On the Bonding Nature of the $N_5^+(=N(N_2)_2^+)$ Cation and Related Species $N(CO)_x^+$, $N(NH_3)_x^+$, and NR_x^+, $x = 1, 2$ and R = He, Ne, Ar, Kr. Do We Really Need the Resonance Concept?

Ioannis S. K. Kerkines, Aristotle Papakondylis, and Aristides Mavridis*

Laboratory of Physical Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, P.O. Box 64 004, 157 10 Zografou, Athens, Greece

We attempt to elucidate the bonding nature of the isoelectronic and isovalent cations $N_5^+(=N(N_2)_2^+)$ and $N(CO)_2^+$, the salts of which have been recently isolated. By performing coupled-cluster RCCSD(T) calculations, we argue against the "resonance" bonding approach as redundant, and we claim that the bonding in the aforementioned species is naturally explained by realizing that the in situ central nitrogen (N^+) finds itself in the first excited ^1D state, thus forming two equivalent dative bonds with N_2 and CO, respectively. To further support our position, we have also studied at the same level of theory the molecules NNH_3^+, $N(NH_3)_2^+$, NR^+, and NR_2^+, where R = He, Ne, Ar, and Kr. It is predicted that the $N(NH_3)_2^+$ system is clearly isolable, whereas under certain conditions, NKr_2^+ (and perhaps NXe_2^+) could also be "trapped" experimentally.

1. Introduction

In 1999, two rather exotic molecular systems were isolated by two independent groups, namely, the isoelectronic and isovalent cations $N_5^+(=N(N_2)_2^+)$[1] and $N(CO)_2^+$.[2] Remarkably, both papers were submitted to the same journal within a time interval of 7 days. The N_5^+ ion was trapped as a $N_5^+AsF_6^-$ salt and described as "a white solid sparingly soluble in anhydrous HF, marginally stable at 22 °C and which can be stored for weeks at −78 °C without noticeable decomposition".[1] Very recently, the Christe group announced the preparation of two new N_5^+ salts, $N_5^+SbF_6^-$ and $N_5^+Sb_2F_{11}^-$, showing surprisingly thermal stability: they decompose at 70 °C, showing also relative stability with respect to impact.[3] The X-ray analysis of the $N_5^+Sb_2F_{11}^-$ crystals revealed the following V-shaped (C_{2v}) structure for the N_5^+ cation[3]


(1)
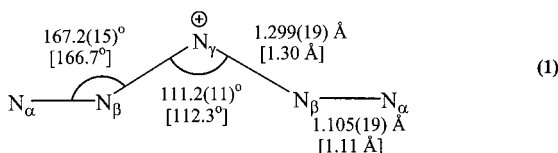
In Scheme 1, values in square brackets refer to theoretical predictions at the density functional B3LYP level of theory for the free N_5^+ cation.[1]

The surprise of the chemical community upon the announcement of a stable polynitrogen species is eloquently described in a *Chemical & Engineering News* report[4] titled, "N_5^+ cation makes explosive debut".

Now, the $N(CO)_2^+$ species was trapped with three different anions, AsF_6^-, $As_2F_{11}^-$, and $Sb_3F_{16}^-$, forming colorless crystals. The $N(CO)_2^+AsF_6^-$ and $N(CO)_2^+As_2F_{11}^-$ salts melt above 0 °C, whereas $N(CO)_2^+Sb_3F_{16}^-$ decomposes slowly at room-

temperature turning brown.[2] Crystals of the $N(CO)_2^+Sb_3F_{16}^-$ salt used for its X-ray crystallographic analysis[2] showed a V-shaped (C_{2v}) structure of the $N(CO)_2^+$ cation, very similar to the N_5^+ structure.

(2)
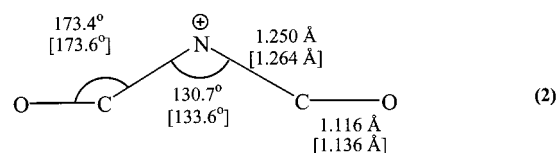
Values in square brackets are theoretical predictions at the CCD/6-31G(d, p) level of theory.[2]

Although the discovery of a stable $N(CO)_2^+$ species is of significant academic importance, its isolation did not attract the attention of the chemical community as in the case of the N_5^+ species. Perhaps because the announcement of the existence of a stable N_5^+ molecule was so unexpected that it completely eclipsed the important fact of the isolation of an isoelectronic, isovalent, and identically bonded (vide infra) to the N_5^+ system[2] or, perhaps, because $N(CO)_2^+$ had already been observed in 1992 in the gas phase by mass spectrometric methods.[5]

As expected, after the isolation of the N_5^+ species, several ab initio and DFT calculations followed,[6−13] focusing mainly on the geometry and stability of N_5^+, and confirming in essence the results of the original publication.[1] However, what has not been resolved yet, at least according to the present authors, is the bonding nature of N_5^+ and related isoelectronic (like $N(CO_2)^+$) or isovalent (like $N(CS)_2^+$, for instance) molecules. As a matter of fact, this is exactly what motivated the present report, that is, a clear understanding of the bonding mechanism of N_5^+ and similar species, based exclusively on *calculable* (or measurable) properties and not on vague or ill-defined concepts, like "resonance". Toward that goal, we have performed accurate-enough, first principles calculations on a series of similarly

bonded systems $N(XY)_x^+$, NR_x^+, and $N(NH_3)_x^+$ where $XY = N_2$, CO, R = He, Ne, Ar, or Kr, and $x = 1$, 2, and their fragments, charged or otherwise (but see below).

2. Chemical Insights

As it was alluded in the Introduction, the favorable explanation concerning the "understanding" of the bonding and stability of N_5^+ is the historically useful but admittedly not well-defined idea of resonance.[14] In the recent article by Christe and co-workers,[3] the bonding in N_5^+ is rationalized by the following series of resonance (sometimes called "canonical") structures:

(3)
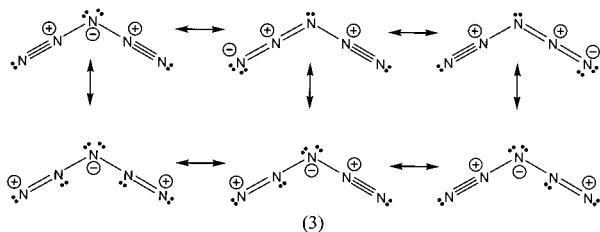
Klapötke[15] explains the stability and bonding of N_5^+ by employing "increased-valence" structures of the type
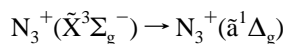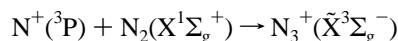

(4)
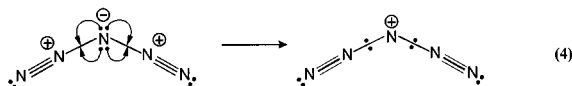
introduced by Harcourt,[16] where thin bonds on the right show fractional electron pair bonds. In another article by Ponec et al.,[10] the N_5^+ bonding is presumably understood by introducing the following "new" resonance scheme.
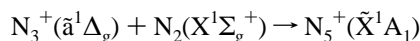

