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On the Stability of $N_5^+N_5^-$

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We investigate the stability of $N_5^+N_5^-$ as an isolated species and in a potential periodic structure. Its barriers toward loss of $N_3^{\cdot}$ from the N_5^+ ion or addition to form N_{10} are 25 and 15 kcal/mol. The barrier toward loss of N_2 from the N_5^- ion is 15 kcal/mol. Increasingly positive charges of the N_5 species in $N_5^{\cdot}$, "$N_5^+N_3^-$", $N_5^+N_5^-$, and N_5^+ are correlated with increased dissociation barriers. Preliminary calculations on quasi-periodic $(N_5^+N_5^-)_2$ clusters and periodic DFT calculations agree on a density of ∼1.9 g/cm^3 and a lattice energy of ∼130 kcal/mol. If a crystalline form of $N_5^+N_5^-$ could be stabilized, it would be an ideal monopropellant since its density is nearly twice that of hydrazine while the energy densities (heat of reaction per gram) are comparable.

Introduction

For several years we have been investigating the prospects for polynitrogen molecules that are unknown experimentally as potential candidates for high energy density forms. We have considered N_4,[1,2] N_5[3], N_6,[1,4] and N_8[1,5] as have other groups.[6−12] A compendium of our calculations for N_2 to N_{10}, including anions and cations, is available.[13] A survey of our work to date is presented in reference 14. Among the many suggestions made in that paper is that of combining the now known N_5^+ [15,16] with the unknown N_5^-.[6,17−21] Strangely, the pentazole anion is unknown in salts such as AgN_5,[22] LiN_5,[3,20] NaN_5,[23] $Mg(N_5)_2$[23] or in ferrocene-type complexes[21,23,24] where N_5^- would replace the cyclopentadienyl rings. However, the pentazole ring is well-known when stabilized by aromatic substituents such as phenyl.[25] The barrier to dissociation of HN_5 into HN_3 and N_2 is 20 kcal/mol[3] and that for N_5^- itself (at the CCSD(T)/cc-pVTZ level, also see ref 6) is 27 kcal/mol, suggesting they should both exist. We have presented the vibrational frequencies and intensities of N_5^-, including those for the Raman active modes[18] and its excitation energies for UV−vis spectroscopy.[13]

Since N_5^+ salts are stable at room temperature, it is natural to combine them with a suitable anion. One natural choice is the azide anion, N_3^-. As part of a study of N_8 we considered such "ion pairs" with fragment charges of ±0.3 and demonstrated that they are not very stable.[5] The barriers toward dissociation or rearrangement to diazidyldiazenes are less than 5 kcal/mol at B3LYP5[26]/aug-cc-pVDZ and just a few kcal/mol larger at MBPT(2)/aug-cc-pVDZ. In dissociative transition states, the already large distance between the N_3 and N_5 fragments increases slightly while the N_5 fragment splits into N_2 and $N_3^{\bullet}$. Even when covalent bonds are formed (diazydyldiazene[5,10,12,27,28,41]), the resulting bond breaks with a barrier of less than 20 kcal/mol.[5] Our prior results suggest that the kinetic stability of N_5^+ can be related to the partial charge it carries in a given environment. To a first approximation, the amount of electron transfer to N_5^+ is determined by its electron affinity and the ionization potentials of the molecules and ions in its environment. Larger charges of the ions are favored when electrostatic interactions with dipoles (polar solvents) or charges (cluster, crystal) reduce the energy.

TABLE 1: Vertical EA and IPs[a] in eV at EOM-CCSD/POL1//B3LYP/aug-cc-pVDZ

N_5^+, EA			N_3^-, IP			N_5^-, IP		
C_{2v}	C_s[b]		$D_{\infty h}$	C_s[b]		D_{5h}	C_s[b]	
B_1	A′	6.04	Π_g	π (nb)[c]	2.53	E_1'	A′	5.58
A_2	A"	5.63	Σ_u	σ LP	7.21	E_1''	A"	5.65
A_1	A′	5.53	Σ_g	σ LP	8.68	E_2'	A′	6.14
A_1	A′	3.93	Π_u	π	8.82	A_1'	A′	9.98

[a] Reference 13. [b] Molecular plane of the complexes. [c] nb = nonbonding.

