Study on the Intermolecular Interaction of CL-20/FOX-7 Cocrystal Explosive

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Abstract. To investigate the intermolecular interactions of CL-20 with high sensitivity/FOX-7 with low sensitivity cocrystal, the structures of four kinds of CL-20/FOX-7 cocrystal I, II, III, IV were studied using a density functional theory (DFT). The intermolecular interaction of four kinds of CL-20/FOX-7 cocrystal and the properties of the explosive were analyzed and predicted using electrostatic potential, electron density topological, reduced density gradient and NBO etc methods. The results show that the interaction energy of four kinds of configurations decreases in the order of structure III > structure II >structure I > structure IV. The nature of the intermolecular interactions of CL-20/FOX-7 cocrystal is a series of weak hydrogen bonding and vdW force, involving N-H…O, C-H…O interactions. The predicted detonation velocity and denotation pressure of CL-20/FOX-7 cocrystal in a 2:1 molar ratio is 9174m/s and 37.68GPa, respectively. And the detonation performance of CL-20/FOX-7 cocrystal explosive is equivalent to HMX.

Keywords: CL-20/FOX-7 cocrystal, intermolecular interactions, binding energy, detonation performance.

1. Introduction

With the continuous development of military science and technology, modern warfare and new weapons have put forward high-energy and high safety requirements for energetic materials [1]. The new generation of high-energy and insensitive energetic materials has become a hot research topic in the field of energetic materials at home and abroad. At present, cocrystal technology, as a new type of modification technology, has received widespread attention from energetic material researchers. Eutectics refer to the formation of multi-component molecular crystals with specific structures and properties by combining two or more different types of molecules in the same lattice through intermolecular non covalent bonds (hydrogen bonds, ionic bonds, van der Waals forces, π - π bonds, etc.) [2-3]. Explosive cocrystal can effectively improve the oxygen balance and sensitivity of some explosives through intermolecular forces, enhancing their explosive heat, work capacity, and safety performance.

Hexanitrohexaazaisowurtzite (CL-20) is currently one of the high-energy elemental explosives, but its application is limited due to its high mechanical sensitivity. 1, 1-diamino-2, 2-dinitroethylene (FOX-7) is a novel high-energy insensitive explosive with an impact sensitivity approximately 5 times that of CL-20 [4]. If CL-20 can be cocrystal with FOX-7 to form a unique structure with both high-energy and low sensitivity characteristics, it will greatly expand the application range of CL-20.

Due to its unique physical and chemical properties, cocrystal explosives are bound to be widely used in military and industrial applications. At present, the development of high-energy insensitive energetic materials mainly relies on experiments, which have the disadvantages of long cycles and significant safety issues. Therefore, theoretical guidance is urgently needed. Nowadays, with the development of computer technology, theoretical simulation methods have become an effective way to study energetic materials. For example, they can verify some theoretical hypotheses of researchers, provide theoretical guidance for experiments, thereby reducing cycles and costs. More importantly, since energetic materials are mostly composed of explosives, they can also improve the safety of the development process [5, 6].

This study established four cocrystal models for CL-20 and FOX-7, and optimized and calculated the CL-20/FOX-7 cocrystal at the B3LYP/6-311++G (d, p) level. By studying the cocrystal structure, electrostatic potential, energy, and induced bonds, combined with electronic density topology and reduced density gradient analysis, the essence of intermolecular interactions in CL-20/FOX-7 cocrystal was revealed, in order to provide theoretical basis for experimental research on CL-20/FOX-7 eutectic.

2. Methodology

Firstly, the crystal structures of CL-20 and FOX-7 were obtained from the Cambridge Crystal Data Center CCDC, and a bimolecular cocrystal structure model was established. The cocrystal molecular structure was optimized using density functional theory (B3LYP 6-311+G (d, p) basis set), and the minimum energy on the lowest potential energy surface was calculated to obtain a stable structure without imaginary frequencies. Calculate the intermolecular binding energy using the M ø ller Plesset method with BSSE (basis set superposition error) correction. Use NBO (natural bond orbital) analysis to study the delocalization of electron transfer, bonding, and intermolecular electron density. Conduct AIM (Atoms in Molecules) analysis based on BCP (Bond Critical Point) theory to obtain the interatomic forces. Based on the above calculations, find the optimal cocrystal configuration with stable structure and lowest energy, and use this configuration to calculate the electronic structure and thermodynamic properties of the compound.