(5)
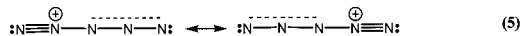
We believe that it is bad philosophy to try to comprehend something, here the bonding of the N_5^+ cation, with something ill-defined, here the concept of resonance. Schemes 3−5, by any means, cannot be considered as a *theory* or as a *model* of explaining the bonding of molecules or as having any *predictive* power. The rationalization comes after the fact ("hindsight") which is "fitted" to the resonance structures, and of course, a new resonance form can always be added to assist the "explanation" in a completely ad hoc manner.
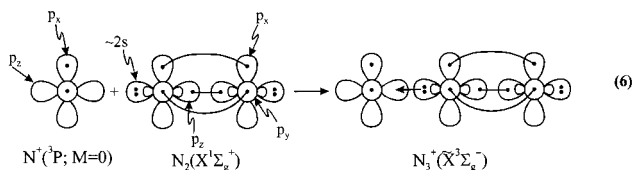
We can imagine now that the N_5^+ cation is composed of N^+ and two dinitrogen (N_2) species and formed by the sequence of reactions

$$N^+(^3P) + N_2(X^1\Sigma_g^+) \rightarrow N_3^+(\tilde{X}^3\Sigma_g^-)$$

$$N_3^+(\tilde{X}^3\Sigma_g^-) \rightarrow N_3^+(\tilde{a}^1\Delta_g)$$

and

$$N_3^+(\tilde{a}^1\Delta_g) + N_2(X^1\Sigma_g^+) \rightarrow N_5^+(\tilde{X}^1A_1)$$

Using valence-bond-Lewis icons (vbL), the first reaction is translated to

(6)

The two N−N bonds of the N_3^+ cation are equal (in the past, people theorized on an unsymmetrical N_3^+),[17] because of the participation in the bonding, by symmetry, of the mirror image of the vbL icon in Scheme 6. We also remind that the ionization energies (IE) of $N(^4S)$ and $N_2(X^1\Sigma_g^+)$ are 14.54[18] and 15.581[19] eV, respectively; therefore, the asymptotic energy fragments of $N_3^+(\tilde{X}^3\Sigma_g^-)$ are indeed $N^+(^3P) + N_2(X^1\Sigma_g^+)$ and not $N(^4S) + N_2^+(X^2\Sigma_g^+)$. Clearly, a second N_2 *cannot be bonded* to $N_3^+(\tilde{X}^3\Sigma_g^-)$, but it can "stick" to it electrostatically by a few kcal/mol, forming a triplet $N_3^+\cdots N_2$ state.[7,20] However, exciting the $\tilde{X}^3\Sigma_g^-$ state of N_3^+ to $\tilde{a}^1\Delta_g$ state, $\Delta E(\tilde{a}^1\Delta_g \leftarrow \tilde{X}^3\Sigma_g^-) = 1.2$ eV (vide infra), creates immediately the proper conditions for the bonding of a second $N_2(X^1\Sigma_g^+)$ molecule, as it is obvious from the following vbL diagram:

(7a)
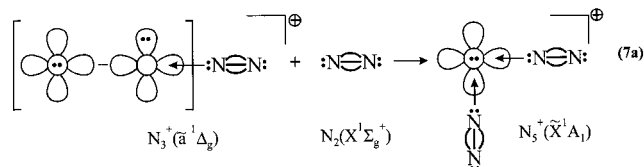
Again, the channel $N_3(\tilde{X}^2\Pi) + N_2^+(X^2\Sigma_g^+)$ is precluded because the IE of $N_2(X^1\Sigma_g^+)$ is larger than that of N_3.[19,29]

Alternatively, we can imagine that two $N_2(X^1\Sigma_g^+)$ moieties are bonded to the $N^+(^1D; 2s^22p^2)$ state, 1.888 eV (=43.53 kcal/mol) above the ground $N^+(^3P)$ state:[18]

(7b)
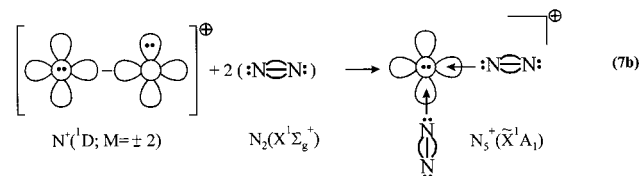
Scheme 7, parts a and b, rationalizes and predicts the binding features of N_5^+, i.e., that (a) the terminal N−N bonds should remain practically intact (triple bonded), (b) the bond to the central nitrogen is, in essence, a "dative" single bond, (c) the charge of the central atom should diminish drastically or even acquire some negative character, (d) the in situ central atom finds itself to the excited $N^+(^1D)$ state, and (e) it dictates the, in general, bent structure of N_5^+. In addition, vbLs 7a and 7b anticipate that by pulling apart N_5^+ according to $N_5^+ \rightarrow N_3^+ + N_2$ we should find N_3^+ in its $\tilde{a}^1\Delta_g$ state, or by pulling away the two N_2 molecules in a symmetrical fashion, $N_5^+ \rightarrow N^+ + 2N_2$, N^+ should be found in a ^1D (s^2p^2) state. Finally, this harpoon-like (dative) bonding clearly implies that the N_5^+ species can be "ripped apart" using a single reference calculational approach like a coupled-cluster (CC) or perturbational (MPn) technique or even at the Hartree−Fock level. Of course, the correct description of N^+ in a pure ^1D state is not feasible at a single-reference level, but we consider this as a minor point for the purpose of the present report.

Bonding mechanisms exemplified through Schemes 6 and 7a,b can be repeated but using the molecules CO ($X^1\Sigma^+$; isoelectronic and isovalent to N_2), CS ($X^1\Sigma^+$; isovalent to N_2), and $NH_3(\tilde{X}^1A_1)$, instead of N_2, thus creating the systems NXY^+, $N(XY)_2^+$ (where $XY = $ CO, CS) and NNH_3^+, $N(NH_3)_2^+$, in complete analogy to the $N_5^+(=N(N_2)_2^+)$ species. Within the same binding model, we can also incorporate the molecules NR^+ and NR_2^+, where R = He, Ne, Ar, and Kr.[21] Indeed, what does one expect to be the bonding mechanism in the

TABLE 1: Energies E (hartree), Bond Lengths r_e (Å), and Ionization Energies IE (eV) of Various Atomic and Molecular Species at the RCCSD(T)/cc-pVTZ Level of Theory (Experimental Values in Parentheses)

species	$-E$	IE[a]	species	$-E$	r_e	IE
N(^{4}S)	54.51433	14.429 (14.54)	N$_2$(X$^1\Sigma_g^+$)	109.37394	1.104 (1.0977)[b]	15.428 (15.581)[b]
N(^{2}D)	54.41354		N$_2^+$(X$^2\Sigma_g^+$)	108.80697	1.123 (1.1164)[b]	
N$^+$(^{3}P)	53.98406		CO(X$^1\Sigma^+$)	113.15558	1.136 (1.1283)[b]	13.895 (14.014)[b]
N$^+$(^{1}D)	53.90674		CO$^+$(X$^2\Sigma^+$)	112.64496	1.123 (1.1151)[b]	
He(^{1}S)	2.900232	24.526 (24.590)	NH$_3$(X̃^{1}A$_1$)[c]	56.47320	1.014 (1.0124)[c]	10.012 (10.070)[d]
He$^+$(^{2}S)	1.998921		NH$_3^+$(X̃^{2}A$_2''$)[e]	56.10527	1.022 (1.014)[f]	
Ne(^{1}S)	128.80245	21.303 (21.559)				
Ne$^+$(^{2}P)	128.01957		N$_2$(X$^1\Sigma_g^+$)[g]	109.40439	1.100	15.542
Ar(^{1}S)	527.04307	15.550 (15.755)	N$_2^+$(X$^2\Sigma_g^+$)[g]	108.83323	1.119	
Ar$^+$(^{2}P)	526.47163		CO(X$^1\Sigma^+$)[g]	113.18791	1.131	13.973
Kr(^{1}S)	2752.24498	13.923 (13.996)	CO$^+$(X$^2\Sigma^+$)[g]	112.67443	1.118	
Kr$^+$(^{2}P)	2751.73333					

[a] Experimental values from ref 18. [b] Experimental values from ref 19. [c] Calculated (expt.) ∠HNH angle 105.6° (106.7°), with experimental values from ref 26. [d] Experimental value from ref 27. [e] ∠HNH angle, by symmetry 120°. [f] Experimental value from ref 28. [g] At the RCCSD(T)/cc-pVQZ level.