Properties of the Pentazole Anion

The transition state for $N_5^- \rightarrow N_3^- + N_2$ was determined at several levels of approximation. At the highest level, CCSD(T)/cc-pVTZ, the dissociation barrier is 27.4 kcal/mol. Our results (see Supporting Information) are similar to those of ref 6: MBPT(2) finds the breaking bonds slightly shorter than the CC methods and B3LYP. On the other hand, the MBPT(2) barrier is a little closer to the CCSD(T) value than the B3LYP value. In this paper, we explore the prospects for making a crystalline $N_5^+N_5^-$ structure. We assess the kinetic stability of N_5^+ in ion pairs with N_3^- and N_5^- and that of the $N_5^+N_5^-$ ion pair with two additional transition states. We also consider the influence of neighboring ions in a crystal by performing calculations on clusters with two $N_5^+N_5^-$ pairs as well as periodic calculations on a possible crystal structure.

Table 1 reports IP- and EA-EOM-CCSD results[13] from ACES II[29] for the four lowest vertical ionized or electron-attached states of N_5^+, N_3^-, and N_5^-. A brief look at the electron affinity (EA) and ionization potentials (IPs) suggests that N_5^+ should be much more ionic and consequentially more stable with N_5^- than with N_3^-. In fact, most simple anions (as opposed to AsF_6^-, etc.) cannot be combined with N_5^+, due to its exceptional vertical EA (6.0 eV). However, N_5^- appears to be a potential exception because of the balance between its vertical IP (5.6 eV) and the EA of N_5^+. Other recent work also reports the $N_5^+N_5^-$ ion pair to be a local minimum of C_{2v} symmetry.[30] At B3LYP/aug-cc-pVDZ, the N5−N3 structure reported in ref 30 has a Gibbs

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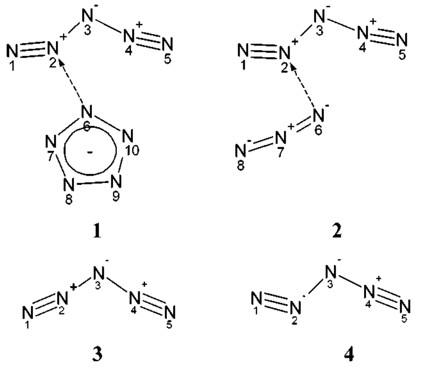


1 2 3 4

Figure 1. Structures of minima.

free energy of 58 kcal/mol, relative to azidylpentazole. That is 28 kcal/mol higher than the isomer in this work (see ref 5).

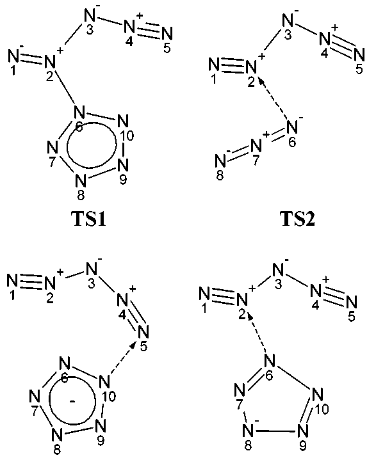
Computational Details

All coupled cluster (CC) calculations were performed with ACES II.[29] To ensure a consistent set of results for the ions, ion pairs, and complexes, their structures were optimized at the MP2/TZVPP[31] level using Turbomole.[32] The RI-[33] and frozen-core approximations were employed. Vibrational frequencies were calculated at the RI-MP2/TZVPP level. Activation energies for the dissociation were approximated by performing a series of partial optimizations with the length of the breaking bond fixed. The electronic structure was explored using the NBO[34]-analysis at the B3LYP5[26]/aug-cc-pVDZ//RI-MP2-fc/TZVPP level. The B3LYP5 calculations were done with Q-Chem 1.2.[35] The B3LYP/aug-cc-pVDZ optimizations used Q-Chem 2.0.[36] Enthalpies were calculated using STTHRM.[37]

