Electrostatic Potentials, Intralattice Attractive Forces and Crystal Densities of Nitrogen-Rich C,H,N,O Salts

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Abstract: The computed electrostatic potentials on C,H,N,O molecular solids and nitrogen-rich C,H,N,O salts are used in analyzing and comparing intralattice attractive forces and crystal densities in these two categories of compounds. Nitrogen-rich C,H,N,O salts are not an assured path to high densities. To increase the likelihood of high densities, small cations and large anions are suggested. Caution is recommended in predicting benefits of nitrogen-richness for explosive compounds.

Keywords: nitrogen-rich; electrostatic potentials; C,H,N,O molecular and ionic compounds; crystal densities

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1. Why "Nitrogen-Rich?"

In the detonation of an explosive compound, an initial stimulus (input of energy) is followed by a series of steps culminating in self-sustaining highly exothermal chemical decomposition releasing large amounts of energy and gaseous products. This results in a high pressure, supersonic shock wave propagating through the system (detonation) [1–5]. Many explosives are composed of appropriate numbers of carbon, hydrogen, nitrogen and oxygen atoms. Their final decomposition products, apart from some solid carbon, are usually mainly large quantities of low molecular mass, very stable gases, e.g., N_2, CO_2, CO, H_2O [6–9]. Due to their low masses, large amounts can be produced per gram of explosive, while their stabilities mean that a great deal of energy is liberated.

An important point is that many C,H,N,O compounds have relatively high densities compared to other organic compounds, in the range 1.50 g/cm^3 to 2.00 g/cm^3 [10–12]. This allows more explosive to be packed into the available volume. The density is in fact one of the primary factors affecting detonation performance [6,9].

During the past two decades, there has been a tendency to focus upon the design and synthesis of "nitrogen-rich" explosive compounds, whether molecular or ionic [13–16], [17] and references therein. While the term is somewhat ambiguous, basically it means replacing some C–H units in a molecular or ionic framework by nitrogens. This is expected to increase the compound's heat of formation (its energy content) and possibly also its density, both of which would be desirable.

An increased density is plausible, because a nitrogen atom has a greater mass but smaller volume than a C–H unit [18]. An increased (more positive) heat of formation is expected because the hypothetical "formation reaction" requires breaking the very strong N≡N bond in N_2 and creating much weaker C–N, C=N, N–N and/or N=N bonds in the explosive [19]. A high heat of formation suggests that the compound has a greater intrinsic energy content, which may result in a larger heat release during detonation.

It should be noted, however, that the effects of increasing the framework nitrogen content may not all be beneficial, as has recently been pointed out [19]. The overall heat release depends upon the

compound's stoichiometry as well as its heat of formation; furthermore, a capability for a very large heat release is likely to be accompanied by excessive sensitivity (vulnerability to accidental detonation). Another consideration is that diminishing the number of hydrogens adversely affects the number of moles of gaseous products per gram of explosive, since more of the heavier N_2 and less of the lighter H_2O are being formed. These issues will be further discussed in a later section.

Our present objectives are to compare molecular and ionic C,H,N,O solids in terms of intralattice forces, electrostatic potentials and crystal densities. At the same time we will consider the effects of nitrogen richness upon the ionic compounds.