NR$^+$ and NR$_2^+$ rare gas series? The following vbL diagrams are revealing:
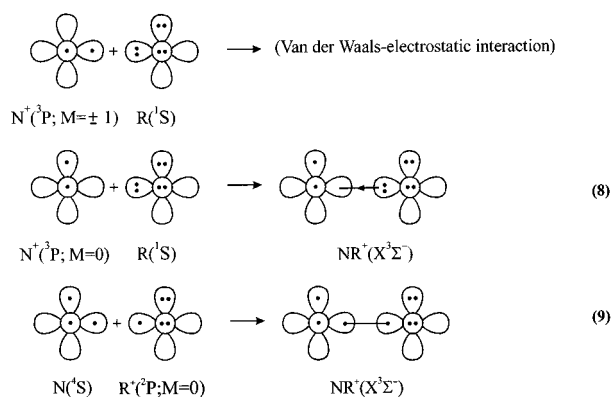
The realization of Schemes 8 and 9 depends on the IE = 14.54 eV of N(^{4}S)[18] vs the IE of R(^{1}S) = He, Ne, Ar, and Kr, 24.580, 21.59, 17.755, and 13.996 eV, respectively;[18] therefore, Scheme 9 takes place only for the Kr atom. To the NR$^+$ X$^3\Sigma^-$ state, no (neutral) second R atom could be bound "chemically", but this can be achieved by exciting the NR$^+$ species to the a$^1\Delta$ state, in complete analogy to Scheme 7a,b.

The calculations that follow for the series N(N$_2$)$_x^+$, N(CO)$_x^+$, N(NH$_3$)$_x^+$, and NR$_x^+$, x = 1, 2 and R = He, Ne, Ar, and Kr, are a very strong indication that the above discussion is on the right track, dismissing at the same time the resonance rationalization as redundant and, therefore, in accordance to Ockham's razor dictum.[22] The system(s) N(CS)$_x^+$, x = 1, 2 are not examined presently because of the vicissitudes of the CS molecule and its relatively low ionization energy; a separate study is intended to be devoted to the N(CS)$_x^+$ molecule(s). Suffice it to say at this point that N(CS)$_2^+$ is a linear (X$^1\Delta$) but very floppy molecule.[23]

For the aforementioned molecular systems, we have performed valence RCCSD(T) calculations in conjunction with correlation-consistent basis sets.[24] By "parenthesis T" it is meant the approximate and practically lowest order noniterative correction to the CCSD (S = T̂$_1$ and D = T̂$_2$) energy from connected triples (T̂$_3$). For all molecules studied, we report total energies, geometries, dissociation energies, and potential energy curves of the processes N$_3^+$ → N$^+$ + N$_2$, NCO$^+$ → N$^+$ + CO, N$_5^+$ → N$^+$ + 2N$_2$, and N(CO)$_2^+$ → N$^+$ + 2CO at the RCCSD(T)/cc-pVTZ level of theory. In addition, and only for the isoelectronic and isovalent species N(N$_2$)$_2^+$ and N(CO)$_2^+$, geometrical structures and bond energies were determined at the RCCSD(T)/cc-pVQZ level.

All of our calculations were performed with the MOLPRO 2000.1 package.[25]

3. Results and Discussion

Table 1 collects absolute energies and IE (ionization energies) of a series of atomic species involved in the molecules studied, as well as total energies, bond lengths (r_e), and IEs of the molecules N$_2$(X$^1\Sigma_g^+$), CO(X$^1\Sigma^+$), NH$_3$(X̃^{1}A$_1$), and their cations, at the RCCSD(T) level of theory. We observe that r_e and IE values are in acceptable agreement with existing experimental results, at least for the purpose of the present work. The largest deviations are observed in the separation energies N(^{2}D) ← N(^{4}S) = 2.743 (2.683) and N$^+$(^{1}D) ← N$^+$(^{3}P) = 2.104 (2.054) eV (values in parentheses have been calculated at the cc-pVQZ level), as compared to the experimental values 2.384 and 1.888 eV,[18] respectively.

Table 2 lists total energies, D_e values, with respect to the N$^+$ + XY/R and N + XY$^+$/R$^+$ channels, geometries, and (Hartree−Fock) Mulliken charges of the molecules N(XY/R)$^+$ (where XY = N$_2$, CO and R = He, Ne, Ar, Kr) and NNH$_3^+$, in their ground triplet and singlet states, as well as energy gaps between singlets and triplets.

3a. N$_3^+$. The formation of the X̃$^3\Sigma_g^-$ state of the N$_3^+$ cation is succinctly described by Scheme 6. Our results (D_e and r_e) are in agreement with experimental values; notice in particular (Table 2) the (Mulliken) charge decrease on the "terminal" nitrogen, from +1 to +0.29 because of the "dative" bond character. Figure 1 shows the potential energy curve (PEC), i.e., a "slice" through the corresponding potential energy surface, of the process N$^+$(^{3}P) + N$_2$(X$^1\Sigma_g^+$) → N$_3^+$(X̃$^3\Sigma_g^-$) at the CCSD(T) level. A similar PEC is presented through the singlet surface of the N$_3^+$ ã$^1\Delta_g$ state, whose bonding nature is described in Scheme 7a, and correlating to N$^+$(^{1}D) + N$_2$(X$^1\Sigma_g^+$). With respect to these fragments (minimal energy path), D_e = 98.3 kcal/mol at r_e = 1.189 Å (Table 2).

3b. NCO$^+$. We could imagine that, at equilibrium, the bonding in the X̃$^3\Sigma^-$ state of NCO$^+$ is formed in a similar fashion as in N$_3^+$, Scheme 6. However, because IE[N(^{4}S)] > IE[CO(X$^1\Sigma^+$)], Table 1, what really happens is described by the following vbL icon, that is, the adiabatic products are
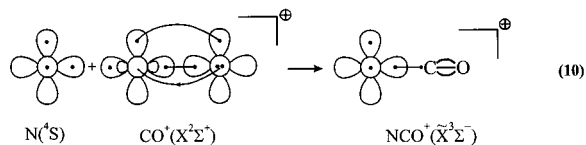
TABLE 2: Total Energies E (hartree), Bond Energies D_e (kcal/mol), Geometries r_e (Å), Mulliken Charges on Nitrogen (q_N), and Singlet−Triplet Separations ΔE (eV) of the Species NXY$^+$/NR$^+$ (XY = N$_2$, CO and R = He, Ne, Ar, and Kr) and NNH$_3^+$ at RCCSD(T)/cc-pVTZ Level of Theory (Experimental Values in Parentheses)
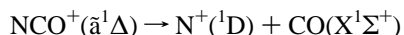
species	$-E$	D_e(N$^+$+XY/R)[b]	D_e(N+XY$^+$/R$^+$)[c]	r_e(N−X/−R)	r_e(X−Y)	q_N[d]	ΔE(S ← T)
N$_3^+$($\tilde{X}^3\Sigma_g^-$)[a]	163.48852	81.9 (81.4)[e]	104.9	1.192 (1.193)[f]	1.192 (1.193)[f]	+0.29	1.393 (1.13)[g]
N$_3^+$($\tilde{a}^1\Delta_g$)[a]	163.43734	98.3	136.1	1.189	1.189	+0.28	
NCO$^+$($\tilde{X}^3\Sigma^-$)	167.32628	117.1	104.8	1.359	1.130	+0.23	1.476
NCO$^+$($\tilde{a}^1\Delta$)	167.27205	131.6	134.0	1.300	1.153	+0.29	
NNH$_3^+$($\tilde{X}^3A_2$)	110.71288	172.1	58.5	1.455[h]	1.030[i]	+0.15	1.984
NNH$_3^+$($\tilde{a}^1A_1$)	110.63997	174.9	76.0	1.436[h]	1.032[i]	+0.12	
NHe$^+$($X^3\Sigma^-$)	56.89178	4.70	237.5	1.566		+0.87	2.117
NHe$^+$($a^1\Delta$)	56.81399	4.40	252.0	1.539		+0.86	
NNe$^+$($X^3\Sigma^-$)	182.80128	9.27	167.8	1.769		+0.88	2.122
NNe$^+$($a^1\Delta$)	182.72330	8.85	182.1	1.762		+0.87	
NAr$^+$($X^3\Sigma^-$)	581.10613	49.6	75.4	1.837		+0.50	2.037
NAr$^+$($a^1\Delta$)	581.03127	51.1	91.7	1.805		+0.45	
NKr$^+$($X^3\Sigma^-$)	2806.33679	67.6	55.9	1.945		+0.37	1.977
NKr$^+$($a^1\Delta$)	2806.26412	70.5	73.6	1.897		+0.30	