The quasi-periodic clusters were optimized using Turbomole at the RI-BP86/SVP level with the *m*3 grid. NBO calculations on the clusters used the cc-pVDZ basis set. The periodic calculations were performed with Crystal98[38] at the BP86/SVP level, including the SVP auxiliary basis set. We used shrinking factors of 8 for the Monkhorst and Gilat-nets. A levelshift of 1 hartree ensured convergence of the energy calculations. We used a modified optimization script that allows referencing of other variables (similar to internal coordinates) and decoupling of intramolecular distances from changes in lattice constants. The optimization was carried out with the simplex scheme.[39] Energy differences are given in kcal/mol, geometry parameters in angstroms and degrees.

Optimized Geometries

The RI-MP2-fc/TZVPP geometries of the $N_5^+N_5^-$ ion-pair **1**, the "$N_5^+N_3^-$" complex **2,** and N_5^+ (**3**) are depicted in Figure 1, together with the MP2/6-31G(d) structure of $^2A'-N_5^{\bullet}$ (**4**). **1** and **2** are minima with C_s symmetry. The C_{2v} symmetric **1′** is just 0.4 kcal/mol higher in energy than **1** and has an imaginary frequency of 123i cm^{-1}. Therefor we expect a vibrationally averaged structure of C_{2v} symmetry. Frequencies and IR intensities of **1** and **2** are given in the Supporting Information. Figure 2 shows the structures of the approximate transition states for loss of $N_3^{\bullet}$ from **1** and **2** (**TS1** and **TS2**), addition of N_5^+ to N_5^- (**TSa**), and loss of N_2 from the N_5^- ion (**TS12**).[40] We think that **TS12** connects **1** and **2**, but the heat of reaction is large enough to cause immediate follow-up reactions, leading to formation of N_2 and probably $N_3^{\bullet}$.



TS1 TS2 TSa TS12

Figure 2. Structures of transition states.

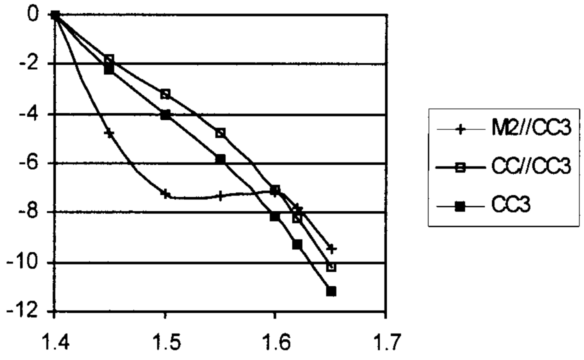


Figure 3. Relative energy (kcal/mol) of $N_5^{\bullet}$ vs N2−N3 distance at CCSD(T)-fc/aug-cc-pVDZ. Single point energies use the same basis set. CC3=CCSD(T)-fc, CC=CCSD-fc, and M2=MBPT(2)-fc.

The bond lengths and angles of **1** and **2** are given in the Supporting Information, together with data for N_5^+ (**3**) and $^2A'-N_5^{\bullet}$ (**4**). $N_5^{\bullet}$ is not a minimum at all levels of theory:[41] We were not able to find a minimum at RI-MP2-fc/TZVPP. A series of partial optimizations at the UHF−CCSD(T)-fc/aug-cc-pVDZ level shows that the MBPT(2)//CCSD(T) energy has a shallow minimum at N2−N3 ~ 1.52 Å while the CCSD and CCSD(T) energies fall monotonically (Figure 3). This could be an artifact of spin contamination in UHF-based MBPT(2) and MP2. Therefore, we interpret the geometry of ref 41 as a point on the dissociation path.

