russian scientists in 1971 and 1990.[4] Although they describe the preparation of 3,3′-azobis(6-phenyl-1,2,4,5-tetrazine) and 3,3′-azobis[6-(4-chlorophenyl)-1,2,4,5-tetrazine], no physical properties or proof of structure were given for the compounds.



Scheme 1. Energy gained in the transformation of a hydrazo group to an azo group in the case of amino-1,2,5-oxadiazoles.

We have previously shown that oxidation of 3-amino-1,2,4,5-tetrazines leads to the formation of *N*-oxides in which the oxide moiety is α to the amino group (Scheme 2).[2b,c] In the case of 3,6-diamino-1,2,4,5-tetrazine (R = NH_2), *N*-oxide groups are formed at the 1- and 4-positions, whereas with 3-amino-1,2,4,5-tetrazines (R = H), N-oxidation occurs at the two ring nitrogen atoms α to the amino group. Stronger oxidizers (hypofluorous acid, peroxytrifluoroacetic acid) can also oxidize an amino group to a nitro group when 3,6-diamino-1,2,4,5-tetrazine is the substrate. Under no circumstances have we observed the formation of an azo or azoxy linkage. Thus the formation of the azo group must be accomplished by a different synthetic approach. Here we describe our synthesis of **1**, as well as some of the properties of this novel high-nitrogen material.



Scheme 2. Oxidation of 3-amino-1,2,4,5-tetrazines. R = NH_2, H; see text for details.

The preparation of **1** is shown in Scheme 3. The 3,5-dimethylpyrazol-1-yl moieties of 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine (**2**) have been shown to be good leaving groups in nucleophilic displacements on 1,2,4,5-tetrazines.[5] With readily available **2** as a starting material,[5a] the hydrazo compound **3** was prepared by treatment of **2** with 0.5 equiv of hydrazine. A variety of oxidizing reagents typically used to oxidize a hydrazo group to an azo moiety (Br_2, NO_2, MnO_2, HgO, HONO) did not lead to the formation of the azo group. Oxidation was only achieved with *N*-bromosuccinimide (NBS), which also brominated the 3,5-dimethylpyrazol-1-yl rings to give the azo compound **4**. The formation of the azo group was confirmed by the absence of signals and stretches for NH in the ^1H NMR and IR spectra as well as elemental analysis. Treatment of **4** with ammonia in acetonitrile yielded a precipitate, which upon analysis showed that complete displacement of the 4-bromo-3,5-dimethylpyrazol-1-yl groups did not occur. However, when the reaction was conducted in dimethyl sulfoxide (DMSO) followed by treatment of the

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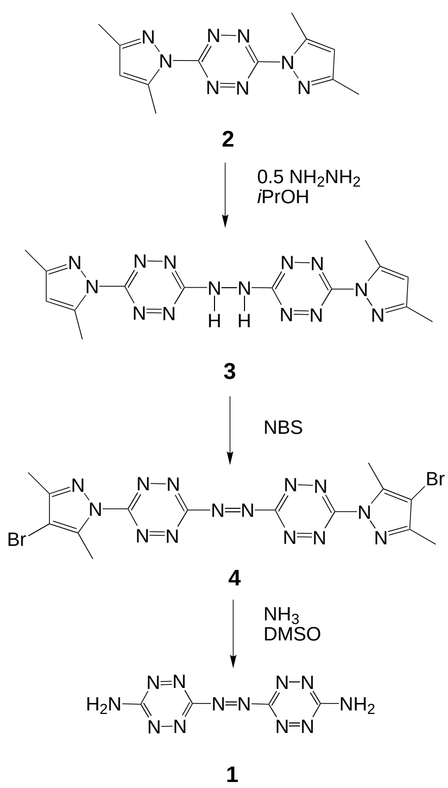

Scheme 3. Synthesis of **1**.

reaction mixture with 2-propanol, a red-brown precipitate was isolated.

According to NMR spectroscopy this material was the bis-DMSO solvate of **1**; however, elemental analysis was inconsistent with the proposed structure, as is typical of compounds high in nitrogen. An X-ray crystal structure analysis[6] of this material confirmed the structure to be the bis-DMSO solvate of **1** (Figure 1), thus providing the first evidence for the synthesis of an azo-1,2,4,5-tetrazine. A density of 1.526 $g cm^{-3}$ was determined from the X-ray crystal structure. The molecules are in an *E* configuration and form planar sheets despite the presence of DMSO molecules in the crystal. We believed that this graphite-like structure would lead to a high density of the neat material. Indeed, a gas pycnometry density of 1.84 $g cm^{-3}$ was determined for pure **1**, which is likely to be the most dense C,H,N molecule known.[7]

