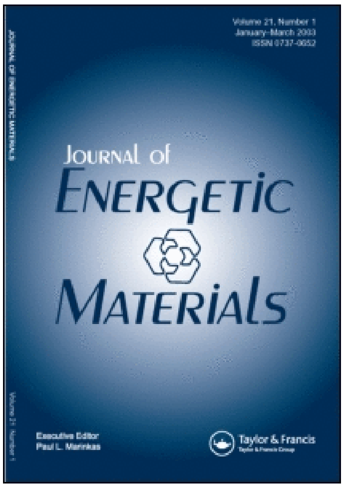

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Crystal Structure of the 1:1 Adduct of Hexanitrostilbene and Dioxan

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The single-crystal structure of the 1:1 HNS-dioxan adduct has been determined. The HNS and dioxan molecules form zigzag chains, which then stack to form sheets. The removal of the dioxan by heating results in the formation of crystalline, desolvated HNS, while the reintroduction of vapor-phase dioxan restores the original HNS-dioxan structure.

Keywords: HNS, crystal structure

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Introduction

Finely divided hexanitrostilbene, commonly known as HNS IV, may be prepared by crash precipitation of a solution of HNS in an organic solvent for example, DMF (N,N-dimethylformamide) or NMP (N-methylpyrrolidin-2-one), in water. It normally has a specific surface area (SSA) of 15–30 m^2g^{-1}. HNS IV that has been prepared by this method usually contains 0.5–1.5 wt% of the original solvent [1, 2], and this cannot be removed by washing with water. Since HNS IV may be required for incorporation into a slapper detonator system, it is deemed necessary to remove this occluded solvent. Harris et al. [1] have described a method for removing this solvent, which involves washing the HNS IV with dioxan in methanol, but although this does remove the occluded DMF or NMP, it also causes a dramatic change in particle shape and size, accompanied by a reduction in SSA. Furthermore, unless the material is further washed with pure methanol, the product contains a considerable amount of dioxan.

We have reported recently [3] that the product formed by the methanol:dioxan wash is, in fact, a 1:1 adduct of HNS and dioxan, with a different crystal structure to that of the HNS IV before washing. The crystal structure of this adduct now has been determined.

Results and Discussion

Crystal Structure of the 1:1 HNS-Dioxan Adduct

The crystal structure of HNS-dioxan is depicted in Figure 1. The asymmetric unit (unprimed labeled atoms) is equivalent to 1/2 molecule of HNS plus 1/2 molecule of dioxan. Both fragments are proximate to crystallographic inversion centers. Analysis of metric data reveals the presence of an interaction between a lone pair on the dioxan oxygen O(7) and the hydrogen atom attached to C(4) of the trinitrophenyl ring [H(4)… O(7) 2.35 Å]. Thus, dioxan and HNS molecules alternate in the gross structure to form chains. In addition, there is evidence for the presence of a potentially important interaction between the second lone pair on O(7) and the center of a phenyl ring in

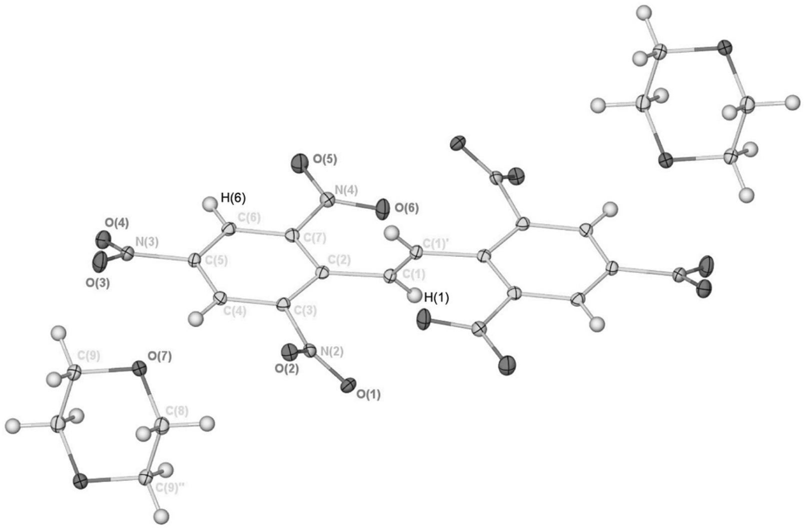

Figure 1. HNS-dioxan adduct.

an adjacent chain. In particular, the O(7) distance to the mean plane of the most proximate phenyl ring is 3.17 Å. The dimensions and shape of the HNS molecules in the adduct are very similar to those in HNS itself [4], but in the latter there are two crystallographically independent HNS molecules.