2. Molecular *vs.* Ionic Crystal Lattices

The discussion in Section 1 applied to both molecular and ionic crystalline C,H,N,O explosives. However there is a major difference in the nature of the intralattice forces that stabilize these two categories of solids. The crystal lattices of molecular compounds are held together by relatively weak Coulombic attractions between molecules that are overall neutral, although having locally positive and negative regions of electrostatic potential. Figures 1 and 2 are the computed electrostatic potentials on the molecular "surfaces" of the molecules 5-nitrotetrazole (**1**) and 3-nitro-1,2,4-triazole (**2**); the surfaces are taken to be the 0.001 au contours of the molecules' electronic densities, as proposed by Bader *et al.* [20]. Such surfaces encompass roughly 97% of the electronic charge and have the advantage that they reflect features such as lone pairs, π electrons and atomic anisotropy that are specific to the particular molecules. Figures 1 and 2 show regions of positive electrostatic potential to be associated with the hydrogens and the central portions of the molecules, and negative regions by the ring nitrogens and nitro oxygens. (All electrostatic potentials being discussed were computed at the density functional B3PW91/6-31G** level).
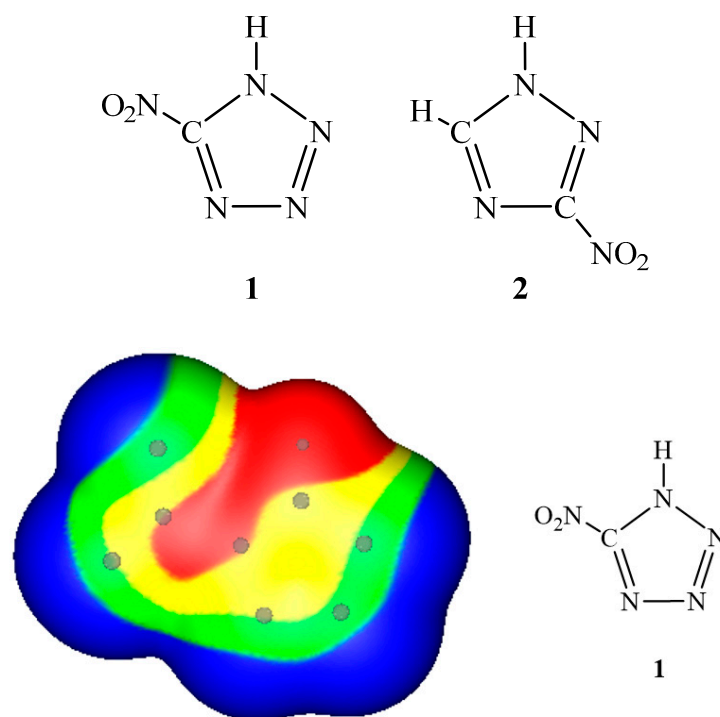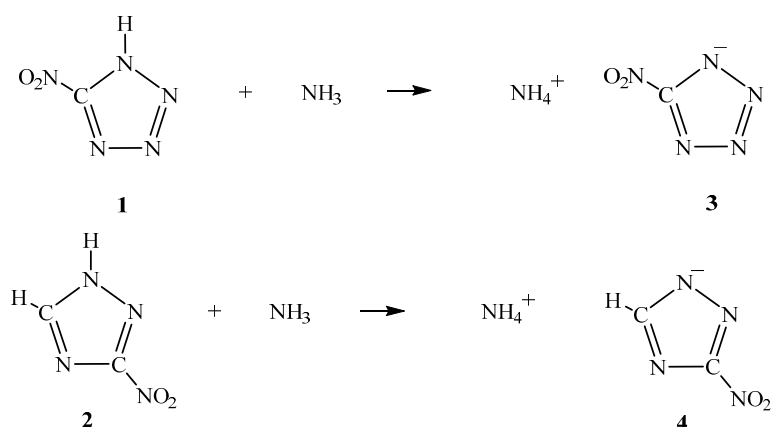

Figure 1. Computed electrostatic potential on 0.001 au molecular surface of 5-nitrotetrazole (**1**). Color ranges, in kcal/mol, are: red, greater than 30; yellow, between 30 and 15; green, between 15 and 0; blue, negative (less than 0). Circles show positions of atoms; NO_2 group is on the left. Most positive potential is 73 kcal/mol by the hydrogen; most negative are −29 kcal/mol by the ring nitrogen at the bottom right.
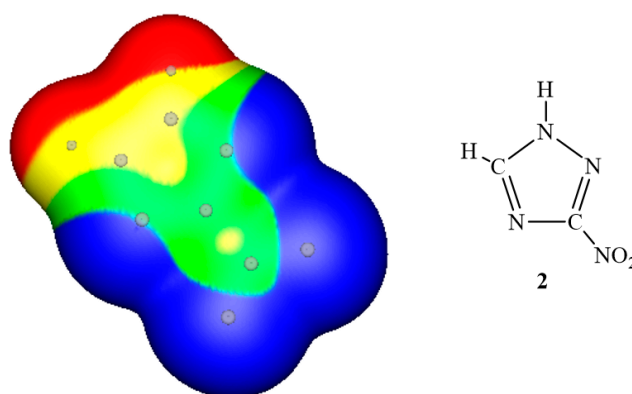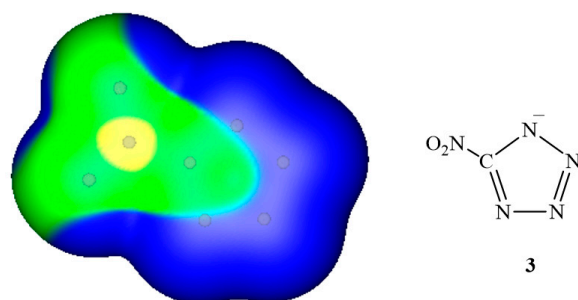
Figure 2. Computed electrostatic potential on 0.001 au molecular surface of 3-nitro-1,2,4-triazole (**2**). Color ranges, in kcal/mol, are: red, greater than 30; yellow, between 30 and 15; green, between 15 and 0; blue, negative (less than 0). Circles show positions of atoms; NO_2 group is on the lower right. Most positive potential is 71 kcal/mol by the N-H hydrogen; most negative are -33 to -39 kcal/mol by the ring nitrogens and the NO_2 oxygens.

