Gitonic Protodiazonium and Bisdiazonium Dications and Their Potential Role in Superacid Chemistry[1]

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Abstract: Energies, electronic structures, and gas phase proton affinities of a series of gitonic protodiazonium and bisdiazonium dications as well as their parent diazonium ions were calculated using ab initio molecular orbital theory. On the basis of computed energetics, decomposition barriers of dications were estimated. NMR chemical shifts of the diazonium ions and protodiazonium dications were calculated using the IGLO method but only the former could be compared with experiment since protodiazonium dications may exist only in low equilibrium concentrations in the superacid media. The potential role of protodiazonium dications in superacid chemistry is discussed.

Introduction

There is continued theoretical and experimental interest in non-benzenoid diazonium ions and their chemistry.[2] The existence of alkyldiazonium ions as intermediates has been well established in a variety of organic reactions.[3] Aliphatic diazonium ions can conveniently be obtained in the strong acid solution without elimination of nitrogen.[2] Diazonium ions like $FN_2^+SbF_6^-$[4] and $H_2NN_2^+$[5] were even isolated and studied by X-ray crystallography. However, the parent diazonium ion HN_2^+ remains elusive in the condensed state. All attempts, including our own,[6] to effect protonation of dinitrogen even in the strongest superacids ($HF–SbF_5$) were inconclusive. However, by using an indirect approach, we were able to diazotize ammonia, bis-trimethylsilylated amines, and isocyanic acid with 99% enriched $^{15}NO^+BF_4^-$, resulting in the formation of $^{14}N^{15}N$, involving the intermediate formation of the parent diazonium ion, HN_2^+. Attempts to observe HN_2^+ by stopped flow NMR by reacting $HN(SiMe_3)_2$ with $^{15}NO^+BF_4^-$ in CH_2Cl_2 were also unsuccessful.[6] We now suggest that the short life time of HN_2^+ in superacid solution may be due to rapid hydrogen exchange, indicative of a second protonation to $H_2N_2^{2+}$ (Scheme 1).

The protonation of diazomethane was shown experimentally to take place either on nitrogen or carbon.[7] In superacids this interconversion can also go through a diprotonated form (Scheme 2) and not through deprotonation–reprotonation reaction (for which there is no evidence).

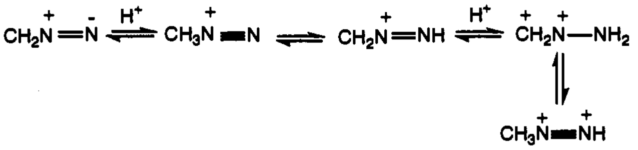
The protonation of hydrazoic acid was shown in our investigations to give the aminodiazonium ion,[8] $H_2NN_2^+$, and subsequent cleavage liberates N_2. This also can be assisted by protosolvation (Scheme 3).[9]

The significance of protosolvation of nonbonded electron pairs on onium ions has been recognized.[9a] Protosolvation plays an important role in strong acid catalyzed electrophilic reactions. Such protosolvation in the limiting case can lead to gitonic (close) dications in which the positive charge bearing centers can be adjacent or geminal compared to distonic (distant) dications.[9b] The present study of diazonium and protodiazonium dications adds further to our understanding of the role of protosolvation in superacid chemistry. We herein report high level *ab initio* calculations to establish the structures and relative stabilities of the diazonium and protodizonium ions. We also report the calculated proton affinities and NMR chemical shifts of diazonium ions as well as bisdiazonium and protodiazonium dications. We further discuss the role of protodiazonium dications in superacid catalyzed reactions.

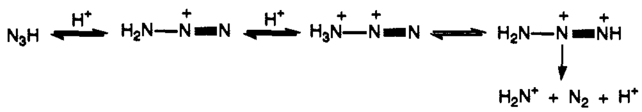
Scheme 1

$$N{\equiv}N \underset{}{\overset{H^+}{\rightleftharpoons}} H{-}\overset{+}{N}{\equiv}N \overset{H^+}{\rightleftharpoons} H{-}\overset{+}{N}{\equiv}\overset{+}{N}{-}H$$

Scheme 2



Scheme 3



Results and Discussion

Ab initio calculations were carried out by using the SPARTAN[10] and GAUSSIAN-92[11] packages of programs. Restricted Hartree–Fock calculations were performed throughout. Optimized geometries were obtained with the standard HF/6-31G** and MP2(FU)/6-31G** levels and for some small systems at the QCISD/6-311++G** level. In order to obtain improved energy comparison, single point energies at the correlated levels of MP2(FU)/6-31G**//HF/6-31G** and MP4(SDTQ)/6-31G**//MP2(FU)/6-31G** were calculated. Vibrational frequencies