[a] Calculated at D_{2h} symmetry. [b] Dissociation with respect to N$^+$(^{3}P) for triplets and to N$^+$(^{1}D) for singlets (XY/R = ground-state singlet). [c] Dissociation with respect to N(^{4}S) for triplets and to N(^{2}D) for singlets (XY$^+$/R$^+$ = ground state doublet). [d] Mulliken charges on the terminal N at the Hartree−Fock level. [e] Experimental value (D_0) from ref 29. [f] Experimental value (r_0) from ref 17. [g] Experimental value from ref 29; at the MRCI/cc-pVQZ level, Rosmus et al. (ref 30) obtained ΔE(S ← T) = 1.30 eV. [h] The N−NH$_3$ distance. [i] The NNH$_2$−H distance, ∠NNH and ∠HNH angles = 109.6° and 109.3° ($^3A_2$), 110.0° and 108.9° ($^1A_1$).
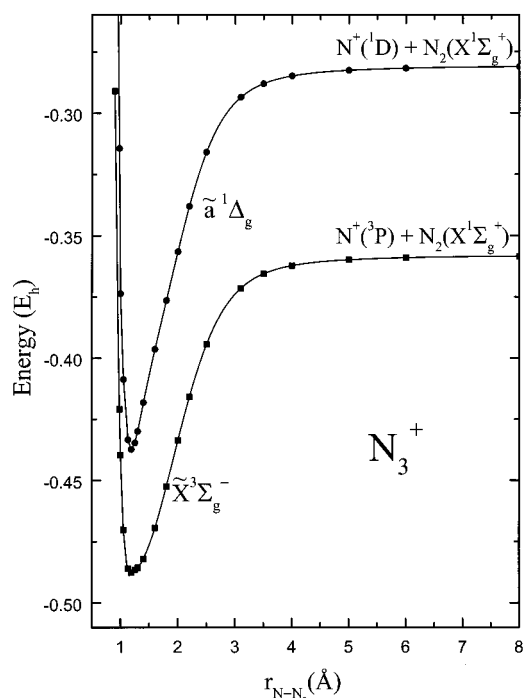
Figure 1. Potential energy profiles of the processes N$_3^+$($\tilde{X}^3\Sigma_g^-$) → N$^+$(^{3}P; M = 0) + N$_2$(X$^1\Sigma_g^+$) and N$_3^+$($\tilde{a}^1\Delta_g$) → N$^+$(^{1}D; M = ±2) + N$_2$(X$^1\Sigma_g^+$) at the RCCSD(T)/cc-pVTZ level.

Figure 2. Potential energy profile of the process NCO$^+$($\tilde{a}^1\Delta$) → N$^+$(^{1}D; M = ±2) + CO(X$^1\Sigma_g^+$) and part of the corresponding curve NCO$^+$($\tilde{X}^3\Sigma^-$) → N(^{4}S) + CO$^+$(X$^1\Sigma^+$); see text. RCCSD(T)/cc-pVTZ level.

N(^{4}S) + CO$^+$(X$^2\Sigma^+$). Scheme 10 suggests that the −C≡O moiety remains practically intact upon bonding and that the complete N−CO PEC cannot be constructed at the RCCSD(T) level because of the covalent character of the N−CO bond. This is exactly what happens: Figure 2 shows the N−CO$^+$ PEC around equilibrium, whereas the NC−O bond length is predicted to be 1.130 Å as compared to 1.123 Å of CO$^+$(X$^2\Sigma^+$), Tables 2 and 1. D_e(N−CO$^+$) = 104.8 kcal/mol with respect to N(^{4}S) + CO$^+$(X$^2\Sigma^+$).

The situation is different however for the $\tilde{a}^1\Delta$ state of NCO$^+$, approximately 1.5 eV above its $\tilde{X}^3\Sigma^-$ state. Whether the reaction

$$\text{NCO}^+(\tilde{a}^1\Delta) \rightarrow \text{N}^+(^1\text{D}) + \text{CO}(\text{X}^1\Sigma^+)$$

or

$$\text{NCO}^+(\tilde{a}^1\Delta) \rightarrow \text{N}(^2\text{D}) + \text{CO}^+(\text{X}^2\Sigma^+)$$

occurs, it depends on the process N(^{4}S) − e$^-$ → N$^+$(^{3}P) → N$^+$(^{1}D) vs N(^{4}S) + CO(X$^1\Sigma_g^+$) → N(^{2}D) + CO$^+$(X$^2\Sigma^+$) + e$^-$. Experimentally, the first one requires 16.428 eV vs 16.398 eV of the second, whereas calculationally, the corresponding values are 16.533 vs 16.638 eV, respectively (Table 1). Indeed, according to our calculations, NCO$^+$($\tilde{a}^1\Delta$) correlates to N$^+$(^{1}D) + CO(X$^1\Sigma^+$); thus, a full PEC could be constructed at the RCCSD(T) level, Figure 2, because of the *dative* character of the N−CO($\tilde{a}^1\Delta$) bond, similar to that of Scheme 6. The N−CO$^+$ D_e is 131.6 kcal/mol with respect to N$^+$(^{1}D) + CO(X$^1\Sigma^+$) or 134.0 kcal/mol with respect to N(^{2}D) + CO$^+$(X$^2\Sigma^+$), a 2.4 kcal/mol difference equal to the difference 16.638 − 16.533 = 0.105 eV reported above.

3c. NNH$_3^+$. The previous bonding scenario can be repeated here; according to Table 2, the least energy paths because of the much higher IE of N(^{4}S) vs NH$_3$ are NNH$_3^+$($\tilde{X}^3A_2$) → N(^{4}S)

TABLE 3: Total Energies E (hartree), Bond Dissociation Energies D_e (kcal/mol), Geometries r_e (Å), θ_e (Degrees), and Mulliken Charges on the Central Nitrogen q_N of the $^1A_1$ State of N(XY)$_2^+$/NR$_2^+$ (XY = N$_2$, CO and R = He, Ne, Ar, and Kr) and N(NH$_3$)$_2^+$($^1A_1$) Molecular Systems at the RCCSD(T)/cc-pVTZ Level

system	−E	D_e → N⁺(^{1}D)[a]	→ N(^{2}D)[b]	D_e → N⁺(^{3}P)[c]	→ N(^{4}S)[d]	r_e(NX/NR)	r_e(X−Y)	θ_e (XNX/RNR)	θ_e (NXY)	q_N[e]
				cc-pVTZ						
N(N₂)₂⁺	272.88521	144.7	182.5	96.2	119.2	1.323	1.116	108.6	167.3	−0.10
N(CO)₂⁺	280.65644	275.2	277.6	226.7	214.3	1.262	1.134	132.3	173.6	−0.11
N(NH₃)₂⁺	167.24857	248.1	161.0	199.6	97.7	1.466	f	105.2	f	−0.38
N(He)₂⁺	59.716693	5.95	253.5	−42.6	190.3	1.762		180.0		+0.86
N(Ne)₂⁺	311.53149	12.5	185.7	−36.1	122.4	1.994		180.0		+0.86
N(Ar)₂⁺	1108.10028	67.4	108.0	18.9	44.7	1.937		104.2		+0.25
N(Kr)₂⁺	5558.54589	93.6	96.7	45.1	33.4	2.034		107.0		+0.05
				cc-pVQZ						
N(N₂)₂⁺	272.95934	146.8	185.7	99.4	123.8	1.318	1.112	108.9	167.3	−0.02
N(CO)₂⁺	280.73596	278.3	281.0	230.9	219.1	1.260	1.131	132.5	173.7	−0.38