The crystal lattices of ionic solids are also held together by Coulombic attractions, but they are quite strong, involving the overall integral positive or negative charges on the ions. Consider the salts resulting from the interactions of **1** and **2** with a base such as NH_3:

Figures 3 and 4 display the electrostatic potentials on the 0.001 au surfaces of the resulting 5-nitrotetrazolate anion (**3**) and 3-nitro-1,2,4-triazolate anion (**4**).
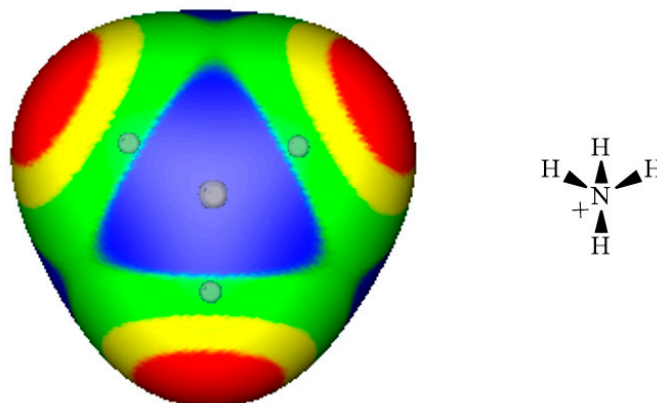

Figure 3. Computed electrostatic potential on 0.001 au anionic surface of 5-nitrotetrazolate anion (**3**). Color ranges, in kcal/mol, are: yellow, between -60 and -80; green, between -80 and -100; blue, more negative than -100. Circles show positions of atoms; NO_2 group is on the left. Most negative potentials are -126 kcal/mol by the ring nitrogens closest to the carbon bearing the NO_2 group.
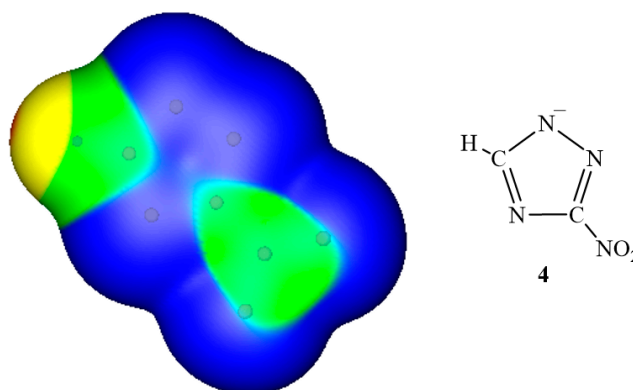
Figure 4. Computed electrostatic potential on 0.001 au anionic surface of 3-nitro-1,2,4-triazolate anion (**4**). Color ranges, in kcal/mol, are: red, less negative than −60; yellow, between −60 and −80; green, between −80 and −100; blue, more negative than −100. Circles show positions of atoms; NO_2 group is on the lower right. Most negative potentials are −133 and −136 kcal/mol by the ring nitrogens closest to the carbon bearing the NO_2 group.

The surfaces of **3** and **4** are completely negative, although with some local variation, which will be discussed later; the surface of the cation NH_4^+ is completely positive (Figure 5), again with some variation. The magnitudes of the electrostatic potentials on the anions **3** and **4** (Figures 3 and 4) and on NH_4^+ (Figure 5) are considerably greater than those on the neutral molecules **1** and **2** (Figures 1 and 2) and on the ammonia molecule (on which they vary from −40 to +24 kcal/mol [21]). It follows that the Coulombic attractions between the ions in the two salts will be much stronger than between the neutral molecules in the molecular solids **1** and **2**.

Figure 5. Computed electrostatic potential on 0.001 au cationic surface of NH_4^+ cation. Color ranges, in kcal/mol, are: red, greater than 178; yellow, between 178 and 174; green, between 174 and 168; blue, less than 168. Circles show positions of atoms. Most positive potentials are 181 kcal/mol by hydrogens.

