Electronic properties and chemical bondings of C–H–N–O compounds

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ABSTRACT

We have performed the density functional theory (DFT) calculations within generalized gradient approximation (GGA) plus TS scheme to calculate the structural and electronic properties of C–H–N–O compounds. Due to the insufficient description of intermolecular interactions within the GGA calculations, the GGA plus TS dispersion correction have been used to optimize the structural parameters. The calculated results based on the GGA + TS calculations are in agreement with the experimental data, indicating that the introduction of TS dispersion correction can effectively obtain the structural properties of C–H–N–O compounds. The electronic properties of nineteen C–H–N–O compounds including density of states, Mulliken charges, bond populations and band structures have been obtained and analyzed. According to these calculated data, the electron distributions and charge transfers have been investigated, which are conducive to clarify the chemical bonding characters and further help to future research of understanding the initial chemistry within the detonating energetic materials.

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1. Introduction

High energy density materials (HEDMs) have received a great deal of scientific attention due to their numerous applications [1–5]. Polynitrogen compounds [1,2], high energy density mixed polymeric phase of CO and N_2 [3], pyridine derivatives [5], and C–H–N–O compounds [6–10] have been widely investigated. Among these HEDMs, the C–H–N–O compounds attract much interest [6–13] due to that they can be used as high explosives [14–21] and fuels [22,23]. Mladenović et al. [6,9] studied the equilibrium structures and energetics of CHNO isomers by using ab initio calculations with coupled cluster techniques and large basis set. The geometries of the minima, the barriers to linearity and isomerization energies, the harmonic vibrational frequencies and the minimum energy paths have been shown and analyzed. Using an ab initio quantum chemical study, Shapley and Bacskay [7]

investigated the potential energy surfaces linked with the HCNO system, which were associated with the possible routes of isomerization and decomposition. The theoretical methods for calculating detonation velocity [14,19], detonation pressure [15,16,21], and detonation temperature [18] of CHNO explosives/mixed explosives have been reported, which effectively predicted the detonation performance. It can be seen that the quest for various C–H–N–O compounds has been widely performed. Hence many molecular crystals have been synthesized to create new CHNO-based explosives. Unfortunately, these crystals have not been fully investigated and were barely compared with each other. In particular, it is well-known that the sensibility of energetic materials to thermal stimulus, mechanical stimulus or initiate detonation is very important to their potential applications, which is associated with chemical reaction processes. Hence, in order to preferably take advantage of energetic materials before the detonation initiation, it is necessary to understand their electronic properties and chemical bondings. Then, we have used the first-principles density functional theory (DFT) to further study the structural and electronic properties of C–H–N–O compounds including HNCO [24], CH_4N_2O [25–31], $CH_4N_4O_2$ [32,33], $CH_5N_3O_4$ [34,35], $CH_6N_2O_3$ [36], CH_6N_4O [37,38], $CH_9N_7O_3$ [39,40], $C_2H_2N_2O$

[41], $C_2H_4N_4O_2$ [42], C_2H_5NO [43], $C_2H_6NO_{4.5}$ [44], $C_2H_6N_2O_4$ [45], $C_2H_7N_3O_3$ [46], $C_3H_3N_3O_3$ [47,48], $C_3H_6N_4O_3$ [49,50], $C_3H_{12}N_6O_3$ [51], $C_5H_4N_4O_3$ [52], $C_5H_7N_5O_2$ [53] and $C_8H_5NO_2$ [54].

2. Method of calculations

All first-principles calculations were carried out within the context of the density-functional theory through the plane-wave ultrasoft pseudopotential. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional [55] was used for treating the exchange-correlation energy. However, it is well-known that DFT calculations are unable to accurately treat the intermolecular interactions of C–H–N–O molecular crystals. Hence the TS dispersion correction [56] as implemented in CASTEP [57] has been adopted in our calculations, which provided obvious improvements for describing the intermolecular interactions. A plane-wave cutoff energy of 380 eV was used here. The valence electron configurations contained H $1s^1$, C $2s^22p^2$, N $2s^22p^3$ and O $2s^22p^4$. These structures were fully relaxed to their equilibrium volumes until the tolerances of total energy within 5.0×10^{-6} eV/atom, maximum force within 0.01 eV/Å, maximum stress within 0.02 GPa and maximum displacement within 0.0005 Å.

