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Theoretical insight into the co-crystal explosive of 2,4,6,8,10,12-hexanitrohexaazaisowurtzitane (CL-20)/1,1-diamino-2,2-dinitroethylene (FOX-7)

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ABSTRACT

Co-crystallization has been widely applied in the energetic field. Theoretical methods including Molecular Dynamics (MD) simulation and quantum-chemical DFT and MP2 calculation were employed to investigate 2,4,6,8,10,12-hexanitrohexaazaisowurtzitane (CL-20) and 1,1-diamino-2,2-dinitroethylene (FOX-7) co-crystal. Different molar ratios of co-formers were studied by MD simulation method. Properties of co-crystallized systems, e.g. oxygen balance (*OB*), density (d_{298k}) and detonation velocity (V_D), were estimated in different molar ratios. The predicted result indicate that CL-20/FOX-7 co-crystal may have the high forming probability in a molar ratio 1:1 and meet a given standard of low sensitive high energetic materials. Analyses of atoms in molecules (AIM), reduced density gradient (RDG) and natural bond orbital (NBO) were utilized to further understand the intermolecular interactions. The bond order analysis of Wiberg bond indices (WBI) confirms the existence of weak hydrogen bond interactions in CL-20/FOX-7 complexes.

1. Introduction

As several stringent requirements for both sensitivity and power of energetic material behavior, many existing energetic materials have been limited for long. Of late, co-crystallization, a technique overcoming this limitation, has attracted great interest in the field of energetic materials [1–3]. Co-crystallization is realized by composing two or more neutral components in a defined molar ratio through non-covalent interactions (e.g. electrostatic interactions, van der Waals forces, π-effects, etc.) [4,5].

Compared with coating, adding insensitive agent and controlling of crystal morphology, co-crystallization has advantages that it could modify the internal composition of energetic material by changing the way of intermolecular combination in molecular level. Therefore, an admirable amount of work was involved in discovering new smart energetic materials through co-crystallization [6–9,3]. On the basis of theoretical and experimental studies for energetic materials, co-crystals only in a defined molar ratio were involved. However, attachment energy in different molar ratios may affect the co-crystal growth. The attachment energy, which gives a useful prediction of the morphology [10] and controls the habit in various crystal growth models [11], is defined as the energy released when an additional growth face of thickness d_{hkl} is attached to the crystal plane [12]. In general, faces with more negative attachment energies have stronger attractive interactions between layers [13]. As this in mind, needed in the energetic material field is the investigation for attachment energies of crystal faces identified by the Miller indices *h k l* in different molar ratios.

Currently, CL-20 was development at China Lake, USA [14,15], which is the most powerful applied explosive with concerns remains over sensitivity to detonation [16]. CL-20 was co-crystallized with several non-energetic materials [17], such as CL-20/DMF (in a 1:2 ratio), CL-20/1,4-dioxane (in a 1:4 ratio), CL-20/HMPA (in a 1:3 ratio) and CL-20/butyrolactone (in a 1:1 ratio). CL-20-based co-crystals of energetic–energetic materials were also prepared, e.g. CL-20/TNT (in a 1:1 ratio) [18,19], CL-20/HMX (in a 2:1 ratio) [20], and CL-20/BTF (in a 1:1 ratio) [21]. Based upon these researches, the stringent requirements for both sensitivity and power of above-mentioned energetic–energetic co-crystals cannot be well satisfied in a certain extent,

Abbreviations: CL-20, 2,4,6,8,10,12-hexanitrohexaazaisowurtzitane; FOX-7, 1,1-diamino-2,2-dinitroethylene; DMF, N,N-dimethylformamide; HMPA, hexamethylphosphoramide; TNT, 2,4,6-trinitrotoluene; HMX, 1,3,5,7-tetranitro-l,3,5,7-tetrazocine; TATB, 1,3,5-triamino-2,4,6-trinitro-benzene; BTF, benzotrifuroxan.

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let alone non-energetic co-crystals. Hence, CL-20 was expected to co-crystallize with some energetic compounds that feature high power and low sensitivity. FOX-7 has been reported as a candidate of the secondary explosive for its low sensitivity and high energy [22–25]. Unfortunately, the CL-20/FOX-7 co-crystal has not been prepared experimentally. Zhou et al. screened several co-formers, including FOX-7, for formation of CL-20-based co-crystals only in a molar ratio 1:1 by the strongest intermolecular site pairing energy method [26]. Landenberger et al. pointed out that traditional screening techniques need to be expanded by considering the kinetic growth methods to more fully access feasible forms in co-crystal discovery [27]. With this in mind, CL-20/FOX-7 co-crystal may amplify the buffering ability of external stimuli to initiation whilst with less dilution of power. It is necessary to go into an admirable amount of work in theoretical study about different molar ratios of co-formers.

Materials Studio (MS) and Gaussian softwares were used cooperatively to profoundly reveal the essence of matter. "Molecular dynamics (MD) simulation" [28] has been used in investigation of co-crystal for energetic materials [29,30]. Intermolecular interactions of co-crystal explosives have been investigated by using density functional theory involving binding energy, atoms in molecules (AIM) and natural bond orbital (NBO) analyses [7]. Plot of the RDG versus sign(λ_2)ρ was used to further understand the internal mechanism of TNT/CL-20 co-crystal [32]. In this work, MD method was employed to study attachment energies of every crystal plane for CL-20/FOX-7 co-crystal in different molar ratios. Here, ε-CL-20 was selected because of its superiorities of density and thermal stability [33–35]. AIM, RDG, and NBO analyses were used to further study for the intermolecular interactions based on the geometry analysis. Properties of oxygen balance (*OB*), density (d_{298k}) and detonation velocity (V_D) were estimated in terms of the methods from Ref. [23].