The differences in the strengths of the intralattice attractive forces in molecular and ionic solids are reflected in the energies required to overcome them. The heat of sublimation of a molecular solid is the enthalpy for the transition from the crystal lattice to separate gas phase molecules. For C,H,N,O molecular explosives, the magnitudes of the heats of sublimation are mainly between 20 and 30 kcal/mol [22]. For ionic compounds, the analogue of the heat of sublimation is the lattice enthalpy, which is the enthalpy required to separate the lattice into free gas phase ions. Lattice enthalpies are generally much greater than heats of sublimation [23]. For C,H,N,O ionic explosives in which the ions have +1 and −1 charges, the estimated lattice enthalpies are between 100 and 200 kcal/mol [24]; for +1

and -2 they are roughly twice as large, and approach 400 kcal/mol for $+2$ and -2. The ionic charges are clearly a major factor.

Another interesting manifestation of the effects of overall ionic charges is evident in estimating "effective" molecular or formula unit volumes, V_{eff}. These are defined for any molecular or ionic solid as,

$$V_{eff} = M/\rho \tag{1}$$

where M is the molecular or formula unit mass and ρ is the crystal density. V_{eff} is the hypothetical volume per molecule or per formula unit (in the case of an ionic compound) that would correspond to the unit cell of the lattice being completely filled. (In reality, there is of course always some free space.) V_{eff} can also be determined by dividing the volume of the unit cell by the number of molecules or formula units that it contains.

For molecular C,H,N,O solids, V_{eff} can be approximated quite well as the volume $V(0.001)$ that is enclosed within the molecule's 0.001 au surface [25–27]:

$$V_{eff} \,(\text{molecular solid}) \approx V(0.001) \tag{2}$$

This is surprising given that $V(0.001)$ is computed for a single isolated molecule, with no consideration of intermolecular interactions within the crystal.

For an ionic C,H,N,O compound, the analogous procedure would be to compute $V(0.001)$ for the positive and negative ions separately and then to estimate V_{eff} for the formula unit by,

$$V_{eff} \,(\text{ionic solid}) \approx a V(0.001)_{cation} + b V(0.001)_{anion} \tag{3}$$

In Equation (3), *a* and *b* are the numbers of cations and anions, respectively, in one formula unit. However Equation (3) is not nearly as good an approximation to the actual V_{eff} for ionic C,H,N,O compounds as Equation (2) is for molecular ones. The V_{eff} obtained by Equation (3) are almost always too large [28,29], often quite significantly so.

Equation (2) is a reasonably good approximation for molecular C,H,N,O solids because the attractive forces between the molecules are relatively weak, and using the volume within the 0.001 au surface of the isolated molecule is therefore acceptable. However Equation (3) is a rather poor approximation for ionic C,H,N,O solids because the attractive forces between the oppositely-charged ions are quite strong, and bring the ions closer together than their 0.001 au volumes would predict.

For both types of solids, the V_{eff} can be improved by taking explicit account of the electrostatic potentials on the molecular or ionic surfaces [24–26]. The corrected V_{eff} can then be used to make reasonably good estimates of crystal densities via Equation (1).
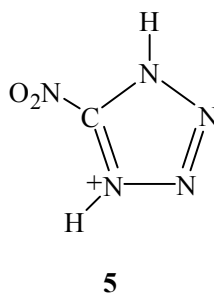
3. Electrostatic Potentials on Ionic Surfaces

On the 0.001 au surface of an ion, the electrostatic potential is everywhere positive or everywhere negative, in accordance with the overall integral charge on the ion (Figures 3–6). However, it should be recognized that for polyatomic ions these surface potentials are frequently far from isotropic. To some extent, they may exhibit patterns that are qualitatively similar to those of the corresponding neutral molecules. (It should be kept in mind that the colors on the surfaces of the neutral molecules, the anions and the cations correspond to different ranges of potentials).

Consider the 5-nitrotetrazolate (**3**) and 3-nitro-1,2,4-triazolate (**4**) anions, Figures 3 and 4. In the parent neutral molecules **1** and **2**, the most positive features are the N-H hydrogens, with maximum potentials of about 70 kcal/mol (Figures 1 and 2). These hydrogens are not present in the anions. However the other positive regions in the neutral molecules—above the rings and the C–NO$_2$ bonds, as well as the C-H hydrogen in **2**—are still in evidence, as being now the least negative regions in the anions. The most negative potentials in the anions (as in the neutral molecules) are associated with the

nitrogens of the rings and the oxygens of the NO_2 groups, reaching magnitudes in the neighborhood of −130 kcal/mol, roughly 100 kcal/mol more negative than in the neutral molecules.