3. Results and discussion

3.1. Structural properties

The space group of orthorhombic HNCO (Isocyanic acid) is Pnma. The N, C and O atoms are located at 4c Wyckoff sites (0.0648,0.25,0.1108), (0.167,0.25,0.2195) and (0.2705,0.25,0.3367) [24], respectively. The space group of tetragonal $CO(NH_2)_2$ (Urea) is $P4\,2_1m$. The C, O, N, H1 and H2 atoms are located at 2c site (0,0.5,0.3283(1)), 2c (0,0.5,0.5963(1)), 4e (0.1447(1),0.6447,0.1784(1)), 4e (0.2552,0.7552,0.2845), 4e (0.1428,0.6428,-0.0339) [25]. The space group of orthorhombic $(NH_2)_2CNNO_2$ (Nitroguanidine) is Fdd2. The C, N1, N2, N3, N4, O1, O2, H1, H2, H3 and H4 atoms are located at 16b sites [32]. The space group of monoclinic $(OC(NH_2)_2H)(NO_3)$(Urea nitrate) is $P2_1/c$. It has one, three, four and five different types of C, N, O and H atoms, respectively, which are located at 4e sites [34]. The space group of orthorhombic $(H_2N)_2CO(H_2O_2)$(Urea hydrogen peroxide) is Pnca. It has two, one, one and three different types of O, C, N and H atoms, respectively. The O1, O2, C, N and H(1-3) atoms are located at 4c, 8d, 4c, 8d and 8d sites [36]. The space group of monoclinic CH_6N_4O (Carbohydrazide) is $P2_1/c$. It has one, four, one and six different types of O, N, C and H atoms, respectively, which are located at 4e sites [37]. The space group of orthorhombic $CH_9N_6NO_3$ (Tri-aminoguanidinium nitrate) is Pbcm. It has one, seven, two and six different types of C, N, O and H atoms, respectively. The C, N(1-7), H(1-3), H(4-6), O1 and O2 atoms are located at 4d, 4d, 4d, 8e, 4d and 8e sites [39]. The space group of orthorhombic $C_2H_2N_2O$ (Cyanoformamide) is Pnma. It has two, two, one and two different types of C, N, O and H atoms, respectively, which are located at 4c sites [41]. The space group of monoclinic $NH_2OCN_2CONH_2$ (Azido-carbonamide) is $P2_1/n$. It has one, two and one different types of O, N and C atoms, respectively, which are located at 4e sites [42]. The space group of trigonal $((CH_3)CO(NH_2))$(Acetamide) is R3c. It has two, one, one and five different types of C, O, N and H atoms, respectively, which are located at 18b sites [43]. The space group of orthorhombic $(NH_4)H(C_2O_4)(H_2O)_{0.5}$ (Ammonium hydrogen oxalate hemihydrate) is Pnma. It has two, five, two and eight different types of C, O, N and H atoms, respectively. The C(1-2), O(1-4), O5, N(1-2), H(1-3,8), H(4-7) atoms are located at 8d, 8d, 4c, 4c, 8d and 4c sites [44]. The space group of monoclinic $N_2H_5HC_2O_4$ (Hydrazinium hydrogen oxalate) is $P2_1/m$. It has one, two, two and four different types of C, N, O and H atoms, respectively. The C1, N(1-2), O(1-2), H(1-2,4) and H3 atoms are located at 4f, 2e, 4f, 4f, and 2e sites [45]. The space group of monoclinic $((NH_2)CO(NH)CO(NH_2))(H_2O)$(Biuret hydrate) is $P2_1/c$. It has two, three and three different types of C, N and O atoms, respectively, which are located at 4e sites [46]. The space group of monoclinic $(CO)_3(NH)_3$ (Cyclo-tricarbonyltriimine) is A2/n. It has two, two, two and two different types of C, N, O and H atoms, respectively. The C1 (N1, O1, H1) and C2 (N2, O2, H2) atoms are located at 4e and 8f sites [47]. The space group of monoclinic $(NH_2)(CO)(NH)(CO)(NH)(CO)(NH_2)$(Triuret) is C2/c. It has three, four, three and six different types of C, N, O and H atoms, respectively, which are located at 8f sites [49]. The space group of tetragonal $(C(NH_2)_3)_2CO_3$ (Guanidinium carbonate) is $P4_12_12$. It has two, three, two and six different types of C, N, O and H atoms, respectively. The C1 and O2 atoms are located at 4a sites, and the others atoms are located at 8b sites [51]. The space group of monoclinic $C_5H_4N_4O_3$ (2,6,8-trioxypurine) is $P2_1/a$. It has five, four and three different types of C, N and O atoms, respectively, which are located at 4e sites [52]. The space group of monoclinic $(C_5H_5N_5O)(H_2O)$(Guanine hydrate) is $P2_1/n$. It has five, five, two and eight different types of N, C, O and H atoms, respectively, which are located at 4e sites [53]. The space group of monoclinic $C_8H_5NO_2$ (Phtalimide) is $P2_1/n$. It has eight, one, two and five different types of C, N, O and H atoms, respectively, which are located at 4e sites [54]. These structures are shown in Fig. 1.

