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DFT Investigation of the Tri(amino)amine $N(NH_2)_3^{2+}$ and the Tri(azido)amine $N(N_3)_3^{2+}$ Dications and Related Mixed Amino(azido)ammonium Ions $(N_3)_xN(NH_2)_{4-x}^+$ ($x = 0$–4)[1]

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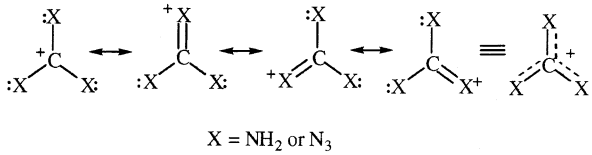
Structures of the tri(amino)amine $N(NH_2)_3^{2+}$ and the tri(azido)amine $N(N_3)_3^{2+}$ dications were calculated at the density functional theory (DFT) B3LYP/6-311+G* level. The tri(amino)amine dication $(NH_2)_3N^{2+}$ (**1**) was found to be highly resonance stabilized with a high kinetic barrier for deprotonation. The structures of diamino(azido)amine dication $(NH_2)_2N(N_3)^{2+}$ (**2**), amino(diazido)amine dication $(NH_2)N(N_3)_2^{2+}$ (**3**), and tri(azido)amine dication $(N_3)_3N^{2+}$ (**4**) were also found to be highly resonance stabilized. The structures and energetics of the related mixed amino(azido)ammonium ions $(N_3)_xN(NH_2)_{4-x}^+$ ($x = 0$–4) were also calculated.

Introduction

The guanidinium ion $(NH_2)_3C^+$ and the triazidocarbenium ion $(N_3)_3C^+$ are highly resonance stabilized ions. These ions owe their thermodynamic stability to the efficient p−p interaction between the positively charged carbon atom and the nonbonded electron pairs on the three adjacent nitrogen atoms (Scheme 1). The guanidinium ion is so stable that it is inert in boiling water.[2] The guanidinium ion can be easily further protonated[3] in superacids to give the N,N-diprotonated guanidinium dication.[4] The triazidocarbenium ion was first prepared in 1966 by Müller and Dehnicke.[5] The ion was characterized by crystal structure determination[6] and NMR and vibrational spectroscopy.[7,8]

Scheme 1



Skancke calculated[9] the structure of the tri(amino)amine dication $(NH_2)_3N^{2+}$, the isoelectronic analogue of the guanidinium ion, focusing on the concept of Y-aromaticity. The structure was calculated at the ab initio MP2/6-31G* level to be a minimum with D_3 symmetry with a planar nitrogen framework. We report now the investigation of the tri(amino)amine $(NH_2)_3N^{2+}$ and the tri(azido)amine $(N_3)_3N^{2+}$ dications as well as the mixed amino−azido dications $(N_3)_xN(NH_2)_{3-x}^{2+}$ ($x = 0-3$) by the density functional theory (DFT) method. The corresponding azido derivatives, amino(azido)ammonium ions $(N_3)_xN(NH_2)_{4-x}^+$ ($x = 0-4$), were also investigated.

Calculations

Calculations were performed with the Gaussian 98 program system.[10] The geometry optimizations were performed using the density functional theory (DFT)[11] method at the B3LYP/6-31G* level.[12,13] Vibrational frequencies at the B3LYP/6-31G*//B3LYP/6-31G* level were used to characterize stationary points as minima (number of imaginary frequencies (NIMAG) = 0) or transition state structures (NIMAG = 1) and to evaluate zero point vibrational energies (ZPEs), which were scaled by a factor of 0.98. Further optimizations were carried out at the higher B3LYP/6-311+G* level. Final energies were calculated at the B3LYP/6-311+G*//B3LYP/6-311+G* + ZPE level. Atomic charges were obtained using the natural bond orbital analysis (NBO) method.[14]

