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Taming CL-20 through hydrogen bond interaction with nitromethane†

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A novel cocrystal explosive comprising CL-20/nitromethane in a 1 : 2 molar ratio was synthesised. Because of the CL-20 molecules were in ε conformation in the cocrystal, they possessed high crystal densities of 1.861 g cm^{-3} at 153 K and 1.821 g cm^{-3} at room temperature. Owing to the strong hydrogen bond interaction between the molecules, the decomposition temperature of the cocrystal was found to be 253 °C, which demonstrated excellent thermal stability among the cocrystals of CL-20. In addition, this cocrystal possessed exceptional sensitivities and comparable detonation properties.

Energetic materials are significant for human development.[1–4] 2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW, also known as CL-20) is a promising energetic material that possesses high density, good oxygen balance, and high explosive power. However, CL-20 is also too sensitive to limit the extensive applications in military products.[5,6]

To modify CL-20, a number of methods have been attempted in recent years, such as preparing nanoscale explosive particles,[7,8] using crystal surface modification,[9] or using the cocrystallisation method.[10–15] Among these methods, cocrystallisation is an interesting approach. In recent years, a larger amount of cocrystals containing CL-20 have been synthesised, such as CL-20/TNT cocrystal,[5] CL-20/HMX cocrystal,[16] and CL-20/TATB cocrystal.[17] To reduce the sensitivity of CL-20 without sacrificing the performance, the conformer of CL-20 in cocrystals should have higher power and lower sensitivity. As a high-energy liquid, nitromethane has moderate energy and good stability. Therefore, nitromethane is an excellent partner for CL-20 in the formation of a high-energy cocrystal. Next, we synthesized a novel cocrystal composed of ε-CL-20 and nitromethane in a molar ratio of 1 : 2 (Fig. 1). Unexpectedly, we found that the CL-20 molecules adopted a ε conformation in the cocrystal, which has not been extensively reported so far.[18,19] Currently, we report that the cocrystals composed of CL-20 molecules in the ε conformation had higher densities. As this conformation of CL-20 molecules has a higher packing coefficient, the density can be increased, and this aspect has great significance.

Cocrystal CL-20/nitromethane was formed from mixed nitromethane solutions by slow evaporation at room temperature. Various methods had been used to characterise the structure and performance of CL-20/nitromethane. In addition, Hirshfeld surface analysis was used to analyse the intermolecular interactions between CL-20 and nitromethane.

The optical micrographs of CL-20/nitromethane cocrystals were obtained on an OLYMPUS BX43 optical microscope. Differential scanning calorimetry (DSC) was conducted on a TA-DSC Q2000 thermal analyzer. Powder X-ray diffraction (PXRD) patterns were obtained on a Bruker D2 Advance diffractometer with a Cu Kα radiation. The impact and friction sensitivity of the cocrystal were measured *via* a BAM fall hammer technique and an FSKM-10 BAM friction apparatus. The detonation properties were calculated by utilizing the EXPLO5 (v 6.02) programme.

This cocrystal formed was a colourless and transparent solid, which had a hexagon-like morphology (Fig. 2a). ε-CL-20 is a spindle-shaped crystal (Fig. 2b). From their differences in the crystalline shape, we can preliminarily determine the

Fig. 1 The cell unit of CL-20/nitromethane cocrystal with each atom labelled.

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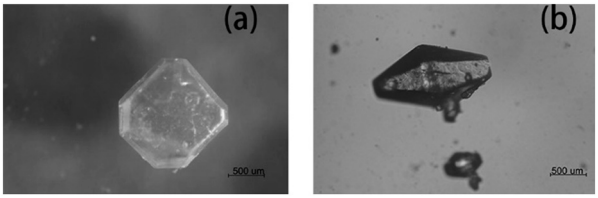

Fig. 2 Microscopic images of CL-20/nitromethane cocrystal (a) and ε-CL-20 (b).

cocrystal. The crystalline structure of this cocrystal was examined *via* single-crystal X-ray diffraction, and it was further distinguished from CL-20 *via* power infrared spectroscopy, X-ray diffraction, and DSC.

PXRD can be used to distinguish the CL-20/nitromethane cocrystal structure from the structures of CL-20 and nitromethane. Based on these PXRD patterns, there are evident differences. Some characteristic peaks of the cocrystal studied are localised at 8.56°, 9.95°, 12.13°, and 15.76°. In the 2θ range of 10–20°, some of the peaks of CL-20 disappeared at 13.80° and 16.38°. Therefore, this evidence implies that this cocrystal is a completely new material.

