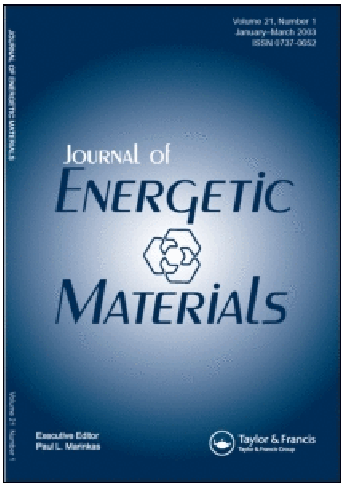

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Hexanitrohexaazaadamantane: A New Potential High-Energy-Density Compound Superior to Hexanitrohexaazaisowurtzitane (CL-20)

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Hexanitrohexaazaadamantane: A New Potential High-Energy-Density Compound Superior to Hexanitrohexaazaisowurtzitane (CL-20)

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To look for new high-energy-density compounds (HEDC) with good performance, molecular mechanics (MM) was first employed to predict the molecular spatial packings (or crystal structures) of hexanitrohexaazaadamantane (HNHAA) and the well-known high-energy-density compound hexanitrohexaazawurtzitane (ε-CL-20). Then, periodic ab initio calculations, using the GGA-RPBE method, were carried out on the band structures of the two predicted crystals. The results showed that they tended to crystallize in the same space group $P2_1/c$, and they have similar density of states (DOS) and comparable band gaps (ΔE, 3.546 and 3.522 eV for HNHAA and ε-CL-20, respectively), which presented similar thermal initiation mechanisms and comparable sensitivity. Furthermore, HNHAA was recommended as a new potential HEDC with better detonation properties than the well-known ε-CL-20,

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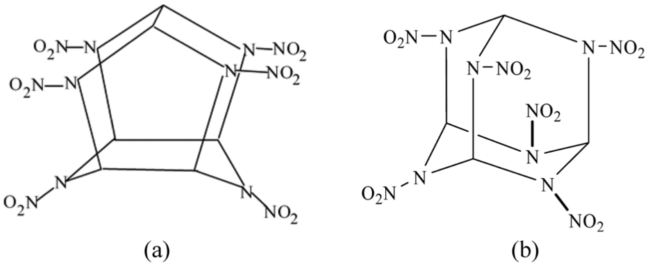
due to its larger density (2.315 g · cm^{-3}) than ε-CL-20 (2.173 g · cm^{-3}).

Keywords: detonation properties, GGA-RPBE method, hexanitrohexaazaadamantane (HNHAA), high-energy-density compound (HEDC), initiation mechanism, sensitivity

Introduction

To meet the development of national defense and national economy, new and higher performances are required for high-energy-density materials (HEDMs). HEDMs consist of high-energy-density compounds (HEDCs), oxidants, and additives (such as binders and insensitive components). It is a heated point for scientists and engineers to look for HEDC in the world energy resource and materials fields [1–7]. Thus, to make a breakthrough in HEDC research, it is a key step to make molecular design and to synthesize new and excellent HEDC.

Among various types of HEDCs, organic cage compounds have attracted much attention. CL-20 (hexanitrohexaazaisowurtzitane; see the molecular structure as Fig. 1a) [1] is a typical example, and its successful synthesis has been praised as a breakthrough in the history of explosives. Due to its good performance in many fields [8–13], such as explosives, propellants, propelling agent formulations, and so on, it is promising to be the most widely used as an HEDC of those synthesized in the past 20 years. We have been trying to find a new potential



(a) (b)

Figure 1. Molecular structures of (a) CL-20, and (b) HNHAA.