[a] With respect to N⁺(^{1}D) + 2XY/2R (ground-state singlet) or N⁺(^{1}D) + 2NH₃($\tilde{X}^1A_1$) for the N(NH₃)₂⁺ case. [b] With respect to N(^{2}D) + XY/R (ground-state singlet) + XY⁺/R⁺ (ground state doublet) or N(^{2}D) + NH₃($\tilde{X}^1A_1$) + NH₃⁺($\tilde{X}^2A_2''$) for the N(NH₃)₂⁺ case. [c] With respect to the ground-state products, N⁺(^{3}P) + 2XY/2R (singlet) or N⁺(^{3}P) + 2NH₃($\tilde{X}^1A_1$), for the N(NH₃)₂⁺ case. [d] With respect to N(^{4}S) + XY/R (ground-state singlet) + XY⁺ (ground state doublet) or N(^{4}S) + NH₃($\tilde{X}^1A_1$) + NH₃⁺($\tilde{X}^2A_2''$) for the N(NH₃)₂⁺ case. [e] Mulliken Hartree−Fock charges. [f] For the detailed geometry of the N(NH₃)₂⁺ complex, see Scheme 12.

+ NH₃⁺($\tilde{X}^2A_2''$) and NNH₃⁺($\tilde{a}^1A_1$) → N(^{2}D) + NH₃⁺($\tilde{X}^2A_2''$) with D_e = 58.5 and 76.0 kcal/mol, respectively. In the singlet state and at the *equilibrium*, we could think that the bonding is of dative character of the NH₃ lone pair to the N⁺(^{1}D) state with a binding energy with respect to N⁺(^{1}D) + NH₃($\tilde{X}^1A_1$) of 174.9 kcal/mol. The neutralization of the terminal nitrogen from +1 to +0.12 upon bonding is characteristic (Table 2).

3d. NR⁺ (R = He, Ne, Ar, and Kr). For the ground-state triplets (X$^3\Sigma^-$) of the NR⁺ series, the bonding mechanism is described by Scheme 8 if R = He, Ne, and Ar and by Scheme 9 for Kr. From Table 2, we observe significantly high binding energies for the NAr⁺ and NKr⁺ triplets, D_e = 49.6 and 55.9 kcal/mol, respectively, and the regular decrease of the nitrogen charge from +0.87 (NHe⁺) to +0.37 (NKr⁺) as expected, testifying to the correctness of Schemes 8 or 9. The same bonding mechanism is followed for the excited singlets (a$^1\Delta$), namely,

$$\left[\text{N}^+(^1\text{D}) \cdots \text{R}(^1\text{S}) \right]^\oplus = \text{N–R}^* (\text{a}^1\Delta) \tag{11}$$
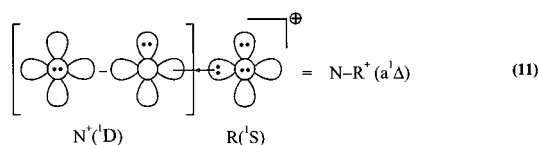
The bonding similarity between triplets and singlets is reflected on the same D_e, r_e, and the charge on the nitrogen (q_N) between these two states.

3e. N$_5^+$. We now move toward our final goal, that is, the clarification of the bonding mechanism of the N(XY)$_2^+$/NR$_2^+$ series, with particular emphasis on the N$_5^+$(=N(N$_2$)$_2^+$) and N(CO)$_2^+$ species, the isolation of which[1,2] triggered the present work. Table 3 presents pertinent numerical results concerning dissociation energies and structural parameters of the series N(XY)$_2^+$/NR$_2^+$ and N(NH₃)₂⁺ in their singlet state. For the N$_5^+$(=N(N$_2$)$_2^+$) and N(CO)$_2^+$ molecules, D_e values and geometries are also reported at the RCCSD(T)/quadruple-ζ level. As expected, going from the triple to the quadruple-ζ basis, the geometrical parameters do not change significantly, nevertheless the reported values at this level are the most accurate so far reported in the literature, and of course, they agree with the crystallographic results, Schemes 1 and 2.

Figure 3 shows a slice through the singlet potential energy surface of N$_5^+$ at the RCCSD(T)/cc-pVTZ level, constructed by pulling apart the two end −N$_2$ fragments, starting from the equilibrium geometry and maintaining the C_{2v} symmetry, while minimizing at the same time the N−N distance of the two terminal −N$_2$ fragments. The asymptotic products are N⁺(^{1}D) + 2N$_2$(X$^1\Sigma_g^+$) as pictured in Scheme 7b. It is also of interest to follow the evolution of Mulliken Hartree−Fock charges of the three distinct nitrogens (N$_\alpha$, N$_\beta$, and N$_\gamma$, see Scheme 1), along the reaction path in the inset of Figure 3, subject to the charge conservation condition $q_{N_\gamma}(r) + 2q_{N_\beta}(r) + 2q_{N_\alpha}(r) = +1$. The central nitrogen (N$_\gamma$) starts with −0.10 e⁻ at equilibrium (see also Table 3) and increases in a sigmoid fashion to +1 at infinity. At equilibrium, N$_\beta$ carries a +0.36 e⁻ charge, diminishes to zero around 2.2 Å, acquires a slight negative charge further apart by induction, and eventually approaches zero. The terminal N$_\alpha$ begins at +0.19 and drops to zero at infinity, slowly and almost linearly. Note also that the N$_\alpha$−N$_\beta$N$_\gamma$ r_e = 1.116 Å (Table 3) is equal to the average of the N$_2$(X$^1\Sigma_g^+$) and N$_2^+$(X$^2\Sigma_g^+$) bond lengths, (1.104 + 1.123)/2 = 1.114 Å, Table 1.

We believe that the above discussion leaves no doubt as to the bonding nature of N$_5^+$($\tilde{X}^1A_1$), i.e., of two dative (harpoon-like) bonds "titrating" the N⁺(^{1}D) atom, Scheme 7b. Instead of writing an ever-increasing number of resonance structures of obscure origin, the simplest and most accurate way to describe the bonding in N$_5^+$ in a chemical symbolic language would be

$$\text{N}{\equiv}\text{N}\diagup\overset{\oplus}{\text{N}}\diagdown\text{N}{\equiv}\text{N}$$
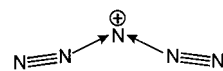
with the understanding that the in situ central nitrogen carries the *memory* of a N⁺ ^{1}D state.

At the RCCSD(T)/cc-pVTZ level, D_e = 98.3 kcal/mol for the process N$_3^+$($\tilde{a}^1\Delta_g$) → N⁺(^{1}D) + N$_2$(X$^1\Sigma_g^+$), Table 2. From Table 3, we see that the breaking of two N−N$_2$ bonds requires 144.7 kcal/mol; therefore, the D_e for the removal of one N$_2$(X$^1\Sigma_g^+$) from N$_5^+$ amounts to 144.7 − 98.3 = 46.4 kcal/mol. Finally, a large (40.6 kcal/mol) inversion barrier accompanied by a significant decrease of the N$_\beta$−N$_\gamma$ distance at linearity (N$_\beta$−N$_\gamma$, 1.210 Å; N$_\alpha$−N$_\beta$, 1.129 Å) is calculated for N$_5^+$ at the same level of theory.