Perform frequency vibration analysis based on the optimized structural model, and derive thermodynamic properties from its ensemble state process. Due to the fact that the harmonic vibration frequency calculated by DFT method is usually greater than its experimental observation value, the frequency range of 0.960 is taken as the correction value for vibration analysis. The enthalpy of formation represents the energy storage of high energy density materials, and the calculation of enthalpy of formation is carried out using the equi bond reaction method [7, 8]. The specific formula is:

$$\Delta H_{298\mathrm{K}} = \sum \Delta_f H_p - \sum \Delta_f H_r = \Delta E_0 + \Delta ZPE + \Delta H_T$$

$$\Delta H_{298\mathrm{K}} = \sum \Delta H_{\mathrm{f,p}} - \sum \Delta H_{\mathrm{f,r}}$$

Based on the estimated density and enthalpy of formation of the compound, the C-J detonation equation of cocrystal compounds is used to search for the C-J point of explosive detonation, the final products under different system states, the calculation of gaseous substances, and the calculation of the free energy of solid substances, in order to estimate the detonation performance of cocrystal compounds. The Monte Carlo method is used to calculate density, and the specific formula is:

$$\rho = \alpha` \left(\frac{M}{V}\right) + \beta`(v_{tot}^2) + \Upsilon`$$

Calculate detonation velocity, detonation pressure, etc. using the Kamlet Jacobs equation:

$$P = 1.558\ \rho 2\Phi$$

$$D = 1.01\Phi 1/2\ (1.011+1.312\ \rho)$$

$$\Phi = 0.4889N\ (MQ)\ 1/2$$

For the energetic material $C_aH_bO_cN_d$, the formula for calculating oxygen balance is:

$$\Omega CO_2 = \frac{c - (2a + 0.5b)}{M} \times 1600$$

3. Results and Discussion

3.1. Analysis of CL-20/FOX-7 Cocrystal Structure

Four CL-20/FOX-7 cocrystal energetic materials were structurally optimized using B3LYP/6-311+G (d, p), and the optimization results are shown in Figure 1. It can be seen that all four sets of cocrystal structures have hydrogen bonding interactions. Among them, the hydrogen bonding interactions of cocrystal I-III are all formed by - NH2 in FOX-7 and - NO2 on CL-20, and cocrystal II and III have strong hydrogen bonding interactions, forming two sets of hydrogen bonds; In complex IV, hydrogen bonds are formed between - NO2 in FOX-7 and - CH - in CL-20. The specific bond length and angle analysis are shown in Table 1.

The H... A distances of the four cocrystal groups are 2.242 Å (N (39) - H (41)... O (11), cocrystal I), 2.202 Å (N (39) - H (41)... O (11), cocrystal II), 2.245 Å (N (42) - H (43)... O (33), cocrystal II), 2.208 Å (N (39) - H (41)... O (16), cocrystal III), 2.212 Å (N (42) - H (43)... O (17), cocrystal III), 2.474 Å (C (7) - H (8)... O (49) Cocrystal IV) belongs to the average value of hydrogen bonding interactions. In addition, the D-H... A bond angles of the four complexes are all between 110°-180°, and the closer the bond angle is to 180°, the stronger the hydrogen bonding effect, and the corresponding hydrogen bond length is shorter, which is consistent with the bond lengths of the four complexes. Therefore, we believe that there is a strong hydrogen bonding interaction between CL-20 and FOX-7.

3.2. Electrostatic Potential and Binding Energy of CL-20/FOX-7 Cocrystal Molecules

The potential energy diagram (MESP) of CL-20/FOX-7 cocrystal molecules is shown in Figure 2. It can be observed that the – NH2 static potential (blue) of FOX-7 overlaps with the – NO2 static potential (red) of CL-20, turning green. Similarly, the – NO2 static potential (red) of CL-20 overlaps with the – NH2 static potential (blue) of FOX-7, turning green. Therefore, it can be considered that a stable cocrystal structure can be formed. Meanwhile, MESP is also related to determining the impact sensitivity of energetic materials. From the figure, it can be seen that the positive electrostatic potential area (blue) of the CL-20/FOX-7 cocrystal much larger than the negative electrostatic potential area (red), indicating that the formation of cocrystal contributes to the reduction of impact sensitivity. In the cocrystal IV structure, due to the weak hydrogen bonding force between FOX-7's - NO2 and CL-20's - CH -, it has little effect on the - NO2 electron cloud of CL-20, resulting in a larger negative electrostatic potential area (red) of cocrystal IV compared to cocrystal I-III. Therefore, cocrystal IV may be the most unstable structure.