Comparing **4** (as a point on the reaction path) to the kinetically stable cation **3** shows some pronounced differences: The N2−N3 bond is 0.2 Å longer in **4** and the N1−N2−N3 angle is 44° smaller. Smaller changes occur in the N3−N4 and N4−N5 bonds. There is no covalent bond between the ions in both **1** and **2** as the interfragment distances are larger than 2 Å. The geometries of the N_5 units of **1** and **2** are intermediate between those of **3** and **4**. The N1−N2−N3 angles are much smaller than in **3** and the N2−N3 distances are longer. In addition, the N3−N4 and N4−N5 bond lengths are intermediate between the values exhibited in **3** and **4**. Many geometrical parameters of the N_5-fragments change smoothly from **3** to **1**, **2**, and **4**. The bond lengths in the N_5 ring of **1** differ by less than 0.02 Å from the pentazole anion (1.334 Å at RI-MP2-fc/TZVPP). These changes fall into the range determined by Gagliardi et al.[30] at the CASPT2(12/10)/ANO−S level. The different symmetry might be due to differences in correlation or the larger basis set in our calculations. The terminal NN bond in the N_3-fragment of **2** is 0.03 Å shorter than in the azide anion.

TS1 shows a large increase in the N2−N3 distance and beginning equilibration of the N3−N4 and N4−N5 bonds. An N2−N6 bond is forming while N1−N2 gets shorter than in N_5^+.

TABLE 2: Relative Enthalpies (298 K) at RI-MP2-fc/TZVPP

with respect to	**1**	**2**
$N_5^+ + N_X^{-\,a}$	−114	−149
N_2	296	241

[a] At RI-MP2-fc/TZVPP, $\Delta_f H_{298}°$ of N_5^+ and N_5^- are 347 and 63 kcal/mol; G3 values are 350 and 61 kcal/mol (ref 41). $\Delta_f H_{298}°$ of N_3^- is 43 kcal/mol; the experimental value is 48.5 ± 2.3 (ref 43).

The product is probably structure **I** of ref 42. **TS2** shows a smaller increase in the N2−N3 distance, some equilibration of the bonds in the forming $N_3^•$, and an increase in the N2−N6 distance. That is quite similar to the calculated behavior at B3LYP5/aug-cc-pVDZ,[5] although the breaking bond is ~0.1 Å shorter at RI-MP2/TZVPP. In **TSa**, the distortion of N_5^+ by N_5^- moved from N2 to N5. The bond lengths in the N_5^+ unit change accordingly. We expect the product to be cis with respect to N4 and N5. The length of the breaking bonds in **TS12** differs by ~0.1 Å. The TS is a little bit earlier than in N_5^- at the same level of theory. Reference 6 as well as our calculations show that B3LYP works reasonably well for geometry and activation energy of that dissociation. The imaginary vibration is consistent with the loss of N9 and N10 from the ring

Relative Enthalpies and Energy Densities

1 has a standard enthalpy of formation ($\Delta_f H_{298}°$) of 296 kcal/mol, 55 kcal/mol higher than **2**. The enthalpies per nitrogen atom are nearly identical at 30 kcal/mol. The enthalpy of reaction for formation of **1** from N_5^+ and N_5^- is −114 kcal/mol. This enthalpy is due to the approach of the oppositely charged ions and subsequent charge transfer from the anion to the more electronegative cation. The larger enthalpy of reaction for the formation of **2** from N_5^+ and N_3^- is mainly due to more charge transfer (see below). The electronic energy of **1** with respect to five N_2 is 288 kcal/mol, 27 kcal/mol larger than the value reported by Gagliardi et al.[7]

The energy density is related to the specific impulse, a very important characteristic of propellants. Since **1** and **2** would ultimately decompose into N_2 molecules, the enthalpy of reaction can be approximated by $\Delta_f H_{298}°$. This results in energy densities of 2.11 and 2.15 kcal/g for **1** and **2**. The ideal (low temperature) dissociation of hydrazine into ammonia, nitrogen, and hydrogen yields 2.14 kcal/g, derived from experimental[44] $\Delta_f H_{298}°$.