According to the SC-XRD analysis, the cocrystal belonged to the monoclinic system with the space group $P2_1/c$, and the cell parameters were as follows: a = 8.9053(18) Å, b = 12.585(3) Å, c = 17.847(4) Å, α = 90°, β = 90.73(3)°, and γ = 90°. The asymmetric unit possessed a formula weight of 560.32, consisting of one CL-20 molecule and two nitromethane molecules. The crystalline system had a sandwich stacking packing style[20] (Fig. 3a and b). In the crystalline system, the CL-20 molecules and nitromethane molecules were arranged in layers; the nitromethane molecules were regularly distributed in the layer of CL-20. According to Fig. 3b, the CL-20 molecules wrapped around the nitromethane molecules through the hydrogen bond interaction. The stacking method was conducive to improve the stability and lower the sensitivity by slipping between layers. The CL-20 molecule is in the ε conformation, which has been previously reported in the literature only twice as a eutectic system (Fig. 4a). According to the image of the hydrogen bonds utilised by the cocrystal (Fig. 4b), there are two main intermolecular interactions, which ranged from 2.442 Å to 2.936 Å. One is the nitro group of nitromethane molecules and the C–H group of CL-20 molecules, and the other is the nitro group of CL-20

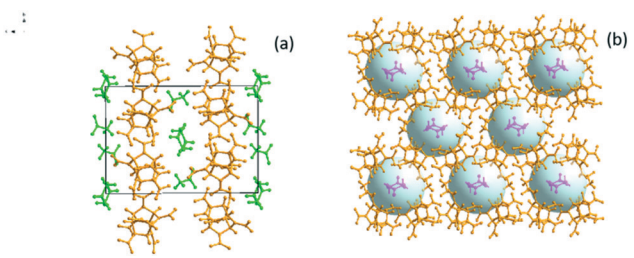

Fig. 3 CL-20/nitromethane cocrystal's sandwich stacking packing style (a) and molecular package diagram (b).

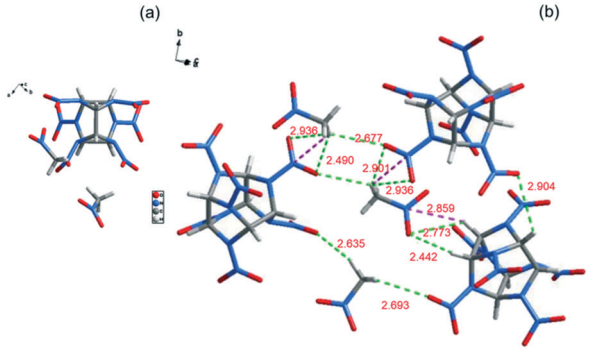

Fig. 4 ε conformation of CL-20 in the cocrystal (a) and hydrogen bond distribution of cocrystal (b).

and the CH_3 group of nitromethane molecules. The layering of the crystal structure is an important structural feature of the known insensitive high-energy materials that were widely used in the rational design of new energy-efficient materials.[21] Notably, the crystal structure can evident that this cocrystal is an insensitive material. The hydrogen bond length of the cocrystal is shown, and the ESI† is displayed, as noted in Fig. S4.

The Hirshfeld surface analysis is an effective method to further research the crystal packing in the cocrystal.[22–24] In this study, the 2D fingerprinting of the crystal and the associated Hirshfeld surface were obtained using the Crystal Explorer software. As shown in Fig. 5, the main contribution to the intermolecular interactions in the cocrystal is from the O···H, O···N and O···O contacts. The O···H contact accounts for more than 50% of the cocrystal, indicating that hydrogen-bonding interactions are the major driving forces in the

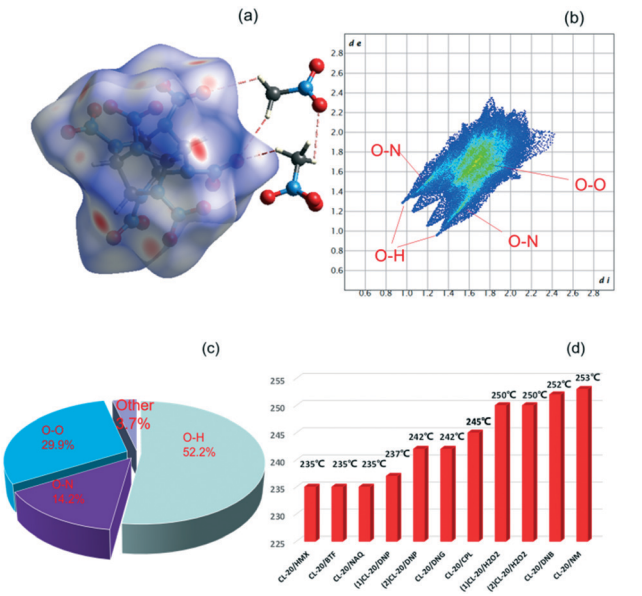

Fig. 5 Hirshfeld surface (a), two-dimensional fingerprint plot (b), intermolecular hydrogen bond (c), and comparison of different cocrystal decomposition temperatures (d).