Based on the optimized structure, we calculated the binding energies of four sets of eutectics, which are within the range of hydrogen bond intermolecular interaction energies: 16 kJ/mol~160 kJ/mol. The order of binding energies of the four sets of eutectics is: cocrystal III (37 kJ/mol)>cocrystal II (16 kJ/mol)>cocrystal I (13 kJ/mol)>cocrystal IV (5 kJ/mol), which is the stability order of the CL-20/FOX-7 eutectic. Overall, it indicates that the CL-20/FOX-7 cocrystal relatively stable, with the stacking of cocrystal II and III structures being the most stable.

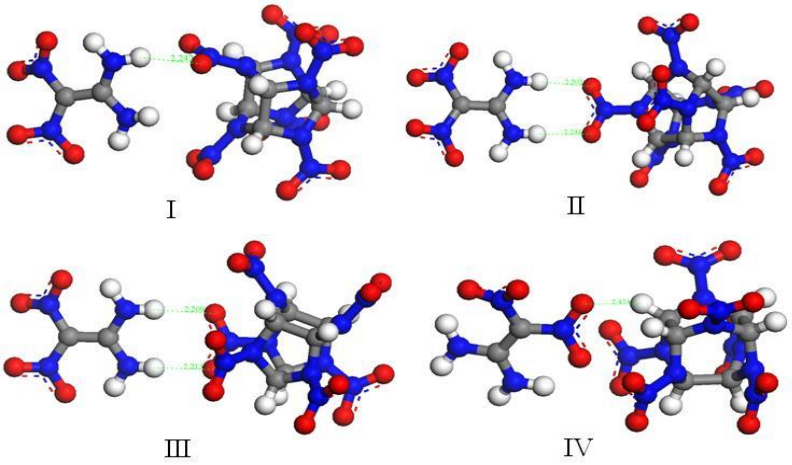

Figure 1. Four predicted structures of CL-20/FOX-7 cocrystal energetic materials

Table 1. Relevant structural analysis of CL-20/FOX-7 cocrystal energetic materials[a]

Structure	hydrogen bond	D-H	H…A	D…A	D-H…A	Winberg BO
I	N(39)-H(41)…O(11)	1.011	2.242	3.202	158.158	0.0126
II	N(39)-H(41)…O(32)	1.009	2.202	3.209	175.447	0.0126
	N(42)-H(43)…O(33)	1.009	2.245	3.251	174.812	0.0118
III	N(39)-H(41)…O(16)	1.009	2.208	3.214	174.396	0.0125
	N(42)-H(43)…O(17)	1.010	2.212	3.217	173.749	0.0130
IV	C(7)-H(8)…O(49)	1.086	2.474	3.043	129.785	0.0058

a: The unit of bond length above is Å, and the unit of bond angle is

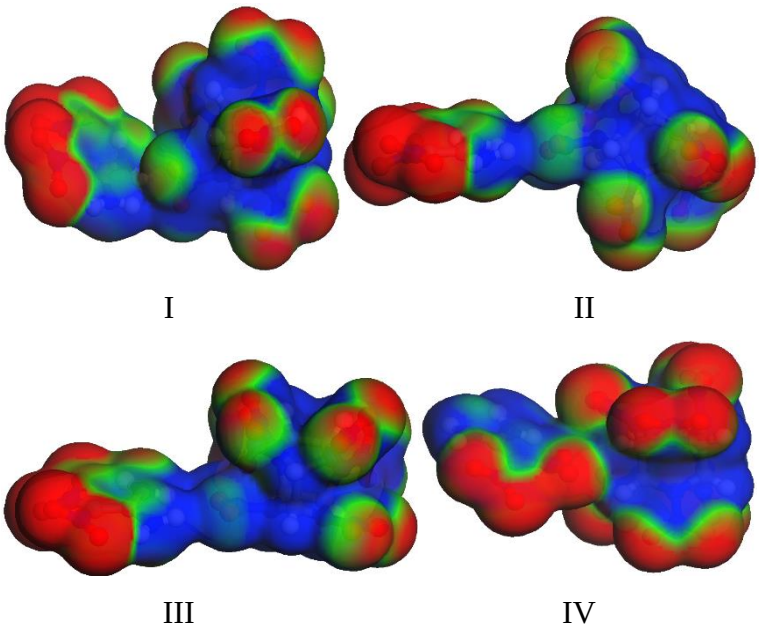

Figure 2. Molecular electrostatic potential energy diagram of CL-20/FOX-7 eutectic