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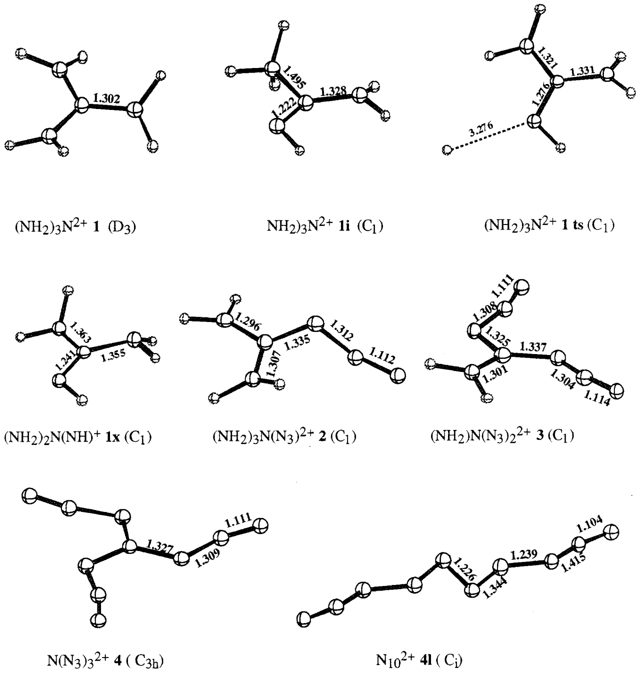
(1) Onium Ions. Part 60. For Part 59 see: Rasul, G.; Prakash, G. K. S.; Olah, G. A. *Proc. Natl. Acad. Sci.*, submitted.
(2) Gund, P. *J. Chem. Educ.* **1972**, *49*, 100.
(3) Rasul, G.; Prakash, G. K. S.; Olah, G. A. *J. Org. Chem.* **1994**, *59*, 2552.
(4) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; Wiley-Interscience: New York, 1985.
(5) Müller, U.; Dehnicke, K. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 841.
(6) Kolitsch, W.; Müller, U. *Z. Anorg. Allg. Chem.* **1974**, *410*, 21.
(7) Müller, U.; Kolitsch, W. *Spectrchim. Acta* **1975**, *31A*, 1455.
(8) Petrie, M. A.; Sheehy, J. A.; Boatz, J. A.; Rasul, G.; Prakash, G. K. S.; Olah. G. A.; Christe, K. O. *J. Am. Chem. Soc.* **1997**, *119*, 8802.
(9) (a) Skancke, A. *J. Phys. Chem.* **1994**, *98*, 5234. (b) Bernhard, H.; Skancke, A. *J. Am. Chem. Soc.* **1993**, *115*, 7465.

10.1021/ic020358r CCC: $22.00



$(NH_2)_3N^{2+}$ **1** (D_3) $NH_2)_3N^{2+}$ **1i** (C_1) $(NH_2)_3N^{2+}$ **1 ts** (C_1)

$(NH_2)_2N(NH)^+$ **1x** (C_1) $(NH_2)_3N(N_3)^{2+}$ **2** (C_1) $(NH_2)N(N_3)_2^{2+}$ **3** (C_1)

$N(N_3)_3^{2+}$ **4** (C_{3h}) N_{10}^{2+} **4l** (C_i)

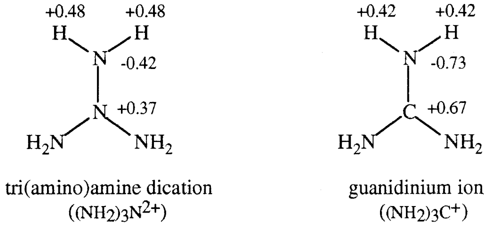
Figure 1. B3LYP/6-311+G* optimized structures of **1**−**4**.

Results and Discussion

The B3LYP/6-311+G* optimized structure (Figure 1) of the tri(amino)amine dication $(NH_2)_3N^{2+}$ is in agreement with previous calculations at the MP2/6-31G* level.[9] The propeller-shaped D_3 symmetry structure **1** is the minimum as confirmed by frequency calculations. The amino groups of the structure are rotated out of the N_4 plane around the $N-NH_2$ bonds by about 25°. Structure **1** is isoelectronic and isostructural with the guanidium ion $(NH_2)_3C^+$.[3] The $N-NH_2$ bond length of **1** is 1.302 Å, slightly shorter than the $C-NH_2$ bond length of the guanidinium ion (1.335 Å) calculated at the same B3LYP/6-311+G* level. This indicates that, similar to the guanidinium ion,[3] the dication **1** is also highly stabilized by resonance interactions between the electron deficient central nitrogen atom and the nitrogen atoms of the amino groups. We have computed the isomeric structure $(NH_3)N(NH_2)(NH)^{2+}$ (**1i**) (Figure 1). However, structure **1i** is significantly (15.9 kcal/mol) less stable than isomer **1**.

