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Towards new green high energy materials. Computational chemistry on nitro-substituted urea

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Abstract As part of a series of studies on new potential green high energy materials, we have calculated the structures and properties of a series of nitro-substituted urea molecules. Our results indicate that nitrated urea molecules have specific enthalpies of decomposition commensurate with current high energy materials. At the same time, they are all low in carbon, suggesting an application as a "green" high energy material.

Keywords DFT calculations · High energy materials · Nitrourea

Introduction

In the search for new high-energy materials, one thought is that they be "green": production of no heavy metals like lead or mercury, and minimal production of carbon-containing products. To that end, molecules with high nitrogen content are being explored as possible high energy (HE) materials [1–5]. Previously, we have used standard computational chemistry techniques to determine the energy contents of molecules that contain large numbers of nitro (NO_2) groups [6–9] on the hypothesis that such molecules would be self-oxidizing as well as benefiting from a large number of N_2 molecules as products.

Urea, NH_2CONH_2, has a storied place in chemical history as the first recognized organic molecule to be synthesized from inorganic sources, by Wöhler [10, 11], thus displacing the theory of vitalism. Urea has the highest nitrogen content (47 % by mass) of any commonly-used agricultural fertilizer, which is 90% + of its use in society. Despite this, urea is not commonly used as a high energy material. Nitrourea, however, is recognized as a high energy material, as are molecules that have a nitrourea functionality like 1,4-dinitroglycouril [12]. However, many cyclic nitrourea compounds suffer from being moisture-sensitive, limiting their use as high energy materials.

Of the various nitrated urea molecules, only nitrourea and (symmetric) dinitrourea have been characterized, with the first mention of dinitrourea being a US patent from 1963 [13]. Renewed interest in dinitrourea as an HE material appears in the literature around 1998. More recently, Ye et al. [14] reported on the crystal structure of N,N'-dinitrourea (DNU) and the HE properties of 11 organic salts of DNU. Densities were found to be between 1.75 and 1.86 g cm^{-3} and detonation properties were found to be similar to those of cyclotrimethylene trinitramine (RDX) and cyclotetramethylene tetranitramine (HMX). They also report an enthalpy of formation for gas-phase DNU of 24.88 kJ mol^{-1}, using the G3MP2 compound method. Qui et al. [15] reported on some calculated densities of nitramines of HE interest, calculating values of 1.52 to 2.44 g cm^{-3} for a variety of compounds, including 1.84 g cm^{-3} for DNU (experimental density 1.98 g cm^{-3}). Their average deviation was only 0.3%. Studies like this are useful because high density is a desirable characteristic for HE materials, among other characteristics like fast velocity of detonation and the formation of the largest possible amount of gaseous decomposition products [12].

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Here we present a survey of the geometries and properties, including thermodynamic properties, of a series of nitrated urea molecules. We include all possible arrangements of nitro groups, from one to four. Finally, we calculate the enthalpy of combustion and/or decomposition on a molar and mass basis, based on the expected reactions using well-known guidelines for HE compounds. While actual performance would be based on a condensed-phase material (as these compounds are likely to be) and not on a gas-phase material, as calculations like this presume, energy per unit mass is still a useful parameter for a high energy material.

Computational details

All calculations were performed using Gaussian03 [16] on a desktop personal computer. In this study, we utilized the hybrid density functional theoretical method using Becke's 3-parameter exchange functional with the correlation functional of Lee, Yang, and Parr (abbreviated B3LYP) [17, 18] along with the standard Gaussian basis set labeled 6-31 G(d,p) [19]. This method/basis set combination has long been considered reliable for predicting thermodynamic properties. Minimum energy geometries were determined for all nitrourea molecules using standard program options, and minima were verified as having no imaginary vibrational frequencies. Vibrational absorption spectra were plotted using the SWizard program [20] using the default 15 cm^{-1} linewidth. No structural parameters were constrained during the structure optimizations, nor was any symmetry imposed.

