

Synthesis and Crystal Structure of Triacetyltribenzyl-Hexaazaisowurtzitane (TATBIW · 0.5 H₂O)

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Abstract: The compound of tetraacetyldibenzylhexaazaisowurtzitane (TADBIW) is an important precursor of synthesizing the high energetic dense compound of hexanitrohexaazaisowurtzitane (HNIW). We can obtain TADBIW by using hydrogenolysis of hexabenzylhexaazaisowurtzitane (HBIW). In the process of hydrogenolysis of HBIW, it will generate a variety of intermediates, one of them is the compound of triacetyltribenzylhexaazaisowurtzitane (TATBIW). We have synthesized the title compound and prepared its single crystal. In the paper, the crystal and molecular structure of TATBIW·0.5H₂O is described. Its crystal belongs to the triclinic and space group P-1. The cell is comprised of two TATBIW and one water molecules. The success of synthesizing TATBIW can help us to research the mechanism of the reduction of HBIW and produce high yields of the end products.

Keywords: Triacetyltribenzylhexaazaisowurtzitane, synthesis, crystal structure.

The hexanitro hexaaza isowurtzitane (HNIW) (2, 4, 6, 8, 10, 12-hexanitro-2, 4, 6, 8, 10, 12-hexaazatetracyclo-[5.5.0.05,9.03,11]-dodecane), more commonly called CL-20, belongs to the family of high energetic dense caged nitramines. It was first synthesized by A.T.Nielsen in 1987¹. HNIW is superior to HMX with respect to density, velocity, detonation pressure and enthalpy of formation. Based on cylinder expansion and tantalum plate acceleration experiments, the HNIW was found to be approximately 14% greater than HMX. The success on synthesizing the polycyclic nitramine explosive HNIW has attracted considerable interest in the area of explosive chemistry. The synthesis of HNIW is generally known by using three-step process, consisting of (1) creation of the basic cage structure in the form of the hexabenzylhexaazaisowurtzitane (HBIW), (2) debenylation of HBIW, (3) nitration to give HNIW². Debenylation of HBIW is an important step in the synthesis of HNIW. At present, we often use reductive hydrogenolysis method to debenzylate HBIW^{3,4}. In the process of reductive acetyldebenylation of HBIW, it would occur in a stepwise manner generating a variety of intermediate polyacetyl polybenzyl derivatives. If we can obtain the intermediates of the reaction, it would help us to research the mechanism of the reduction of HBIW.

The authors have been successful on synthesizing the title compound which should be the intermediate of reductive acetyldebenylation. TATBIW · 0.5 H₂O crystal structure

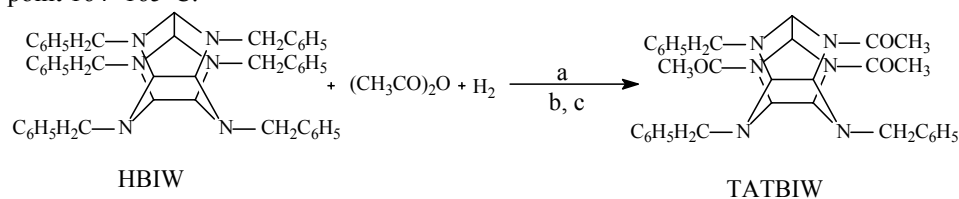
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was measured by X-ray diffraction technique.

Experimental

The synthesis of TATBIW

The reaction was run using 50 g of HBIW, 100 mL of DMF, 100 mL of acetic anhydride, 1.5 mL of bromobenzene and 885 mg Pearlman's catalyst (dry weight of catalyst was 350 mg). The vessel was purged three times with hydrogen, the temperature of the reaction was 19°C, and then the reaction mixture was stirred. Over the next two hours, approximately 70% of hydrogen (based on the theoretic consuming hydrogen if HBIW converted completely to the end product of TADBIW) was consumed and the reaction temperature rose from 19°C to 25°C. The reaction was ceased, the catalyst was filtrated off and the solution was concentrated by rotary evaporation. White solid was obtained by washing with ethanol and air dried to afford 22 g (55%) of TATBIW. The crude product was purified by recrystallization from acetonitrile to give pure product with a melting point 164~165°C.