In Figure 6 is the electrostatic potential on the 0.001 au surface of the positive 5-nitrotetrazolium cation, **5**, formed by protonating one of the ring nitrogens in **1**. Now there are two N–H hydrogens, and they have the most positive potentials, 174 kcal/mol. The regions above the ring and the C–NO_2 bond are also strongly positive, with maxima of about 152 kcal/mol. The most negative (*i.e.*, least positive) regions are by the non-protonated ring nitrogens and the NO_2 oxygens. All of this is analogous to what is seen in the potential of the parent molecule in Figure 1 (except of course that the values of the electrostatic potential are now all positive).

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Figures 3–6 show that it would be misleading to focus only upon the overall charges on polyatomic ions, ignoring the variations in the electrostatic potentials on their surfaces. What also needs to be taken into account are the polarizing effects of the ions upon each other. The influence of these factors upon crystal densities will be discussed in the next section.
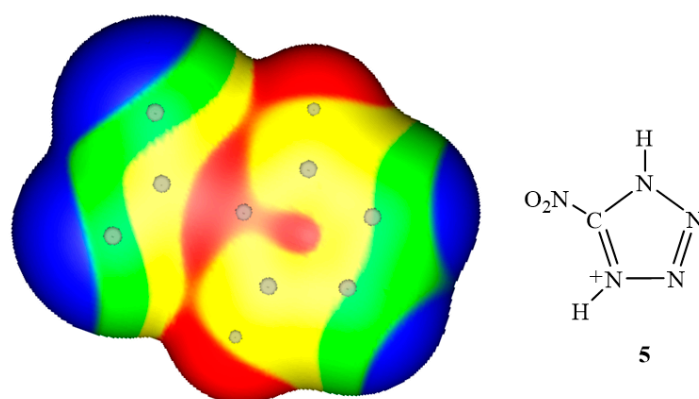
Figure 6. Computed electrostatic potential on 0.001 au cationic surface of 5-nitrotetrazolium cation (**5**). Color ranges, in kcal/mol, are: red, greater than 150; yellow, between 150 and 120; green, between 120 and 90; blue, less than 90. Circles shown positions of atoms; NO_2 group is on the left. Most positive potentials are 174 kcal/mol by hydrogens.

## 4. Crystal Densities and Electrostatic Potentials

It has already been pointed out that replacing C-H units in molecular or ionic frameworks by nitrogen atoms could reasonably be expected to increase the crystal densities. The strongly attractive forces between oppositely-charged ions might be anticipated to have a similar effect. What is in fact observed?

In 2007, Rice *et al.* compiled a database of experimental crystal densities of 180 C,H,N,O molecular solids [26]. They were mainly nitroaromatics, nitroaliphatics, nitramines and nitrate esters. Many of them had all-carbon frameworks. In 2011, Gao and Shreeve tabulated the experimental densities of more than 230 C,H,N,O salts [15], in which one or both ions were usually tetrazole or triazole

derivatives, with a few being derivatives of imidazole or pyrazole. Thus these can be viewed as largely nitrogen-rich salts.

Figure 7 compares the distributions of densities, on a percentage basis, within these two categories of compounds. The comparison shows clearly that nitrogen-rich salts do not represent an assured path to high densities. It has been suggested that a density greater than 1.80 g/cm^3 is "an essential requirement for advanced energetic materials" [30]. This criterion is satisfied by about 22% of the molecular compounds in Figure 7 but only about 6% of the ionic ones, even though the latter were predominantly nitrogen-rich while many of the former were not.
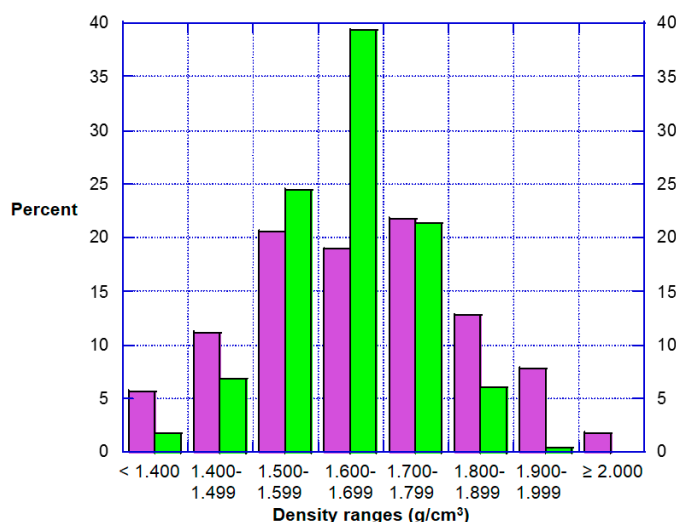
Figure 7. Crystal density distributions of C,H,N,O molecular compounds (**purple**) and nitrogen-rich C,H,N,O ionic compounds (**green**). Vertical axes are percentages.

