A computational study of novel nitratoxycarbon, nitritocarbonyl, and nitrate compounds and their potential as high energy materials

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ABSTRACT

The Hartree–Fock RHF/6-31G* and density functional B3LYP/6-31G(d) methods were used to determine the structures and properties of the isomers of the first three members of the series $C_n(CO_3N)_{2n+2}$ ($n = 0, 1, 2$). The first member of the series, $C_0(CO_3N)_2$, has six possible isomers, di(nitrato-O-)acetylene, cis- and trans-di(nitrato-O,O-)ethylene, the novel di(nitrato-O,O,O-)ethane or bis(nitratoxycarbon), di(nitroso)oxalate and the mixed isomer nitroso(nitrato-O,O,O-)acetate. The most stable of these isomers, both at the Hartree–Fock or density functional levels of theory, is di(nitroso)oxalate, followed by nitroso(nitrato-O,O,O-)acetate, and bis(nitratoxycarbon). The electronic energy of the mixed isomer closely approximates the mean of the energies of di(nitroso)oxalate and bis(nitratoxycarbon). Neither the cis- nor the trans-di(nitrato-O,O-)ethylene could be optimized to a stable minimum on the Hartree–Fock or density functional potential energy surfaces, and the di(nitrato-O-)acetylene isomer was a stable minimum with the Hartree–Fock method but not at the density functional level of theory. Of the two higher members of the series investigated, $C_n(CO_3N)_{2n+2}$ ($n = 1, 2$), each has two isomers: the nitritocarbonyl-substituted systems — analogous to di(nitroso)oxalate — and the nitratoxycarbon-substituted systems (neglecting mixed isomers containing both nitritocarbonyl and nitratoxycarbon moieties). In these compounds, while the nitritocarbonyl derivatives were found to be significantly more stable thermodynamically than the nitratoxycarbon derivatives, both systems were stable minima on both potential energy surfaces and may be of interest as high-energy materials.

1. Introduction

High-energy materials — substances whose characteristics include strained rings and/or cages, high nitrogen contents, and high densities [1] — often contain nitrogen oxide moieties, such as the nitrocarbons which contain the N-bound nitro group ($-NO_2$). Examples of these molecules include the nitrocubanes [2] and hexanitrobenzene [3]. Other nitrogen oxide substituents on organic molecules include the N-bound nitroso group ($-NO$) in nitrosocubanes [4] and the mono-O-bound nitroxy group ($-ONO_2$) in nitroxycubanes [1] and pentaerythritol tetranitrate (PETN) [5]. (In the latter case, the nitroxy group is formed through the nitration — addition of an NO_2 moiety — to the alcohol rather than the direct incorporation of a nitroxy group.) The nitroxy moiety is more exactly described as an O-bound nitrate group and, as such, leads to the question of whether a nitrate group can bond to a carbon center with more than one of the nitrate oxygen atoms, such as is illustrated in Fig. 1. Apparently, the nitrato-O,O- and the nitrato-O,O,O-bonding modes have not yet been observed or

investigated in an organic system. (The novel nitrato-O,O,O-moiety is referred to herein as a nitratoxycarbon substituent for the sake of nomenclature simplicity and to emphasize that all three of the oxygen atoms in the group are bound to the carbon center.)

Simple organic molecules (essentially alkane, alkene, or alkyne derivatives) with nitrate groups bound to a carbon atom may be envisioned and, if fully substituted, will have the general formula $C_n(CO_3N)_{2n+2}$, where $n = 0, 1, 2, 3$, and so forth. When $n = 0$, the isomeric molecules (**1**, cis-**2**, trans-**2**, **3**, **4**, and **5**) depicted in Fig. 2 arise. Of these six molecules, none have been reported experimentally, and calculated results have been reported in the literature only for the di(nitroso)oxalate, **4** [6].