The packing arrangement in the supramolecular structure of the solvated adduct is shown in Figure 2, revealing that chains of HNS and dioxan molecules form sheets, which in turn are stacked to form the supramolecular array, wherein all HNS units are parallel. This contrasts with the molecular arrangement in the previously reported [4] structure of HNS, wherein similar parallel packing of the molecules occurs within the two-dimensional sheet structure, but the sheets themselves are angled relative to each other, rendering a ‘‘herringbone pattern’’ in the gross structure (Figure 3).

Reversible Removal of Dioxan from the Adduct

We have reported [3] that heating the HNS-dioxan adduct above the boiling point of dioxan serves to eliminate the

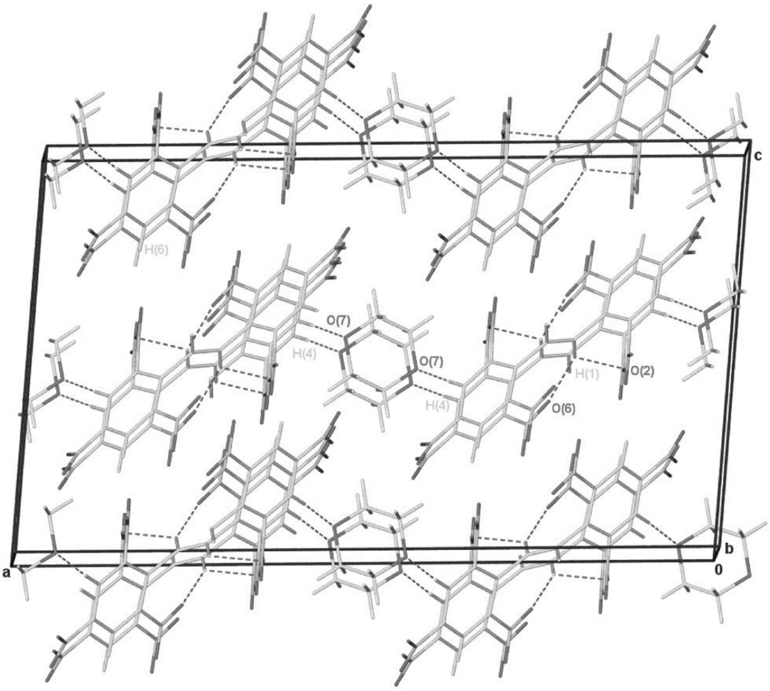

Figure 2. HNS-dioxan adduct.

dioxan and concomitantly results in the formation of microcrystalline HNS, bearing a similar crystal morphology (by powder X-ray diffraction [XRD]: see Figure 4 (a)) and (b) to that of unsolvated HNS, in addition to retaining the needle shape of the crystals (see Figure 5). We have now shown that exposure of this desolvated material to dioxan vapor results in the uptake of one equivalent of dioxan (as evidenced by mass increase, mass loss on thermogravimetric (TG) analysis, and ^{1}H NMR spectroscopy) to reform the HNS-dioxan adduct (indicated by Fourier transform infrared [FTIR] spectroscopy and powder XRD; see Figure 4 (c)). For comparison, the XRD powder plots for the HNS-dioxan adduct and HNS itself, simulated from the single-crystal XRD data, are shown in Figure 6. The reversible loss and restoration of dioxan from this material must involve considerable realignment within the