Electronic Structure

The electronic structure of **1** is closely related to the electronic structures of the fragments. The Lewis structure of the N_5^+ unit (see Natural Localized MOs, Supporting Information) has two terminal triple bonds and two single bonds. Three lone pairs are in the molecular plane while the second lone pair at N3 is a somewhat delocalized π orbital. The Lewis structure of the N_5^- unit is as expected: five nearly nonpolar σ-bonds, five lone pairs in the molecular plane, and an aromatic set of three π-bonds. The π electrons are somewhat polarized toward N6. The lone pair at N6 donates 0.26 electrons into the N1−N2 antibonding π-orbital in the molecular plane. This accounts for most of the electron transfer between the ions. It also explains why the N1−N2 bond is longer than in N_5^+.

The Lewis structure of **2** can be understood in terms of interacting N_5^+ and N_3^- fragments, too. The bonding in the N_5 unit is similar to that in **1**. The main difference is that the N1−N2 π-bond in the molecular plane is polarized toward the terminal nitrogen atom instead of the usual polarization toward the inner nitrogen. The N_3 unit differs from N_3^- by a strong delocalization of the N6 π-lone pair into the N1−N2 π antibond (both π-bonds are in the plane of the complex). 0.68 electrons are transferred by this interaction, accounting for most of the charge transfer between the ions. The partial population of the N1−N2 π antibond explains its elongation with respect to N_5^+ and **1**.

The atomic charges (Table 3) show that $N_5^+N_5^-$ should be called an ion pair while "$N_5^+N_3^-$" is better described as a complex with strong electron transfer. The N_5 units of **1** and **2** receive significant amounts of electron density: N_5^- donates about one-third of an electron while N_3^- transfers two-thirds of an electron. The additional electron density mainly reduces the positive charges at N1 and N2, apparently preparing the N_5 unit for dissociation into N_2 and $N_3^•$.

Dissociation of the N_5 Unit and Other Reactions

The N_5^+ cation, **3**, is kinetically stable enough for use as a high energy density material. The barrier to dissociation is 52 kcal/mol at MP2/6-311+G(d).[6] The $N_5^•$ radical ($^2A'$, **4**) however, is not stable. The equilibrium N2−N3 distance of $N_5^•$ is more than 0.15 Å longer than the equilibrium N2−N3 distances of **1** or **2** (Table 1). The subunits into which **4** dissociates have fragment charges of nearly zero (Table 3). To explore the correlation between the charge of the N_5 unit and the stability with respect to loss of $N_3^•$, we computed approximate activation energies. The energy curves obtained by optimizing the geometries of **1** and **2** with the N2−N3 bonds frozen (**1*** and **2***) are shown in Figure 4a.

The N2−N3 bond in "$N_5^+N_3^-$" dissociates with a barrier of 12 kcal/mol, 6 kcal/mol higher than the B3LYP5 value in ref 5. Breaking the N2−N3 bond in **1** requires about 25 kcal/mol. Figure 5 plots dissociation barriers versus the charge of the N_5 fragment in the minimum structures. The observed increase in stability with decreasing charge transfer from the anion to N_5^+ suggests that a more electronegative anion might form ion pairs with larger kinetic stability of the N_5^+ cation. The stability might also be increased by placing the complex in an environment that stabilizes the ions. One such environment is a crystal where each ion is surrounded by several counterions.

While the barrier toward loss of $N_3^•$ from **1** is high enough to make experimental observation possible, this is not the only probable reaction. We approximated the barrier toward addition of N_5^+ and N_5^- by doing a series of partial optimizations with the N_5−N_{10} distance frozen (Figure 4b). The barrier is ~16 kcal/mol. $\Delta_a H_{298}°$ for the loss of N_2 from the ring is 14.5 kcal/mol at B3LYP/aug-cc-pVDZ. Reference 6 as well as our results show that B3LYP describes the loss of N_2 from isolated N_5^-

TABLE 3: Atomic Charges at B3LYP/aug-cc-pVDZ//RI-MP2-fc/TZVPP

	N1	N2	N3	N4	N5	N6	N7	N8	N9	N10	ΣN1··N5	ΣN1,N2
3	0.33	0.22	−0.10	0.22	0.33						1.00	0.55
1	0.17	0.17	−0.15	0.22	0.22	−0.20	−0.11	−0.10	−0.09	−0.13	0.63	0.34
2	0.05	0.06	−0.17	0.24	0.15	−0.35	0.16	−0.14			0.33	0.11
4[a]	0.03	−0.04	−0.24	0.21	0.04						0.	−0.01

[a] B3LYP/aug-cc-pVDZ//MP2(fu)/6-31G(d), geometry from ref 41.

