Theoretical Study on CL-20-Based Cocrystal Energetic Compounds in an External Electric Field

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ABSTRACT: An external electric field has great effects on the sensitivity of cocrystal energetic materials. In order to find out the relationship between the external electric field and sensitivity of cocrystals 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane/ benzotrifuroxan (CL-20/BTF), 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane/3,4-dinitropyrazole (CL-20/DNP), and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane/1-methyl-3,5-dinitro-1,2,4-triazole (CL-20/MDNT), density functional theory at B3LYP-D3/6-311+G(d,p) and M062X-D3/ma-def2 TZVPP levels was employed to calculate frontier molecular orbitals, atoms in molecules (AIM) electron density values, bond dissociation energies (BDEs) of the N–NO2 bond, impact sensitivity (H10), electrostatic potentials (ESPs), and nitro group charges (QNO2) in this work. The results show that a smaller highest occupied molecular orbital—lowest unoccupied molecular orbital gap and the BDEs, as well as H10, tend to have a larger sensitivity along with the positive directions in the external electric field. Moreover, a smaller local positive ESP (Vmax) leads to better stability in the negative electric field. The sensitivity of cocrystal molecules decreases gradually in the negative external electric field with the increase of negative nitro group charges. Finally, the change in the bond lengths, AIM electron density values, and nitro group charges correlate well with the external electric field strengths.

1. INTRODUCTION

High energy density materials have attracted considerable attention because of their good properties.1−3 The study of the external electric field effect on a molecule has critical guiding significance for the study of the properties of energetic materials and the purposeful synthesis of new explosives with high-performance indices,4,5 such as safety and stability, difficulty in trigger, and more energy when they explode. The high nitrogen content and prominent thermal stability enable them to have potential applications in many fields such as explosives, propellants, and so on.6 2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) is a kind of cage nitramine explosive, which has exceedingly high energy density and detonation performance.7 However, because of its high mechanical sensitivity, which can significantly damage the safety, the application prospect of CL-20 is seriously limited. Cocrystallization is becoming an increasingly hot topic in the field of energetic materials.8−14 As a new modification technique, cocrystallization involves combining two or more different kinds of molecules into the same crystal lattice through noncovalent bonds to form multicomponent crystals with specific structures and properties.15−18 In order to solve the faults in the mechanical sensitivity of CL-20, using energy-insensitive materials with a lower mechanical sensitivity as ligands to form a cocrystal with CL-20 can effectively improve the density, thermal stability, and mechanical sensitivity. Recently, CL-20 has been cocrystallized with azole compounds19,20 [dinitropyrazole (DNP), 1-methyl-3,5-dinitro-1,2,4-triazole (MDNT), and benzotrifuroxan (BTF)];21 there were no nitro group and hydrogen atom. For example, Yang21 prepared a CL-20/BTF cocrystal and found that it displayed superior detonation power compared to BTF. In 2017, Rodzevich et al.22 studied the effect of the external electric field on the decomposition rate of silver azide by an experimental method. Politzer23,24 and Song et al.25 predicted the influence of the external electric field on the explosive sensitivity by means of investigations into their molecular and electronic structures and energy gaps of the frontier molecular orbitals (FMOs) and electrostatic potentials (ESPs). However, properties such as sensitivity of these three cocrystal molecules under an electric field are seldom studied, so this work aims to find out the relationship between the external electric field and sensitivity of these cocrystals using quantum chemistry.

Ping et al.26 explored the effect of the external electric field on the C–NO2 or N–NO2 bonds by AIM analysis; Lv et al.27 discussed the effects of the external electric field on the bond dissociation energies and barrier heights of the cleavage
The transfer of electrons and nitro oxygen plays an important role in the trigger reaction of energetic materials, and N−NO2 is often the trigger bond of nitramine explosives. Therefore, in order to reveal the nature of molecular orbital (LUMO), which are called FMOs, are two important aspects of reaction mechanisms. Particularly, their energy gap can determine the kinetic stability, chemical reactivity, and optical polarizability of an energetic material.