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Table 1. Total Energies (–au), ZPE (kcal/mol), Relative Energies (kcal/mol), and Proton Affinities (kcal/mol) of **1**–**37** in the Gas Phase[a]

ion	HF/6-31G** //HF/6-31G**	MP2(FU)/6-31G** //HF/6-31G**	MP2(FU)/6-31G** //MP2(FU)/6-31G** (ZPE)	MP4SDTQ/6-31G** //MP2(FU)/6-31G**	rel energy	proton (expt) affinity
1	108.94395	109.25467	109.26157 (2.9)	109.27299	119.7	121.2 (118.2)[b]
2	109.13622	109.45234	109.45975 (9.2)	109.47385	0.0	–59.0
3	109.05935	109.37055	109.37649 (5.8)	109.39343	47.1	
4	109.04326	109.36571	109.37381 (13.9)	109.38490	60.5	
5	108.99211	109.31354	109.32110 (9.9)	109.33277	89.2	
6	147.84782	148.32336	148.32716 (18.6)	148.35145	219.2	220.7 (216.0)[c]
7	148.22128	148.68018	148.68871 (26.9)	148.71395	0.0	–23.5
8	148.15163	148.61682	148.61900 (26.4)	148.65046	39.3	
9			148.65493 (30.9)	148.67941	25.7	
10	148.13847	148.60419	148.61284 (29.8)	148.64104	48.7	
11	148.21385	148.66659	148.66920 (33.3)	148.70127	14.4	
12			148.57339 (27.0)	148.59730	73.3	
14	163.84290	164.35241	164.36135 (12.6)	164.38092	187.6	197.5
15	164.16197	164.65260	164.66143 (20.0)	164.68324	5.4	7.9
16	164.09933	164.61288	164.61831 (18.8)	164.64430	28.6	
17	164.18084	164.66739	164.67653 (27.4)	164.70356	0.0	
18	164.13247	164.63828	164.64395 (25.4)	164.66739	20.7	
20	207.83103	208.32250	208.33359 (5.5)	208.35095	0.0	–66.4
21	207.72536	208.22673	208.23688 (10.9)	208.25236	67.3	
22	207.66486	208.16181	208.17694 (9.0)	208.20116	97.5	
23	207.68017	208.17905	208.18947 (6.5)	208.20476	92.7	
25	183.68012	184.20071	184.21368 (6.3)	184.22908	137.5	140.0 (136.5)[b]
26	183.92343	184.42400	184.43472 (12.1)	184.45333	2.5	
27	183.88691	184.42735	184.43884 (12.5)	184.45802	0.0	–38.2
28	183.85890	184.37346	184.38410 (16.6)	184.40131	39.7	
29	183.85874	184.35590	184.36735 (17.7)	184.39105	47.2	
31	200.78749	201.39056	201.40716 (8.6)	201.43032	15.8	17.3
32	200.83102	201.42701	201.44039 (15.2)	201.46605	0.0	
33	200.69934	201.32546	201.34895 (13.1)	201.37512	55.0	
34	200.69664	201.29827	201.31348 (9.3)	201.33667	75.3	
35	200.64194	201.25809	201.27699 (9.2)	201.29933	98.6	
37	216.67182	217.29351	217.31316 (8.5)	217.34706		

[a] Relative energies based on MP4(SDTQ)/6-31G**//MP2(FU)/6-31G** + ZPE and proton affinities based on MP4(SDTQ)/6-31G**//MP2(FU)/6-31G**. Zero point vibrational energy (ZPE) at the MP2(FU)/6-31G**//MP2(FU)/6-31G** level is scaled by a factor of 0.93. [b] Reference 35. [c] Reference 36.

at the MP2(FU)/6-31G**//MP2(FU)/6-31G** level were used to characterize stationary points as minima and to evaluate zero point vibrational energies (ZPE) which were scaled by a factor of 0.93.[12] Gas phase proton affinities were calculated for 300 K on the basis of MP4(SDTQ)/6-31G**//MP2(FU)/6-31G** energies. Calculated energies and proton affinities are listed in Table 1.

For simplification only the MP2(FU)/6-31G** geometries and MP4(SDTQ)/6-31G**//MP2(FU)/6-31G** energies will be discussed throughout the text unless otherwise stated.

NMR chemical shifts were calculated at the IGLO DZ and IGLO II levels using MP2(FU)/6-31G** (gas) geometry according to a reported method.[13] Huzinaga[14] Gaussian lobes were used for the two different basis sets as follows: (basis DZ) C or O, 7s3p contracted to [4111,21]; H, 3s contracted to [21]; (basis II) C or O, 9s5p1d contracted to [51111,2111,1]; d exponent, 1.0; H, 5s1p contracted to [311,1]; p exponent, 0.70. Calculated and experimental NMR chemical shifts are listed in Table 2.