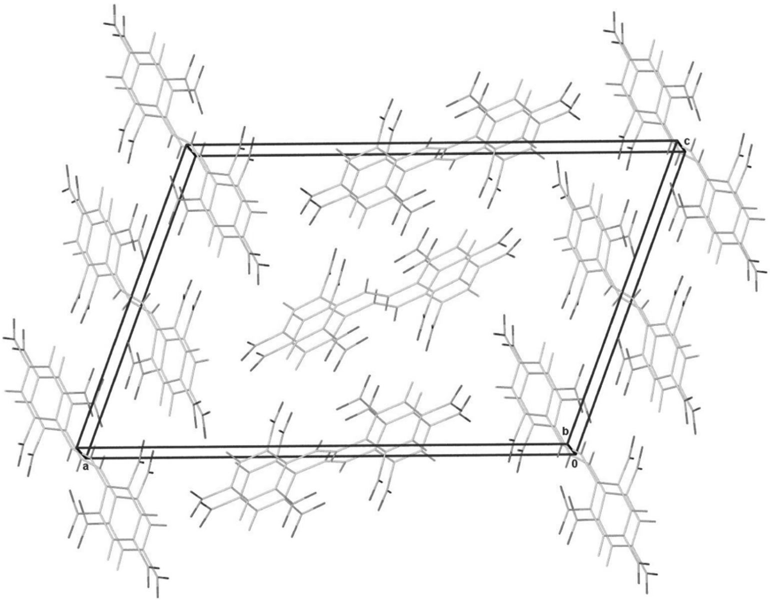

Figure 3. HNS.

structure to accommodate the ‘‘herringbone pattern’’ present in the HNS structure.

Experimental

HNS II (1.39 g) was dissolved in NMP (60 ml) and filtered through a sintered glass funnel (grade 3). The solution was then injected with rapid stirring into distilled water (270 ml) over a period of 1 hr. Saturated, aqueous aluminium nitrate solution (8 drops) was added to the suspension to coagulate the product, and the mixture was allowed to settle for 90 minutes. After decanting off the clear liquid, the remaining suspension was filtered through two layers of Whatman No. 42 filter paper and washed with distilled water (4 × 30 ml). This was then immediately rinsed through with methanol:-dioxan (4:1 by volume, 4 × 20 ml). After drying in a vacuum desiccator the yield was 1.34 g. It contained 0.01 wt% NMP