We analyze and discuss the calculated structural properties of C–H–N–O compounds. Table 1 shows the calculated lattice constants of C–H–N–O compounds along with the available experimental values [24–54]. It is well-known that the DFT-GGA calculations significantly overestimate the volumes of molecular crystals [58,59]. Here we use the GGA-PBE and TS dispersion correction to obtain the ground-state properties of C–H–N–O compounds. According to the calculated results, the rates of volume change are 6.159%, -0.938%, 7.240%, 1.822%, -1.594%, 0.037%, 0.537%, -1.146%, -0.385%, -6.114%, 2.734%, 4.129%, -0.578%, 4.040%, -1.139%, -6.122%, 1.087%, 6.601%, -4.022% for isocyanic acid, urea, nitro-guanidine, urea nitrate, urea hydrogen peroxide, carbohydrazide, triaminoguanidinium nitrate, cyanoformamide, azidocarbonamide, acetamide, ammonium hydrogen oxalate hemihydrate, hydrazi-nium hydrogen oxalate, biuret hydrate, cyclo-tricarbonyltriimine, triuret, guanidinium carbonate, 2,6,8-trioxypurine, guanine hydrate, phtalimide, respectively. We can see that some structural parameters are in good agreement with the previous experimental results, but some values are slightly overestimated or under-estimated. Compared with the results overestimated by about 20.7% using the GGA calculations [58], our results within the GGA-PBE plus TS are better, meaning that the TS dispersion correction can effectively improve the description of intermolecular interactions.

3.2. Electronic properties and chemical bondings

Fig. 1 shows the total and partial density of states (TDOS and PDOS) of C–H–N–O compounds. For HNCO compound, we can see that there are six parts in TDOS. The part 1 around −20.860 eV is mainly dominated by O-2s states and is partially dominated by O-2p, C-2s and C-2p states. The part 2 around -16.494 eV is mainly dominated by N-2s states and is partially dominated by N-2p, C-2s and C-2p states. The part 3 around −8.024 eV is dominated by the hybridization between N-2p and H-1s states. The part 4 from −6.609 to −3.034 eV comes from the hybridizations between O-2p and C-2p states as well as N-2p and C-2p states. The upper valence bands are mainly due to O-2p and N-2p states. The conduction bands are mainly contributed by C-2p states and are