Protodiazonium Dication. Protonated dinitrogen has been observed in the gas phase by mass spectrometry and ICR studies.[15] HN_2^+ was also detected in the interstellar cloud, indicative of ion–molecule reactions in extraterrestrial space.[16] The predicted equilibrium structure of HN_2^+ from several *ab initio* calculations was found to be linear.[17]

The calculated structures of dinitrogen and its possible protonated forms are depicted in Figure 1. Bridged structure **3** is a transition state as shown by frequency calculation at the MP2(FU)/6-31G**//MP2(FU)/6-31G** level. The energy barrier for the possible N_α–N_β rearrangement of protonated dinitrogen **2** through transition state **3** is quite high (47.1 kcal/mol).

Further protonation of **2** leads to linear diprotonated dinitrogen i.e the protodiazonium dication **4**.[18] The dissociation of **4** into **2** and H^+ is thermodynamically preferred by 60.5 kcal/mol, although a kinetic barrier of 28.7 kcal/mol has to be overcome through the transition state **5**. This is in agreement with the reported barrier of 29.9 kcal/mol at the HF/4-31G level[19] and close to our QCISD/6-311++G**//QCISD/6-311++G** level calculated value of 30.7 kcal/mol.

We have also optimized the structures **1**-**5** at the QCISD/6-311++G** level but the geometries and relative energies do not differ much from the MP2(FU)/6-31G** optimized values (Figure 1 and Table 1).

Considerable kinetic barriers for proton loss from dications were reported earlier.[20] It was shown theoretically by Dunitz and Ha[21] that bonding interactions can counteract strong electrostatic charge–charge repulsion sufficiently to result in kinetically stable species. Previously it was suggested that calculated barriers were overestimated at the Hartree–Fock level.[22a] Correlated levels lower the activation energy slightly,

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(18) Protonation on NH nitrogen of **2** would lead to N,N-diprotonated dinitrogen dication which is 65.0 kcal/mol less stable than the dication **4** at the MP4(SDTQ)/6-31G**//MP2(FU)/6-31G** level.

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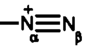
Table 2. Calculated NMR Chemical Shifts (Experimental Value)[a]


$R-\overset{+}{\underset{\alpha}{N}}\equiv N_{\beta}$

		DZ//MP2(FU)/6-31G**			II//MP2(FU)/6-31G**		
ion	formula	$^{15}N_\alpha$	$^{15}N_\beta$	others	$^{15}N_\alpha$	$^{15}N_\beta$	others
2	HN_2^+	217.0	367.3		239.9	383.1	
4	$H_2N_2^{+2}$	194.2	194.2		225.8	225.8	
7	$H_3CN_2^+$	237.9	379.9	$^{13}C = 54.1$ (44.5)[b]	270.3	391.8	$^{13}C = 44.4$
8	$H_2CN_2H^+$	371.5	479.0	$^{13}C = 106.1$ (76.6)[b]	440.0	488.8	$^{13}C = 97.8$
9	$H_3CN_2H^{+2}$	242.9	213.5	$^{13}C = 79.2$			
11	$H_3CN_2H^{+2}$	424.0	214.3	$^{13}C = 137.6$			
15	$H_2NN_2^+$	191.6	357.9 (266.2)[c]	$^{15}N = 76.4$ (68.6)[c]	233.9	369.5	$^{15}N = 84.0$
17	$H_3NN_2^{+2}$	166.7	387.3	$^{15}N = 54.7$	207.7	404.8	$^{15}N = 93.9$
20	FN_2^+	199.6	332.0	$^{19}F = 445.2$	227.2	305.1	$^{19}F = 208.6$
21	FN_2H^{+2}	198.2	173.0	$^{19}F = 453.1$	223.6	175.8	$^{19}F = 224.6$
26	HON_2^+	212.5	326.7		308.7	103.7	
27	ON_2H^+	282.0	111.1		241.5	320.9	
28	HON_2H^{+2}	197.4	155.2		227.9	174.6	
29	$H_2ON_2^{+2}$	151.3	365.0		191.7	373.1	
31	NCN_2^+	194.4	317.3	$^{13}C = 110.4$ $^{15}N = 324.1$	224.5	356.3	$^{13}C = 97.2$ $^{15}N = 368.0$
32	$HNCN_2^{+2}$	172.0	401.7	$^{13}C = 87.4$ $^{15}N = 81.6$	207.6	435.2	$^{13}C = 76.0$ $^{15}N = 132.1$
37	N_4^{+2}	159.1	331.0		192.0	376.5	

[a] ^{15}N, ^{13}C, and ^{19}F NMR chemical shifts are referenced to NH_3, TMS, and $CFCl_3$, respectively. [b] Reference 7. [c] Reference 8.