3f. N(CO)$_2^+$. The above discussion for the N$_5^+$ molecule holds also for the N(CO)$_2^+$($\tilde{X}^1A_1$) species. From Table 3, it is

**4440** *J. Phys. Chem. A, Vol. 106, No. 17, 2002*

Kerkines et al.
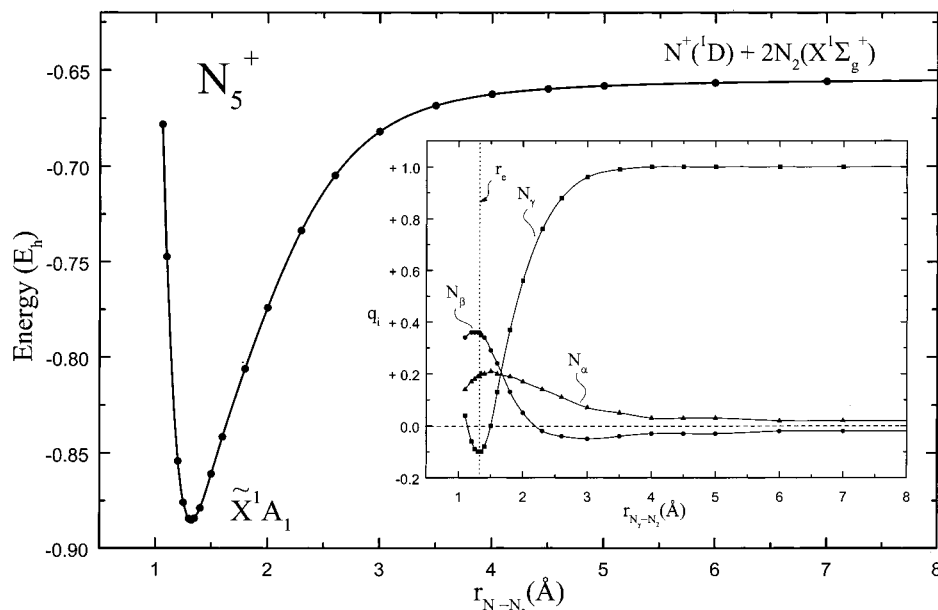
Figure 3. Symmetric opening of N_5^+ to $N^+(^1D) + 2N_2(X^1\Sigma_g^+)$ at the RCCSD(T)/cc-pVTZ level. The inset shows Hartree−Fock Mulliken charges (q_i, $i = \alpha$, β, γ) on the N_α, N_β, and N_γ atoms as a function of the $N_\gamma-N_2$ distance. The r_e dotted line indicates the equilibrium $N_\gamma-N_2$ distance.
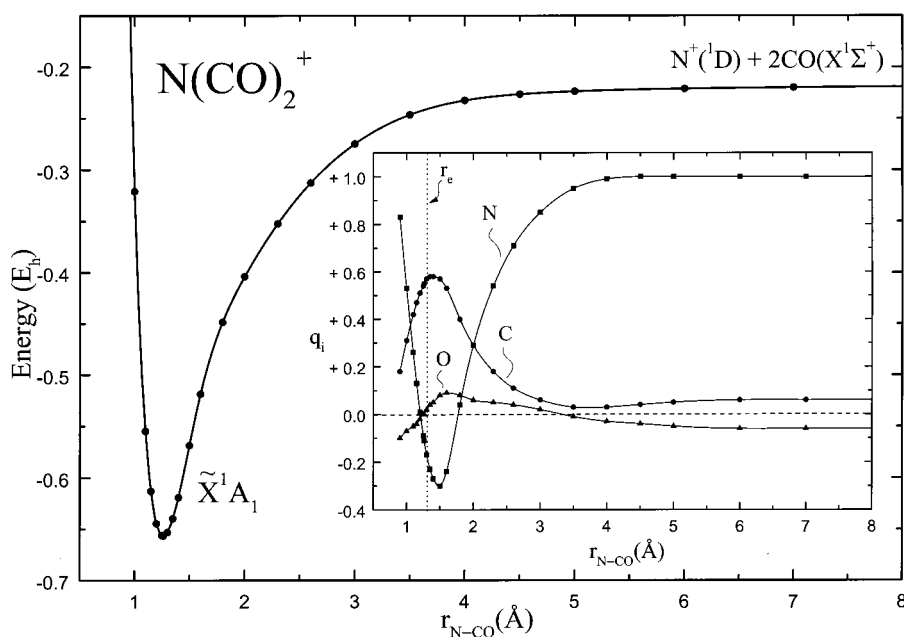

Figure 4. Symmetric opening of $N(CO)_2^+$ to $N^+(^1D) + 2CO(X^1\Sigma^+)$ at the RCCSD(T)/cc-pVTZ level. The inset shows Hartree−Fock Mulliken charges on the N, C, and O atoms as a function of the N−CO distance. The r_e dotted line indicates the equilibrium N−CO distance.

seen that the nitrogen atom carries a negative charge of 0.1 e^- at the Hartree−Fock/cc-pVTZ level, where the NC−O bond distance is very similar to that of the free $CO(X^1\Sigma^+)$ or $CO^+(X^2\Sigma^+)$, Table 1, and in the light of section 3b (NCO$^+$), we are rather certain that the bonding is similar to that of $N(N_2)_2^+$, Scheme 7b, i.e. with the in situ N^+ in the ^1D state. A
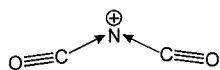

similar potential energy diagram to that of $N(N_2)_2^+$ (Figure 4) is shown in Figure 4. The two CO molecules are pulled away in a symmetrical fashion while optimizing at the same time the C−O distance. In the inset, we observe the (HF) charge

evolution for the three unique atoms, essentially identical to that of $N(N_2)_2^+$. What is remarkable is the very high D_e value for the process $N(CO)_2^+(\tilde{X}^1A_1) \rightarrow N^+(^1D) + 2CO(X^1\Sigma^+)$, $D_e = 275.2$ kcal/mol (Table 3), twice as large of the $N(N_2)_2^+$ corresponding value. This could be attributed to the availability of the σ lone pair of electrons residing on the carbon atom (:C≡O), thus rendering the dative mechanism more efficient. Knowing the D_e value for the reaction $NCO^+(\tilde{a}^1\Delta) \rightarrow N^+(^1D) + CO(X^1\Sigma^+)$ to be 131.6 kcal/mol (Table 2), the D_e for abstracting one $CO(X^1\Sigma^+)$ from $N(CO)_2^+$ is $275.2 - 131.6 = 143.6$ kcal/mol at the triple-ζ level. At the same level of theory, we find that $N(CO)_2^+$ is rather floppy; the barrier to linearity (N−C, 1.233 Å; C−O, 1.138 Å) is calculated to be 3.0 kcal/mol, in accord with previous calculations.[2,31]
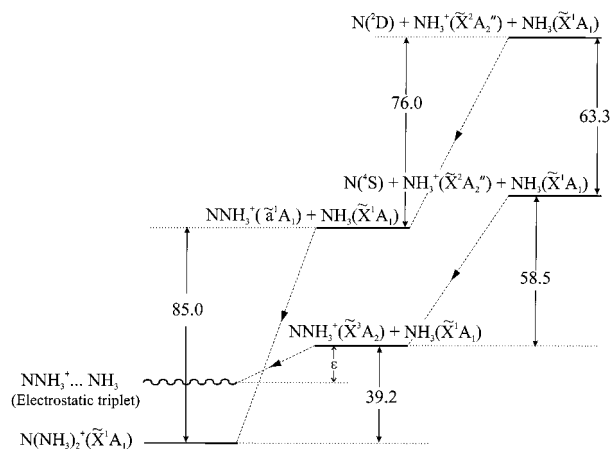
Figure 5. Energetics of the singlet $N(NH_3)_2^+(\tilde{X}^1A_1)$ and triplet $NNH_3^+\cdots NH_3$ formations at the RCCSD(T)/cc-pVTZ level of theory. All numbers are in kcal/mol; ϵ signifies the electrostatic binding energy $NNH_3^+(\tilde{X}^3A_2)\cdots NH_3$.