Deprotonation of **1** was calculated to be substantially endothermic by 67.3 kcal/mol. We have identified the transition state **1ts** for deprotonation of **1**, which lies 110.8 kcal/mol above **1**. Thus, the dication **1** has a very high kinetic barrier for dissociation into the monocation **1x** and H^+. The optimized structure of **1x** is given in Figure 1.

Scheme 2



tri(amino)amine dication ($(NH_2)_3N^{2+}$)   guanidinium ion ($(NH_2)_3C^+$)

The NBO[14] charges of the tri(amino)amine dication **1** (Scheme 2) were calculated at the B3LYP/6-311+G*//B3LYP/6-311+G* level. For comparison, NBO charges of the guanidinium ion were calculated (Scheme 2) at the same level. The calculated charges of the central and amino nitrogens and the hydrogen atoms of **1** are +0.37, −0.42, and +0.48 au, respectively. Thus, the hydrogen atoms of **1** bear the most of the positive charges. The NH_2 group (+0.54 au) of the dication as a whole bears more positive charge than the central nitrogen atom. However, unlike the dication **1**, in the monocationic guanidinium ion, the NH_2 group (+0.11 au) bears substantially less positive charge than the central carbon atom (+0.67 au). These comparisons indicate that, in the dication **1**, the charges are more delocalized compared to the charge in the guanidinium ion.

We have calculated the structures and energetics of the diamino(azido)amine dication $(NH_2)_2N(N_3)^{2+}$ (**2**) and the amino(diazido)amine dication $(NH_2)N(N_3)_2^{2+}$ (**3**) at the B3LYP/6-311+G* level (Figure 1). Both structures are almost planar with the amino groups being slightly rotated out of the N_4 plane around the $N-NH_2$ bonds. The $N-NH_2$ bond lengths of the dications **2** and **3** are very close to that of the dication **1**. Compared to $N-NH_2$, the N−N (N_3) bond lengths of the dications **2** and **3** are slightly longer at about 1.33 Å.

The minimum energy structure of the tri(azido)amine dication $(N_3)_3N^{2+}$ corresponds to C_{3h} symmetry form **4** (Figure 1). Structure **4** is isoelectronic and isostructural with the trisazidocarbenium ion $(N_3)_3C^+$.[5−8] The central N−N bond length of **4** is 1.328 Å, shorter than the C−N bond length of the triazidocarbenium ion (1.349 Å) calculated at the same B3LYP/6-311+G* level. From this comparison, it appears that the dication **4** is structurally similar to the triazidocarbenium ion[8] and is also highly resonance stabilized. Recently, Klapötke et al. calculated the structure of neutral $(N_3)_3B$, which is an isoelectronic analogue of $(N_3)_3N^{2+}$.[15]

For comparison, the C_i symmetry isomer **4l** of the dication **4** was calculated (Figure 1) and found to be a minimum on the potential energy surface. The structure **4l** was found to be only 0.3 kcal/mol less stable than **4** (Table 1). In a related study, recently Olah et al. reported[16] the DFT calculated

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(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998.

(11) Ziegler, T. *Chem. Rev.* **1991**, *91*, 651.

(12) Becke's three parameter hybrid method using the LYP: Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(13) Correlation functional: Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(14) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

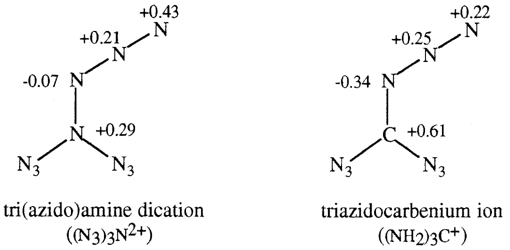
(15) Fraenk, W.; Habereder, T.; Hammerl, A.; Klapötke, T. M.; Krumm, B.; Mayer, P.; Nöth, H.; Warchhold, M. *Inorg. Chem.* **2001**, *40*, 1334.

Table 1. Total Energies (−au), ZPE,[a] and Relative Energies (kcal/mol)[b]

no.	B3LYP/6-31G*//B3LYP/6-31G*	ZPE	B3LYP/6-311+G*//B3LYP/6-311+G*	rel. energy (kcal/mol)
1	221.76450	54.1	221.82413	0.0
1i	221.73866	54.2	221.79896	15.9
1ts	221.57435	46.4	221.63523	110.8
1x	221.64487	47.4	221.70629	67.3
2	329.96876	44.9	330.05618	
3	438.17944	35.8	438.29478	
4	546.39720	27.2	546.54042	0.0
4l	546.39207	24.3	546.53463	0.3
1b	386.40051	63.2	386.50897	
2b	494.61097	53.4	494.74638	
3b	602.82189	43.7	602.98425	
4b	711.03917	34.2	711.22865	
5	517.85929	15.6	518.01259	
6	582.26181	21.7	582.43074	
7	646.65987	28.0	646.84370	

[a] Zero point vibrational energies (ZPEs) at B3LYP/6-31G*//B3LYP/6-31G* scaled by a factor of 0.98. [b] At B3LYP/6-311+G*//B3LYP/6-311+G* + ZPE level.