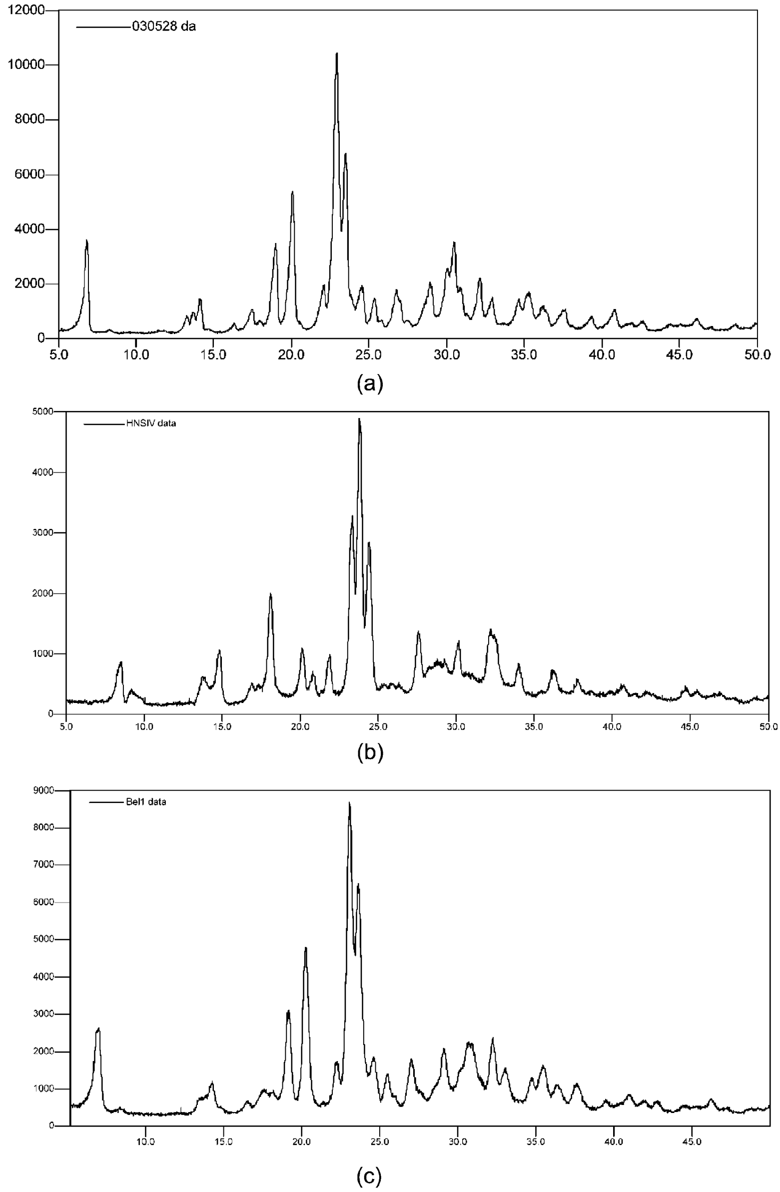

Figure 4. XRD powder plots of (a) HNS-dioxan adduct, (b) adduct after removal of dioxan by heating, (c) product from exposure of (b) to dioxan vapor.

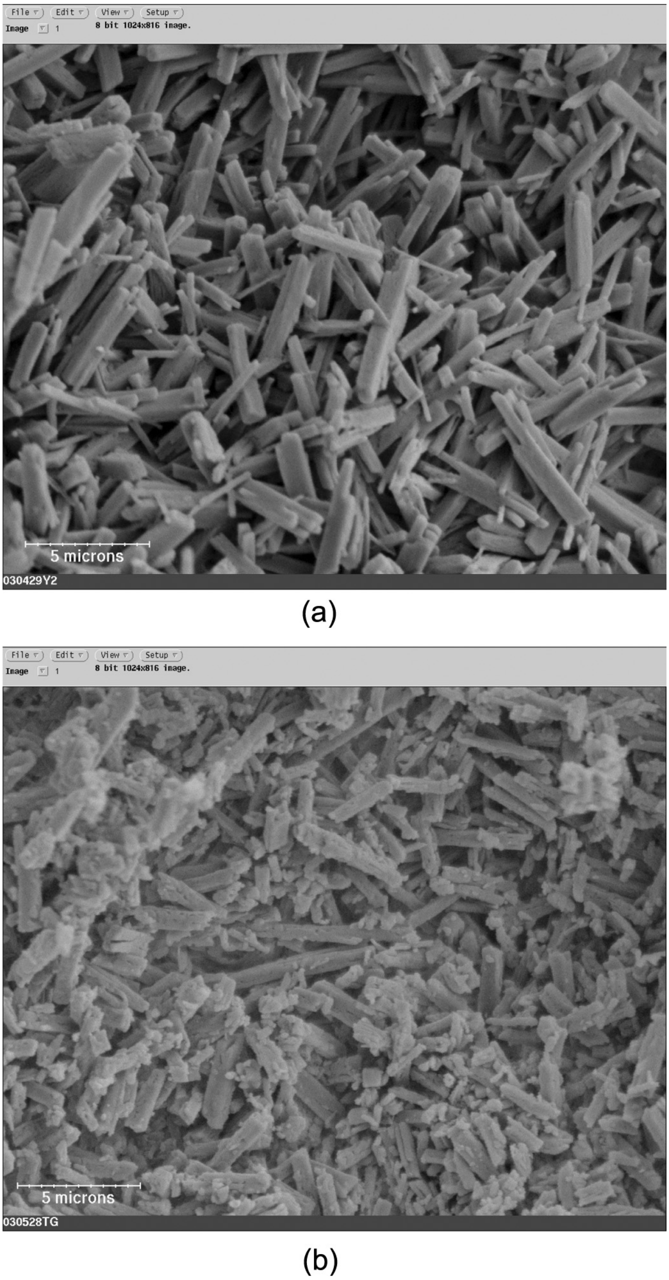

Figure 5. SEM pictures of (a) HNS-dioxan adduct, (b) adduct after removal of dioxan by heating.