The HOMO is spread over the molecule of MDNT under the positive electric field and in the absence of an electric field. However, under the negative electric field, the HOMO is mainly distributed on the skeleton carbon atom and nitro group of CL-20. Based on the above changes in three cocrystal molecules, it can be seen that the negative electric field changes the distribution of the HOMO, and the distribution of the LUMO is altered by the positive electric field. It should be noted that the LUMO of CL-20/DNP changed under the negative electric field.

Evidence suggests that FMOs play a significant role in chemical reactivity; larger HOMO and LUMO energy gaps lead to lower chemical reactivity, making the molecule more stable. As can be seen from the energy gaps (Table 1), it is revealed that the order of energy gaps under the positive electric field and in the absence of an electric field is CL-20/MDNT > CL-20/DNP > CL-20/BTF. Under the negative electric field, the sequence for the gaps is CL-20/DNP > CL-20/MDNT > CL-20/BTF. As a result, CL-20/BTF has maximum sensitivity in the external electric field.

2.2. Change in the Trigger Bond. Exploring the trigger bond is a vital means to explore the influence of the external electric field on the sensitivity of cocrystal materials. In this section, we present the study of the change in the trigger bond of CL-20 cocrystals under different electric fields. Furthermore, the well-known concept of bond critical point (BCP) is also associated with the topological analysis of electron density ρ(r), which was formulated in the “quantum theory of atoms in molecules” theory of Bader and co-workers. The AIM methodology provides a unique tool for the study of bonding interactions. A lot of research works have demonstrated that the shorter the trigger bond is, the larger the dissociation energy and the bond strength will be. Therefore, the sensitivity finally decreases. In this work, N−NO2 is found to be the trigger bond after bond order analysis. The bond lengths and AIM analysis of N−NO2 are shown in Table 2.

AIM theory can analyze the bond strength by characterizing the topological property parameters (such as the total electron density and potential energy density) at the BCP. As can be seen from Table 2, a longer trigger bond length (R_{N−N}), a lower total electron density (ρ), and a larger potential energy (V(r)) will lead to a weaker bond strength with the increase of the positive field. This makes the bond length become longer and the sensitivity higher. The change trends of the ρ and V(r) values along the negative directions in the external electric field are opposite to those along the positive directions. Table 2 shows the order of R_{N−N} in the positive electric field, which is CL-20/MDNT > CL-20/DNP > CL-20/BTF, and the sequence for the negative electric field is CL-20/MDNT < CL-20/DNP < CL-20/BTF, and the sensitivity higher. The change trends of the ρ and V(r) values along the negative directions in the external electric field are opposite to those along the positive directions. Table 2 shows the order of R_{N−N} in the positive electric field, which is CL-20/MDNT > CL-20/DNP > CL-20/BTF, and the sequence for the negative electric field is CL-20/MDNT < CL-20/DNP < CL-20/BTF, and the sensitivity higher. The change trends of the ρ and V(r) values along the negative directions in the external electric field are opposite to those along the positive directions. Table 2 shows the order of R_{N−N} in the positive electric field, which is CL-20/MDNT > CL-20/DNP > CL-20/BTF, and the sequence for the negative electric field is CL-20/MDNT < CL-20/DNP < CL-20/BTF, and the sensitivity higher.
CL-20/DNP < CL-20/BTF. Therefore, CL-20/BTF is the most sensitive of the three cocrystals.

Analyzing the $\Delta R_{N-N}$ (the differences between the bond lengths in the electric fields and those without an electric field), $\Delta \rho$ (the differences between the total electron density of the BCP in the electric field and that without an electric field), and $\Delta V(r)$ (the differences between the potential energy density in the electric fields and those without an electric field) is helpful for us to explore the influence of the external electric field on the trigger bond.\textsuperscript{38}

Topological analysis of the electron charge density and its Laplacian function constitutes a powerful tool to investigate the electronic properties of the molecular system and allows an in-depth examination of the interatomic interactions.\textsuperscript{39} The Laplacian of the electron density ($\nabla^2 \rho$) value at the BCP indicates that when $\nabla^2 \rho < 0$, the electronic charge is concentrated in the internuclear region and is therefore shared by two nuclei.\textsuperscript{35} Thus, there is a covalent interaction between the three cocrystal molecules.