On the other hand, when $n = 1$ or higher, because of the inability of the molecules to form carbon–carbon double or triple bonds or maintain bonding to the "NO$_3$" substituent without the addition of hydrogen atoms or other substituents, only two alkane-derivative isomers are expected to be observed: the nitritocarbonyl analogs of di(nitroso)oxalate and the nitratoxycarbon systems (ignoring "mixed" isomers containing both the nitritocarbonyl and the nitratoxycarbon substituents for the sake of simplicity and computational time and resources). These isomers are illustrated in Fig. 3 for $n = 1$ (**6** and **7**) and in Fig. 4 for $n = 2$ (**8** and **9**). If mixed isomer

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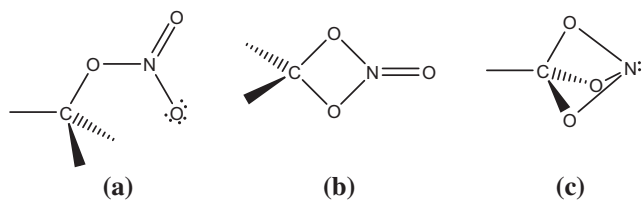E-mail address: rwz7001@humboldt.edu (R.W. Zoellner).

Fig. 1. Potential bonding modes for a nitrate group to a carbon center: (a) nitrato-*O*-, (b) nitrato-*O,O*-, and (c) nitrato-*O,O,O*-. The latter mode is referred to as a nitratoxycarbon moiety for the sake of simplicity, and might also engage in additional bonding modes through the formal lone pair of electrons on the nitrogen atom.

systems were to be considered as well, there are three additional mixed isomers for the $n = 1$ system and eight additional mixed isomers for the $n = 2$ system.

The novelty of these systems with regard to the bonding modes of a nitrate group to a carbon atom and the question regarding the possible existence of these novel molecules — the highly symmetrical methane derivative system **7**, originally constructed with simple ball-and-stick physical models, was the impetus for the interest in these systems — led to the present computational investigation of these molecules. Herein are reported the results for the Hartree–Fock and density functional computational investigation of the molecules with the general formula $C_n(CO_3N)_{2n+2}$ ($n = 0, 1, 2$) at the RHF/6-31G* and B3LYP/6-31G(d) levels of theory.

2. Computational details

All Hartree–Fock calculations were carried out using the *PC Spartan Pro* computational package [7] at the RHF/6-31G* level of theory without the imposition of any symmetry constraints. Similarly, all density functional calculations were carried out using the *Gaussian 03W* computational package [8] at the B3LYP/6-31G(d) level of theory without the imposition of any symmetry constraints. Vibrational frequencies were calculated for each molecule with each method to assure that a stable minimum on the potential energy surface had been located.

3. Results and discussion

3.1. $C_0(CO_3N)_2$

The computational results for the six isomers with the formula $C_n(CO_3N)_{2n+2}$ ($n = 0$) are summarized in Table 1. Neither the *cis*- or the *trans*-isomer of **2** could be optimized as a minimum on the

RHF/6-31G* or on the B3LYP/6-31G(d) potential energy surfaces: At the Hartree–Fock level of theory, the three calculated imaginary frequencies exhibited by each isomer represented vibrational modes which could be associated with ring-opening followed by a twisting motion, resulting in the transformation of either of the **2** isomers to **1** (but not to **4**), while at the density functional level of theory, the systems optimized to two NO moieties and an O_2CCO_2 structure. All attempts to locate a stable minimum for either of the **2** isomers failed at both levels of theory.