3g. $N(NH_3)_2^+$. When the geometry of the $N(NH_3)_2^+$ molecule is minimized at the RCCSD(T)/cc-pVTZ level under C_{2v} symmetry, the following structure is obtained. Interestingly
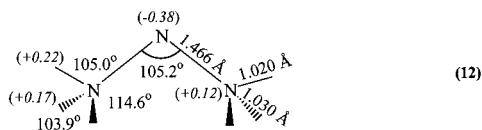

enough, the $\angle NNN$ angle is practically the same as the corresponding angle of the $N(N_2)_2^+$ system. Notice the very large negative Mulliken-HF charge on the central nitrogen, -0.38 e$^-$. From Tables 2 and 3, we deduce that the $D_e = 76.0$ kcal/mol for the process $NNH_3^+(\tilde{a}^1A_1) \rightarrow N(^2D) + NH_3^+(\tilde{X}^2A_2'')$, thereby the second NH_3 molecule enters with a binding energy of $161.0 - 76.0 = 85.0$ kcal/mol. Or, using pictures:
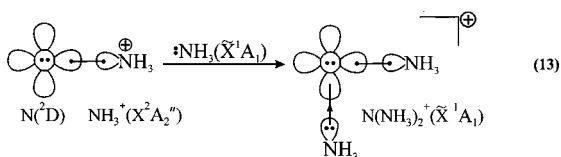
Of course, the two N−N bonds are equivalent.

To the best of our knowledge, neither experimental nor theoretical results exist in the literature concerning the $N(NH_3)_2^+$ cation. What is of interest from an experimental point of view, however, is that the $^1A_1$ $N(NH_3)_2^+$ species according to the energy diagram of Figure 5 is *isolable* at the RCCSD(T)/cc-pVTZ level. The wiggly line represents the level of the electrostatic interaction $N(NH_3)^+\cdots NH_3$, ϵ; assuming that ϵ is smaller than 39 kcal/mol, a reasonable hypothesis, $N(NH_3)_2^+(^1A_1)$ is the ground state. We would like to mention at this point that the homologous species $N(PPh_3)_2^+$ and $P(PPh_3)_2^+$, where Ph = phenyl group (C_6H_5), have been isolated.[32]

3h. NR_2^+; R = He, Ne, Ar, and Kr. When Scheme 11 is followed for the $NR^+(a^1\Delta)$ series, a second R atom can be inserted in the available p (p_π) orbital of the in situ $N^+(^1D)$ atom, resulting in the NR_2^+ singlet series of molecules. Table 3 reports atomization energies with respect to different channels, along with structural equilibrium parameters at the RCCSD(T)/cc-pVTZ level of theory. From Table 3, we observe the stark difference between the atomization energies of the two pairs of molecules NHe_2^+, NNe_2^+ and NAr_2^+, NKr_2^+, 5.95, 12.5 and 67.4, 93.6 kcal/mol, respectively. In addition, the first two
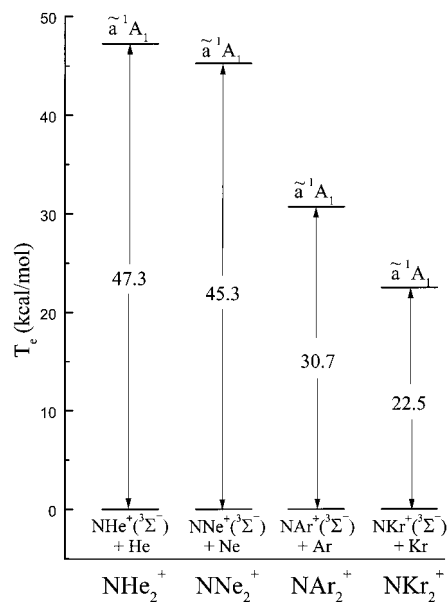
Figure 6. Singlet−triplet separations of $NR^+(^3\Sigma^-)$ + R(^1S) and $NR_2^+(\tilde{a}^1A_1)$, R = He, Ne, Ar, and Kr. All numbers should be increased by the corresponding electrostatic interactions $NR^+(^3\Sigma^-)\cdots R$; see text.

species are linear ($\angle RNR = 180°$), whereas the other two are strongly bent and with similar $\angle RNR$ angles, similar also to the $\angle N_\beta N_\gamma N_\beta$ of N_5^+. The atomization energies of the NR_2^+ series increase almost linearly with the polarizabilities of the R atoms (0.204456, 0.3946, 1.646, and 2.48 Å^3 for He, Ne, Ar, and Kr, respectively[33]) and inversely proportional to their electron-donor ability, i.e., to their IE values (Table 1). This is also evident from the charge on the N atom that decreases dramatically from He to Kr (Table 3).

Quite interestingly, the atomization energy of NHe_2^+ with respect to $N^+(^1D) + 2He(^1S)$, 5.95 kcal/mol, is nearly equal to the atomization energy of $LiHe_2(\tilde{A}^2B_1)$ with respect to $Li(^2P) + 2He(^1S)$, 5.57 kcal/mol.[34] The latter molecule is bent but extremely floppy having an inversion barrier of 32 cm^{-1};[34] on the other hand NHe_2^+ is linear but also floppy: bending NHe_2^+ from 180° to 120° requires 1.83 kcal/mol, at the RCCSD(T)/cc-pVTZ level.

The NNe_2^+ species is also linear, with an atomization energy of 12.5 kcal/mol with respect to $N^+(^1D) + 2Ne(^1S)$, and equally floppy, with NHe_2^+ requiring 1.66 kcal/mol to become bent at 120°.

The picture changes when we move to the NAr_2^+ and NKr_2^+ species: although the binding process is the same, i.e., two dative bonds, the atomization energies change drastically because of much larger polarizabilities and much smaller IEs of Ar and Kr as compared to He and Ne. As a result, atomization energies as large as 93.6 kcal/mol are calculated for NKr_2^+ at severely bent geometries and with respect to $N^+(^1D) + 2R(^1S; Ar, Kr)$. In addition, $NAr_2^+(\tilde{a}^1A_1)$ and $NKr_2^+(\tilde{a}^1A_1)$ are bound with respect to $N^+(^3P) + 2Ar$ and $N(^4S) + Kr^+ + Kr$ by 18.9 and 33.4 kcal/mol, respectively. Figure 6 shows the energy separation (T_e) between the NR_2^+ (singlets) and $NR^+ + R$ (triplets). The energy differences shown should be increased by the electrostatic interaction, $NR^+(^3\Sigma^-)\cdots R$, not larger than 5−6 kcal/mol for the Kr, and much smaller for the He atom (for instance, the electrostatic binding energy of $LiKr^+(X^1\Sigma^+)$ is 9.0 kcal/mol[19]). Notice that moving from He to Kr, T_e decreases significantly, and it is not unreasonable to propose that the $NKr_2^+(\tilde{a}^1A_1)$ (and maybe NAr_2^+) species could be experimentally trapped as a salt with an appropriate counterion.