3.3. NBO Analysis of CL-20/FOX-7 Eutectic

NBO analysis is an effective method for studying intra - and intermolecular interactions. In terms of occupied Lewis and unoccupied non Lewis localized orbitals, its analysis can be used to investigate charge transfer or conjugation effects in their molecular systems. In order to investigate and explain the electron density transfer between CL-20 and FOX-7 after cocrystal formation, and further understand intermolecular interactions, we conducted a second-order perturbation evaluation of the

donor acceptor energies (E (2)) of four CL-20/FOX-7 eutectics. We performed NBO analysis at the B3LYP/6-311+G (d, p) level, and the corresponding results are shown in Table 2.

Table 2. NBO analysis of CL-20/FOX-7 cocrystal energetic materials

Co-structure	Donor NBO(i)	Acceptor NBO(j)	E(2) kJ/mol	E(j)-E(i) a.u.	F(i,j) a.u.
I	LP(1) O11	BD*(1) N39-H41	0.81	1.28	0.029
	LP(2) O11	BD*(1) N39-H41	2.48	0.77	0.040
	LP(3) O11	BD*(1) N39-H41	0.08	0.75	0.008
	LP(1) O11	BD*(1) N42-H43	0.05	1.27	0.007
	LP(1) O11	BD*(1) N42-H43	0.11	0.74	0.009
II	LP(1) O32	BD*(1) N39-H41	1.13	1.29	0.034
	LP(2) O32	BD*(1) N39-H41	2.61	0.78	0.041
	LP(3) O32	BD*(1) N39-H41	0.08	0.76	0.008
	LP(1) O33	BD*(1) N42-H43	0.91	1.29	0.031
	LP(2) O33	BD*(1) N42-H43	2.43	0.78	0.040
	BD* N31-O33	BD*(1) N42-H43	0.12	0.23	0.013
III	LP(1) O16	BD*(1) N39-H41	1.19	1.29	0.035
	LP(2) O16	BD*(1) N39-H41	2.63	0.78	0.041
	LP(1) O17	BD*(1) N42-H43	1.08	1.29	0.033
	LP(2) O17	BD*(1) N42-H43	2.67	0.78	0.042
IV	LP(1) O49	BD*(1) C7-H8	0.45	1.21	0.021
	LP(2) O49	BD*(1) C7-H8	0.41	0.70	0.015
	LP(1) O49	BD*(1) C28-H29	0.26	1.21	0.016
	LP(2) O49	BD*(1) C28-H29	0.38	0.70	0.015

From Table 2, it can be seen that there is no covalent bonding between N-O and H in the nitro group, but some weak hydrogen bonds are formed. The donor acceptor energy data indicate that the main intermolecular interactions for the formation of cocrystal I come from LP (1) O11 → BD * (1) N39-H41, with E (2)=2.48 kJ/mol; The main intermolecular interactions for the formation of cocrystal II come from LP (2) O32 → BD * (1) N39-H41 and LP (2) O33 → BD * (1) N42-H43, with E (2) values of 2.61 and 2.43 kJ/mol, respectively; For the formation of cocrystal III, the main intermolecular interactions come from LP (2) O16 → BD * (1) N39-H41 and LP (2) O17 → BD * (1) N42-H43, with E (2) values of 2.63 and 2.47 kJ/mol, respectively; For the formation of cocrystal IV, the main intermolecular interactions come from LP (2) O49 → BD * (1) C7-H8 and LP (2) O49 → BD * (1) C7-H8, with E (2) values of 0.45 and 0.41 kJ/mol, respectively; In addition, cocrystal III and IV have more intermolecular interactions, so CL-20 and FOX-7 are more likely to form cocrystal by stacking these two types.

3.4. RDG Analysis of CL-20/FOX-7 Eutectic

Based on the reduced density gradient function and the sign of electron density multiplied by the second Hessian eigenvalue (sign (λ 2) ρ), Erin et al. [9] proposed a method for detecting non covalent interactions in real space. Low density values typically indicate weaker van der Waals forces, while slightly higher density values indicate slightly stronger non covalent interactions (including hydrogen bonding attraction and spatial repulsion). To further investigate the intrinsic mechanism of CL-20/FOX-7 eutectic, we plotted its sign (λ 2) ρ - RDG diagram, as shown in Figure 3.