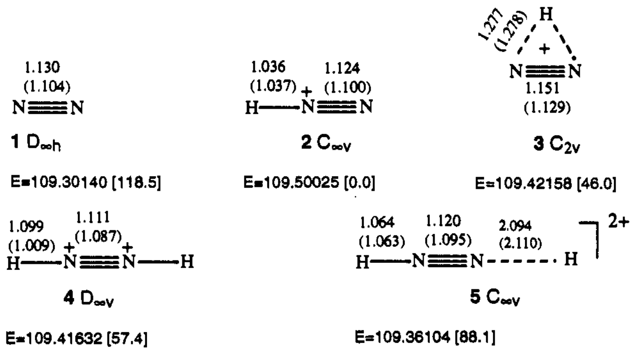
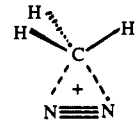


Figure 1. MP2(FU)/6-31G** optimized geometries of **1-5**. QCISD/6-311++G** optimized parameters are given in parentheses. The energies (–a.u.) and relative energies (given in square bracket, in kcal/mol) are based on QCISD/6-311++G**//QCISD/6-311++G** and QCISD/6-311++G**//QCISD/6-311++G** + ZPE (see Table 1), respectively.

but even with G2 theory significant barriers exist for smaller dications. At HF/6-31G*//HF/6-31G* level the deprotonation barrier for $HCOH^{2+}$ is 22.7 kcal/mol. The G2 method still gives a calculated gas phase barrier of 19.5 kcal/mol.[20]

One can question the relevance of kinetic stability of these dications with respect to their actual observation in the gas phase or in condensed phase superacid media especially if the protonation energies of the monocations are largely endothermic? We have previously reported[22b] by *ab initio* calculations that NO_2H^{2+} also has a significant kinetic barrier of 17 kcal/mol for deprotonation at the HF/6-31G*//HF/6-31G* level. However, the protonation energy of NO_2^+ was calculated to be +85.1 kcal/mol at the same level. More recently, Schwarz *et al.* were able to observe[22c] NO_2H^{2+} in the gas phase by dissociative electron impact ionization of HNO_3. Furthermore, their high level *ab initio* calculations (MRCI + D level corrected for ZPVE at MP2/6-311G**) showed a kinetic barrier of 16.7 kcal/mol for deprotonation of NO_2H^{2+} thus confirming our earlier calculational results.[22b] Consequently it is possible to observe small dications of sufficient kinetic stability even though they are difficult to obtain by direct protonation.

Diprotonated Diazomethane (Protomethyldiazonium Dication). The protonation of diazomethane **6** in superacids was shown[7] to take place either on carbon or on nitrogen to produce **7** and **8**, respectively. At our highest level, C-protonated diazomethane **7** is 39.3 kcal/mol more stable than N-protonated diazomethane **8**. The species **7** has also been calculated earlier by *ab initio* theory.[23] In fact protonation on both termini of diazomethane **6** can be observed only under conditions of kinetic control in extremely acidic FSO_3H/SbF_5 solution. When the acidity is reduced (i.e. FSO_3H) only the thermodynamically stable C-protonated diazomethane **7** was observed.[7] In our calculations we did not consider the bridged structure of $CH_3N_2^+$ because it was found to be significantly less stable than the previously open structure **7**.[23b,23c]



We have also calculated three possible structures of diprotonated diazomethane; N-protonated **9** (which is isoelectronic to protonated acetonitrile), C-protonated **10**, and allene type **11** (Figure 2). Previously, Lammertsma showed[24] that the structure **9** is a transition state and not a minimum at the HF/3-21G level. We also could not find a minimum for **9** at the Hartree–Fock level using the 6-31G** basis set but were able to obtain a minimum at the correlated level of MP2(FU)/6-31G**. Frequency calculation at the same correlated level (i.e. MP2(FU)/6-31G**//MP2(FU)/6-31G**) shows that the structure **9** is indeed a minimum as there is no imaginary frequency. The dissociation barrier for **9** via transition state **12** into **7** and H^+ was found to be 47.6 kcal/mol, although dissociation is favored by 25.7 kcal/mol. On the other hand, kinetic barrier of dissociation of **9** into CH_3^+ and HN_2^+ is only 3.0 kcal/mol. Lammertsma has also showed[24] calculationally that the hypercoordinated structure **10** could be a viable species in the gas phase. At our highest level we found that the structure **10** is 23.0 kcal/mol less stable than the cation **9**. Interestingly, the global minimum for the diprotonated diazomethane is N,N-diprotonated diazomethane **11** which is 11.3 kcal/mol more stable than the structure **9**. Another possible structure **13** for diprotonated diazomethane