HEDC [14–16]. Previous studies on the gas molecules of polynitrohexaazaadamantanes (PNHAA) have indicated that the three PNHAA with 4–6 nitro groups complied with the quantitative energy standard (density $\rho > 1.9\,\mathrm{g \cdot cm^{-3}}$, detonation velocity $D > 9.0\,\mathrm{km \cdot s^{-1}}$, and detonation pressure $P > 40\,\mathrm{GPa}$) and the stability requirement (the dissociation energy of trigger bond $E > 120\,\mathrm{kJ \cdot mol^{-1}}$) as a feasible HEDC [16]. As is the case with CL-20, these three PNHAA belong to nitramine series. Besides, based on the studies on their gas molecules, it was found that the theoretical density (ρ_0) of hexanitrohexaazaadamantane (HNHAA, $2.08\,\mathrm{g \cdot cm^{-3}}$; see the molecular structure as in Fig. 1b) was a little larger than that of the most stable polymorph of CL-20 (ε-CL-20, $2.04\,\mathrm{g \cdot cm^{-3}}$). Here, ρ_0 of each compound was obtained from the average mole volume divided by the molecular weight. The mole volume, defined as the volume inside a contour of 0.001 $\mathrm{e \cdot Bohr^3}$ density [17], was calculated by a Monte Carlo method, based on the fully optimized structures at the DFT-B3LYP/6–31G* level, and this method has been proved reliable [18]. The approximity of the ρ_0 of HNHAA and CL-20 predicted the comparability of their detonation properties (detonation velocity and detonation pressures, the most important parameters to balance the performance of an HEDC) between HNHAA and CL-20. Besides, the calculations at the UB3LYP/6-31G* level have shown that the dissociation energy ($E_{\text{N-NO}_2}$) of N-NO_2 trigger bond of HNHAA ($142.65\,\mathrm{kJ \cdot mol^{-1}}$) was comparable with that of CL-20 ($143.93\,\mathrm{kJ \cdot mol^{-1}}$) [19], predicting their similar thermal stability. Therefore, from the studies on the gas molecules, HNHAA was recommended as a potential HEDC.

However, most high-energy materials exist in an agglomerate phase, especially in a crystal form; thus, investigations on crystals are more applicable than on gas molecules. And it agrees with the trend from ‘‘molecule chemistry’’ to ‘‘material chemistry’’ by paying more emphasis on the studies of crystals of high energy materials. In this article, by comparing the ε-CL-20 crystal obtained from theoretical prediction with that from experiments, molecular mechanics (MM) was firstly proved to be feasible in predicting molecular spatial packing (or crystal structures); then periodic ab initio calculations were carried out to calculate the band structures of the predicted crystals of ε-CL-20 and HNHAA. Compared with the structures and properties of ε-CL-20, HNHAA was finally predicted as a feasible HEDC superior to ε-CL-20.

Prediction of Molecular Packing

To predict the crystal structure of a molecule, the most important step is to choose a proper force field type. Of various force fields, it is well known that the Compass [20] and Dreiding [21] force fields are the most suitable for compounds containing C, H, O, and N atoms [20–23]. By comparing the optimized molecule structures of HNHAA from the two force fields with that from the density functional method with the GGA-RPBE (generalized gradient approximation—revised Perdew-Burke-Ernzerhof) [24] exchange-correlation functional, respectively. In Fig. 2, it is found that the two force fields are both suitable for HNHAA, although the Compass can produce a more consistent structure with that from GGA-RPE than the Dreiding. Furthermore, the following calculations showed that COMPASS is quite suitable for ε-CL-20. For convenient comparisons, we will provide the molecular packings for HNHAA and ε-CL-20

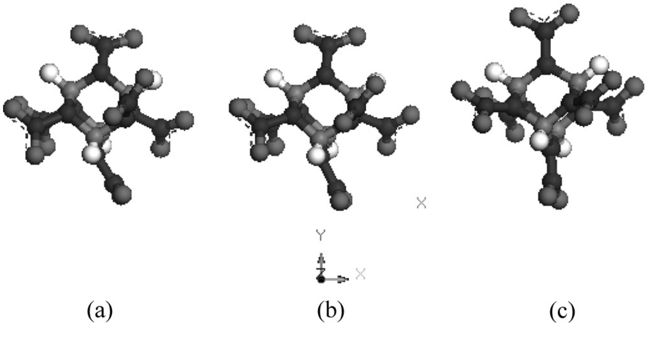


Figure 2. Optimized molecular structures of 2,4,6,8,9,10-hexanitrohexaazaadamantane obtained from three methods: (a) GGA-RPBE, (b) Compass, and (c) Dreiding.

using both Compass and Dreiding by the Polymorph module in MS 3.0 [25].