To show the influence clearly, the fitting results of $\Delta R_{N-N}$, $\Delta \rho$, and $\Delta V(r)$ of the three cocrystal molecules in the electric field are listed in Table 3 and Figures 2–4. The linear correlation coefficients $R^2$ change in the range of 0.922–0.992, which indicates that $\Delta R_{N-N}$, $\Delta \rho$, and $\Delta V(r)$ correlate well with the electric field intensity.

In order to further explore the effect of the external electric field on cocrystal sensitivity, the bond dissociation energy ($E_{BDE}$), interaction energy ($E_{int}$), and impact sensitivity ($H_{50}$) under different electric fields are calculated. The calculated results are shown in Table 4. As can be seen from Table 4, $E_{int}$ of CL-20 cocrystals increases under the negative external electric field, while under the positive electric field, some of these crystals grow, while others decrease, which indicates that the effect of the external electric field on $E_{int}$ is complicated.

The bond dissociation energy (BDE) is beneficial for us to understand the thermal stability and the decomposition process of an energetic material.\textsuperscript{40} From Table 4, it is seen that the greater the electric field intensity is, the smaller the $E_{BDE}$ and $H_{50}$ become, and the sensitivity of explosives tends to become higher finally under the positive electric field. The change trends of the $E_{BDE}$ and $H_{50}$ values along the negative direction in the external electric field are opposite to those along the positive direction.

In conclusion, the ranking for the BDE under the positive electric field is CL-20/DNP > CL-20/MDNT > CL-20/BTF and the sequence under the negative field is CL-20/MDNT > CL-20/DNP > CL-20/BTF. However, at $-0.010$ a.u., the $E_{BDE}$ of CL-20/DNP is larger than that of others. The order of impact sensitivity is CL-20/MDNT > CL-20/DNP > CL-20/BTF.

2.3. Electrostatic Potential. ESP is a measurable and fundamentally significant physical property of compounds as it provides information about the distribution of charge density and molecular reactivity.\textsuperscript{41} The maximum and minimum surface ESPs of CL-20 cocrystals are displayed in Figure 5.

In this section, the ESP of three cocrystal molecules is calculated with the help of Multiwfn at 0.001 e·Bohr$^{-3}$ electron density and the 0.25 Bohr lattice point spacing surface. Figure 5a–c shows that the positive ESPs (red areas) are mainly distributed on the parent skeleton, while the negative ESPs (blue areas) are concentrated on the edges of the molecules, especially on the nitrogen and oxygen atoms of nitro groups, mainly due to their higher electronegativity.
As can be seen from Table 5, with the increase of the positive electric field, the maximum and minimum of positive surface potentials of both CL-20/BTF and CL-20/MDNT increase, but the maximum of positive ESPs for CL-20/DNP increases at first and then decreases. With the increase of the negative electric field, the maximum and minimum of positive surface potentials of both CL-20/DNP and CL-20/MDNT increase, but the maximum of positive ESPs of CL-20/BTF decreases at first and then increases. The varieties of ESPs are
consistent with this point, which indicates that the external electric field has a significant effect on the movement of charge. In the presence of the external electric field, as can be seen from Figure 5a, the ESP of the intersection for CL-20/BTF changes from red to light blue and a part of the red region changes to blue, indicating that the positive ESP between molecules decreases and a part of the positive ESP changes into negative ESP. In Figure 5b,c, the ESP of the intersection
for CL-20/DNP and CL-20/MDNT changes from light blue to light pink, and the color of the blue region becomes lighter, indicating that the negative ESP between molecules changes into a positive ESP and a part of the negative ESP decreases. All the above changes indicate that the changes in the charge distribution of cocrystals bring about sensitivity changes.