As Zhang *et al.* have pointed out [30], the interactions between polyatomic ions are directional, reflecting the nonisotropic natures of the electrostatic potentials on their surfaces (Figures 3–6). Zhang *et al.* argued that closer packing and higher densities could be promoted by taking advantage of interactions such as hydrogen bonding, and drew attention to the hydroxylammonium ion, H$_3$N-OH$^+$, as being effective for this purpose.

It must be noted that Dunitz *et al.* found no general relationship between density and hydrogen bonding for a database of hydrocarbon, C,H,O and C,H,N molecular solids [31]. However that conclusion may not be relevant to the present systems of functionalized C,H,N,O salts.

It was demonstrated quite some time ago that hydrogen bonding ability can be related to the magnitude of the positive electrostatic potential on the hydrogen [32,33]. In Table 1 are listed the most positive calculated ionic surface potentials associated with the hydrogens in a series of monopositive cations that are commonly found in C,H,N,O salts. The hydroxylammonium ion clearly stands out; it has the single most positive potential, 190 kcal/mol near the hydroxyl hydrogen, plus three more of about 181 kcal/mol by the other hydrogens. There is in fact a continuous very strongly positive region encompassing all of the hydrogens, ranging in magnitude from 177 to 190 kcal/mol (Figure 8). The next most positive ion in Table 1 is the ammonium ion, NH$_4^+$, which has four hydrogen maxima of 181 kcal/mol, but they are separated by distinctly less positive regions (Figure 5).

The presence of several highly positive sites on H$_3$N-OH$^+$ shows it to be a likely candidate for strongly attractive directional interactions with polyatomic anions; NH$_4^+$ would be the next most likely in Table 1. Does this translate into higher densities? Dunitz *et al.* found no general relationship between density and lattice energies for their database of hydrocarbon, C,H,O and C,H,N molecular solids [31], mentioned above, but again this may not be relevant to the present functionalized C,H,N,O ionic solids.

　　　We have surveyed 87 nitrogen-rich C,H,N,O salts that have been synthesized during the past five years [16,30,34–46]. (Only anhydrous salts were considered.) 41 of them, or 47%, have crystal densities ≥ 1.80 g/cm^3. This is a remarkable increase over the 6% in the earlier work that is represented in Figure 7; some reasons for this will be proposed later.

　　　In twelve of these 87 compounds, the cation is H$_3$N-OH$^+$. All twelve have densities ≥ 1.80 g/cm^3. In four of them, the density is 1.90 g/cm^3 or more. Thus, the hydroxylammonium ion does promote high densities in C,H,N,O salts, as is suggested by the electrostatic potential on its surface (Figure 8) and as was argued by Zhang *et al.* [30]. NH$_4^+$ is the cation in nine of the compounds surveyed, and six of them have densities ≥ 1.80 g/cm^3, with one being 1.90 g/cm^3. The H$_3$N–OH$^+$ and NH$_4^+$ cations clearly increase the likelihood of a C,H,N,O salt having a high density.
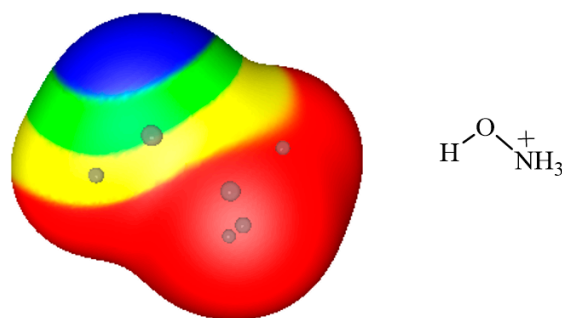
Figure 8. Computed electrostatic potential on 0.001 au cationic surface of NH$_3$OH$^+$ cation. Color ranges, in kcal/mol, are: red, greater than 165; yellow, between 165 and 140; green, between 140 and 110; blue, less than 110. Circles show positions of atoms; OH group is on the left. Most positive potential is 190 kcal/mol by the OH hydrogen.

Table 1. Most positive electrostatic potentials on the 0.001 au surfaces of some C,H,N,O monopositive cations.