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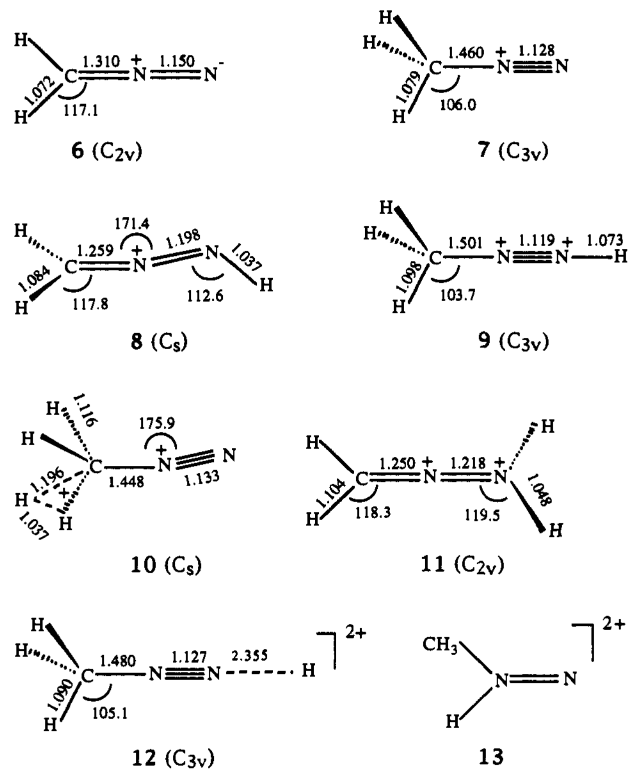
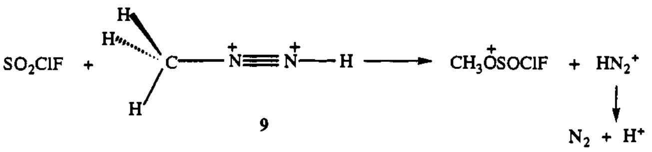


6 (C_{2v}) 7 (C_{3v}) 8 (C_s) 9 (C_{3v}) 10 (C_s) 11 (C_{2v}) 12 (C_{3v}) 13

Figure 2. MP2(FU)/6-31G** optimized geometries of **6–12**.

Scheme 4

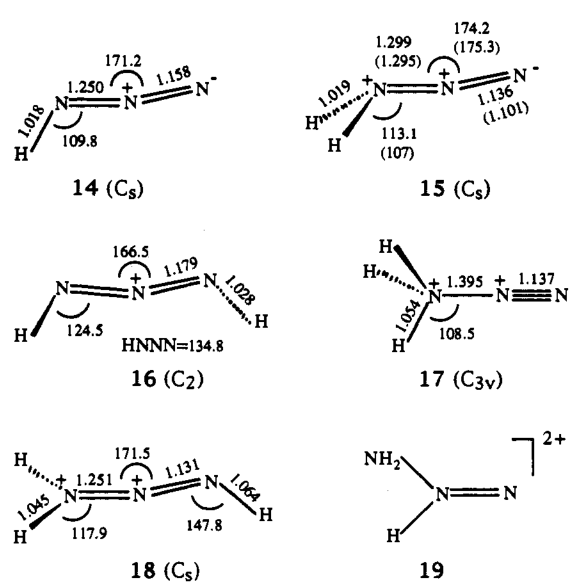


dissociates into CH_3^+ and HN_2^+ upon optimization at the HF/6-31G* level.

From kinetic studies it was shown[7] that the displacement of nitrogen from the methyldiazonium ion **7** is a nucleophilic substitution type of reaction. Weakly nucleophilic SO_2ClF is known to displace nitrogen from methyldiazonium ion. The rate of this reaction increases with increase in acidity. It is now suggested that this enhanced reactivity of **7** in superacidic systems is more probably due to the protomethyldiazonium dication **9** in equilibrium with **7** (Scheme 4).

Protoaminodiazonium Dication. Christie, Bau, *et al.*, recently reported[5] the X-ray crystal structure of aminodiazonium ion **15**. This gives an opportunity to compare the calculated structure with the experimental one. Previously Olah and his associates had already established[8] by ^1H and ^{15}N NMR spectroscopy that the protonation of hydrazoic acid **14** took place exclusively on NH nitrogen to form aminodiazonium ion **15**. *Ab initio* studies were also reported[25] on the structures and stabilities of halogen azides XN_3 (X = F, Cl, Br, I) and HN_3. Joint *ab initio* and mass spectrometric study of protonated hydrazoic acid ($H_2N_3^+$) were also reported by Cacace et al.[26] We have considered several possible protonated hydrazoic acid structures and the data is tabulated in Figure 3 as well as Table 1. A possible protonated form of $H_2N_3^+$ is **16** which is 23.2 kcal/mol less stable than **15** (Table 1) and is not observed in the superacid solution.

