



Theoretical analysis of the formation driving force and decreased sensitivity for CL-20 cocrystals



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ABSTRACT

Methods that analyze the driving force in the formation of the new energetic cocrystal are proposed in this paper. Various intermolecular interactions in the 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo [5.5.0.0^{5,9}.0^{3,11}]dodecane (CL-20) cocrystals are compared with those in pure CL-20 and coformer crystals by atom in molecule (AIM) and Hirshfeld surface methods under the supramolecular cluster model. The driving force in the formation of the CL-20 cocrystals is analyzed. The main driving force in the formation of the cocrystal CL-20/HMX comes from the O···H interactions, that in the formation of the cocrystal CL-20/TNT from the O···H and C···O interactions, and that in the formation of the cocrystal CL-20/BTF from the N···H and N···O interactions. Other interactions in the CL-20 cocrystals only contribute to their stabilization. At the same time, the reasons for the decreased impact sensitivity of the CL-20 cocrystals are also analyzed. They are the strengthening of the intermolecular interactions, the reducing of the free space, and the changing of the surrounding of CL-20 molecule in the CL-20 cocrystals in comparison with those in the pure CL-20 crystal.

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1. Introduction

Cocrystallization is a solid state engineering strategy that gives the compound better property by combining two or more species with non-covalent bonds. Cocrystallization is widely applied to pharmaceuticals [1], optical materials [2], and semiconducting materials [3]. Recently, cocrystallization technique has also attracted the researcher's attention working on energetic materials. Energetic cocrystals are expected to give better properties, i.e., low impact sensitivity, high density and thermal stability. CL-20 is an important energetic material, but its sensitivity is very high. Therefore, the cocrystallization method is applied in order to decrease its sensitivity. For example, Bolton and his coworkers have prepared the cocrystal CL-20/HMX (octahydro-1,3,5,7-terranitro-1,3,5,7-tetra-Zocine), and have found it has high explosive power density and good impact sensitivity [4]. They also have obtained the

cocrystal CL-20/TNT (2,4,6-trinitrotoluene), and have found its impact sensitivity is reduced to approximate half of the pure ϵ -CL-20 [5]. Yang and his coworkers have prepared the cocrystal CL-20/BTF (benzotrifuroxan), and have predicted that the cocrystal CL-20/BTF would exhibit excellent detonation properties as compared with the pure BTF crystal [6]. Now the experimental researcher intuitively expects that the driving force in the formation of the CL-20 cocrystals is attributed to hydrogen bonds and lone pair/ π interactions [4], but theoretically, the formation mechanism of these cocrystals has not been explored in detail. In order to design more new energetic cocrystals, the present work uses the supramolecular cluster model to analyze the molecular packing in CL-20 cocrystals, and uses theoretical methods, such as AIM electronic density topology and Hirshfeld surface analysis, to analyze the various intermolecular interactions among different CL-20 cocrystals. The changes in the strength and number of different types of interactions in the CL-20 cocrystals are compared to those in pure ϵ -CL-20 crystal and pure coformer crystals. The driving force in the formation of the CL-20 cocrystals is analyzed. At the same time, the

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reasons of the low sensitivity of the CL-20 cocrystals are also analyzed.

2. Methodology

Firstly, the supercell was constructed from the experimental crystal structure [4–6], and then one molecule in the supercell was selected as the central molecule. The molecular cluster with the radius of 10 Å from the centroid of the central molecule was chosen as the model cluster. Each peripheral molecule in molecular clusters forms a dimer with the selected central molecule. For each CL-20 cocrystal, the CL-20 and the coformer molecule were taken as the central molecules, respectively. In consideration of the structural error of each dimer caused by the optimization at low calculation level and the computing time at high calculation level, no geometry optimization was performed for each dimer, and the single point energy calculation was directly carried out. The single point energy calculation was done at the wB97XD/6–311++G (d,p) level with the counterpoise (CP) correction for basis set superposition error (BSSE) in Gaussian 09 [7]. The strength of intermolecular interactions in each dimer was analyzed in AIM2000 software [8].

It is known that the relative contact distance between the two atoms can be displayed by the color of the associated Hirshfeld surface of the crystal, and the relative contribution of the various contacts to the Hirshfeld surface can be displayed by the color of two-dimensional fingerprints of the crystal. Therefore the various intermolecular interactions in CL-20 cocrystals were analyzed by the associated Hirshfeld surfaces and two-dimensional fingerprints [9]. For each point on the Hirshfeld surface, the normalized contact distance (d_{norm}) is defined by an equation (1) in which d_i is the distance measured from the surface to the nearest atom interior, and d_e is that measured from the surface to the nearest atom exterior, respectively, where r_i^{vdw} and r_e^{vdw} are the van der Waals radii of these two atoms.

$$d_{norm} = \frac{d_i - r_i^{vdw}}{r_i^{vdw}} + \frac{d_e - r_e^{vdw}}{r_e^{vdw}}. \quad (1)$$

The Hirshfeld surfaces are displayed using a red-white-blue color scheme, where red highlights shorter contacts, white for contacts around the van der Waals separation, and blue is for longer contacts. Each point on the standard fingerprint represents a bin formed by discrete intervals of d_i and d_e and the points on the surfaces are colored as a function of the fraction of the surface points in the bin. For instance, the blue color indicates a few points while the green color means moderate points and the red color suggests many points. Hirshfeld surface and two-dimensional fingerprint analyses were performed in CrystalExplorer3.0 [10].