After proper minimum-energy structures were determined, the enthalpy changes of the following gas-phase isodesmic reactions were determined using B3LYP/6-31G (d,p) structure/energy calculations for all species:

$$\begin{aligned}&NH_2C(O)NH_2 + (x/2)N_2O_4\\&\rightarrow C(O)N_2H_{4-x}(NO_2)_x + (x/2)H_2\end{aligned} \tag{1}$$

$$\begin{aligned}&C(O)N_2H_{4-x}(NO_2)_x + 2xNH_3\\&\rightarrow NH_2C(O)NH_2 + (x/2)HNO_2 + (x/2)N_2H_4.\end{aligned} \tag{2}$$

Reaction (1) uses the simpler molecular species, while reaction (2) is based on the reaction used by Ye et al. [14] and is used for comparison. After the enthalpy changes of each reaction were determined, the enthalpies of formation of the particular nitrourea molecule was determined using that enthalpy of reaction and the experimental enthalpies of formation of the other species. The experimental enthalpies of formation of other species was taken from the NIST Chemistry Webbook [21]. This website has some conflicting data for the enthalpy of formation of hydrazine, NH_2NH_2. To be consistent with the work of Ye et al. [14], we used $\Delta H_f\ [NH_2NH_2]=95.35$ kJ mol^{-1} in all calculations involving reaction (2).

Once the enthalpies of formation were determined, the enthalpies of combustion and/or decomposition were determined using standard Hess'-law techniques and enthalpy of formation data from the NIST Chemistry Webbook [21]. Of the nitrourea compounds, the derivative with one nitro group has a negative oxygen balance (OB%; [22]). As such, this derivative has combustion and decomposition reactions. The combustion reaction for the mononitro derivative is

$$NH_2C(O)NH(NO_2) + 3/4O_2 \rightarrow CO_2 + 3/2H_2O + 3/2N_2, \tag{3}$$

where we are assuming that all products are in the gas phase (this affects the enthalpy data for H_2O only). The decomposition reaction of the mononitro derivative is given by the Kistiakowsky-Wilson rules [23], and is

$$\begin{aligned}NH_2C(O)NH(NO_2) \rightarrow\ &1/2CO + 1/2CO_2\\&+ 3/2H_2O + 3/2N_2.\end{aligned} \tag{4}$$

The OB% of the higher-substituted urea molecules are all positive, so there is sufficient oxygen to completely oxidize all necessary atoms. The decomposition reactions are