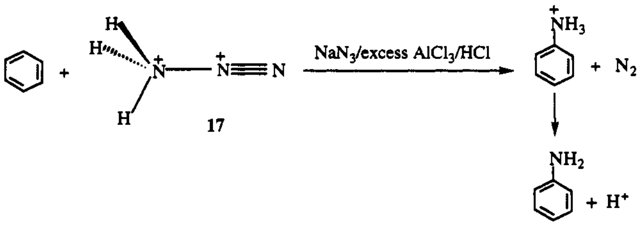
The experimental data[5] of **15** (shown in parentheses in Figure 3) agrees rather well with the MP2(FU)/6-31G** optimized geometry as shown in Figure 3. In both geometries the NH_2 group is pyramidal and the N–N–N bond angle is close to 175°. This agreement indicates that the structure of the aminodiazonium ion is indeed best represented by **15**, with little or no contribution from the planar C_{2v} structure **15a**.

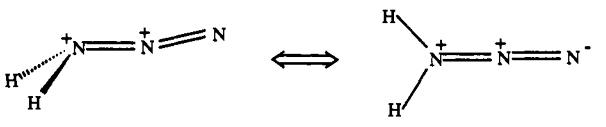


14 (C_s) 15 (C_s) 16 (C_2) 17 (C_{3v}) 18 (C_s) 19

Figure 3. MP2(FU)/6-31G** optimized geometries of **14–18** (experimental data).

Scheme 5





15 15a (C_{2v})

Two possible structures of the protoaminodiazonium dications, **17** and **18** were also calculated. N (NH_2)-protonated aminodiazonium ion **17** is isoelectronic and isostructural with C-protonated diazomethane **7** (Figures 2 and 3). Similar to N-protonated diazomethane **8**, terminal N-protonated aminodiazonium dication **18** is 20.7 kcal/mol less stable than **17**. The diprotonated structure **19** collapses to **18** without any activation barrier at the HF/6-31G* level of optimization.

The importance of the protoaminodiazonium dication lies in its ability of electrophilic amination of aromatics.[8] Olah and co-workers demonstrated that the aminodiazonium ion **15** (prepared *in situ* from NaN_3/excess $AlCl_3$/HCl or from $(CH_3)_3SiN_3/CF_3SO_3H$) can be used as an efficient direct aminating agent for aromatics. It is now suggested that the reaction *de facto* proceeds probably through the activated protoaminodiazonium dication **17** which may be present in some limited equilibrium with **15** (Scheme 5) in the superacid medium.

Protofluorodiazonium Dication. The structure of fluorodiazonium ion (both calculated and established by X-ray[4]) is linear (Figure 4). Terminal N-protonation gives linear protodiazonium dication **21**. F-Protonation would give the bent structure **22**. Although **22** is a minimum on the potential energy surface, it is 30.2 kcal/mol less stable than **21**. Dissociation of **21** into **20** and

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(25) Otto, M.; Lotz, S. D.; Frenking, G. *Inorg. Chem.* **1992**, *31*, 3647.

(26) Cacace, F.; Attina, M.; Petris, G. D. *Gazz. Chim. Ital. Soc.* **1990**, *120*, 691.

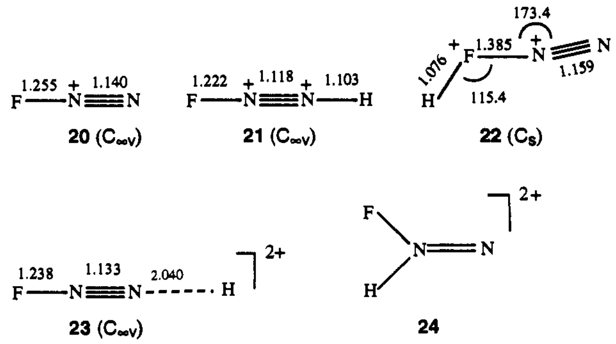


Figure 4. MP2(FU)/6-31G** optimized geometries of **20–23**.

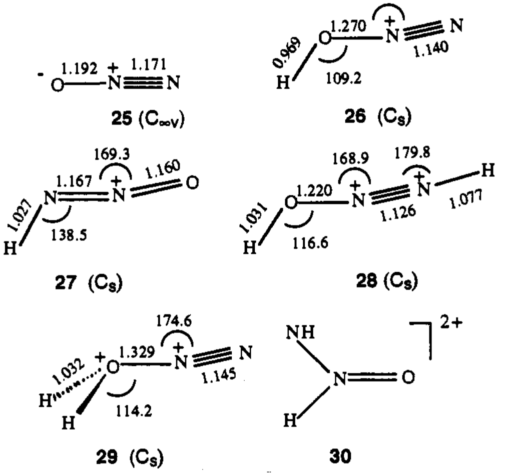


Figure 5. MP2(FU)/6-31G** optimized geometries of **25–29**.