3. Results and discussion

3.1. The statistical analysis and comparison of intermolecular interactions in the CL-20 cocrystals

3.1.1. The statistical analysis and comparison of intermolecular interactions in the cocrystal CL-20/HMX

As for the cocrystal CL-20/HMX, a supercell was constructed from $2 \times 2 \times 2$ experimental unit cells. One CL-20 molecule and one HMX molecule in the supercell were taken as the centers, respectively. All the molecules within the sphere with 10 Å radius from the centroid of the selected central molecule form one model cluster. The CL-20 and HMX thus have their own model cluster as shown in Fig. 1. The central molecule is shown in the ball and stick style and the element color, and the peripheral molecules are

shown in the line style and different custom colors. The dimer consisting of the peripheral molecule and the central molecule is chosen to analyze the intermolecular interactions in the cocrystal cell. In order to include all the possible intermolecular interactions in the cocrystal cell, two model clusters for CL-20 and HMX respectively are analyzed. The union of these two clusters contains 11 different dimers. The structure of each dimer is directly taken from the experimental crystal data, and then the single point energy calculation is carried out at the level wB97XD/6–311++G (d,p). The formation energy of each dimer, $\Delta E(\Delta E = E_{AB} - E_A - E_B)$, is calculated, and shown in Table 1. From Table 1 it can be seen that the highest formation energy for these dimers with the centroid–centroid distance below 10 Å is -8.2 kJ/mol. It indicates that the formation energy of the dimer with the centroid–centroid distance above 10 Å would be less negative, and the intermolecular interactions in these dimers can be neglected for the driving force of the cocrystal formation. Therefore, it indicates the size of the selected model cluster is reasonable. From Table 1 it can also be seen that the formation energies of Dimer_1, Dimer_2 and Dimer_3 are much lower than those of others. They are -40.5 , -33.5 , -32.6 kJ/mol, respectively. The structures of Dimer_1, Dimer_2 and Dimer_3 are shown in Fig. 1, and the structures of other dimers are shown in Fig. S1 in the supporting information.

The various intermolecular bonds in the dimers above are analyzed by the AIM method. The pure crystal ϵ -CL-20 and β -HMX are also analyzed in the same way. As seen in Fig. 1 and Table 1, the formation energy of the heterodimer Dimer_1 consisting of one CL-20 molecule and one HMX molecule is the lowest, and it means that the intermolecular interactions in Dimer_1 are the strongest. The Dimer_1 contains multiple hydrogen bond interactions. Among these hydrogen bonds the two short O \cdots H bond lengths are 2.319 and 2.443 Å, and the electronic density of their corresponding bond critical points (BCP) is 0.0103 and 0.0100 e/bohr³, respectively [8]. The formation energy of the homodimer Dimer_2 consisting of two CL-20 molecules is -33.5 kJ/mol, and its formation energy is mainly due to the O \cdots N and O \cdots O interactions. The bond length of the strongest O \cdots N interaction in it is 2.625 Å, and its BCP electronic density is 0.0133 e/bohr³. The formation energy of the heterodimer Dimer_3 consisting of one CL-20 molecule and one HMX molecule is -32.6 kJ/mol. It contains one strong O \cdots H bond, and the O \cdots H bond length is 2.357 Å with BCP electronic density of 0.0109 e/bohr³.

Fig. 2a–c and a'–c' show the comparison of the strength and number of the same type of intermolecular interactions in the cocrystal CL-20/HMX, pure crystal ϵ -CL-20 and pure crystal β -HMX, respectively. The Fig. 2a shows that the shortest hydrogen bond length in the cocrystal CL-20/HMX is shorter than that in the pure crystal ϵ -CL-20 and the pure crystal β -HMX. The corresponding hydrogen bond strength in the cocrystal CL-20/HMX is stronger than that in the pure crystal CL-20 and β -HMX. The Fig. 2b' shows that the number of the relative short hydrogen bond is much more than that in the pure crystal ϵ -CL-20 and β -HMX. It can be concluded that the hydrogen bond interactions make a great contribution to the formation of the CL-20/HMX cocrystal. As seen in Fig. 2b and b', for the O \cdots O interactions, there is no obvious difference in the strength and number between the cocrystal CL-20/HMX and its corresponding pure crystals. They have no contribution to the competitive formation of the cocrystal CL-20/HMX, and only have contribution to the stabilization of the cocrystal CL-20/HMX. As seen in Fig. 2c and c', for the N \cdots O interactions, two short N \cdots O bonds exist in the cocrystal CL-20/HMX, but they exist in the homodimer CL-20. They have no contribution to the formation of the cocrystal CL-20/HMX and only have contribution to the stabilization of the cocrystal CL-20/HMX.

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