At the Hartree–Fock level of theory, the most stable of these isomers is di(nitroso)oxalate (**4**), 664.4 kJ/mol more stable than di(nitrato-*O*-)acetylene (**1**), which itself is 365.0 kJ/mol more stable than bis(nitratoxycarbon) or di(nitrato-*O-O-O*-)ethane (**3**). Unsurprisingly, the electronic energy of the mixed isomer, **5**, is almost exactly intermediate between the energies of **3** and **4**, and **5** is also calculated to be thermodynamically more stable than **1** by 159.6 kJ/mol. At the density functional level of theory, similar observations can be made, save for the result that **1** is not a stable minimum on the potential energy surface, but rather optimizes to two ONO groups and an OCCO moiety. The order of electronic energies at the density functional level is the same as with the Hartree–Fock calculations: **4** is the most stable, **3** is least stable, and **5** is nearly exactly intermediate between these two molecules. However, the energy differences are larger; **4** is more stable than **5** by 446.1 kJ/mol and more stable than **3** by 909.0 kJ/mol. Such huge energy differences may indicate that significant difficulties will need to be overcome in order to synthesize **3** or **5**, and that **4** may always be the preferred product in any synthesis. The di(nitrato-*O*-)acetylene species may not be accessible under any circumstances given that **1** is not a stable minimum on the density functional energy surface despite being a minimum on the Hartree–Fock energy surface.

Structurally, the computationally stable molecules do not appear to deviate greatly from what might be considered normal with respect to their overall conformations and bond distances; the calculated structures for these molecules are illustrated in Fig. 5. In **1**, the planar mono-oxygen-bound nitrate groups are rotated with respect to each other about the very nearly linear O—C≡C—O moiety, forming a dihedral angle of 90.32°; at 1.173 Å the C≡C distance is a bit shorter than expected and remarkably similar to the triple bond length observed in hexafluoro-2-butyne, F_3C—C≡C—CF_3, 1.199 Å [9]. Given the expected highly electron-withdrawing nature of the nitrate group (the trifluoromethyl group has $R = 0.64$ and $F = 0.76$ [10]), such a similarity is not unusual. Nitrogen–oxygen single bond lengths are expected to be approximately 1.40 Å in length, while N—O double bonds are expected to be approximately 1.21 Å [11]. In **1**, the N—O
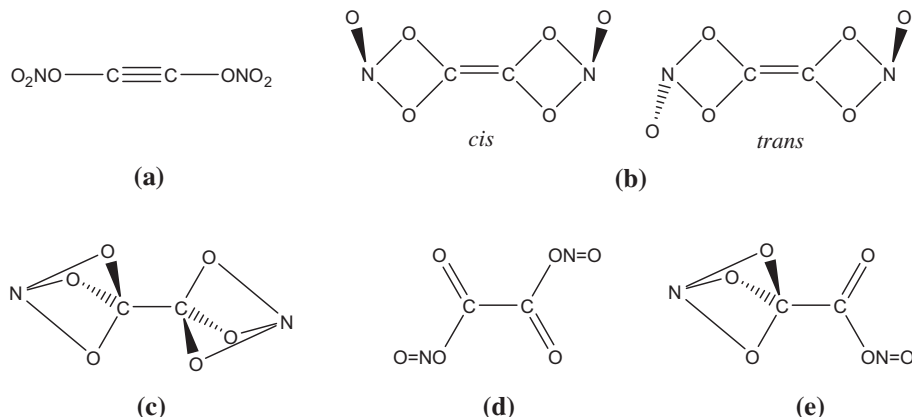