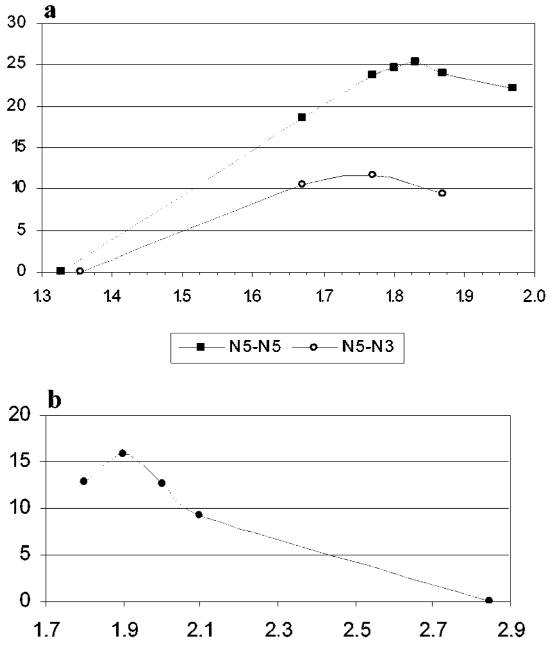


Figure 4. Electronic Energy (kcal/mol) with respect to **1** or **2** from partial optimizations at RI-MP2-fc/TZVPP. (a) Energy of **1*** and **2*** as a function of the N2−N3 distance. (b) Energy of **1*** as a function of the N5−N10 distance.

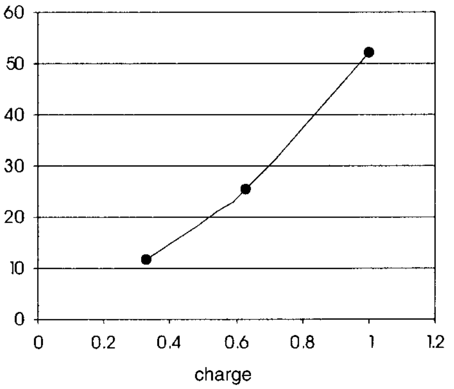


Figure 5. Dissociation barrier (kcal/mol) vs charge of the N_5-fragment in the equilibrium structure.

reasonably well. If it works as well here, N_5^- is destabilized by charge transfer, too.

Quasi-Periodic Cluster Calculations and Periodic Calculations

To explore the influence of multiple counterions on geometry and fragment charge of the N_5^+ ion, we optimized two clusters. These clusters consist of two N_5^+ and two N_5^- ions in a hypothetical $N_5^+N_5^-$ crystal that has each ion surrounded by six counterions and preserves the C_s symmetry found in **1**. That crystal would have space-group *Cm*. We achieve quasi-periodicity by forcing all N_5^+ and all N_5^- ions to share the same geometry. They are also restricted to have the same orientation in parallel (or identical) planes. Of course, this approach is qualitative, but it should provide a first impression of the differences between vacuum and crystal. We will compare our results with a periodic calculation later. Approximations to the lattice vectors **a** and **b** of a crystal can be determined from the N6→N16 and N13→N3 vectors in **5** (Figure 6). The N6→N16 vector in **6** can be used to approximate **e** which is equal to $^1/_2$(**a**+**b**+**c**). From these data, we evaluated the pseudo-lattice constants in Table 4.