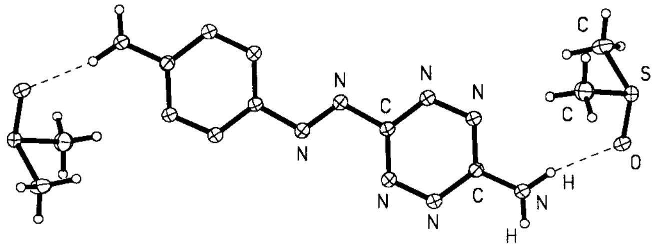

Figure 1. A drawing of one formula unit of the bis(DMSO) solvate of **1** (half of this is the asymmetric unit of the crystal, that is, the labeled atoms). There are strong linear hydrogen bonds linking every amino hydrogen atom with a neighboring DMSO; two are shown as dashed lines. Each DMSO oxygen atom also accepts two hydrogen bonds (not shown), thus linking molecules of **1** into long planar ribbons. Side-by-side ribbons are parallel and coplanar, so they form extended planar (average deviation 0.08 Å) sheets. The perpendicular distance between adjacent sheets is only 3.22 Å, which is even shorter than the interplanar spacing in graphite (3.4 Å).

The DMSO solvate was easily broken by treatment with boiling water to give pure **1**. The pure material is thermally stable to 252 °C (differential scanning calorimetry), and the heat of formation was measured to be +862 $kJ mol^{-1}$ by combustion calorimetry. This is a very high heat of formation and when normalized, a value of 43.1 kJ per atom is realized. Some sensitivity properties include a drop weight impact value of 70 cm (the value for the popular high-explosive HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) is 25 cm), despite the fact that there are no oxygen atoms in the molecule. The compound is insensitive to initiation by spark (>0.36 J) or friction (BAM, >36 kg).[8] We are currently evaluating the oxidation of **1** with oxygen transfer reagents.[9]

Experimental Section

3: To **2** (270.0 g, 1.0 mol) in 2-propanol (2 L) in a mechanically stirred 5-L, 3-necked flask was added anhydrous hydrazine (16.0 g, 0.5 mol) all at once with efficient stirring. The mixture was refluxed for 2 h and allowed to cool and stir overnight. The orange product was filtered and washed with 2-propanol to give 143.0 g of pure **3**. The mother liquor was allowed to stand for a few weeks and refiltered to provide an additional 7.3 g of product identical to the first crop (total yield 79%); m.p. 215–217 °C. IR (KBr): $\tilde{\nu} = 3194, 1575, 1490, 1415\ cm^{-1}$; ^1H NMR (270 MHz, $[D_6]$DMSO, 25 °C, TMS): $\delta = 2.21$ (s, 6H), 2.49 (s, 6H), 6.22 (s, 2H), 11.2 (brs, 2H); ^{13}C NMR (270 MHz, $[D_6]$DMSO, 25 °C, TMS): $\delta = 12.3$, 13.0, 109.5, 142.3, 151.3, 158.9, 162.7; elemental analysis calcd for $C_{14}H_{16}N_{14}$: C 44.21, H 4.24, N 51.55; found: C 43.95, H 4.40, N 51.39.

4: *N*-Bromosuccinimide (267.4 g, 1.5 mol) was dissolved in acetonitrile (2 L) in a 5-L, 3-necked flask equipped with a mechanical stirrer. Compound **3** (143.0 g, 0.38 mol) was added portionwise over 15 min, and the mixture was allowed to stir for 1 h. The purple precipitated product was filtered and washed with *tert*-butyl methyl ether and air-dried to yield 197.0 g of **4** (98%); m.p. 195–197 °C. IR (KBr): $\tilde{\nu} = 1501, 1450\ cm^{-1}$; ^1H NMR (270 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.44$ (s, 6H), 2.84 (s, 6H); ^{13}C NMR (270 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 13.0$, 14.4, 104.4, 142.2, 155.3, 159.3, 167.9; elemental analysis calcd for $C_{14}H_{12}N_{14}Br_2$: C 31.36, H 2.26, N 36.57; found: C 30.99, H 2.21, N 36.51.

1: Ammonia was bubbled rapidly through DMSO (1 L) in a 4-L beaker until 7.0 g (0.41 mol) were absorbed. To this was added **4** (110.4 g, 0.206 mol) with stirring within 1 min. The reaction mixture was allowed to stir for 15 min and then diluted with 2-propanol (1 L). The red solid was filtered, washed with 2-propanol, and air-dried to yield 34.3 g of **1** $\cdot$ 2DMSO (44%). This material was boiled in water (250 mL) for a few minutes to break the DMSO solvate, filtered, washed with water, and air-dried to give pure **1**; m.p. 252 °C (decomp.). IR (KBr): $\tilde{\nu} = 3372, 3283, 3194, 1629, 1506\ cm^{-1}$; ^1H NMR (270 MHz, $[D_7]$DMF, 25 °C, TMS): $\delta = 8.93$ (brs, 4H); ^{13}C NMR (270 MHz, $[D_7]$DMF, 25 °C, TMS): $\delta = 163.6$, 167.9; elemental analysis calcd for $C_4H_4N_{12}$: C 21.82, H 1.83, N 76.35; found: C 21.46, H 2.11, N 67.70.