- a) Pearlman's catalyst
 b) PhBr
 c) DMF

The preparation of crystal

Dissolve the purified TATBIW in an acetonitrile-water mixture and evaporate slowly the solvent at room temperature to obtain a colorless transparent single crystal of TATBIW · 0.5 H₂O.

Structure Determination and Result

The data of the crystal of TATBIW · 0.5 H₂O were collected at room temperature on a Rigaku RAXID RAPID IP diffractometer with MoK (λ=0.071073 nm) radiation. The crystal is triclinic system and P-1 space group with unit cell dimensions a=0.9893(2) nm, b=1.2624(3) nm, c=1.3396(3) nm, α=97.17(3)°, β=97.26(3)°, γ=104.18(3)°, v=1.5963(6) nm³, Z=2, D_c=1.194 g·cm³. The final R1=0.0591, wR2=0.1777 for 6139 unique reflections. The crystal structure was solved by direct method and subsequent Fourier differential techniques and refined by full-matrix least square using the SHELXL-97 program. All non-hydrogen atoms were located theoretically and refined with anisotropic thermal parameters. All hydrogen atoms were located theoretically and refined with riding mode position parameters and fixed isotropic thermal parameters. The final cyclic

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of full-matrix least square refinement was converged with $\omega = 1/[\sigma^2(F_o2) + (0.0472P)^2 + 0.0000P]$, where $P = (F_o2 + 2F_c2)/3$. The maximum and minimum residual peaks on the final difference Fourier map amount to 0.270 and -0.140 eÅ⁻³, respectively.

In TATBIW there are two types of C atoms with sp^3 and sp^2 hybrid status (marked with C_{sp^3} and C_{sp^2} respectively) and some differences existed among the lengths of C sp^3 -N bonds (0.1446~0.1474 nm) and the lengths of C sp^2 -N bonds (0.1345~0.1362 nm). The bond length of N (3) -C (27) is 0.1502 nm, the bond length of N (1) -C (13) and N (2) -C (20) are 0.1455 nm and 0.1473 nm respectively. This means that the N (3) -C (27) bond is the weakest in the cage. If we continue to acetyldebenzylate TATBIW, the N-benzyl group in the five-membered ring is superior to be substituted by acetyl group. This is proved by experiment.

The molecular structure and packing diagram are shown in **Figure 1** and **Figure 2** respectively. It can be seen that TATBIW is a caged polycyclic molecule composed of one six-membered ring and two five-membered rings. Three of the acetyl groups are all located in the two five-membered rings. The single bond length of C (5) and C (6) which connects two five-membered rings is 0.1600 nm. The cell is comprised of two TATBIW and one water molecules. In the packing of the unit cell, the two waters are connected with hydrogen bonds.