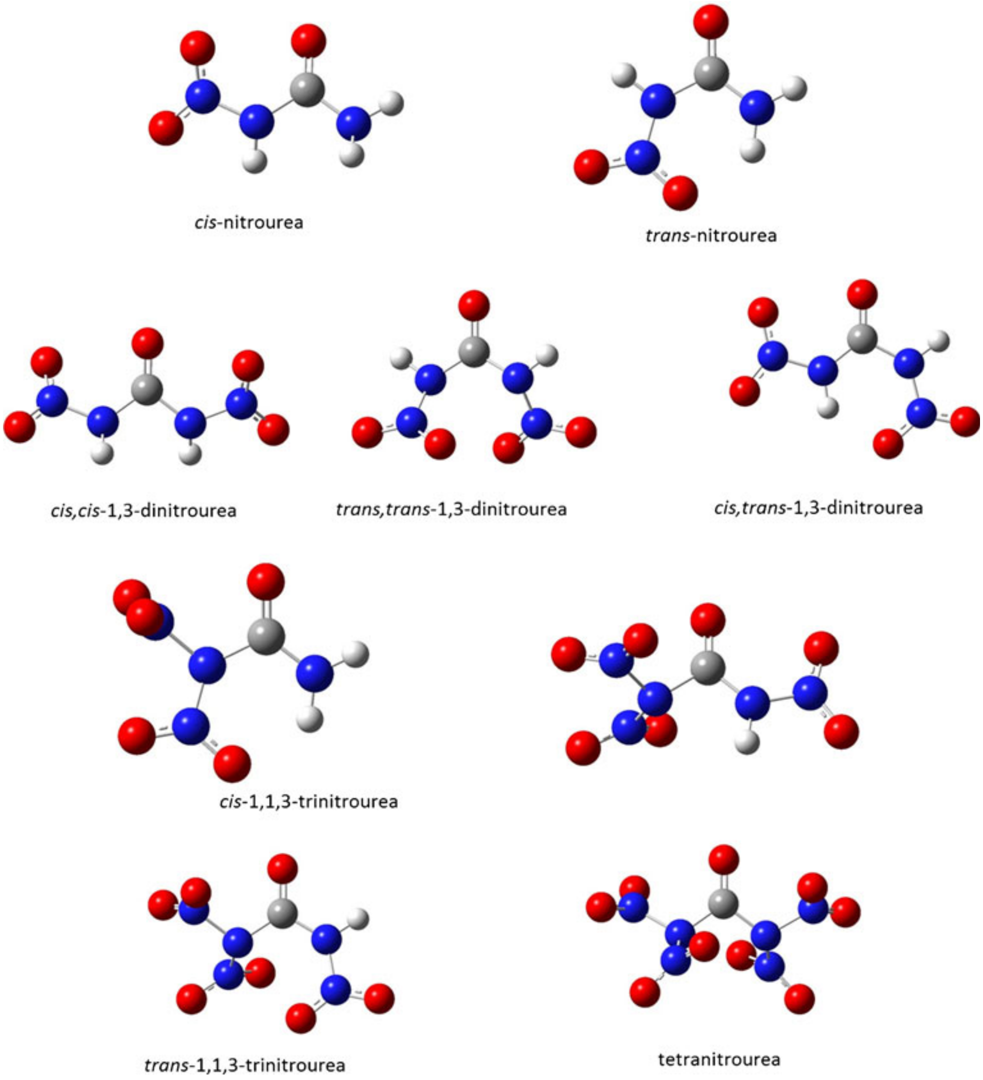
$$\begin{aligned}C(O)N_2H_{4-x}(NO_2)_x \rightarrow\ &CO_2 + ((4-x)/2)H_2O\\&+ ((2+2x)/2)N_2\\&+ ((5x-6)/4)O_2,\end{aligned} \tag{5}$$

where again in reactions (4) and (5) we are assuming that all products are in the gas phase. In reaction (5), x varies from 2 to 4. Specific enthalpies of combustion and decomposition were determined by dividing the molar enthalpies of reaction by the molar mass of the urea derivative.

Results and discussion

Figure 1 shows the structures of the optimized molecules for this study. There are several isomers for each level of nitration, depending on the orientation of a unique nitro group with respect to the carbonyl oxygen atom. We have used the prefix *cis* to represent an isomer in which the nitro group is pointing in the same direction as the carbonyl oxygen atom, and the prefix *trans* to represent an isomer in which the nitro group is pointing in the opposite direction as the carbonyl oxygen atom. For dinitrourea, there is also linkage isomerism, as the nitro groups can bond to the same

Fig. 1 Nitrourea molecules examined in this study



cis-nitrourea

trans-nitrourea

cis,cis-1,3-dinitrourea

trans,trans-1,3-dinitrourea

cis,trans-1,3-dinitrourea

cis-1,1,3-trinitrourea

trans-1,1,3-trinitrourea

tetranitrourea

amine nitrogen atom or different amine nitrogen atoms. Thus, there are two different nitrourea rotational isomers, four different dinitrourea molecules (three of which are rotamers), two trinitrourea rotamers, and a single tetranitrourea molecule. The rotational potential energy diagrams of the rotamers and inversion at the N atoms were not explored. However, all of the isomers presented here represent actual minimum-energy structures, as confirmed by vibrational analyses (discussed below).

Table 1 lists notable structural parameters of each nitrourea molecule. Complete Cartesian coordinates of the optimized structures are available as Supplementary Material. One of the more obvious trends is the significant increase (by ~0.1 Å) in the C-N bond length when one or more NO_2 groups are attached to that nitrogen atom. We also note that the NO_2 group nearest to the C = O moiety (in the *cis* position) typically shows a longer bond to the adjacent N atom in the urea backbone as well as a slightly larger O-N-O bond angle. Although dihedral angles are not reported in Table 1, Fig. 1 shows that the *cis* nitro group twists significantly if there is a *trans* nitro group attached to the same nitrogen atom, likely because of electrostatic repulsions from oxygen atoms in the carbonyl group and the *trans* NO_2 group. Similarly, in molecules with two *trans* NO_2 groups, the groups twist noticeably, again likely due to the proximity of two oxygen atoms in the respective groups.

