Journal of Molecular Structure 1110 (2016) 91–96

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Crystal structure, spectrum character and explosive property of a new cocrystal CL-20/DNT

Ke Liu, Gao Zhang*, Jieyu Luan, Zhiqun Chen, Pengfei Su, Yuanjie Shu

Xi'an Modern Chemistry Research Institute, Xi'an 710065, China

ARTICLE INFO

Article history:
Received 4 November 2015
Received in revised form
27 November 2015
Accepted 13 January 2016
Available online 15 January 2016

Keywords:
Cocrystal
CL-20
Energetic material
Crystal structure
Characterization

ABSTRACT

A new cocrystal explosive of 2,4,6,8,10,12-hexanitrohexaazaiso-wurtzitane(CL-20) and 2,5-dinitrotoluene(DNT) in a molar ratio of 1:2 has been prepared by slow solvent evaporation method. Crystal structure of the cocrystal characterized by single crystal X-ray diffraction (SXRD) reveals that the cocrystal is formed by intermolecular hydrogen bond interactions and belongs to the triclinic system with P^{-1} group. Moreover, the obivious differences of powder X-ray diffraction (PXRD) patterns, infrared spectroscopy and Raman spectroscopy confirm that the intermolecular interactions have great influence for the crystal structure and formation of cocrystal. The cocrystal exhibits a lower impact height of 44 cm, suggesting a substantial reduction of sensitivity in comparison with CL-20. And thermal test results showed cocrystal obtains a lower melting point than DNT, which means huge advantages in blasting engineering.

1. Introduction

Energetic materials (explosives, propellants and pyrotechnics) are normally defined as a class of compounds storing vast amount of chemical energy [1], which will be released under some stimuluses like impact, shock or thermal effects [2,3,4]. Even though energetic materials have been widely studied and applied in civilian and military field [5], the contradiction between safety and power always exists. So it is particularly crucial for energetic materials to find the fine balance between high detonation performance and low sensitivity especially under the modern battlefield environment. Although researches on new explosive molecules are always carring on, the modification of existing materials still offers great opportunities to enhance the complex properties with less cost and fewer efforts. Various methods such as creating polymer bonded explosives(PBXs) [6] and recrystallizing from solvents have been adopted to solve the contradiction and modify the properties of energetic materials. Cocrystallization is to combine two or more kinds of molecules in one crystal lattice by intermolecular weak interactions such as hydrogen bonds [7], π−π stacking, ionic bonds and van der Waals forces, which has been widely used as a modification method in pharmaceutical chemicals for the improvement in solubility and stability than crystals of pristine compounds [8,9,10]. Therefore cocrystallisation would potentially provide a way to achieve the combination of high energy and low sensitivity on the molecular level [11,12].

2,4,6,8,10,12-hexanitrohexaazaisowurtzitane(HNIW), also known as CL-20, is the most powerful commercially available explosive for practical application at present [13,14]. It exhibits a better oxygen balance than other explosives which have been widely used such as RDX and HMX. While its high impact sensitivity and production cost distinctly limit the widely industrial application [15]. [16] Cocrystallization of CL-20 and other insensitive explosives have been researched in order to improve the security and comprehensive properties of CL-20, and series of cocrystals based on CL-20 to lower the sensitivity have been synthesized [17,18,19]. However, the formation of CL-20 cocrystals are hard to be predicted and normally difficult to be obtained for the lack of strong predictable interactions in the chemical structures of the components. So the preparation and characterization of some new CL-20 cocrystal will help the research of mechanism and subsequence of cocrystal design. The compound 2,5-dinitrotoluene (DNT) is a kind of less sensitive and inexpensive energetic material which is normally applied as organic chemistry intermediate and the substitute for TNT. In comparison with other similar reported cocrystals, we presents a new cocrystal of CL-20 with higher ratio of insensitive explosive addition (1:2). The crystal structure was determined by single crystal X-ray diffraction (SXRD). And the

* Corresponding author.
E-mail address: zgg1965@163.com (G. Zhang).

http://dx.doi.org/10.1016/j.molstruc.2016.01.027
0022-2860/

intermolecular interactions of hydrogen bonding between CL-20 and DNT molecules in the cocrystal were investigated and confirmed by infrared and Raman spectroscopy.

2. Experimental

2.1. Materials

Powdered ε −CL-20 and 2,5-DNT was obtained from Xi'an Modern Chemistry Research Institute. Ethyl acetate was reagent grade and obtained from Guangdong Guanghua Chemical Reagent Chemical Technology Company.

2.2. Preparation method

A molar ratio of 1:2 mixture of CL-20 (438 mg) and DNT (182 mg) was put into about 10 mL ethyl acetate at room temperature, then stir the solution with a magnetical strring machine. The glass vial filled with the solution was covered with a piece of Parafilm with a few holes to control the evaporation rate. After about 3 days evaporation the new cocrystal of CL-20/DNT was formed.

2.3. Optical microscopy

Optical micrographs of the CL-20/DNT cocrystals were taken under the ZEZSS 2000-C optical microscope.