Scheme 3



tri(azido)amine dication ($(N_3)_3N^{2+}$)

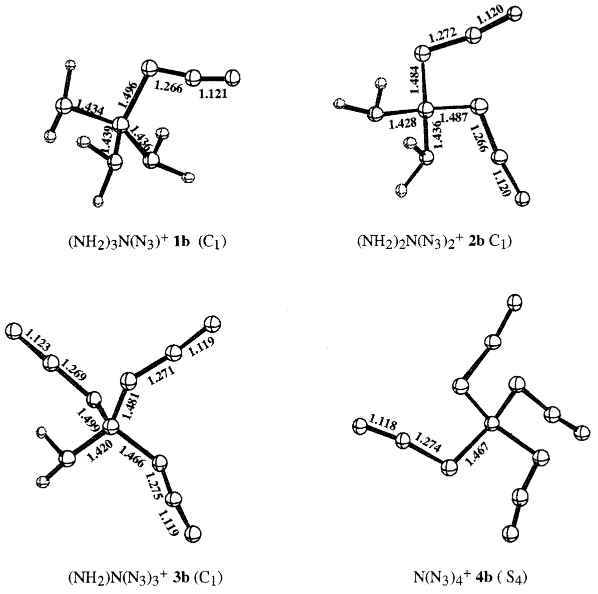
triazidocarbenium ion ($(NH_2)_3C^+$)

structures of N_6^{2+}. Previously, Christe et al. have prepared and characterized the intriguing all nitrogen N_5^+ cation as the $N_5^+AsF_6^-$, $N_5^+SbF_6^-$, and $N_5^+Sb_2F_{11}^-$ salts.[17,18] Christe et al. have also obtained the structure of N_5^+ by single-crystal X-ray diffraction studies.[18] The DFT-calculated[17] structure of N_5^+ agrees very well with the X-ray structure,[18] thus validating the suitability of the DFT-hybrid method for this type of nitrogen compounds.

The NBO charges of the tri(azido)amine dication **4** were calculated and compared with the calculated NBO charges of its isoelectronic analogue, triazidocarbenium ion (Scheme 3). The calculated charge of central nitrogen of dication **4** is only +0.29 au.

Thus, the N_3 groups of **4** (+0.57 au) bear the bulk of the positive charges. In contrast, the central carbon of triazidocarbenium ion (+0.61 au) bears most of the positive charge.

Interaction of **1** with the azide (N_3^-) ion yielding the tri(amino)azidoammonium ion $(NH_2)_3N(N_3)^+$ (**1b**) was calculated (Figure 2) and found to be expectedly highly exothermic by 248.3 kcal/mol. Similarly, interactions of **2**, **3**, and **4** with the azide (N_3^-) ions yielding $(NH_2)_2N(N_3)_2^+$ (**2b**), $(NH_2)N(N_3)_3^+$ (**3b**), and $(N_3)_4N^+$ (**4b**), respectively, were also calculated (Figure 2). All of these interactions were computed to be similarly exothermic, by about 252 kcal/mol. In the structure **4b**, the four azido groups are oriented pseudo-tetrahedrally. The crystal structure of the tetraazidoborate anion $(N_3)_4B^-$ has recently been reported by Klapotke et al.[15] The $(N_3)_4B^-$ anion is isoectronic with the $(N_3)_4N^+$ cation.



$(NH_2)_3N(N_3)^+$ **1b** (C_1)

$(NH_2)_2N(N_3)_2^+$ **2b** C_1)

$(NH_2)N(N_3)_3^+$ **3b** (C_1)

$N(N_3)_4^+$ **4b** (S_4)

Figure 2. B3LYP/6-311+G* optimized structures of **1**−**4b**.