Figures 2, 3 and 4 shows the calculated vibrational spectra of the nitrourea molecules, calculated to verify that the structures as determined were truly minimum-energy. In Fig. 2, the *cis* and *trans* isomers of nitrourea have similar spectra except for the region below 1000 cm^{-1} and above 3500 cm^{-1}. The region above 3500 cm^{-1} is the N-H stretching region, and for the *cis* isomer the two N-H stretches on the terminal NH_2 group are only about 5 cm^{-1} apart and so are unresolved in the spectrum. However, for the *trans* isomer, the NO_2 group is near enough to the terminal NH_2 group that it perturbs one of the N-H stretching frequencies, resulting in a splitting of 47 cm^{-1}

Table 1 Notable structural parameters of the nitrourea molecules. (Distances in Å, angles in degrees.*)

Molecule	r(C=O)	r(C-N)	r(N-N)	α(N-C-N)	α(H-N-N)	α(N-N-N)	α(O-N-O)
cis-nitrourea	1.206	1.375, 1.438	1.410	109.3	108.2	—	128.0
trans-nitrourea	1.216	1.346, 1.435	1.353	116.5	119.9	—	126.3
cis,cis-1,3-dinitrourea	1.196	1.418	1.422	106.1	109.3	—	128.9
trans,trans-1,3-dinitrourea	1.213	1.398	1.423	118.5	109.8	—	128.5
cis,trans-1,3-dinitrourea	1.204	1.427, 1.379	1.390, 1.413	113.5	112.4, 113.9	—	126.7, 128.6
1,1-dinitrourea	1.210	1.342, 1.472	1.422, 1.536	115.5	—	110.4	127.2, 131.4
cis-1,1,3-trinitrourea	1.193	1.374, 1.497	1.425, 1.473, 1.503	106.7	112.1	115.3	129.5, 129.6, 130.6
trans-1,1,3-trinitrourea	1.204	1.386, 1.443	1.415, 1.489, 1.514	116.1	111.8	111.9	128.6, 130.2, 130.9
tetranitrourea	1.193	1.438	1.515, 1.505	107.9	—	111.8	130.8, 131.0

*In entries that have more than one value, the order is: side with lone nitro group first; *trans* nitro group before *cis* nitro group if there are both.

for the two N-H stretches and making them more easily resolved. This provides a distinctive signature of this rotational isomer that might be observed in the gas phase or in a cryogenic matrix.

A similar circumstance is seen in Fig. 3 for the two isomers of dinitrourea that have different N-H environments, *cis,trans*-1,3-dinitrourea and 1,1-dinitrourea. Because it is a linkage isomer, 1,1-dinitrourea shows a distinctly different spectrum than the other dinitrourea derivatives.

Table 2 lists the oxygen balances and the enthalpies of reaction for the various nitrourea molecules, using reactions (1) and (2) from above. The enthalpies of formation that we predict are consistent between the two reactions, suggesting some level of confidence in the values. The ΔH_f values determined using reaction 2 are about 1 – 2 kJ mol^{-1} per NO_2 group lower than the ΔH_f values determined using reaction 1. We note, however, that Ye et al. [14] used G3MP3 calculations to report a ΔH_f value of 24.88 kJ mol^{-1} for dinitrourea, which we deduce is what we are calling the *cis,cis*-1,3-dinitrourea isomer

Given the agreement in the ΔH_f values that we calculate for both Reactions (1) and (2), we are curious about the ~80 kJ mol^{-1} discrepancy with the previous study [14]. As a check, we recalculated the energies for *cis,cis*-1,3-dinitrourea and the other species in reaction (2) using the G3MP2 compound method in an attempt to verify Ye et al.'s work. For completeness, we are listing the explicit results in Table 3. Results are the "G3MP2 enthalpy" values from the Gaussian output file. Using these data and the known enthalpies of formation data from the NIST