H^+ via transition structure **23** has a 25.3 kcal/mol kinetic barrier. Another possible structure, **24** is converted into **21** at the HF/6-31G* level of optimization.

Protohydroxydiazonium Dication. The *ab initio* study of protonated nitrous oxide is also relevant concerning our previous attempts[27] to prepare and characterize the hydroxydiazonium ion **26** by NMR spectroscopy under stable ion conditions. For the two possible forms of protonated nitrous oxide, O-protonated nitrous oxide (hydroxydiazonium ion) **26** is only 2.5 kcal/mol more stable than N-protonated nitrous oxide **27** (Figure 5). However, neither of these ions has been observed by NMR in superacid solutions. In contrast, the methoxydiazonium ion ($CH_3ON_2^+$) is quite stable.[27] Similar calculations on protonated NPO and PNO were reported by Davy and Schaefer.[28]

The failure to observe the hydroxydiazonium ion **26** in superacids at low temperature is now suggested to be due to possible fast intermolecular exchange resulting from a second protonation via the protohydroxydiazonium dication (either **28** or **29**). Our calculations show that the structure **28**, i.e O,N-diprotonated nitrous oxide, is more stable than the O,O-diprotonated nitrous oxide **29** by 7.5 kcal/mol at the highest level of theory used. At the HF/6-31G* level of optimization the structure **30** dissociated into HN^+ and HNO^+.

Protocyanodiazonium Dication. Aromatic cyanation via the cyanodiazonium ion (generated *in situ*) was studied by Olah and his associates[29] and Eberson and co-workers.[30] However, direct observation of the cyanodiazonium ion was unsuccessful.[29] The linear structure **31** was found to be the global minimum (Figure 6).

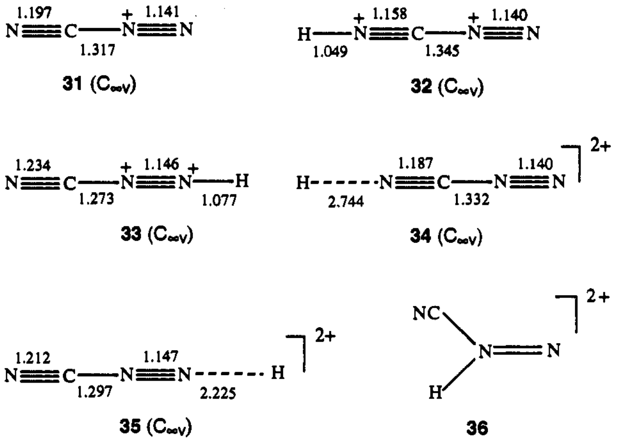


Figure 6. MP2(FU)/6-31G** optimized geometries of **31–35**.

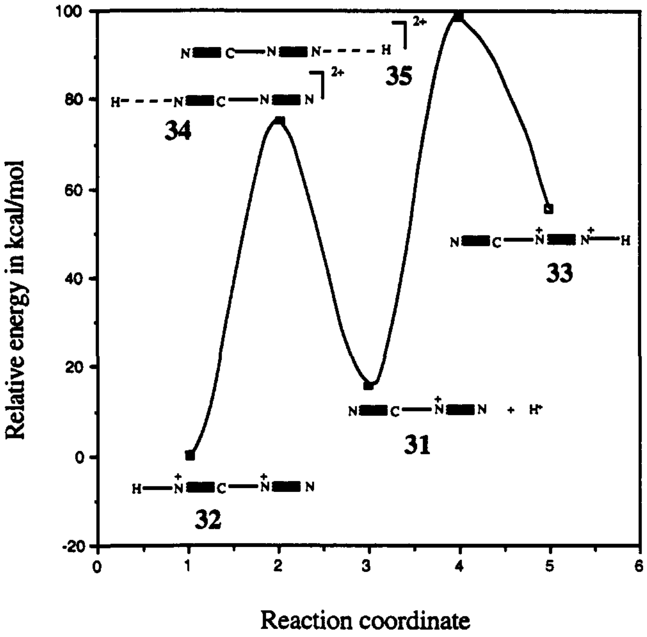
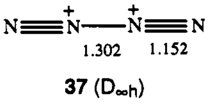


Figure 7. Potential energy surface of protonated cyanodiazonium dication.



$$N{\equiv}\overset{+}{N}{-}\overset{+}{N}{\equiv}N$$

Figure 8. MP2(FU)/6-31G** optimized geometries of **37**.