Structure **4b** corresponds to molecular formula N_{13}^+, and this was calculated by Christe et al.[19] at the ab initio MP2/6-31G* level. Our DFT results agree very well with the computed MP2/6-31G* results.[19] Bartlett has calculated[20] the structures and energies of neutral and monocationic as well as monoanionic forms of polynitrogen species ranging from N_2 to N_{10} using DFT and ab initio methods. All of them were found to be stable minima on their potential energy surfaces. Glukhovtsev et al.[21] have calculated the structures and stabilities of neutral polynitrogen molecules (N_4, N_6, N_8, N_{10}, and N_{12}) by ab initio and DFT methods. Calculated vibrational frequencies of selected ions (**1**, **4**, and **4b**) are given in Table 2.

In 1991, Pyykkö and Runeberg calculated a series of ABCBA-type compounds including N_5^+ at the MP2/6-31G* level.[22] In 1992, one of us (G.R.) proposed and calculated the N_5^+ cation and suggested its possible synthesis.[23] However, this was not further pursued or published. The reaction of FN_2^+ with HN_3 was utilized by Christe et al. to synthesize the N_5^+ cation.[17,18] We have now investigated a similar reaction of tetrafluoroammonium ion NF_4^+ with hydrazoic acid HN_3 computationally at the B3LYP/6-311+G*//B3LYP/6-311+G* + ZPE level (to the possible preparation of tetra(azido)ammonium ion **4b**, Scheme 4). Highly energetic diazonium ions such as $FN_2^+AsF_6^-$ and

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(16) Olah, G. A.; Prakash, G. K. S.; Rasul, G. *J. Am. Chem. Soc.* **2001**, *123*, 3308.

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

(18) Vij, A.; Wilson, W. W.; Vij, V.; Tham, F. S.; Sheehy, J. A.; Christe, K. O. *J. Am. Chem. Soc.* **2001**, *123*, 6308.

(19) Michels, H. H.; Montgomery, J. A.; Christe, K. O.; Dixon, D. A. *J. Phys. Chem.* **1995**, *99*, 187.

(20) Bartlett, R. J. *Chem. Ind. (London)* **2000**, *4*, 140. For more information see: http://www.qtp.ufl.edu/~bartlett/polynitrogen.doc.gz.

(21) Glukhovtsev, M. N.; Jiao, H.; Schleyer, P. v. R. *Inorg. Chem.* **1996**, *35*, 7124.

(22) Pyykkö, P.; Runeberg, N. *THEOCHEM* **1991**, *234*, 279.

(23) Rasul, G. Written proposal for Ph.D. examination, University of Southern California, 1992.

Table 2. B3LYP/6-31G*//B3LYP/6-31G* Calculated Frequencies[a] and IR Intensities

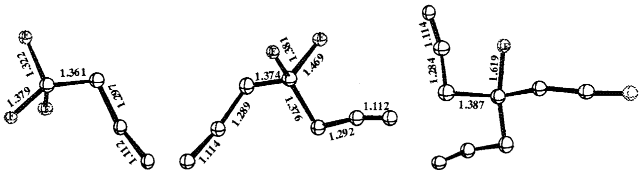
no.	frequencies in cm^{-1} (IR intensities in km/mol)
1	474 (0), 477 (71), 517 (614), 522 (2), 628 (74), 672 (200), 1052 (0), 1191 (0), 1199 (13), 1627 (88), 1644 (526), 1675 (0), 3394 (1233), 3438 (0), 3539 (183), 3546 (736)
4	82 (4), 127 (1), 184 (0), 235 (0), 401 (5), 439 (10), 477 (0), 495 (0), 623 (5), 694 (20), 845 (0), 1054 (98), 1168 (0), 1331 (1054), 2319 (0), 2328 (66)
4b	65 (2), 180 (1), 252 (54), 340 (2), 372 (37), 382 (5), 441 (4), 446 (72), 509 (10), 521 (13), 533 (20), 640 (10), 748 (30), 798 (42), 871 (206), 901 (144), 1077 (71), 1129 (62), 1184 (50), 1206 (162), 1357 (8), 1390 (12), 1453 (4), 1672 (54), 1679 (75), 1689 (16), 2259 (168), 3449 (60), 3452 (21), 3459 (42), 3547 (55), 3561 (45), 3571 (60)

[a] Not scaled.