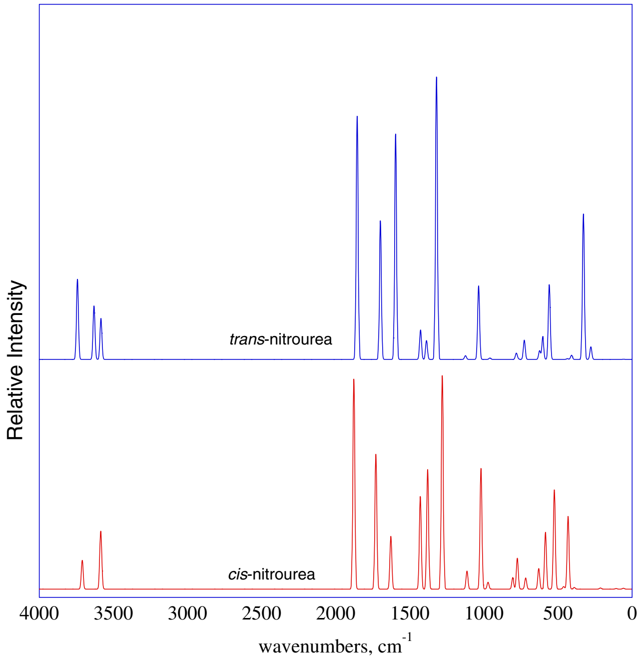


Fig. 2 Calculated vibrational spectra of *cis*- and *trans*-nitrourea

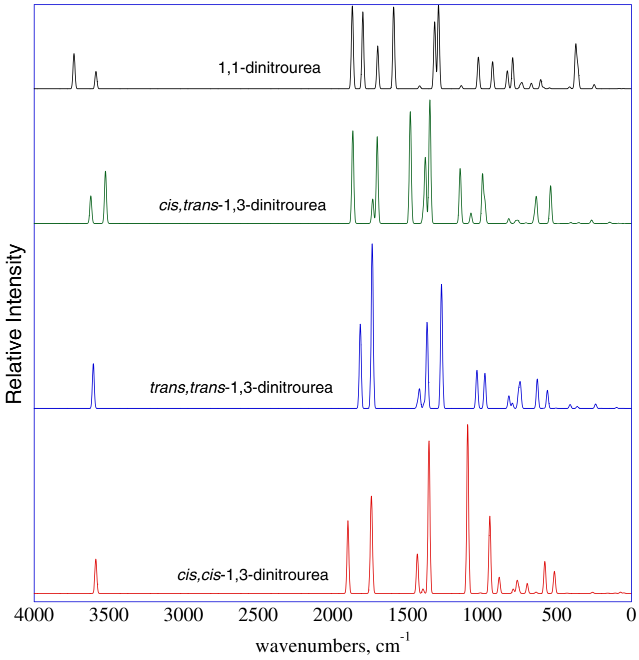


Fig. 3 Calculated vibrational spectra of the four isomers of dinitrourea

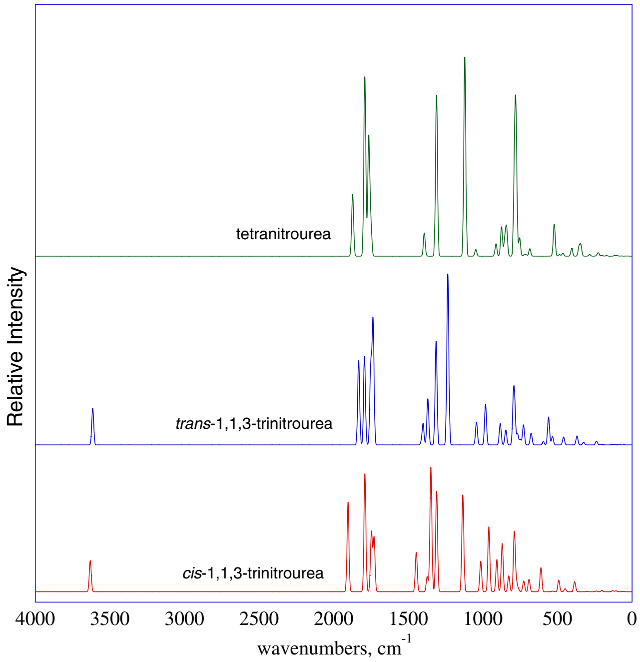


Fig. 4 Calculated vibrational spectra of trinitroureas and tetranitrourea

web site [21], we calculate an enthalpy of reaction of 32.2 kJ for reaction (2) and a resulting enthalpy of formation for *cis,cis*-1,3-dinitrourea of -46.7 kJ mol^{-1}, which is entirely consistent with the values presented in Table 2 for the other methods and reactions used in this study. Unless some systematic error is uncovered, we stand by the enthalpy of formation values presented here.

The two mononitrourea derivatives differ by over 35 kJ mol^{-1} because of differences in the positions of the single NO_2 group. The *trans* rotamer is more stable, as it minimizes oxygen-oxygen atom repulsion between the NO_2 and carbonyl groups; the *trans* isomer also benefits by some intramolecular hydrogen bonding between the NO_2 and NH_2 groups (O—H distance is only 1.98 Å). The relative stabilities of the 1,3-dinitrourea molecules follow a similar trend. The *cis*,*cis* isomer is least stable, as expected by the proximities of the NO_2 groups to the carbonyl oxygen atom. Contrarily, the *trans*,*trans* isomer is not the most stable, as this puts oxygen atoms from the two NO_2 groups in proximity. In fact, in the optimized structure of *trans,trans*-1,3-dinitrourea the NO_2 groups take advantage of the tetrahedral geometry of the N atoms in the urea backbone, forming a 67-degree nonbonding dihedral angle as defined by the atoms N-N—N-N. This allows the NO_2 groups to avoid each other somewhat, but still imparts this isomer with a stability of only about 14 kJ mol^{-1} over the *cis*,*cis* isomer. The *cis,trans*-1,3-dinitrourea structure benefits energetically from another intramolecular hydrogen bond (O—H distance is 1.90 Å), making it more stable than the other two rotamers despite the O—O proximity between the other nitro group and the carbonyl group. The linkage isomer 1,1-dinitrourea is actually the least stable, likely due to proximity of the two NO_2 groups on the same N atom and despite the 1.97-Å distance between the O and H atoms on different parts of the molecule.