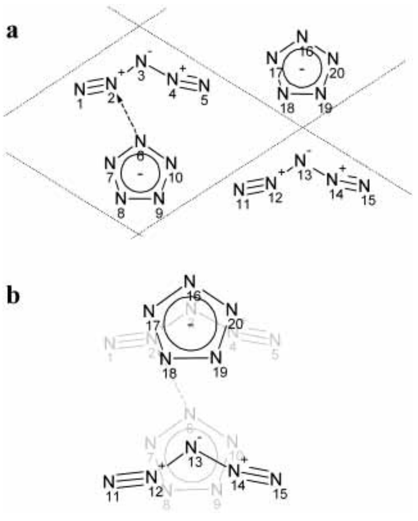


Figure 6. Quasi-periodic two-ion-pair clusters at RI−BP86/SVP. (a) **5**: Side by side in one plane with cell boundaries. (b) **6**: Two parallel planes. The gray ions are behind the black ones.

TABLE 4: Pseudo-Lattice Parameters for *Cm* (in Angstroms and Degrees) and Density in g/cm^3

a	b	c	α	ρ
6.81	6.64	6.06	115	1.87

TABLE 5: Partial Charges in Isolated 1 and Dimers 5 and 6

	1	5	6
N1	0.17	0.25	0.23
N2	0.17	0.21	0.21
N3	−0.16	−0.15	−0.12
N4	0.23	0.21	0.24
N5	0.20	0.20	0.23
N6	−0.20	−0.23	−0.23
N7	−0.09	−0.15	−0.14
N8	−0.11	−0.13	−0.15
N9	−0.08	−0.11	−0.14
N10	−0.13	−0.12	−0.15
ΣN1···N5	0.61	0.72	0.79

Cartesian coordinates and absolute energies are given in the Supporting Information. It is noteworthy that **a** and **b** are very similar: This shows that N_5^+ has very similar interactions to the left and to the right. The same can be concluded from the internal geometries of the N_5^+ and N_5^- ions. If both ions were undistorted, they would (as a pair) have C_{2v} symmetry. While the ions in **5** and **6** have C_s symmetry, they are much closer to C_{2v} than the ions in **1**. Differences between bond lengths or angles that would be equivalent in C_{2v} are often less than one-third as large as in **1**. Attempts to optimize clusters with four ion pairs failed because too many frozen variables created numerical problems.

We also calculated partial charges for **1**, **5** and **6** at the B3LYP/cc-pVDZ//RI-BP86/SVP level. Table 5 shows that the introduction of a second counterion reduces the electron transfer from N_5^- to N_5^+ by 0.1−0.2 electrons. According to the correlation in Figure 5 this should increase the kinetic stability of the N_5^+ by 5 to 10 kcal/mol. The partial charges are also more symmetric within the ions—especially in **6**—even though the electronic structure of the dimers was not forced to be periodic. The difference between the charges of atoms related by quasi-periodicity can be as large as 0.11 e$^-$.

Table 6 shows that the interaction energy Δ*E* is roughly proportional to the number of ion pairs in the cluster. The interaction energy per ion pair (Δ*E*/*Z*) is most negative for **1**.

TABLE 6: Electronic Energies (RI-BP86/SVP) of Quasi-Periodic Clusters with Respect to Separated Ions in kcal/mol

	1	5	6
ΔE	−125.9	−235.2	−240.0
$\Delta E/Z$	−125.9	−117.6	−120.0

TABLE 7: Lattice Parameters for *Fmm*2 (in Angstroms and Degrees) and Density in g/cm^3

a	b	c	ρ
11.44	5.91	7.23	1.90

Both **5** and **6** have an interaction between the tip of the V-shaped N_5^+ and the N_5^--ring. This interaction and the interaction of the terminal atoms of N_5^+ with N_5^- are not quite as good as the interaction in **1** because lone-pairs are located there and dampen the electrostatic attraction to a small degree. Additionally, the geometry constraints used to enforce quasi-periodicity will make the interaction energies of **5** and **6** a little less negative. Our calculations suggest that the interaction energy of a $N_5^+N_5^-$ crystal is more negative than −126 kcal/mol.