Scheme 4

	ΔH (kcal/mol)
$NF_4^+ + HN_3 \longrightarrow F_3NN_3^+\ \mathbf{5} + HF$	-44.6
$\mathbf{5} + HN_3 \longrightarrow F_2N(N_3)_2^+\ \mathbf{6} + HF$	-37.3
$\mathbf{6} + HN_3 \longrightarrow FN(N_3)_3^+\ \mathbf{7} + HF$	-33.9
$\mathbf{7} + HN_3 \longrightarrow N(N_3)_4^+\ \mathbf{4b} + HF$	-16.5

$NF_4^+BF_4^-$ were isolated by Christe et al. and characterized by X-ray crystallography.[24,25] Formation of the trifluoroazidoammonium ion $F_3NN_3^+$ (**5**) from the reaction of NF_4^+ with HN_3 was computed to be exothermic by 44.6 kcal/mol. Formation of $F_2N(N_3)_2^+$ (**6**) from **5** with a further molecule of HN_3 was computed to be exothermic by 37.3 kcal/mol. Similarly, subsequent formation of $FN(N_3)_3^+$ (**7**) and $N(N_3)_4^+$ (**4b**) were also found to be exothermic by 33.9 and 16.5 kcal/mol, respectively. Thus, the overall formation of tetra(azido)ammonium ion **4b** from NF_4^+ and HN_3 is a thermodynamically favorable process. However, success of the reaction will probably depend on kinetic stabilities of the ions, **5**−**7**. Calculated structures of **5**−**7** are displayed in Figure 3. In structure **6**, one of the N−F (1.469 Å) bonds is considerably longer than the other (1.381 Å). Structure **7** showed a very long N−F bond length of 1.619 Å. Thus, the ion **7** may be considered as a loosely held complex of $N(N_3)_3^{2+}$ and F^-.



$F_3NN_3^+$ **5** (C_s) $F_2N(N_3)_2^+$ **6** (C_1) $FN(N_3)_3^+$ **7** (C_3)

Figure 3. B3LYP/6-311+G* optimized structures of **5**−**7**.

Scheme 5

	ΔH (kcal/mol)
$FN_2^+ + HN_3 \longrightarrow N_5^+ + HF$	-72.6

For comparison, we have also calculated the reaction of FN_2^+ with HN_3 (Scheme 5) at the same level of theory. Formation of the N_5^+ cation from the reaction of FN_2^+ with HN_3 was found to be exothermic by 72.6 kcal/mol.

Conclusions

Structures and energies of the tri(amino)amine $N(NH_2)_3^{2+}$ and the tri(azido)amine $N(N_3)_3^{2+}$ dications were calculated using the DFT method at the B3LYP/6-311+G* level. Similar to the guanidinium ion $(NH_2)_3C^+$,[3] the D_3 symmetry tri(amino)amine dication $(NH_2)_3N^{2+}$ (**1**) is highly stabilized by resonance interactions between the electron deficient central nitrogen atom and the amino groups. Dication **1** has a high kinetic barrier for deprotonation. Structures of the diamino(azido)amine dication $(NH_2)_2N(N_3)^{2+}$ (**2**), the amino(diazido)amine dication $(NH_2)N(N_3)_2^{2+}$ (**3**), and the tri(azido)amine dication $(N_3)_3N^{2+}$ (**4**) were also computed. The minimum energy structure of the tri(azido)amine dication $(N_3)_3N^{2+}$ corresponds to the C_{3h} symmetry form **4**. Dication **4** was also shown to be highly resonance stabilized. Structures of the mixed amino−azido derivatives $(N_3)_xN(NH_2)_{4-x}^+$ ($x = 0-4$) of the corresponding dication were determined. Vibrational frequencies of the selected ions (**1**, **4**, and **4b**) were also calculated. Possible formation of tetra(azido)ammonium ion $N(N_3)_4^+$ (**4b**) from the reaction of NF_4^+ with HN_3 was computed and discussed.

Acknowledgment. This work was supported by the National Science Foundation and the Office of Naval Research.

Supporting Information Available: Cartesian coordinates and total energies (hartrees) of the optimized geometries (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) Moy, D.; Young, A. R. *J. Am. Chem. Soc.* **1965**, *87*, 1889. Christe, K. O.; Wilson, W. W.; Savodny, W. *J. Mol. Struct.* **1971**, *8*, 245. Christe, K. O.; Wilson, R. D.; Wilson, W. W.; Bau, R.; Sukumar, S.; Dixon, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 3795.

(25) Christe, K. O.; Lind, M. D.; Thorup, N.; Russell, D. R.; Fawcett, J.; Bau, R. *Inorg. Chem.* **1988**, *27*, 2450.