The way the two nitro groups adopt positions with respect to each other on one side of the molecule, neither of the trinitrourea rotamers benefit significantly from hydrogen bonding. Hence, the *trans* isomer is slightly more stable than the *cis* isomer. Tetranitrourea is significantly more unstable than the trinitrourea molecules, doubtless due to the crowding required by having four NO_2 groups in the molecule.

Given the enthalpies of formation, it is straightforward to determine the enthalpies of combustion (for nitrourea only) and decomposition (for all molecules). Table 2 also lists the enthalpies of decomposition for these molecules, assuming an enthalpy of formation using our Reaction (1). Table 2 also lists the enthalpies of combustion for the two nitrourea molecules. The final column in Table 2 lists the specific enthalpies of decomposition (or combustion, for nitrourea) for these substances. We find a similar conclusion that we did with other highly nitrated molecules: while the enthalpy of decomposition increases (that is, gets more negative)

Table 2 Enthalpies of reaction for the nitrourea molecules. All values are kJ mol^{-1} unless otherwise indicated

Molecule	OB%	ΔH_f, Rxn 1	ΔH_f, Rxn 2	ΔH_{dec}*	ΔH_{dec}, kJ g^{-1}*
cis-nitrourea	-7.6	-153.1	-154.5	-461.2 (-602.8)**	-5.07 (-6.62)
trans-nitrourea	-7.6	-190.3	-191.3	-424.5 (-566.0)	-4.66 (-6.22)
cis,*cis*-1,3-dinitrourea	+21.3	-55.6	-60.2	-579.7	-3.86
trans,*trans*-1,3-dinitrourea	+21.3	-70.1	-74.7	-565.2	-3.77
cis,*trans*-1,3-dinitrourea	+21.3	-86.7	-91.2	-548.7	-3.66
1,1-dinitrourea	+21.3	-47.7	-52.2	-587.6	-3.92
cis-1,1,3-trinitrourea	+36.9	69.5	61.4	-583.2	-2.99
trans-1,1,3-trinitrourea	+36.9	68.7	60.2	-582.6	-2.99
tetranitrourea	+46.7	223.0	211.5	-616.5	-2.57