Figure 1 The molecule structure of TATBIW

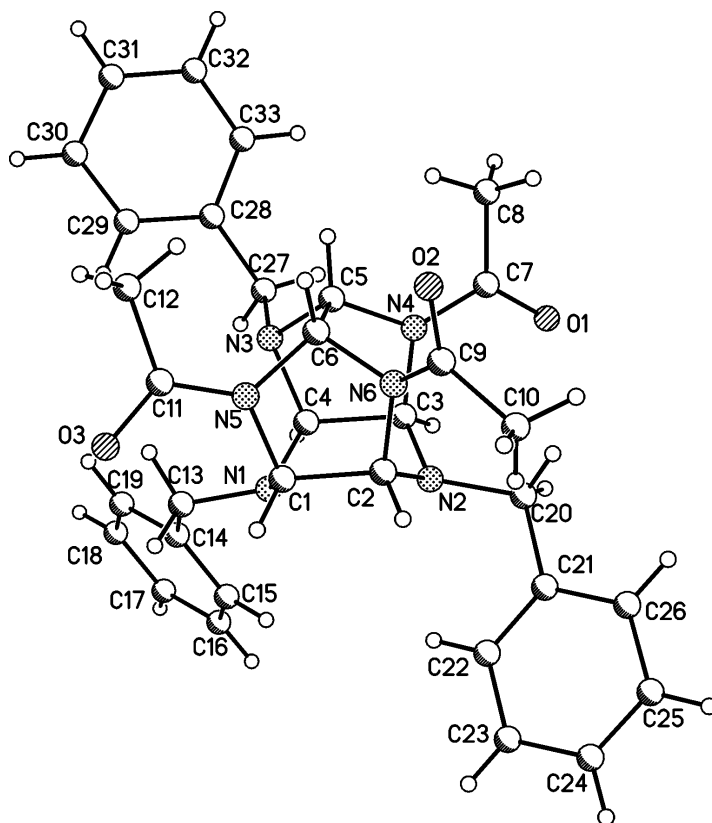
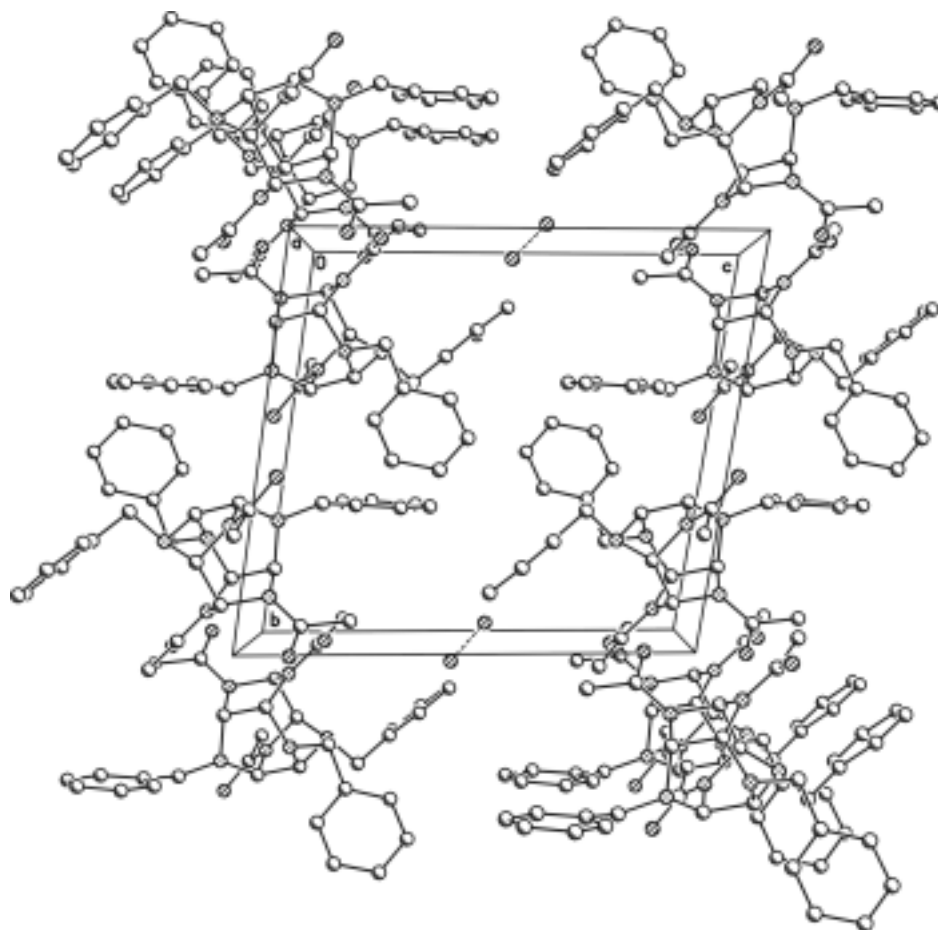


Figure 2 The packing of the unite cell**References**

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