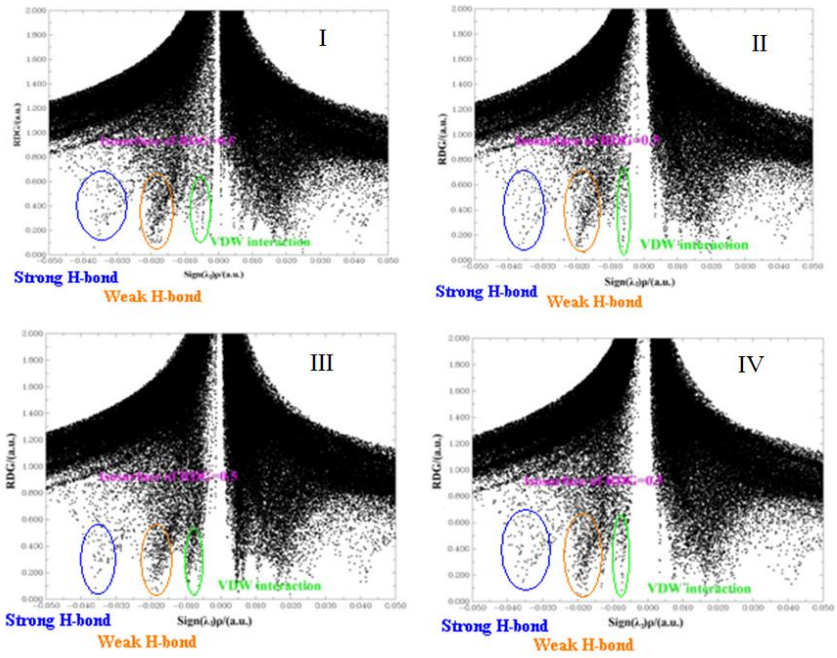

Figure 3. Sign (λ 2) ρ - RDG diagram of CL-20/FOX-7 eutectic

From Figure 3, it can be seen that strong and weak hydrogen bonds, as well as van der Waals forces, are distributed in all four configurations within the range of electron density values ρ between 0.04-0 a.u. When the electron density value ρ is 0.03-0 a.u, the low-density and low gradient region with sign (λ 2) ρ value close to 0 corresponds to the equipotential surface between the nitro group of CL-20 and the amino group of FOX-7, where weak hydrogen bonding (0.03-0.01 a.u) and van der Waals forces (0.01-0 a.u) can be clearly observed. When the electron density value ρ is in the range of 0.04-0.03 a.u, the electron density value in this range is slightly higher, corresponding to the equipotential surface between the nitro and amino groups of FOX-7 molecule itself, where strong hydrogen bonding can be clearly observed (0.04-0.03 a.u). Based on the above analysis, it can be concluded that weak hydrogen bonding and van der Waals forces are the main interactions between CL-20/FOX-7 cocrystal molecules.

3.5. AIM Analysis of CL-20/FOX-7 Cocrystal Structure

According to Bader's "intramolecular atom (AIM)" theory [10], the topological properties of electron density distribution in a molecule depend on the gradient vector field $\nabla \rho$ and Laplacian quantity $\nabla 2\rho$ of electron density. AIM is a commonly used tool for characterizing the nature of chemical bonds, and the nature of bonds can be determined through analysis and calculation of compounds. By calculating the AIM of the compound, the parameters of the chemical bond saddle point (BCP) can be obtained: total electron energy density (H), potential energy density (V (r)), and kinetic energy density. Another effective reference for analyzing the nature of chemical bonds is the energy of chemical bonds. There is a certain relationship between the energy of a key and its bonding nature. The relationship between the binding energy range and the type of chemical bond is as follows: when the binding energy of the compound is between 4-160 kJ/mol, it is hydrogen bonding; When the binding energy is between 2-4 kJ/mol, it is the van der Waals force; When the binding energy is about 400 kJ/mol, the chemical bond is a covalent bond. The analysis results of four CL-20/FOX-7 cocrystal energetic materials are shown in Table 3.