Fig. 2. Isomers of $C_0(CO_3N)_2$: (a) di(nitrato-*O*-)acetylene (**1**), (b) the *cis*- and *trans*-isomers of di(nitrato-*O,O*-)ethylene (*cis*-**2** and *trans*-**2**), (c) bis(nitratoxycarbon) or di(nitrato-*O,O,O*-)ethane (**3**), (d) di(nitroso)oxalate (**4**), and nitroso(nitrato-*O,O,O*-)acetate (**5**).
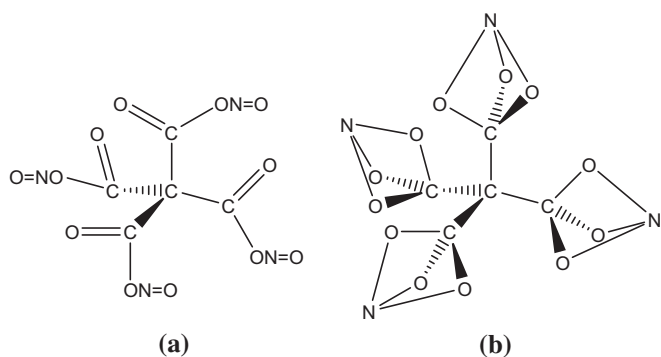
Fig. 3. Isomers of $C_1(CO_3N)_4$: (a) tetrakis(nitritocarbonyl)methane (**6**) and (b) tetrakis(nitratoxycarbon)methane (**7**).

bond length of 1.392 Å is consistent with a single bond, while the terminal N=O bond lengths of 1.167 Å and 1.171 Å appear to indicate strong double bond character. However, regardless of the "commonplace" nature of the calculated structure of **1** at the

Hartree–Fock level of theory, the inability to locate a stable minimum for **1** on the density functional potential energy surface may indicate that **1** is not a realistic synthetic target.

The calculated structure of the highly symmetrical but least stable isomer, **3**, bis(nitratoxycarbon), consists of a central C—C single bond of 1.504 Å (HF) or 1.508 Å (df) in length bracketed by two O,O,O-bound nitrate groups. While certainly unprecedented, these unusually-bound nitrate groups appear to be structurally relatively commonplace. The three C—O single bonds of the nitrate groups, at 1.382 Å (HF) or 1.426 Å (df), are shorter than or comparable to the 1.43 Å expected [11], while the N—O bonds are slightly longer than expected for an N—O single bond [11]. In the calculated infrared spectrum of **3**, the vibrations associated with these bonds are strongly coupled, as might be expected given the similarities of the masses of the atoms associated with the vibrations. Thus, this bonding mode for a nitrate group appears to be computationally supportable, even if thermodynamically disfavored. Structurally, the nitratoxycarbon portion of the mixed isomer **5** is nearly identical to the nitratoxycarbon moieties of **3**.

The most stable isomer with the formula $C_0(CO_3N)_2$, di(nitroso)oxalate (**4**), is calculated to be approximately planar,
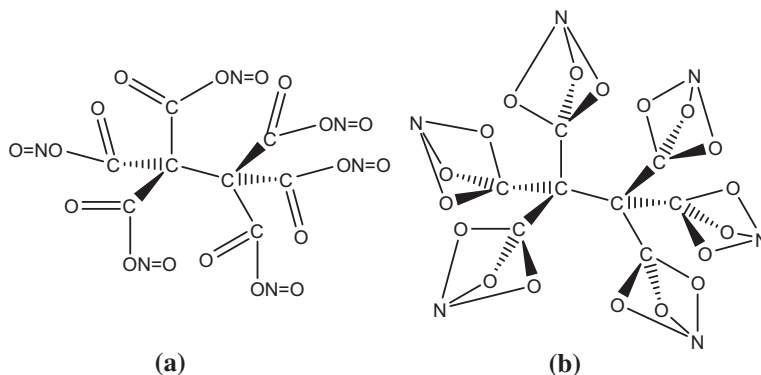

Fig. 4. Isomers of $C_2(CO_3N)_6$: (a) hexakis(nitritocarbonyl)ethane (**8**) and (b) hexakis(nitratoxycarbon)ethane (**9**).

Table 1
Selected calculated properties for the six isomers with the formula $C_n(CO_3N)_{2n+2}$ ($n = 0$).