Cation	Most Positive Potentials, kcal/mol
hydroxylammonium	190, 181, 181, 180
ammonium	181, 181, 181, 181
5-nitrotetrazolium	174, 174, 153, 152
hydrazinium	173, 173, 172
3,3-dinitroazetidinium	172, 172
5-aminotetrazolium	172, 172
methylammonium	169, 169, 169
1,1-dimethylhydrazinium	164, 164, 156
azidoformadinium	165, 157, 143
t-butylhydrazinium	161, 158, 154
1,5-diaminotetrazolium	164, 141, 130, 130
1-isopropyl-3,3-dinitroazetidinium	158, 158, 143
hydroxyguanidinium	157, 152, 143, 136
guanidinium	154, 154, 154
aminoguanidinium	154, 151
1,5-diamino-4-methyltetrazolium	149, 137
N,N,N-trimethylhydrazinium	142, 142, 130
triaminoguanidinium	136

　　　In Table 2 are the most negative calculated ionic surface potentials of a series of mononegative anions often found in C,H,N,O salts. In general, their magnitudes are less than those of the most positive potentials on the cations in Table 1. It is further notable that the smaller ions tend to have the strongest potentials, whether positive or negative. This may be in part because the overall charge of

the ion is not as delocalized [47]; another factor of course, for a given ionic framework, is the effects of the functional groups.

Table 2. Most negative electrostatic potentials on the 0.001 au surfaces of some C,H,N,O mononegative anions.

Anion	Most Negative Potentials, kcal/mol
nitrate	−151, −151, −151
nitroformate	−142, −142, −123, −120, −120
azide	−139, −139
5-aminotetrazolate	−137, −137, −137
3-nitro-1,2,4-triazolate	−136, −133
4-nitro-1,2,3-triazolate	−132, −124, −124, −123
dinitramide	−131, −126, −126, −121, −121
5-nitrotetrazolate	−126, −126, −118, −118, −116
4,5-dinitroimidazolate	−125, −125, −119
3,5-dinitropyrazolate	−123, −123
3,5-dinitro-1,2,4-triazolate	−119, −119, −119, −119
picrate	−119, −119
2,4,5-trinitroimidazolate	−116, −116, −115, −114

In using electrostatic potentials such as those in Figures 1–6 and 8 to interpret and predict molecular and ionic interactions, it is important to keep in mind that these potentials are typically computed for the ground states of the molecules or ions, *prior* to any interaction [48–50]. Accordingly they do not reflect the polarizing effect that each molecule's or ion's electric field has upon the charge distribution of the other. This polarization, which is stabilizing, is of course particularly significant when resulting from the strong electric fields of ions.

The degree to which the charge distribution of a molecule, atom or ion is affected by an external electric field is determined by its polarizability. It is well known that polarizability generally increases with size [51–57] and in going from cations to neutral molecules to anions [58], as the outer electrons become less tightly bound. It is therefore to be expected that the intralattice attractive interactions in ionic compounds will be stronger when they have large polarizable anions in conjunction with cations having several highly positive polarizing sites. Hydroxylammonium and ammonium salts with large C,H,N,O anions fit this description, which helps to explain their frequently high densities.

Why are the recently-prepared nitrogen-rich salts more likely to have high densities than the earlier ones represented in Figure 7? Several factors may be involved. In the newer compounds, there is a greater emphasis upon small cations and large anions. This results in strong intralattice attractions due to the highly-positive potentials of small cations (Table 1) and the high polarizabilities of large anions, and evidently promotes higher densities. In contrast, a significant number of the salts represented in Figure 7 involved large cations, which have low polarizabilities and weaker positive potentials, and often large anions, which have weaker negative potentials (Table 2). Furthermore, even when these compounds did have a large anion and small cation, the latter was very rarely the hydroxylammonium while the anion was often relatively poor in oxygens or even just C,H,N in composition; all of this diminishes the opportunities for strong hydrogen bonding.

While C,H,N,O salts with large cations are less likely to have high densities, it is not precluded, as can be seen from the examples in Table 3. Note that the negative ion in three of the four compounds is NO_3^-, which has the most negative potentials in Table 2.
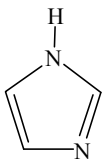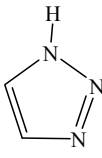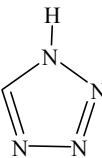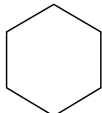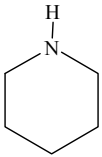
Table 3. Some C,H,N,O nitrogen-rich salts with large cations and small anions that have experimental densities greater than 1.80 g/cm^3.

| Salt	Density, g/cm^3	Reference
oxalhydrazinium dinitrate	1.945	44
1-amino-3-nitroguanidinium nitrate	1.91	38
oxalhydrazinium nitrate	1.840	44
5-aminotetrazolium dinitramide 1.833	1.833	29

5. Discussion and Summary

Is nitrogen richness beneficial? For unsubstituted molecules, replacing a C–H unit by a nitrogen does tend to increase the density (Table 4). When functional groups are present, however, it is less straightforward; for example, 1,3,5-trinitrobenzene (**6**) and 2,4,6-trinitropyridine (**7**) have essentially the same densities, 1.76 g/cm^3 [2] and 1.751 g/cm^3 [59], respectively. Rice *et al.* compiled the densities of 38 "high-nitrogen" C,H,N,O molecular solids [26]; only four had densities greater than 1.80 g/cm^3.