Table 3. Important bonding topological parameters and AIM analysis of CL-20/FOX-7 cocrystal energetic materialsa

cocrystal structure	Interaction	ρ	$\nabla^2\rho$	V(r)	H	E_{HB}
I	N(39)-H(41)…O(11)	0.0125	0.0457	-0.0078	0.0017	-10.03
II	N(39)-H(41)…O(32)	0.0133	0.0486	-0.0082	0.0019	-10.78
	N(42)-H(43)…O(33)	0.0126	0.0451	-0.0077	0.0016	-9.96.
III	N(39)-H(41)…O(16)	0.0132	0.0483	-0.0082	0.0019	-10.54
	N(42)-H(43)…O(17)	0.0130	0.0477	-0.0081	0.0018	-10.43
IV	C(7)-H(8)…O(49)	0.0071	0.0302	-0.0050	0.0011	-6.52

a: The unit of EHB is kJ/mol, and other units are a.u.

From the above table, it can be seen that the electron density of the four cocrystal structures ranges from 0.0071 to 0.0133 a.u., which is consistent with the typical range of hydrogen bonding interactions (0.002 to 0.04 a.u.). The Laplace quantities $\nabla^2\rho$ are all positive values, and the electron energy density (H) ranges from 0.0011 to 0.0019 a.u., indicating that the chemical bond interactions in cocrystal are closed shell interactions. In addition, the two types of hydrogen bonds obtained (N-H... O and C-H... O) have bond lengths between 2.202 and 2.474 Å, which is smaller than the sum of the van der Waals radii of hydrogen atoms (1.2 Å) and oxygen atoms (1.52 Å) (2.72 Å). The above indicates that the interaction between CL-20 and FOX-7 is non covalent.

Among the four cocrystal structures, the binding energy (EHB) of cocrystal II and III is higher than that of cocrystal I and IV, indicating that the intermolecular forces between II and III are stronger. Therefore, hydrogen bonds (N-H... O and C-H... O) are the main stabilizing forces for the CL-20/FOX-7 eutectic, and due to their strong binding energy, cocrystal II and III are more easily formed.

3.6. Performance Prediction of CL-20/FOX-7 Cocrystal

The typical definition of high-energy and low sensitivity compounds is a detonation velocity greater than 8500 m/s and a specific drop height H50 greater than 50 cm. By calculating the density, detonation velocity, and other properties of cocrystal energetic materials, relevant information on their energy and safety can be obtained, and materials that meet the requirements of high energy and low sensitivity can be screened. The properties of CL-20/FOX-7 cocrystal with different molar ratios were calculated using Monte Carlo method and K-J equation, respectively. Table 4 shows the predicted results of density, detonation velocity, detonation pressure, and oxygen balance for CL-20/FOX-7 eutectic.

Table 4. Performance prediction of CL-20/FOX-7 cocrystal energetic materials

CL-20: FOX-7	ρ(g/cm^3)	D(m/s)	P(GPa)	OB
2: 1	1.99	9174	37.68	-28.1
1: 1	1.97	9132	37.12	-31.6
1: 2	1.95	9081	36.73	-35.2

From the above table, it can be seen that the CL-20/FOX-7 cocrystal energetic material has a high energy level. With the increase of CL-20 content, the density, detonation velocity, and detonation pressure of CL-20/FOX-7 cocrystal all show an upward trend. Due to the small molecular weight of FOX-7 itself, its mass proportion in the above molar ratios is not high. Therefore, the density of the cocrystal formed is around 2.00g/cm3, which is close to the density of CL-20. When CL-20: FOX-7=2:1, the predicted detonation velocity reaches 9174m/s and the predicted detonation pressure reaches 37.68GPa, which is basically equivalent to the energy of HMX.

4. Conclusions

(1) The four cocrystal structures of CL-20/FOX-7 were analyzed using density functional theory at the B3LYP/6-311++G (d, p) level, including structural analysis, electrostatic potential analysis,

NBO analysis, electronic density topological properties, and graphical analysis. The results indicate that there are intermolecular interactions in the system, and the order of the magnitude of these interactions is: Structure III>Structure II>Structure I>Structure IV. Cocrystal IV may be the most unstable structure. In addition, there are not only weak hydrogen bonding interactions between molecules, but also van der Waals forces, mainly manifested as N-H... O, C-H... O interactions. Hydrogen bonding is the main stabilizing force for CL-20/FOX-7 eutectic, and due to its strong binding energy, cocrystal II and III are more easily formed.

(2) CL-20/FOX-7 cocrystal energetic material has a high energy level. When CL-20: FOX-7=2:1, the predicted detonation velocity reaches 9174m/s and the predicted detonation pressure reaches 37.68GPa, which is basically equivalent to the energy of HMX.

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