Politzer and Murray showed that the smaller the local positive ESP ($V_{s \text{max}}$) of the trigger bond is, the lower the sensitivity of the explosive will become, making the molecules more stable. To study the variations in the properties of the trigger bond under the external electric field, the $V_{s \text{max}}$ is calculated and the results are displayed in Table 5. The results obtained show that the $V_{s \text{max}}$ tends to be larger at a higher positive electric field intensity, so the sensitivity increases gradually. Table 5 shows the calculated results for $V_{s \text{max}}$. The sequence for $V_{s \text{max}}$ is CL-20/DNP < CL-20/MDNT < CL-20/BTF. Therefore, CL-20/BTF has a maximum sensitivity of the three cocrystals.

The higher the ratio of positive ESPs, the better the stability of the molecular structure. The ratio of the surface area of electrostatic surface potentials and positive electrostatic surface potentials of complexes is shown in Table 6. With the increase of the positive electric field strength, the ratio of the positive ESP and the negative ESP increases, indicating that the negative ESP between molecules changes to light pink, and the color of the blue region becomes lighter, and the color of the light pink region becomes lighter.

Table 6. Ratio of Positive ESPs and the Surface Area of ESPs of CL-20 Cocrystals

| compound   | external electric field/a.u. | $A_{\text{neg}}/\AA^2$ | $A_{\text{pos}}/\AA^2$ | $A_{\text{neg}}/\AA^2$ | ratio$_{\text{pos}}$ (%) |
|------------|------------------------------|-------------------------|-------------------------|-------------------------|--------------------------|
| CL-20/BTF  | 0.010                        | 1576.19                 | 832.34                  | 743.85                  | 52.81                    |
|            | 0.005                        | 1576.74                 | 857.72                  | 719.02                  | 54.40                    |
|            | 0.000                        | 1575.86                 | 873.92                  | 701.94                  | 55.45                    |
|            | $-0.005$                     | 1577.29                 | 905.52                  | 671.77                  | 57.41                    |
|            | $-0.010$                     | 1575.55                 | 918.24                  | 657.31                  | 58.28                    |
| CL-20/DNP  | 0.010                        | 1544.57                 | 803.03                  | 741.54                  | 51.99                    |
|            | 0.005                        | 1545.70                 | 820.78                  | 724.92                  | 53.10                    |
|            | 0.000                        | 1462.24                 | 826.03                  | 636.21                  | 56.49                    |
|            | $-0.005$                     | 1487.69                 | 887.92                  | 599.78                  | 59.68                    |
|            | $-0.010$                     | 1565.58                 | 982.15                  | 583.43                  | 62.73                    |
| CL-20/MDNT | 0.010                        | 1505.56                 | 853.82                  | 651.74                  | 56.71                    |
|            | 0.005                        | 1477.95                 | 847.97                  | 629.98                  | 57.37                    |
|            | 0.000                        | 1521.22                 | 875.62                  | 645.60                  | 57.56                    |
|            | $-0.005$                     | 1517.27                 | 891.87                  | 625.40                  | 58.78                    |
|            | $-0.010$                     | 1508.19                 | 887.87                  | 620.32                  | 58.87                    |

Table 7. Charges of the Nitro Group in Complexes

| compound   | external electric field/a.u. | $Q_{\text{NO2}}$/a.u. | $\Delta Q_{\text{NO2}}$/a.u. |
|------------|------------------------------|------------------------|-------------------------------|
| CL-20/BTF  | 0.010                        | 0.0781                 | 0.0815                        |
|            | 0.005                        | 0.0377                 | 0.0411                        |
|            | 0.000                        | $-0.0034$              | 0.0000                        |
|            | $-0.005$                     | $-0.0455$              | $-0.0421$                     |
|            | $-0.010$                     | $-0.0889$              | $-0.0855$                     |
| CL-20/DNP  | 0.010                        | 0.0387                 | 0.0733                        |
|            | 0.005                        | 0.0214                 | 0.0560                        |
|            | 0.000                        | $-0.0346$              | 0.0000                        |
|            | $-0.005$                     | $-0.0732$              | $-0.0386$                     |
|            | $-0.010$                     | $-0.1270$              | $-0.0924$                     |
| CL-20/MDNT | 0.010                        | 0.0426                 | 0.0668                        |
|            | 0.005                        | 0.0186                 | 0.0428                        |
|            | 0.000                        | $-0.0242$              | 0.0000                        |
|            | $-0.005$                     | $-0.0770$              | $-0.0528$                     |
|            | $-0.010$                     | $-0.1310$              | $-0.1068$                     |

Table 7. Charges of the Nitro Group in Complexes

Figure 6. Fitting results of the charges of the nitro group of CL-20/BTF, CL-20/DNP, and CL-20/MDNT in the electric field.