4. Synopsis

For the series of molecules $N(N_2)_x^+$, $N(CO)_x^+$, $N(NH_3)_x^+$, and NR_x^+, where $x = 1, 2$ and R = He, Ne, Ar, and Kr, we have obtained structural parameters and bonding energetics using RCCSD(T) methods coupled with triple and quadruple-ζ correlation-consistent basis sets. The motivation of the present work was to elucidate the bonding nature, mainly of N_5^+ and $N(CO)_2^+$, two recently isolated species.[1,2] We argue, that the much used resonance concept for explaining the bonding of N_5^+ is of no use, as a matter of fact is misleading, and that the bonding can be understood by using *calculable* properties. Obviously, molecules are formed by atoms in well-defined stationary states, ground or otherwise.

All of the above, seemingly unrelated molecular systems ($x = 2$), can be easily understood by realizing that the in situ central nitrogen N^+ finds itself in the first excited ^1D state, forming two dative (harpoon-like) bonds originating from the two substituents.

For the systems $N(N_2)_2^+$ and $N(CO)_2^+$, our calculated structural parameters at the quadruple-ζ level are the best so far reported in the literature; in addition, and for the first time, we report singlet potential energy curves of the processes $N(XY)_2^+ \rightarrow N^+(^1D) + 2XY$, where $XY = N_2(X^1\Sigma_g^+)$, $CO(X^1\Sigma^+)$. The binding energies with respect to the ground states $NXY^+(\tilde{X}^3\Sigma^-) + XY(X^1\Sigma^+)$ are 14.3 and 109.6 kcal/mol for $XY = N_2$ and CO, respectively. This means that the $N(CO)_2^+$ system is much more stable than N_5^+, as indeed has been proven experimentally. Of course, resonance structures of $N(CO)_2^+$ similar to those of $N(N_2)_2^+$ do not support, explain, or predict the much larger stability of $N(CO)_2^+$ vs $N(N_2)_2^+$.

Within the same spirit, our study has been extended to the systems $N(NH_3)_2^+$ and NR_2^+, R = He, Ne, Ar, and Kr, where writing resonance structures is rather far-fetched. Nevertheless, the $N(NH_3)_2^+$ singlet state is clearly isolable according to our results, whereas very large binding energies are observed for the NAr_2^+ and NKr_2^+ systems. As a matter of fact the NKr_2^+ cation could be even isolable, with the singlet state being a little bit more than 23 kcal/mol above the global electrostatic $NKr^+\cdots Kr$ triplet minimum. Although we do not have any numerical data for the NXe_2^+ molecule, it is rather obvious that this system could be also isolable if combined with an appropriate counterion.

References and Notes

(1) Christe, K. O.; Wilson, W. W.; Sheehy, J. A.; Boatz, J. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2004.

(2) Bernhardi, I.; Drews, T.; Seppelt, K. *Angew. Chem., Int. Ed.* **1999**, *38*, 2232.

(3) Vij, A.; Wilson, W. W.; Vij, V.; Tham, F. S.; Sheehy, J. A.; Christe, K. O. *J. Am. Chem. Soc.* **2001**, *123*, 6308. See also, *Chem. Eng. News* **2000**, *78*, 41.

(4) Rawls, R. *Chem. Eng. News* **1999**, *77*, 7.

(5) Sülzle, D.; O'Bannon, P. E.; Schwarz, H. *Chem. Ber.* **1992**, *125*, 279.

(6) Xu, W.-G.; Li, G.-L.; Wang, L.-J.; Li, S.; Li, Q.-S. *Chem. Phys. Lett.* **1999**, *314*, 300.

(7) Nguyen, M. T.; Ha, T.-K. *Chem. Phys. Lett.* **2000**, *317*, 135.

(8) Wang, X.; Hu, H.; Tian, A.; Wong, N. B.; Chien, S.-H.; Li, W.-K. *Chem. Phys. Lett.* **2000**, *329*, 483.

(9) Nguyen, M. T.; Ha, T.-K. *Chem. Phys. Lett.* **2001**, *335*, 311.

(10) Ponec, R.; Roithová, J.; Gironés, X.; Jug, K. *J. Mol. Struct. (THEOCHEM)* **2001**, *545*, 255.

(11) Li, Q. S.; Wang, L. S. *J. Phys. Chem. A* **2001**, *105*, 1203.

(12) Fau, S.; Bartlett, R. J. *J. Phys. Chem. A* **2001**, *105*, 4096.

(13) Gagliardi, L.; Orlandi, G.; Evangelisti, S.; Roos, B. O. *J. Chem. Phys.* **2001**, *114*, 10733.

(14) See, for example: Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960; pp 10−14. What Pauling defines as "resonance" is a combination of the variational principle for normal (=ground) states and configuration interaction.

(15) Klapötke, T. M. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2536.

(16) Harcourt, R. D. *Eur. J. Inorg. Chem.* **2000**, 1901 and references therein.

(17) Friedmann, A.; Soliva, A. M.; Nizkorodov, S. A.; Bieske, E. J.; Maier, J. P. *J. Phys. Chem.* **1994**, *98*, 8896 and references therein.

(18) Moore, C. E. *Atomic Energy Levels*; NRSDS−NBS Circular No.35, U.S. GPO: Washington, DC, 1971.

(19) Huber, K. P.; Herzberg, G. H. *Molecular Spectra and Molecular Strucure; Vol. IV: Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.

(20) Pyykkö, P.; Runeberg, N. *J. Mol. Struct. (THEOCHEM)* **1991**, *234*, 279.

(21) See, for instance: Kerkines, I. S. K.; Mavridis, A. *J. Phys. Chem. A* **2001**, *105*, 1983.

(22) Ockham's razor maxim says: *Pluralitas non est ponenda sine necessitate*; that is, "multiplicity ought not to be posited without necessity", see, for example, *Encyclopedia Britannica* 1971; vol. 16, p 858.

(23) Unpublished results of this laboratory.

(24) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(25) MOLPRO is a package of ab initio programs written by Werner, H.-J. and Knowles, P. J. with contributions from Amos, R. D.; Bernhardsson, A.; Berning, A.; Celani, P.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Hetzer, G.; Korona, T.; Lindh, R.; Lloyd, A. W.; McNicholas, S. J.; Manby, F. R.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pitzer, R.; Rauhut, G.; Schütz, M.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T.

(26) Herzberg, G. *Molecular Spectra and Molecular Strucure, vol. III: Electronic Spectra and Electronic Structure of Polyatomic Molecules*; Van Nostrand Reinhold: New York, 1966.

(27) Lias, S. G. Ionization Energy Evaluation. In *NIST Chemistry Webbook; NIST Standard Reference Database Number 69*; Linstrom, P. J., Mallard, W. G., Eds.; July 2001, National Institute of Standards and Technology: Gaithersburg, MD, 20899 (http://webbook.nist.gov/).

(28) Lee, S.; Oka, T. *J. Chem. Phys.* **1991**, *94*, 1698.

(29) Dyke, J. M.; Jonathan, N. B. H.; Lewis, A. E.; Morris, A. *Mol. Phys.* **1982**, *47*, 1231.

(30) Bennett, F. R.; Maier, J. P.; Chambaud, G.; Rosmus, P. *Chem. Phys.* **1996**, *209*, 275.

(31) Carvalho, M. C.; Juliano, V. F.; Kascheres, C.; Eberlin, M. N., *J. Chem. Soc., Perkin Trans. 2* **1997**, 2347.

(32) Schmidpeter, A.; Lochschmidt, S.; Sheldric, W. S. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 226 and references therein. See also Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; J. Wiley & Sons: New York, 1999; pp 404−405.

(33) Polarizability values from: Miller, T. M.; Bederson, B. *Adv. At. Mol. Phys.* **1977**, *13*, 1.

(34) Kerkines, I. S. K.; Mavridis, A. *J. Phys. Chem. A* **2000**, *104*, 408.