2. Computational methods

2.1. Molecular dynamics calculations

The unit cell models of ε-CL-20 [14] and FOX-7 [36] were constructed according to their cell parameters, respectively. Initial models were relaxed (COMPASS force-field, Smart algorithm) to produce a stable conformation by Discover module (optimized cell parameters are shown in Table 1). 1.0×10^{-5} kcal/mol of accuracy was required for discover minimization convergence. The crystal morphologies of CL-20 and FOX-7 in vacuum were predicted by Growth morphology model of Morphology module. Details of the CL-20 and FOX-7 crystal habits and several important surfaces (*h k l*) are listed in Table 2, respectively.

Different co-crystal molar ratios can be treated by substituted method: molecules of CL-20 super cells were substituted by equal number of FOX-7 at molar ratios of 11:1 to 1:1 (CL-20:FOX-7), Molecules of FOX-7 super cells were substituted by equal number of CL-20 at molar ratios of 1:2 to 1:11 (CL-20:FOX-7). Substituted molecules in this method were determined by the Miller indices *hkl*. Relevant parameters in accordance with option selected (molar ratios, mass ratios, super cell patterns and the number of substituted molecules) are listed in Table 3.

After building and geometry optimization of substituted models, NVT ensembles and temperature of 298 K were employed when models were simulated by MD simulation. Andersen was set as the temperature control method [28]. COMPASS force-field was assigned for above all simulations [37,38], and summation methods for electrostatic and van der Waals were Ewald and

Table 1
Experimental and computational data of cell parameters.

	CL-20			FOX-7		
	Expl.[a]	Comp.	Relative error (%)	Expl.[b]	Comp.	Relative error (%)
a (Å)	8.85	9.06	−2.33	6.94	6.19	10.76
b (Å)	12.56	12.84	−2.29	6.64	6.50	2.00
c (Å)	13.39	13.51	−0.95	11.34	12.31	−8.54
α (°)	90.0	90.0		90.0	90.0	
β (°)	106.8	103.8	2.87	90.6	92.2	−1.76
γ (°)	90.0	90.0		90.0	90.0	
ρ (g cm^{-3})	2.044	1.906	6.75	1.883	1.968	−4.51
Space group	P21/N			P21/N		
Crystal system	Monoclinic			Monoclinic		
Z	4			4		

[a] The data from Ref. [14].
[b] The data from Ref. [36].

Table 2
The morphologically important faces of CL-20 and FOX-7 crystals in vacuum.

	(*h k l*)	Mul.[a]	d_{hkl}[b]	E_{att} (Tot)[c]	E_{att} (vdW)[c]	E_{att} (Elect)[c]	Tot facet area (%)
CL-20	(0 1 1)	4	9.18	−359.83	−345.27	−14.57	34.00
	(1 1 0)	4	7.26	−397.70	−371.59	−26.11	21.79
	(1 0 −1)	2	8.27	−351.92	−328.32	−23.60	16.71
	(0 0 2)	2	6.56	−394.10	−385.65	−8.45	9.44
	(1 1 −1)	4	6.96	−407.99	−383.30	−24.69	6.86
	(0 2 1)	4	5.77	−410.83	−391.80	−19.08	6.71
	(1 0 1)	2	6.62	−456.73	−447.65	−9.12	4.50
FOX-7	(0 1 1)	4	5.75	−147.91	−106.21	−41.71	49.42
	(1 0 1)	2	5.44	−180.76	−103.19	−77.57	18.52
	(1 0 −1)	2	5.62	−182.34	−104.87	−77.47	16.07
	(0 0 2)	2	6.15	−211.85	−104.51	−107.35	8.21
	(1 1 −1)	4	4.25	−199.74	−121.56	−78.18	7.60
	(1 1 0)	4	4.48	−224.07	−128.09	−95.98	0.19

[a] The number of a certain crystal face *(h k l)* of a grown crystal.
[b] Lattice-plane spacing.
[c] All energies in this paper are in kJ/mol.

Table 3
Corresponding relationships of the molar ratios, mass ratios, super cell patterns and the number of substituted molecules.

Molar ratio (CL-20:FOX-7)	Mass ratio[a]	Super cell	Total number of molecules	Number of substituted molecules
11:1	0.970	4 × 3 × 2	96	8
10:1	0.967	11 × 2 × 2	176	16
9:1	0.964	5 × 2 × 2	80	8
8:1	0.959	3 × 3 × 2	72	8
7:1	0.954	4 × 2 × 2	64	8
6:1	0.947	7 × 2 × 2	112	16
5:1	0.937	3 × 2 × 2	48	8
4:1	0.922	5 × 2 × 2	80	16
3:1	0.899	2 × 2 × 2	32	8
2:1	0.856	3 × 2 × 2	48	16
1:1	0.748	2 × 2 × 2	32	16
1:2	0.597	3 × 2 × 2	48	16
1:3	0.497	2 × 2 × 2	32	8
1:4	0.425	5 × 2 × 2	80	16
1:5	0.372	3 × 2 × 2	48	8
1:6	0.330	7 × 2 × 2	112	16
1:7	0.297	2 × 2 × 2	64	8
1:8	0.270	3 × 3 × 2	72	8
1:9	0.248	5 × 2 × 2	80	8
1:10	0.228	11 × 2 × 2	176	16
1:11	0.212	3 × 2 × 2	96	8

[a] The mass percent of CL-20.