Protonation on cyanodiazonium ion **31** can take place in two possible ways. Protonation on cyano nitrogen gives **32** and the protonation on terminal diazo nitrogen gives **33**. Energetically **32** is 55.0 kcal/mol more stable than **33**. Both **32** and **33** have considerable kinetic barriers toward dissociation into cyanodiazonium ions **31** and H^+ (Figure 7) and the barriers are 75.3 and 43.6 kcal/mol, respectively. However, thermodynamically **32** is unfavorable and **33** is favorable toward dissociation into cyanodiazonium ions **31** and H^+ by 15.8 kcal/mol and 39.2 kcal/mol, respectively. Diprotonated structure **36** is converted into **33** upon optimization at the HF/6-31G* level. Shudo *et al.* have reported[31] efficient cyanation of aromatics with sodium cyanide or trimethylsilyl cyanide in trifluoromethanesulfonic acid. The reaction is best explained to proceed through the protonated nitrilium dication.[31]

Bisdiazonium Dication. We have also calculated the structure and energetics of the interesting bisdiazonium dication (N_4^{2+}) **37** at the MP2(FU)/6-31G** level (Figure 8). Frequency calculations at the MP2(FU)/6-31G**//MP2(FU)/6-31G** level

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(30) Eberson, L.; Nilsson, S.; Rietz, B. *Acta Chem. Scand.* **1972**, *26*, 3870.

(31) Yato, M.; Ohwada, T.; Shudo, K. *J. Am. Chem. Soc.* **1991**, *113*, 691.

shows that the novel diazonium dication **37** is a minimum as there is no imaginary frequency.[32]

We have also attempted to generate **37** experimentally[33] by the diazotization of the aminodiazonium ion **15** with $NO^+BF_4^-$ in Magic Acid/SO_2ClF at −78 °C. However, no further diazotization of the aminodiazonium ion was observed.

Proton Affinities. We have calculated proton affinities[20] for the studied protodiazonium, bisdiazonium, and related dications and monocations using MP4(SDTQ)/6-31G**//MP2(FU)/6-31G** energies and MP2(FU)/6-31G**//MP2(FU)/6-31G** zero point vibrational energies (ZPE). The calculated proton affinities match with the available experimental data very well (**Table 1**). For instance, the calculated proton affinities of N_2 and N_2O are 119.7 and 140.0 kcal/mol, respectively, which agree well with the corresponding experimental values of 118.2 and 136.5 kcal/mol. The highest proton affinity of 17.3 kcal/mol among the diazonium ions is calculated for cyanodiazonium ion **8** (the protonated product is **32**). The proton affinities of the diazonium ions are considerably higher than the proton affinity of oxonium ions[20] except for HN_2^+ **2** and FN_2^+ **20**. The G2 calculated proton affinity of H_3O^+ ion is −60.4 kcal/mol. The observed hydrogen–deuterium exchange of the oxonium ion in superacids upon increase in acidity was suggested to result in an associative mechanism involving a tetracoordinated oxonium dication.[34]

IGLO Calculated NMR Chemical Shifts. We have also calculated the ^{15}N and ^{13}C NMR chemical shifts of discussed representative ions with the use of Kutzelnigg and Schindler's IGLO (individual gauge for localized orbitals) method.[13] Due to the presence of nonbonded electrons on nitrogen, ^{15}N NMR chemical shifts are more dependent on solvents and temperature than ^{13}C NMR chemical shifts; consequently, calculated ^{15}N NMR chemical shifts (Table 2) can be expected to differ more from experimental values. The calculated chemical shifts, although only approximate, can still be indicative of the expected chemical shifts. As protodiazonium dications can be present only in very low concentrations in rapid equilibrium with the respective monocations in the superacid media it is not surprising that NMR studies gave no indication of their presence.

Conclusions

In superacid media the nonbonded nitrogen electron pairs of diazonium ions are capable of undergoing further protonation (or protosolvation) to form highly reactive superelectrophilc gitonic dications. The chemical reactivity of some of the diazonium ion systems in superacids is suggested to be due to such activation. The *de facto* protonated diazonium and bisdiazonium dications were calculationally studied as they relate to the idealized gas phase. It should be recognized that the suggested superelectrophilic reactivities in the condensed phase can be brought about by "electrophilic assistance" i.e. protosolvation of the diazonium ions. In the study of the behavior of aliphatic nitriles and HCN in superacidic media, Shudo *et al.* have previously provided examples for the related role of gitonic dications ($RCNH_2^{2+}$) in their electrophilic reactions.[31]

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Supplementary Material Available: Contains calculated frequencies at the MP2(FU)/6-31G**//MP2(FU)/6-31G** level (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(32) Structures including cyclic D_{2h}, T_d, and other lower symmetric structures are not minima at the HF/6-31G** level and dissociate into two N_2 fragments.

(33) Diazotizations were carried out using commercially avaiable $NO^+BF_4^-$ (Aldrich) according to the reported method of ref 29.

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