Table 1 Physiochemical properties of nitromethane/CL-20 cocrystal

Comp.	T_d[a] (°C)	D[b] (g cm^{-3})	v_D[c] (m s^{-1})	P[d] (GPa)	IS[e] (J)	FS[f] (N)	ΔH_f[g] (kJ mol^{-1})
Cocrystal	253	1.821	8873	35.3	22	170	312.2
CL-20/TNT	—	1.76	8426	32.3	30	58	—
RDX	204	1.80	8795	34.9	7.5	120	70.3
HMX	287	1.91	9144	39.2	7.4	120	74.8
ε-CL-20	243	2.04	9406	44.6	4	94	397.8

[a] Decomposition temperature. [b] Crystal density. [c] Calculated detonation velocity. [d] Calculated detonation pressure. [e] Impact sensitivity. [f] Friction sensitivity. [g] Calculated heat of formation.

formation of this cocrystal.[25] The strong hydrogen-bonding interactions are conducive to the accumulation of crystals, which might also be a reason for the higher density of this cocrystal. As the second contacts in the cocrystal, the O···O contact can be ascribed to the interaction between the nitro groups surrounding the hexaazaisowurtzitane cage and the nitromethane chain. Finally, the O···N contacts that occurred between the nitro groups contributed to about 14% of the intermolecular interactions.

The packing coefficient (PC) was a significant factor for investigating the density changes, which could be calculated according to an existing empirical formula. The PC of this cocrystal studied herein was calculated to be 77.66%, which is higher than most of CL-20 cocrystals. The higher PC once again shows the ε conformation of the CL-20 molecule's advantages of stacking in crystals. PC is closely related to the density of the compound; the higher the PC, the higher is the density. The PC of this cocrystal is higher than that of γ-CL-20 (75%) but lower than that of ε-CL-20 (79%). The lower PC of this cocrystal compared with that of ε-CL-20 can be attributed to the directional interactions. By using directional interactions as driving forces, the distance between the two components of the cocrystal is increased; however, this method used also destroyed the maximum accumulation of the crystal's close packing pattern. Hence, maybe because of this reason there was a decrease in the density of the cocrystal.

To explore the value of CL-20/nitromethane cocrystal in practical applications, we conducted a systematic study on its various properties, which include thermal stability, detonation properties, and sensitivity. Thermal stability was determined by DSC at a heating rate of 10° min^{-1} in N_2. The decomposition temperature of the cocrystal was higher than that of CL-20 at 253 °C. Thus, the thermal stability was quite good among the cocrystals of CL-20 (Fig. 5d). However, there were two exothermic peaks at 146 °C and 165 °C, which might be caused due to the partial melting of the crystal.

Sensitivity is one of the most important characteristics of the energetic materials and a main indicator for evaluating their safety, which directly affected their application value. According to Table 1, the impact sensitivity of the cocrystal is 22 J, and the friction sensitivity is 170 N, which is better than that of CL-20 (4 J, 94 N) and HMX (7.0 J, 120 N). Higher hydrogen-bonding interactions between CL-20 and nitromethane molecules and the layered stacking found in the cocrystal might be the main reasons for the good sensitivities (Fig. 5c). In order to further explore the reasons for the low sensitivities of the cocrystal, we calculated the noncovalent interaction, which was based on the significant correlation between the sensitivity of energetic materials and intramolecular interactions.[26] According to Fig. S4, ESI,† the cocrystals contain interactions between the molecules, which can effectively buffer the mechanical actions to enhance stability.[27–29] In addition, density is a critical factor to determine the performance of high-energy materials. The crystallographic densities of the cocrystal were 1.861 g cm^{-3} at 153 K and 1.821 g cm^{-3} at room temperature, which were better than that of RDX (1.816 g cm^{-3}). Higher density signified that it possessed a good detonation performance; the calculated detonation velocity of the cocrystal is 8873 m s^{-1}, and the detonation pressure was 35.3 GPa, which is better than that of RDX (8795 m s^{-1}, 34.9 GPa) (Fig. 6). Therefore, the CL-20/nitromethane cocrystal is expected to replace HMX as a good explosive because of its low sensitivity and excellent detonation performance.

In summary, we synthesised and characterised a novel, high-energy cocrystal of CL-20/nitromethane in a 1 : 2 molar ratio, yielding the cocrystal in the ε conformation. Higher intermolecular interactions and layered stacking of the CL-20/nitromethane cocrystal produced significant stability, higher density, and lower sensitivity than that of RDX.

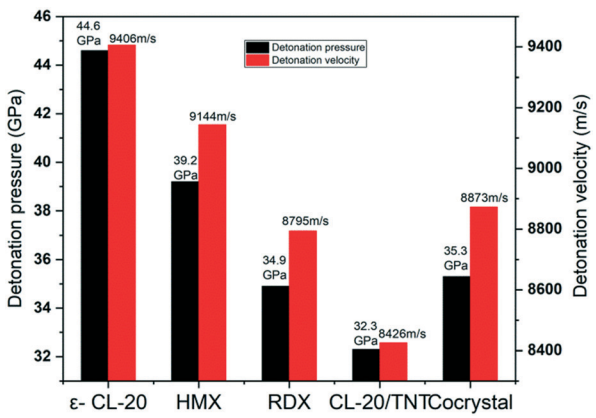

Fig. 6 Detonation performance of cocrystal and respective components as well as references.

Author contributions

Wenjin Zhang: investigation, data curation and writing – original draft. Penghao Lv and Lingxiang Bao: conceptualization

and methodology. Fei Teng: visualization and software. Chenghui Sun: writing – review and editing, and funding acquisition. Siping Pang: supervision and funding acquisition.

Conflicts of interest

There are no conflicts of interest to declare.

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