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[6] Crystal data for **4** ($C_8H_{16}N_{12}O_2S_2$): $M_r = 376.45$, triclinic, space group $P\bar{1}$; $a = 5.3757(4)$, $b = 9.197(1)$, $c = 9.3683(8)$ Å, $\alpha = 67.564(7)$, $\beta = 75.634(7)$, $\gamma = 76.442(7)^\circ$, $V = 409.65(6)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.526$ mg mm^{-3}; 1392 data measured to $2\theta_{max} = 115^\circ$; $R = 0.0279$, $wR2 = 0.0745$ for all 1106 unique reflections. X-ray intensity data were measured on a Bruker diffractometer with $Cu_{K\alpha}$ radiation ($\lambda = 1.54178$ Å) at $T = 294$ K. The structure were solved with the aid of program XS, and refined with full-matrix least-squares program XL, from SHELXTL software (SHELXTL96 G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467). The XL program minimizes F^2 differences, and uses all data; that is, weak data are not considered "unobserved", and are included in the R factors reported. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-138299. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Synthesis of Prussian Blue Nanoparticles and Nanocrystal Superlattices in Reverse Microemulsions**

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Among known molecular magnets, Prussian blue (*catena*-[MFe^{III}{Fe^{II}(CN)$_6$}] (M = Li, Na, K, NH$_4$)) and related cyanometallate-based coordination polymers offer a range of compounds with unique versatility. The variety of structures and magnetic properties of this family of compounds has been extensively investigated,[1] and recently reviewed.[2] Although much work has focused on the relationship between the unit-cell structure and magnetic properties, relatively few attempts have been made towards understanding and controlling the growth mechanism of these magnetic coordination polymers. This is an important aspect in the study of molecular magnets because compounds with appropriate magnetic properties require further fabrication and processing if functional devices and materials are to be produced.

Recently, organic supramolecular templates and organized reaction media have been used for the construction of higher-order assembly of traditional inorganic solids, such as silica,[3] calcium carbonate,[4] and iron oxides.[5] These processes allow the control of properties such as particle size, particle shape, surface texture, and organization to be integrated directly into the synthesis method. It seems feasible that similar strategies could also be developed for the coupled synthesis and construction of both molecular materials and coordination polymers to produce complex functional materials that are organized beyond the length scale of the unit cell. As a first step towards this objective, we address the possibility of coupling the synthesis of Prussian blue crystals with its emergent properties such as size, shape, and higher-order assembly.

Periodically banded arrangements (Liesgang bands) have been produced previously for the precipitation of Prussian blue on perfluorinated membranes.[6] Similarly, a dissipative structure has been briefly reported.[7] More recently, the growth of Prussian blue under Langmuir monolayers[8] and in the interlayer spaces of lamellar vesicles has been described.[9] These studies have focused on the spatial confinement of Prussian blue rather than the colloidal and mesoscale properties of the constituent crystals. Herein, we show that by confining the synthesis to nanoscale water droplets formed in reverse microemulsions prepared from the anionic surfactant sodium bis(2-ethylhexyl)sulfosuccinate (AOT), hydrophobic Prussian blue nanoparticles with a uniform shape and size can be routinely prepared. A related material, [Cu$_2${Fe(CN)$_6$}], has been recently synthesized in microemulsion media, although the resulting nanoparticles were highly disorganized.[10] In our experiments, the growth of the nanoparticles within the restricted reaction field is controlled by a multistep process involving the slow photoreduction of $[Fe(C_2O_4)_3]^{3-}$ to produce Fe^{II} ions that subsequently react with $[Fe(CN)_6]^{3-}$ ions to generate nuclei and clusters of Prussian blue encapsulated within the water droplets. Growth of the molecular magnet occurs by further exchange and fusion between microemulsion droplets to produce nanoparticles encapsulated in a shell of surfactant molecules. Moreover, the highly hydrophobic surface properties of the Prussian blue nanoparticles enable the facile preparation of self assembled nanoparticle arrays with 2-D and 3-D superlattice ordering.

AOT reverse microemulsions containing 0.3 M ammonium iron(III) oxalate and 0.3 M ammonium ferricyanide aqueous nanodroplets at $w = 5-20$ ($w = [H_2O]/[AOT]$) were transparent yellow fluids that were stable in the dark at room temperature. Exposure of the microemulsions to daylight transformed them to a transparent blue solution in two days and no precipitate was observed for two weeks. UV/Vis absorption spectra showed a broad band at 680 nm consistent with the Prussian blue $\{Fe^{III}[(t_{2g})^3(e_g)^2]Fe^{II}[(t_{2g})^6]\} \rightarrow \{Fe^{II}[(t_{2g})^4(e_g)^2]Fe^{III}[(t_{2g})^5]\}^*$ electronic transition.[11] FT-IR spectra contained a major band at 2069 cm^{-1} that corresponds to the Fe–CN stretching mode in the cyanometallate lattice.

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