It is well known that among the 230 space groups, quite a small fraction is typical of organic crystals. It has been found that over 80% organic compounds crystallize in the 7 typical space groups ($P2_1/c$, P-1, $P2_12_12_1$, $P2_1$, Pbca, $C2/c$, and Pna2_1) on the basis of statistical data [26]. This provides us with the possibility to confine the global search to the most frequent groups only. In each space group, a most stable polymorph with the least energy will be found, and finally seven most stable polymorphs will be obtained in the 7 space groups. By comparing energies of the seven stable polymorphs, the polymorph with the lowest energy is recommended as the most reasonable molecular packing (crystal structure) of the compound.

The origin molecule of ε-CL-20 was derived from the experiment [27]. Table 1 lists the unit cell parameters of the packing with the least energy in seven space groups using Compass. Here, the energy is defined as the average molecular energy of the packing.

As seen in Table 1, there are certain energy differences per molecule among the packings with the least energy in the seven space groups, the ε-CL-20 molecule in $P2_1$ packing has the lowest energy, and it appears that ε-CL-20 tends to crystallize in $P2_1$. Meanwhile, it is found that the obtained E, ρ, and cell parameters of the packings in $P2_1/c$ and Pna2_1 are almost the same. This indicates that it is possible for ε-CL-20 to crystallize in the $P2_1/c$ or Pna2_1. It is most interesting that the predicted cell parameters in these two space groups are much approximate to the experimental values. Therefore, this method used to predict molecular packing has been proved reliable to some extent in working as a good assistant tool of experiment to investigate the crystal properties of known or unknown organic compounds.

Pivina et al. have previously predicted that HNHAA belonged to P-1 [28] by using the atom-atom potential method (AAPM) [29]. However, our calculations from the Compass force field in Table 2 show that HNHAA tends to crystallize in $P2_1/c$, in which the HNHAA molecule has the lowest energy (E, −3574.32 kJ). To testify to the reliability of the prediction, molecular packing calculations for HNHAA using Dreiding were

Table 1
Molecular packings obtained from Compass for ε-CL-20 in seven space groups

Space groups	$P2_1/a$[a]	$P2_1/c$	$P2_12_12_1$	P-1	Pbca	$C2/c$	Pna2_1	$P2_1$
Z	4	4	4	4	8	8	4	2
E	−1400.51	−1409.66	−1406.32	−1395.66	−1397.25	−1400.01	−1409.66	−1416.35
a	13.70	12.64	7.58	7.69	15.76	27.25	12.64	11.68
b	12.55	7.740	23.54	21.01	13.66	7.65	13.69	7.57
c	8.83	13.69	7.55	9.21	12.86	25.65	7.74	7.62
α	90.00	90.00	90.00	41.67	90.00	90.00	90.00	90.00
β	111.18	90.00	90.00	51.48	90.00	150.26	90.00	94.25
γ	90.00	90.00	90.00	75.97	90.00	90.00	90.00	90.00
ρ	2.055	2.173	2.160	2.080	2.102	2.196	2.173	2.166

[a] Crystal structure from experiment; see Baur and Kassner [26].

Units: Z, the number of molecules in one unit cell; energy (E, energy of per molecule), kJ/mol; density (ρ), $\mathrm{g \cdot cm^{-3}}$; cell parameters (a, b, and c: Å; α, β, and γ: °).

Table 2
Molecular packings obtained from Compass for HNHAA in seven space groups

Space groups	$P2_1/c$	$P2_12_12_1$	P-1	Pbca	$C2$/c	Pna2_1	$P2_1$
E	−3574.32	−3567.34	−3572.98	−3563.62	−3565.25	−3561.32	−3558.94
a	7.13	13.35	7.76	13.41	12.47	14.23	7.39
b	12.83	7.16	7.11	13.25	7.76	7.08	12.43
c	14.57	12.76	12.69	13.50	24.79	11.81	7.52
α	90.00	90.00	78.33	90.00	90.00	90.00	90.00
β	117.49	90.00	95.77	90.00	100.06	90.00	115.23
γ	90.00	90.00	60.94	90.00	90.00	90.00	90.00
ρ	2.315	2.245	2.346	2.283	2.319	2.301	2.192

Table 3
Molecular packings obtained from Dreiding for HNHAA in seven space groups