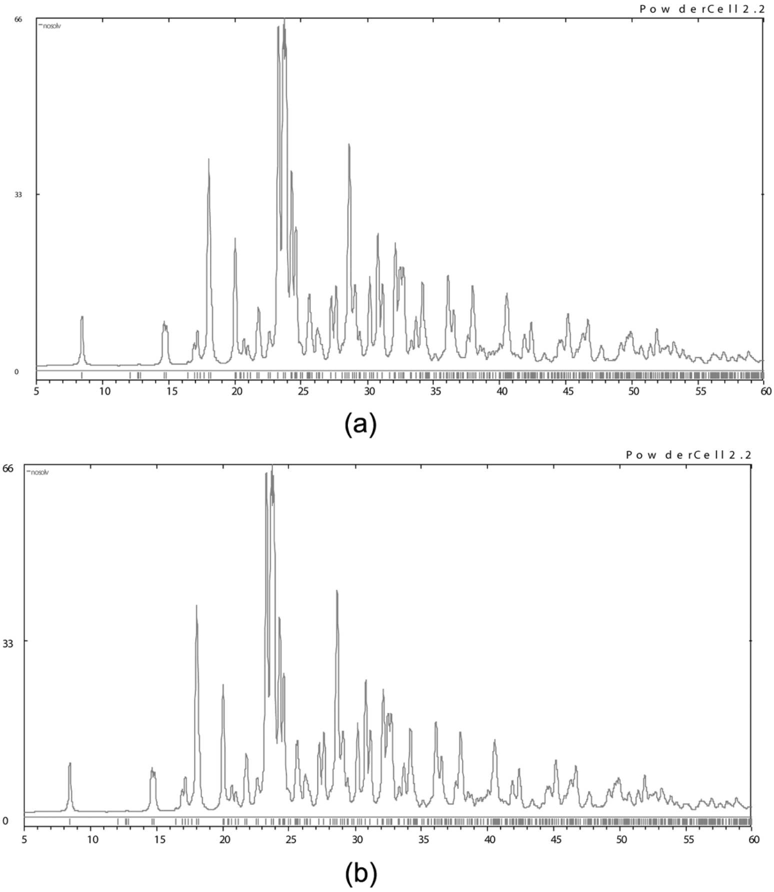

Figure 6. Simulated XRD powder plots from single-crystal data: (a) HNS-dioxan adduct, (b) HNS.

(by ^{1}H NMR). The product was shown to be a 1:1 adduct of HNS and dioxan by ^{1}H NMR spectroscopy, differential scanning calorimetry, TG, FTIR spectroscopy, and powder XRD [3].

Crystals of the adduct for structure determination were grown by slowly adding (by syringe pump during 24 hr) an equal volume of dioxan to a saturated solution of HNS II in NMP (10 ml), and then leaving the resultant suspension for several days. Rapid mixing gave an homogeneous solution before crystals began to separate, and the resultant crystals were always manifested as very fine needles.

Warning. HNS and HNS-dioxan are potentially explosive and should be treated with appropriate precautions.

Crystallography

Crystal data for HNS-dioxan: $C_{18}H_{14}N_6O_{14}$, $M = 538.35$, colorless, tabloid, $0.30 \times 0.15 \times 0.08\,\mathrm{mm}^3$, monoclinic, space group C2/c (No. 15), $a = 25.5400(1)$, $b = 5.5070(2)$, $c = 14.8570(3)$ Å, $\beta = 95.0380(10)^\circ$, $V = 2081.55(9)$ Å^3, $Z = 4$, $Dc = 1.718\mathrm{g/cm}^3$, $F000 = 1104$, MoK radiation, $\lambda = 0.71073$ Å, $T = 150(2)$ K, $2\theta\mathrm{max} = 55.1^\circ$, 17,483 reflections collected, 2382 unique ($\mathrm{Rint} = 0.0408$). Goodness of $\mathrm{fit} = 1.059$, $R1 = 0.0354$, $wR2 = 0.0927$ (R indices based on 1953 reflections with $I > 2\sigma(I)$ (refinement on $F2$)), 176 parameters, 1 restraint, $\mu = 0.151\,\mathrm{mm}^{-1}$.

CCDC 246308 contains the supplementary crystallographic data for HNS-dioxan. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-366033; deposit@ccdc.cam.ac.uk.

Acknowledgments

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