The three cocrystal crystals are listed in Table 3, and their result is $R_{\text{CL-20/BTF}}^2 = 0.999$, $R_{\text{CL-20/DNP}}^2 = 0.972$, and $R_{\text{CL-20/MDNT}}^2 = 0.975$. It can be seen that there is a good linear relationship of the charge of the nitro group in the electric field. The results show that the electric field has a major influence on the negative charge of the nitro group.

3. CONCLUSIONS

In this work, the FMOs, AIM topological analysis, ESP, and charge of the nitro group of CL-20 cocrystals are investigated systematically using DFT. The results are summarized as follows:
1 The electron structure analysis showed that the positive electric field causes the energy gap of the CL-20 cocrystals to decrease, while the negative electric field makes the energy gap larger. CL-20/BTF has the smallest energy gap and its chemical reactivity is higher than that of other compounds. Therefore, CL-20/BTF is the most sensitive of the three cocrystals.

2 By analyzing the BDEs of N=NO2 and $H_{\text{form}}$, we can draw the conclusion that with the increase of the positive electric field, the smaller bond dissociation energy, impact sensitivity, and the longer trigger bond length tend to have a larger sensitivity. Under the negative electric field, the situation is the opposite to that of the positive electric field. AIM theory reveals the reason for the change in the bond length.

3 The analysis of ESP shows that the $V_{e\text{max}}$ of the three cocrystal molecules tends to be larger at higher positive electric field intensities, so the sensitivity increases gradually. However, this result is in contrast to the negative electric field.

4 The larger the negative electric field, the more the negative charge of the nitro group, causing the sensitivity to decrease. All these theoretical investigations can help us to understand the initiation mechanism of more complex energetic materials in the external electric field and will certainly be useful in determining the safe use of explosives, avoiding catastrophic explosions in the external electric field.

4. COMPUTATIONAL DETAILS

All the calculations were performed with the Gaussian 16 package,[44] based on DFT. The molecular structure was fully optimized by using the B3LYP-D3/6-311+G(d,p) method in the external electric field as well as in the absence of a field. The stable structure was judged by the “no imaginary frequency” criterion. Then, the M062X-D3 method was selected to calculate the molecular single-point energy of explosives with the ma-def2 TZVPP basis group. In order to further reveal the effect of the external electric field on the sensitivity of CL-20 cocrystals, the changes in the trigger bond and the molecular surface ESP were explored under the external electric field.

The external electric field perpendicular to the trigger-linkage directions has no obvious effects on the bond strength,[29] and only those parallel to the potential trigger-linkage directions is effective. To determine the positive direction of the electric field, VMD software was used to make the trigger bond parallel to the X-axis, and the positive direction of the X-axis is defined as the positive direction of the external electric field. The positive direction of the electric field is defined as $N \rightarrow NO_2$, and the field strength of the applied electric field is as follows: $\pm 0.005$, $0.000$, and $\pm 0.010$ a.u., respectively. Figure 7 shows the related molecular structures of the explored cocrystals, all of which were optimized at the B3LYP-D3/6-311+G(d,p) level. As can be seen from Figure 7, there is no intermolecular hydrogen bonding in CL-20/BTF because of the special structure of BTF. The intermolecular hydrogen bonding of CL-20/DNP is C=H⋯O and N=H⋯O, and the length of the C=H⋯O and N=H⋯O bonds are 2.728 and 2.097 Å. For CL-20/MDNT, the intermolecular hydrogen bonding is C=H⋯O, and the length of two C=H⋯O bonds is 2.954 and 2.388 Å.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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