Space groups	$P2_1/c$	$P2_12_12_1$	P-1	Pbca	C2/c	Pna2_1	$P2_1$
E	−1250.07	−1243.59	−1248.86	−1242.33	−1246.52	−1243.72	−1242.25
a	13.51	13.52	8.16	28.06	28.05	13.94	7.87
b	8.223	12.96	7.98	6.79	8.05	8.33	6.79
c	13.71	6.85	14.21	14.97	14.99	12.52	12.97
α	90.00	90.00	77.61	90.00	90.00	90.00	90.00
β	117.32	90.00	15.03	90.00	120.56	90.00	90.02
γ	90.00	90.00	120.52	90.00	90.00	90.00	90.00
ρ	1.930	1.988	1.897	1.921	1.879	1.883	1.972

further carried out, and the results are shown in Table 3. From this table, it is also shown that it is the $P2_1/\mathrm{c}$ space group, in which HNHAA molecules has the lowest energy (E, $-2800.14\,\mathrm{kJ}$) and the cell parameters are similar to those from Compass. From the above, it can be predicted that HNHAA tends to crystallize in the same space group $P2_1/\mathrm{c}$ as ε-CL-20 does; in addition, by comparing the unit cell parameters (a, b, and c) of corresponding reasonably predicted packings of HNHAA and ε-CL-20, it is interesting that their unit cell parameters are close to each other, correspondingly. Meanwhile, as we all know, the loaded density of explosive is the most important factor to determine the detonation properties (such as detonation velocity D and detonation pressure P, and D and P are usually proportional to ρ^2). Here, the COMPASS calculations indicate that the density (ρ) of HNHAA crystal is ($2.315\,\mathrm{g}\cdot\mathrm{cm}^{-3}$) somewhat larger than that of ε-CL-20 ($2.173\,\mathrm{g}\cdot\mathrm{cm}^{-3}$). According to this, it is predicted that if HNHAA can be successfully synthesized, its detonation properties may be superior to those of ε-CL-20, one of the most important HEDC in the field of energy sources currently.

Periodic ab Initio Calculations

The investigation on the electronic structure (band structure) of HEDC is of much importance to understand its related properties. Density of states (DOS) is a presentation of the band structure of a crystal, and PDOS, in which DOS is projected on atom-centered orbital, such as s and p states of C, N, and O atoms, can be used to understand the probability of electron distribution in each energy band and to investigate the constitution of energy bands (DOS). In this article, the DOS and PDOS of the predicted crystal of ε-CL-20 and HNHAA, as in Figs. 3 and 4, were both provided from the GGA-RPBE method in the DMol^3 [30, 31] module of the MS3.0 program. The calculation accuracy was set as fine with the DNP basis set, and all electrons were included.

Comparing Figs. 3a and 3b, it is found that DOS or PDOS of predicted crystal of ε-CL-20 is similar to that of its experimental

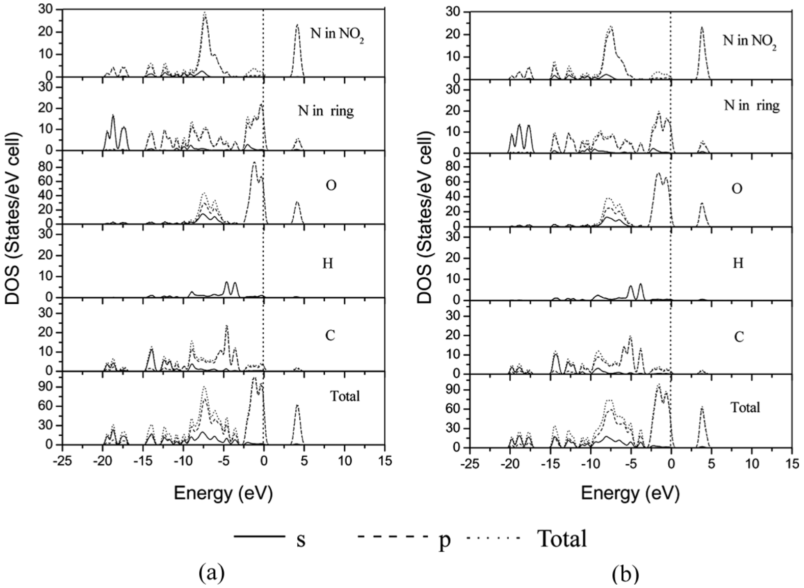


Figure 3. DOS (PDOS) of ε-CL-20 using the GGA-RPBE method: (a) experimental crystal and (b) predicted crystal.