Table 4. Some experimental densities and heats of formation, ΔH_f.

Compound	Structure	Density [a] g/cm^3	ΔH_f [b] kcal/mol (cal/g)
1 *H*-imidazole		1.0303	11.9 (175)
1 *H*-1,2,3-triazole		1.1861	—
1 *H*-tetrazole		1.4060	56.4 (805)
cyclohexane		0.7739	−37.68 (−447.7)
piperidine		0.8606	−20.66 (−242.6)

[a] Reference [58]; [b] Reference [60].

NO₂

O₂N NO₂

6

O₂N N NO₂

NO₂

7
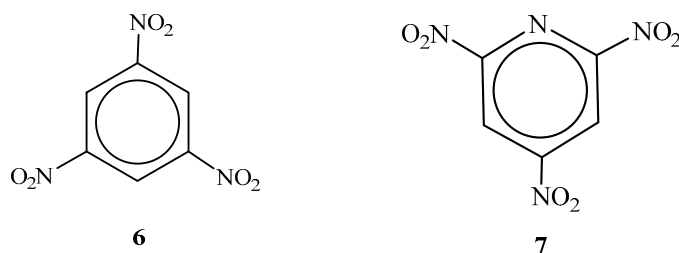
For C,H,N,O salts as well, nitrogen richness is not sufficient to make likely a density $\geqslant 1.80$ g/cm^3. This is shown by Figure 7. To increase the probability of a high density, the salt should also have a large anion and a small cation, preferably $H_3N\text{-}OH^+$ or NH_4^+.

A greater nitrogen/carbon ratio does frequently result in a more positive heat of formation, ΔH_f (Table 4). Thus the values for **6** and **7** are -10.4 kcal/mol (-48.8 cal/g) and 18.8 kcal/mol (88.0 cal/g), respectively [2]. This may (or may not) lead to a greater heat release Q upon detonation, as shall be seen. For an explosive X, Q is typically taken to be the negative of the enthalpy change per gram of X in the overall detonation reaction:

$$Q = -\frac{1}{M_X}\left[\sum_i n_i \Delta H_{f,i} - \Delta H_{f,X}\right] \tag{4}$$

In Equation (4), M_X is the mass of X in g/mol, n_i is the number of moles of final detonation product i, having molar heat of formation $\Delta H_{f,i}$, and $\Delta H_{f,X}$ is the molar heat of formation of the explosive X.

From Equation (4), the detonation heat release Q is greater as the heat of formation $\Delta H_{f,X}$ of the compound is more positive and as the heats of formation $\Delta H_{f,i}$ of the products are more negative. Replacing C–H units by nitrogens is likely to increase $\Delta H_{f,X}$ but it may also decrease the amounts of the three common detonation products that have negative heats of formation: CO_2 (g), -94.05 kcal/mol; CO (g), -26.42 kcal/mol; H_2O (g), -57.80 kcal/mol [60]. Producing one less mole of CO_2 would negate a quite considerable increase of 94 kcal/mol in $\Delta H_{f,X}$; two fewer moles of H_2O would cancel an increase of 115 kcal/mol! Of course, a larger N/C ratio means that more N_2 is formed as a product, which may be viewed as desirable since N_2 is (at the moment) considered to be environmentally benign; however its heat of formation is zero, so it does not contribute to the detonation heat release Q. Increasing the N/C ratio may therefore have two opposing effects, one making Q larger and the other making it smaller.

There are yet other factors to take into account. A larger value of Q is associated with a higher level of detonation performance [6], but it is also linked to greater sensitivity [5,19,61,62], *i.e.*, undesirable vulnerability to accidental detonation caused by an unintended stimulus such as shock or impact. Finally, if the increase in N_2 is accompanied by a decrease in the lighter product H_2O, then the volume of gas produced per gram of compound will be less—adversely affecting detonation performance [6].

So, given all these conflicting factors, our answer to the question posed at the beginning of this section, "Is nitrogen richness beneficial?" is an unequivocal yes and no! Putting it more elegantly, one should not generalize; it depends upon the particular case.

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