Isomer[a]	Electronic energy	Dipole moment	Selected vibrational frequencies (cm^{-1}, uncorrected)	Selected structural parameters (Å)
1$_{HF}$	−633.327474 a.u.	0.967 D	2666.4 [v(C≡C)]; 1076.4, 1443.1 [v(C—O)]; 1561.8, 1671.0, 1976.1, 1980.3 [v(N—O$_2$)]	1.173 (C≡C); 1.309 (C—O); 1.392 (O—N); 1.167, 1.171 (N=O)
1$_{df}$	No minimum[b]	–	–	–
cis-**2**$_{HF}$	No minimum	–	−293.7, −223.0, −57.0 [imaginary]	–
cis-**2**$_{df}$	No minimum[c]	–	–	–
trans-**2**$_{HF}$	No minimum	–	−294.2, −222.8, −58.0 [imaginary]	–
trans-**2**$_{df}$	No minimum[c]	–	–	–
3$_{HF}$	−633.191867 a.u.	0.007 D	1444.4, 1256.2, 1255.6, 1208.8, 1205.0, 1155.0, 1154.9, 1106.6, 1004.8 [v(C—O), v(N—O)][d]	1.504 (C—C); 1.382 (C—O); 1.444 (N—O)
3$_{df}$	−636.504644 a.u.	0.000 D	1268.4, 1065.5, 1065.2, 1017.8, 1011.7, 963.0, 962.7, 922.2, 836.3 [v(C—O), v(N—O)][d]	1.508 (C—C); 1.426 (C—O); 1.515 (N—O)
4$_{HF}$	−633.580517 a.u.	0.351 D	2114.6, 2098.9, 2079.8, 2061.1 [v(C=O), v(N=O)][d]; 1284.6, 1121.0 [v(C—O)]; 865.7, 733.9 [v(N—O)]	1.173 (C=O); 1.535 (C—C); 1.334 (C—O); 1.420 (N—O); 1.136 (N=O)
4$_{df}$	−636.850845 a.u.	0.578 D	1929.7, 1918.6, 1830.7, 1827.8 [v(C=O), v(N=O)][d]; 1266.0, 1134.7, 969.7, 867.9 [v(C—O), v(N—O)][d]	1.204 (C=O); 1.552 (C—C); 1.349 (C—O); 1.589 (N—O); 1.149 (N=O)
5$_{HF}$	−633.388274 a.u.	2.102 D	2118.7, 2080.8 [v(C=O), v(N=O)][d]; 1341.8, 1211.8, 1199.9, 1178.0, 1114.4, 1004.0 [v(C—O), v(N—O)][d]	1.399, 1.400, 1.394 (C—O$_3$); 1.440, 1.443, 1.442 (O$_3$—N); 1.518 (C—C); 1.172 (C=O); 1.328 (C—O); 1.442 (N—O); 1.132 (N=O)
5$_{df}$	−636.680938 a.u.	3.607 D	1973.2, 1845.3 [v(C=O), v(N=O)][d]; 1197.9, 1021.2, 1005.2, 987.0, 947.8, 847.2 [v(C—O), v(N—O)][d]	1.509 (O$_3$—N); 1.530 (C—C); 1.203 (C=O); 1.337 (C—O); 1.602 (N—O); 1.140 (N=O)

[a] Hartree–Fock results are indicated by the subscript "HF" and density functional results are indicated by the subscript "df".
[b] Optimizes to a system containing two ONO groups and an OCCO group.
[c] Optimizes to a system containing two NO groups and an O$_2$CCO$_2$ group.
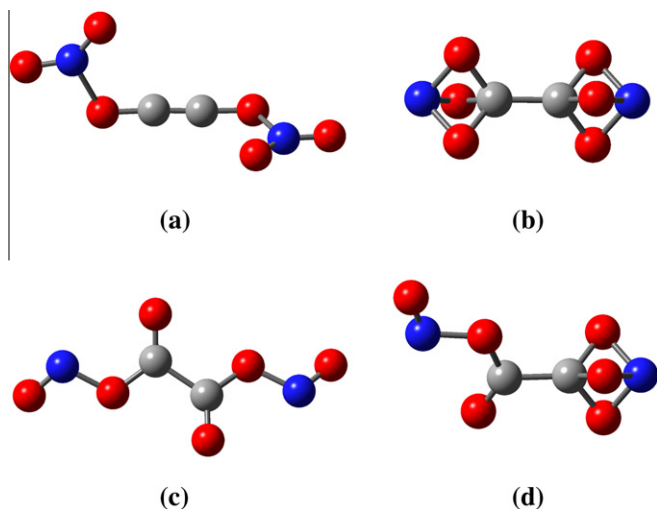[d] Strongly coupled.