2.4. X-ray diffraction

Powder X-ray diffraction patterns were collected with a EMPYREAN, Cu-Kα radiation (λ = 0.15405 nm). The voltage and current applied were 40 kV and 40Ma, respectively. And the data were collected over the range from 5° to 90°.

The single crystal X-ray diffraction data was collected with a Bruker SMART APEX CCD II detector (graphite-monochromated, Mo-Kα radiation). During the data collection the temperature was kept at 296 K. 14,718 diffraction data were collected and 5032 were unique with the R(int) = 0.0148 in the theta range of 1.68°−24.55°. The cocrystal structure was solved by direct method of SHELXS, structure solution program using direct method and refined with SHELXL.

2.5. Infrared spectroscopy

The infrared spectra was obtained by Fourier transform techniques with a NEXUS B70 spectrometer with KBr pellets. Each spectrum was scanned in the range of 400−4000 cm^{-1}, and the resolution ratio is 4 cm^{-1}.

2.6. Raman spectroscopy

The Raman spectroscopy was carried out with a RENISHAW inVia Raman instrument, and the excitation source is a 785 nm laser with about 250 mW power. The spectra resolution of the Raman system is 1 cm^{-1}.

2.7. Differential scanning calorimetery (DSC)

Differential scanning calorimetery (DSC) was carried out with a NETZSCH5 instrument. The sample (0.62 mg) was heated from room temperature to 400 °C at a heating rate of 10 K/min in a nitrogen steam. The tests were conducted under the pressure of 3 GPa for that the DNT sample is easy to sublimate, and to confirm the coherence of tests, the cocrystal sample and CL-20 sample were under the same test condition.

2.8. Impact sensitivity test

The impact sensitivity was conducted according to the GJB772A-97standard method 601.2 [20]. The test conditions are: drop weight, 5 kg; sample mass, 50 mg; trial quantity, 20. For the varing of the impact energy in each trial, the ultimate impact energy is determined statistically with 50% probability of ignition.

3. Results and discussion

3.1. Morphology

The crystal morphology of CL-20, DNT and CL-20/DNT cocrystal explosive is shown in Fig. 1. The cocrystal was light yellow prisms with integrated crystal surfaces. It can be easily distinguished from single component of CL-20(colorless fusiform crystal) and DNT (yellow needle shape crystal) for the cocrystal's unique shape and the light yellow color.

3.2. Powder X-ray diffraction

The powder X-ray diffraction patterns of the cocrystal and coformers are shown in Fig. 2. As illustrated in Fig. 2, there are obvious differences among these powder X-ray diffraction patterns. Some main peaks like 9.1° in pure DNT and 30.3° in pure CL-20 disappeared in the new cocrystal diffraction pattern. While a new sharp peak in 25.9° appeared in the cocrystal diffraction pattern. And these differences of PXRD patterns can indicate that the cocrystal is a totally new non-solvated crystalline phase rather than the crystal transformation product.

3.3. Single crystal X-ray diffraction

According to the data collected by single crystal XRD, the crystallographic data of the cocrystal have been deposited with the Cambridge Crystallographic Data (CCDC) with the depository number of 1409272. The crystal structure of CL-20/DNT cocrystal was identified by single crystal X-ray diffraction and the crystallographic data of cocrystal are presented in Table 1. Selected bond lengths and bond angles of the cocrystal have been listed in Table 2. It confirms that the CL-20/DNT cocrystal belongs to triclinic system with P^{-1} group and the cell parameters a = 0.8145(2) nm, b = 1.3612(4) nm, c = 1.5415(4) nm and α = 114.692°, β = 98.584°, γ = 93.619°. From Fig. 3 it can be seen that the cocrystal asymmetric unit consists of one CL-20 molecule and two DNT molecules. As shown in Fig. 4, the formation of CL-20/DNT cocrystal mainly contributes to these intermolecular interactions which bring different kinds of molecules together rather than crystallize separately. In the cocrystal structure, the intermolecular hydrogen bond interactions between nitro groups and methyl groups are the main drive forces of the formation of cocrystal, and the hydrogen bond distances and angles data in the cocrystal have been listed in Table 3. The hydrogen bond interactions found in the CL-20/DNT cocrystal mainly includes two types of interactions: (1) The hydrogen bonding between one H atom from the CL-20 molecular ring and one oxygen atom from the nitro group of DNT, such as the hydrogen bond of C(15)−H(15) … O(1), C(16)−H(16) … O(4) and C(19)−H(19) … O(8); (2) The hydrogen bonding between the H atom from methyl group in DNT molecule and the oxygen atom from the nitro group of CL-20, such as the intermolecular hydrogen bonding interactions of C(1)−H(1A) … O(19) and C(8)−H(8B) … O(9), the two interactions are the main interactions connecting CL-20 and DNT molecules, which have bond distances of 2.60 Å, 2.72 Å, and bond angles of 120°,144°. In the cocrystal the two kinds of components build a network molecular structure by hydrogen