*Using the ΔH_f from Rxn 1

**The values in parentheses are for the combustion reaction (3)

Table 3 Raw data and derived values for reaction (2) using G3MP2 calcuations

Species/quantity	Enthalpy value (h, unless otherwise labeled)
cis,*cis*-1,3-dinitrourea	-633.45548
NH_3	-56.46636
urea	-224.96312
HNO_2	-205.47737
NH_2NH_2	-111.69540
ΔH [Rxn(2)], kJ	32.2
ΔH_f [dinitrourea], kJ mol^{-1}	-46.7

with increasing nitro content, the amount of energy per unit mass decreases as the nitro content increases, decreasing by half when going from nitrourea (-5.07 kJ g^{-1}) to tetranitrourea (-2.57 kJ g^{-1}).

This is not to imply that nitrourea molecules may be poor HE materials. Table 4 shows a comparison of the specific enthalpies of decomposition for a series of current high-energy materials, along with a summary of those for the nitrourea compounds. Not only are their specific enthalpies of decomposition commensurate with some other commonly-used HE materials, but the second column of data indicates that the nitrourea system is relatively low-carbon. That is, they are relatively “green”, here used to describe materials that yield low amounts of carbon-containing products. If their densities, velocities of detonations, sensitivities, etc., are favorable, highly nitrated urea compounds may represent a new class of green high energy materials.

Dinitrourea was originally synthesized [24] by mixing urea in a mixture of 95% sulfuric acid in 100% nitric acid at 5 °C for 30 min. After that time, the mixture was cooled to 0 °C and a white precipitate formed, which was washed with trifluoroacetic acid to remove any remaining acid reactant. Given that this is a standard nitration reaction, one wonders if higher nitration occurred or would occur if reaction times were longer and the reaction temperature were lowered (if possible for this solvent mixture). Perhaps tests of the remaining supernatant would demonstrate the presence of higher nitrated ureas, as there seems no inherent mechanistic barrier to the addition of more than two NO_2 groups to the parent molecule. Care should be taken, however, as Murray, Concha, and Politzer have argued [25] that increasing the number of nitro groups decreases the C-NO_2 or (relevant here) N-NO_2 bond energies, increasing the likelihood of sudden decomposition.

Table 4 Comparisons of specific enthalpies of decomposition and carbon content of other HE materials with nitrourea (previous data taken from reference 23)

HE material	Formula	% carbon by mass	$\lvert\Delta H_{dec}\rvert$ kJ/g
nitroglycerine	$C_3H_5N_3O_9$	15.9	6.19
ethylene glycol dinitrate	$C_2H_4N_2O_6$	15.8	6.66
pentaerythritol tetranitrate	$C_5H_8N_4O_{12}$	19.0	5.79
cyclotrimethylenetrinitramine	$C_3H_6N_6O_6$	16.2	5.04
cyclotetramethylene-tetranitramine	$C_4H_8N_8O_8$	16.2	5.01
nitroguanidine	$CH_4N_4O_2$	11.5	2.47
picric acid	$C_6H_3N_3O_7$	31.4	3.25
tetryl	$C_7H_3N_5O_8$	29.5	4.34
triaminotrinitrobenzene	$C_6H_6N_6O_6$	27.9	3.50
hexanitrostilbene	$C_{14}H_6N_6O_{12}$	37.3	3.94
trinitrotoluene	$C_7H_5N_3O_6$	46.9	4.25
******************			
nitrourea	$CH_3N_3O_3$	13.2	4.87*
dinitrourea	$CH_2N_4O_5$	8.00	3.80*
trinitrourea	CHN_5O_7	6.16	2.99*
tetranitrourea	CN_6O_9	5.00	2.57

*average values

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