Fig. 5. Calculated structures for the computationally stable isomers of $C_0(CO_3N)_2$ at the Hartree–Fock level of theory: (a) di(nitrato-*O*-)acetylene (**1**), (b) bis(nitratoxycarbon) (**3**), (c) di(nitroso)oxalate (**4**), and (d) nitroso(nitrato-*O,O,O*-)acetate (**5**). Structures at the density functional level of theory for **3**, **4**, and **5** are similar. Gray spheres represent carbon, red spheres represent oxygen, and blue spheres represent nitrogen. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

exhibiting a central dihedral angle ∠O═C—C═O of 150.6° (HF) or 143.4° (df) and ∠O—C—C—O of 152.2° (HF) or 146.3° (df); the carbonyl groups are oriented in an *anti*-fashion about the central C—C single bond, which is a slightly longer than expected 1.535 Å (HF) or 1.552 Å (df) in length. (Although no structural parameters were reported [6], the illustration of di(nitroso)oxalate in [6] is remarkably similar to that, Fig. 1c, in the present study.) The carbonyl C═O distances at 1.173 Å (HF) or 1.204 Å (df) are comparable to the expected 1.20 Å [11], and the remaining distances characterizing the O═N—O—C moieties are typical. Strong vibrational coupling between the C═O and N═O bonds, and between the C—O and N—O bonds is also observed. As was the case in the comparison of the structures of **3**,**4**, and **5**, the nitritocarbonyl portion of **5** is nearly identical to the nitritocarbonyl moieties of **4**.

The mixed isomer, **5**, contains both the nitratoxycarbon and the nitritocarbonyl group connected by a C—C single bond 1.518 Å (HF) or 1.530 Å (df) in length. As was observed for **3** and **4**, strong vibrational coupling between the C═O and N═O bonds, and between the C—O and N—O bonds is noted here as well. Essentially, **5** is best described as a "hybrid" of **3** and **4**.

3.2. $C_1(CO_3N)_4$ and $C_2(CO_3N)_6$

The computational results for the isomers with the formula $C_n(CO_3N)_{2n+2}$ ($n = 1,2$) are summarized in Table 2. (Mixed isomers have been neglected for the sake of simplicity and to reduce computational time and resources, but based on the calculated properties for **5** compared to those of **3** and **4**, these mixed isomers are expected to again exhibit structural and electronic properties that are intermediate between the parent nitritocarbonyl and nitratoxycarbon systems.) At both the Hartree–Fock and density functional levels of theory, the more stable isomers are, as expected, the higher nitritocarbonyl analogs of di(nitroso)oxalate, **6** and **8**, which are thermodynamically more stable that their nitratoxycarbon isomers **7** and **9** by a massive 2067.3 kJ/mol and 3146.9 kJ/mol, respectively, at the Hartree–Fock level of theory, and by 1831.5 kJ/mol and 2787.2 kJ/mol, respectively at the density functional level of theory.

Structurally, these four molecules are best described as simply longer-chair analogs of **3** and **4**. Bond lengths are reasonable for C—C single bonds, carbonyl groups, and C—O, N—O, and N═O bonds: As observed in **3** and **4**, the C═O and N═O bonds are slightly shorter than expected, while the C—O and N—O bonds are slightly longer than expected. Fig. 6 depicts the computationally determined structures for **6** and **7**, while the structures of **8** and **9** are illustrated in Fig. 7. As is apparent from the figures, the nitratoxycarbon systems, **7** and **9**, are quite compact molecules, and although the differences in energy between them and the nitritocarbonyl systems indicate that they may be difficult to synthesize, the nitratoxycarbon systems might exhibit the high densities that may be a requirement for high energy materials [1].