To check the conclusions drawn from the quasi-periodic structures, we optimized a possible crystal structure of $N_5^+N_5^-$. We chose the space group *Fmm*2 where both ions are restricted to C_{2v} symmetry. This seems justified since the quasi-periodic clusters are closer to C_{2v} symmetry than the ion-pair **1** and because of the small energy difference between **1** and **1′** at RI-MP2-fc/TZVPP. We are aware that $N_5^+N_5^-$ might crystallize in a different way, but our results would still be an upper bound to the interaction energy and quite probably a lower bound to the density.[45]

Table 7 shows the optimized lattice parameters and the resulting density. The density is ~1.5% larger than that derived from the quasi-periodic calculations. The geometry of the ions is similar to that of the isolated ion pair.

An empirical scheme for the estimation of lattice potential energies, related to Bartlett's relationship,[47] was recently proposed by Jenkins et al.[45] The relationship usually deviates less than 10% from the experimental values. Using formulas 3 and 4 of that publication and the approximate unit cell parameters from Table 4, we calculate a lattice potential energy of 137 kcal/mol. The same relationship predicts 138 kcal/mol for the BP86/SVP optimized crystal structure. The lattice potential energy is defined with the energy of the vibrating crystal being zero, i.e., it is approximately the negative of the interaction energy. Considering the difference with respect to zero point energies, the agreement between the upper limit of the interaction energy (−126 kcal/mol) and the lattice potential energy (137 kcal/mol) is reasonable.

Summary and Conclusions

We have shown that the ion pair $N_5^+N_5^-$ is a minimum on the N_{10} surface. There are lower energy structures, including an N_{10} analogue to azidylpentazole and the bipentazole[7,20,47] initially proposed in 1992.[3] The transition state between these two structures has not been located. Gas-phase $N_5^+N_5^-$ has enough charge separation to be called an ion pair. However, the corresponding "$N_5^+N_3^-$" structure has so much electron transfer that it should be called a complex. The relatively ionic structure of $N_5^+N_5^-$ is due to the unusually large ionization potential of N_5^-. In the gas phase, $N_5^+N_5^-$ has a barrier of 25 kcal/mol toward loss of $N_3^\cdot$ from the N_5^+ fragment, twice as high as the corresponding barrier in "$N_5^+N_3^-$". A correlation between dissociation barriers and charge of the N_5 fragment at the equilibrium geometry suggests that a larger positive charge of N_5^+ be accompanied by greater kinetic stability. Quasi-periodic cluster calculations show increased partial charges of the N_5^+ fragment. This would appear to move the dissociation barrier into a practically useful range. The N_5^+ fragments in the clusters also exhibit smaller deviations from C_{2v} symmetry, resulting in shorter and presumably more stable N2−N3 bonds. While N_5^+ in the crystal may be sufficiently stable, the preparation of the crystal from a solution might be difficult. Both the addition of N_5^+ to N_5^- and the loss of N_2 from the N_5^--ring have (in the gas-phase) barriers of ~15 kcal/mol.

To assess the performance of $N_5^+N_5^-$ as a propellant, we calculated its energy density. The lattice energy is estimated to be 120 to 140 kcal/mol. This represents a lower bound since better crystal structures may exist. The density of crystalline $N_5^+N_5^-$ is approximately 1.9 g/cm^3. The densities from the quasi-periodic and periodic calculation differ by less than 2%. These values result in an energy density of 2.11 kcal/g, similar to the optimal value calculated for hydrazine. However, the density of crystalline $N_5^+N_5^-$ is about twice as large as that of hydrazine, which might allow for smaller and therefore lighter rockets. The density of crystalline $N_5^+N_5^-$ is also important for its possible use as an explosive.

The periodic calculation might also be interesting with respect to recent reports on solid forms[48] of nitrogen, generated under extreme pressures. The very large ionization potential of N_5^- suggests that it may form very stable salts with cations that are less electronegative than N_5^+. Investigations of the kinetic stability of cyclic $N_5^\bullet$ are in progress.

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Supporting Information Available: Cartesian coordinates of all structures, vibrational frequencies of minima, natural localized molecular orbitals, overlap-weighted NAO bond orders, and absolute energies are presented. This material is available free of charge via the Internet at http://pubs.acs.org.

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