crystal. This further proves the reliability of the crystal structures obtained from MM method. Figures 3a and 3b also show that the upper valence bands of ε-CL-20 mainly consist of the *p* states of N atoms in the ring and O atoms, and the lower conduct bands mainly the *p* states of N and O atoms in $–NO_2$. This indicates that the $N–NO_2$ fragment is the active center of ε-CL-20. It is also noted that near the Fermi energy, the *p* states of N in $–NO_2$ overlap with those of N atoms in the ring. According to the principle of energy matching, these *p* states contribute the $N–NO_2$ bond. Thus, the $N–NO_2$ bond tends to be the trigger bond of ε-CL-20 during thermolysis. This is in good agreement with experiments [32, 33] and that drawn from bond dissociation energy calculations on its gas molecule [34]. The DOS or PDOS of predicted HNHAA in Fig. 4 are similar to that of ε-CL-20 because they both belong to organic cage nitramine series, their crystals are in the same space group $P2_1/c$, and they have the same number 6 of $N–NO_2$ in each molecule.

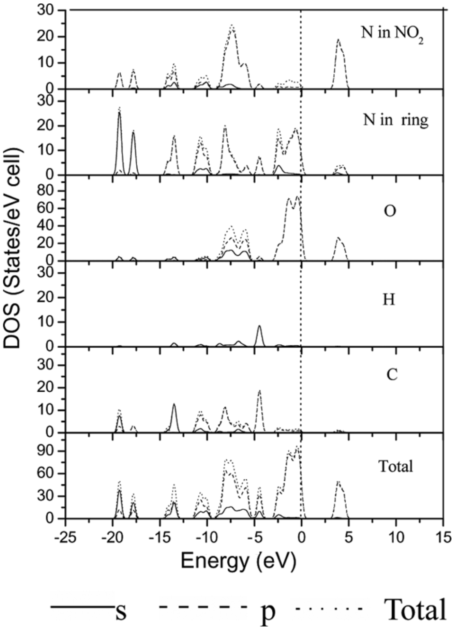


Figure 4. DOS (PDOS) of HNHAA using the GGA-RPBE method.

Based on their similar energy band structures, DOS or PDOS, ε-CL-20, and HNHAA are predicted to show similar properties; e.g., from the PDOS of HNHAA, the N–NO_2 bond is accordingly considered as the trigger bond during thermal decomposition, which is also in accord with that drawn from theoretical studies on its gas molecule [16].

As a high-energy material, to some extent, whether it can be used or how to put it into use is determined by its sensitivity, which is related to its structure. Previous theoretical studies have mainly concentrated on the relationship between the sensitivity and gas molecular structural parameters. Based on the research on the band structures of metal-azides in cluster modeling using an empirical quantum chemistry method (DV-Xα), the principle of easiest transition (PET) has been suggested to predict their relative sensitivity by our research group [35].

In the principle, the band gap (ΔE) between the highest occupied crystal orbital (HOCO) and the lowest unoccupied crystal orbital (LOCO) is used as a criterion to predict the sensitivity of the materials with similar structures and pyrolysis mechanism; the smaller the ΔE, the easier the electron transits, and the greater the sensitivity will be. Many experimental results have been well illustrated on the principle [35–37]. It is most important that this principle has also been found to be suitable for molecular crystals [38]. Here, our calculated ΔE for the predicted crystal of HNHAA (3.546 eV) almost equals that of ε-CL-20 (3.522 eV). However, the ordering of their ΔE is different from that of their dissociation energies ($E_{\mathrm{N-NO_2}}$) of gas molecules (142.65 and 143.93 $\mathrm{kJ \cdot mol^{-1}}$, respectively.) [39], and this may be due to the different molecular interactions in their crystals.

Conclusions

Based on theoretical studies on the potential high-energy-density compounds hexanitrohexazaadamantane (HNHAA) and ε-CL-20, several conclusions are obtained. HNHAA was predicted to crystallize in the same space group $P2_1/c$ as ε-CL-20 by an MM method. From the periodic calculations on the two crystals with the GGA-RPBE method, their similar band gaps (ΔE) presented similar sensitivities, which agreed well with those drawn from the bond dissociation energies of their gas molecules. It is worth noting that the density (ρ) of HNHAA crystal was predicted to be larger than that of ε-CL-20, and thus HNHAA promises to be a new potential HEDC superior to the well-known CL-20 due to its better detonation properties (such as detonation velocity and detonation pressure).

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