The concept of oxygen balance [1,12] may also indicate that these molecules may be of interest as high energy systems. Oxygen balance, Ω, is a measure of whether a molecule contains sufficient oxygen to fully oxidize the other atoms in the molecule without the addition of external supplies of oxygen or another oxidizer.

For a molecule containing only carbon, hydrogen, oxygen, and nitrogen, Ω, as a percentage, is given by formula (1).

$$\Omega(\%) = [-32(c + 0.25h - 0.5o)]/M \times 100 \quad (1)$$

In this formula, c is the number of carbon atoms, h is the number of hydrogen atoms, o is the number of oxygen atoms in the formula, and M is the molar mass. For the molecules described here, $\Omega = 21.6\%$ for isomers **1** ($C_2O_6N_2$), 10.4% for isomers **2** ($C_5O_{12}N_4$), and 6.8% for isomers **3** ($C_8O_{18}N_6$). All of these molecules exhibit a positive oxygen balance according to formula (1), indicating that

Table 2
Selected calculated properties for the isomers[a] with the formulas $C_n(CO_3N)_{2n+2}$ ($n = 1,2$).

Isomer[a]	Electronic energy	Dipole moment	Selected vibrational frequencies (cm^{-1}, uncorrected)	Selected structural parameters (Å)
6$_{HF}$	−1305.05242 a.u.	0.027 D	2114.7, 2105.6, 2097.9, 2097.3, 2071.1, 2064.4, 2058.5, 2058.2 [ν(C═O), ν(N═O)][b]	1.539 (C—C); 1.174 (C═O); 1.335 (C—O); 1.427 (N—O); 1.134 (N═O)
6$_{df}$	−1311.82785 a.u.	0.003 D	1937.9, 1926.3, 1920.8, 1920.8, 1843.2, 1839.6, 1828.1, 1828.1 [ν(C═O), ν(N═O)][b]	1.551 (C—C); 1.203 (C═O); 1.351 (C—O); 1.590 (N—O); 1.148(C═O)
7$_{HF}$	−1304.26501 a.u.	0.019 D	1597.8, 1568.5, 1568.1, 1566.5 [ν(C—C)]	1.526 (C—C); 1.394 (C—O); 1.442 (N—O)
7$_{df}$	−1311.13027 a.u.	0.001 D	1421.0, 1370.6, 1370.5, 1370.4 [ν(C—C)]	1.532 (C—C); 1.427 (C—O); 1.512 (N—O)
8$_{HF}$	−1976.49832 a.u.	1.531 D	2119.1, 2108.5, 2107.5, 2104.9, 2100.2, 2095.2, 2071.0, 2067.4, 2059.4, 2053.6, 2049.5, 2047.8 [ν(C═O), ν(N═O)][b]	1.588 (C—C); 1.548 (C—C)$_{ave}$; 1.174 (C═O); 1.332 (C—O); 1.432 (N—O); 1.133 (N═O)
8$_{df}$	−1986.78564 a.u.	1.698 D	1943.7, 1932.0, 1931.4, 1929.7, 1915.8, 1908.9, 1839.7, 1837.6, 1827.8, 1825.1, 1823.3, 1817.6, [ν(C═O), ν(N═O)][b]	1.585 (C—C); 1.562 (C—C)$_{ave}$; 1.203 (C═O); 1.349 (C—O); 1.592 (N—O); 1.148 (N═O)
9$_{HF}$	−1975.29972 a.u.	0.041 D	1584.8, 1560.3, 1541.5, 1540.2, 1534.9, 1533.9 [ν(C—C)]	1.603 (C—C); 1.543 (C—C)$_{ave}$; 1.396 (C—O); 1.439 (N—O)
9$_{df}$	−1985.72405 a.u.	0.001 D	1395.8, 1378.1, 1337.5, 1337.4, 1334.5, 1334.3 [ν(C—C)]	1.606 (C—C); 1.540 (C—C)$_{ave}$; 1.429 (C—O); 1.509 (N—O)

[a] Neglecting mixed isomers for the sake of simplicity and computational time.
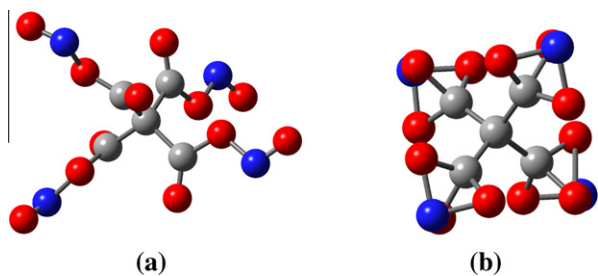[b] Strongly coupled.

Fig. 6. Calculated structures for the computationally stable isomers of $C_1(CO_3N)_4$: (a) tetrakis(nitritocarbonyl)methane **(6)** and (b) tetrakis(nitratoxycarbon)methane **(7)**. Gray spheres represent carbon, red spheres represent oxygen, and blue spheres represent nitrogen. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
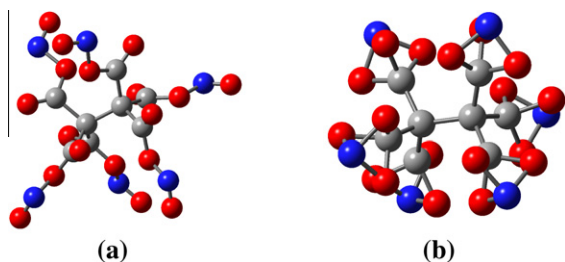

Fig. 7. Calculated structures for the computationally stable isomers of $C_2(CO_3N)_6$: (a) hexakis(nitritocarbonyl)ethane **(8)** and (b) hexakis(nitratoxycarbon)ethane **(9)**. Gray spheres represent carbon, red spheres represent oxygen, and blue spheres represent nitrogen. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

no additional oxygen or other oxidizers will be necessary in order for the molecules to be completely oxidized. However, the oxygen balance does not indicate whether a molecule will or will not be unstable or explosive, only whether there is sufficient oxygen present in the formula for all atoms in the formula to be completely oxidized during decomposition [12].

4. Conclusions

The six isomers with the formula $C_0(CO_3N)_2$ and the two homo-substituted isomers each with the formula $C_n(CO_3N)_{2n+2}$ ($n = 1, 2$) have been investigated at the RHF/6-31G* and B3LYP/6-31G(d) levels of theory. In all cases, the nitritocarbonyl isomer (**4**, **6**, and **8**) was by far the thermodynamically more stable and thus the most likely to be able to be synthesized. However, the di(nitrato-*O*-)acetylene isomer of $C_0(CO_3N)_2$ was a stable minimum on the Hartree–Fock potential energy surface, but not on the density functional potential energy surface, so that even in light of similarities between **1** and hexafluoro-2-butyne, this molecule may not be a reasonable synthetic target, even though **1** is unlikely to convert to **4** if a synthesis is attempted. The nitratoxycarbon isomers (**3**, **7**, and **9**) are much higher in energy that their corresponding nitritocarbonyl isomers. However, the compact structural nature of the nitratoxycarbon systems may make them (or their mixed substituent analogs, such as **5**) interesting targets for synthesis. In addition, the nitratoxycarbon moiety might also be stabilized by complexation to a metal center through the formal lone pair of electrons on the nitrogen atom of the group.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.comptc.2011.10.011.

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