Allenediazonium ions and their protonation chemistry: a DFT study†

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The parent allenediazonium monocation $H_2C{=}C{=}CH(N_2^+)$ and ten of its substituted derivatives $XYC{=}C{=}C(Z)N_2^+$ (with F, CF_3, Me, OMe, and Me_2N as substituents) were studied by DFT at the B3LYP/6-31++G** level. Except for the Me_2N-substituted derivative that forms a monocation–N_2 complex, structurally intact allenediazonium ions were obtained as minima in all cases. Protonation studies at various sites were performed on allenediazonium cations, and relative energies of the resulting minima were used to identify the energetically most favored dications. In the majority of cases, protonation at the central carbon of the allenic moiety (C_2) is most favored, forming delocalized allyl cation–N_2^+ species. The same dication structure is formed *via* initial C_3-protonation, followed by a formal hydride shift, in cases where a carbocation-stabilizing group is placed at C_3. When a CF_3 group is placed at C_3, initial protonation at C_1 resulted in a 1,3-fluorine shift, to generate a fluoroallyl cation linked to a $CH_2N_2^+$ moiety. Structural features in the allenediazonium monocations and their protonated dications were examined, taking into account their geometrical features, computed charges, and the GIAO NMR shifts.

Introduction

The available literature on vinyldiazonium ions is relatively extensive, encompassing their isolation in specific cases as stable salts, X-ray analysis, generation from suitable precursors under stable ion conditions for direct NMR studies, and theoretical studies.[1,2] The commonly employed strategy for their experimental generation involves *O*-alkylation (*O*-protonation) of suitably substituted diazoketones or diazoesters. It is known that alkenediazonium ions exhibit vastly different relative stabilities depending on their structures, ranging from those that can be isolated as salts and stored at room temperature for an extended period of time,[3–5] to those that require *in situ* generation and trapping,[6] to those that can be generated under stable ion conditions at low temperature in superacids for direct NMR studies.[7,8]

Although only a limited number of studies point to generation of ethynyldiazonium cations under solvolytic conditions,[9] several theoretical studies on these species have been published.[10]

In comparison, no studies pertaining to the "missing relative", namely allenediazonium ions $XYC_3{=}C_2{=}C_1(Z)N_2^+$ seem to exist. Weakly-bound complexes of $C_3H_3^+$ cations with dinitrogen have been studied by IR-photodissociation spectroscopy and by *ab initio* calculations.[11] Electron impact ionization of parent allene generated two isomeric $C_3H_3^+$ cations, namely the cyclopropenyl cation and the propargyl cation, and these gave weakly-bound complexes with dinitrogen. In the case of propargyl cation, the complex in which N_2 was bound to the acetylenic-H is a global minimum, whereas the complex with N_2 bound to a CH_2 proton is a local minimum (from MP2 calculations).[11]

Electrophilic addition to allenes has been studied in a number of cases,[12] demonstrating that the kinetically favored protonation leads to a vinyl cation intermediate. Thus HX addition to simple allenes gives vinyl halides as initial products. Kinetic studies and solvent isotope effect measurements in strong acids underscored the importance of vinyl cation formation (attack at C_1).[12] Several examples of addition of *in situ*-generated carbenium ions to allenes have also been reported that involve allyl cation as intermediate (attack at C_2).[13] Addition of PhSeX to allenes was consistent with attack at C_2 and allyl cation generation.[13] For Me_3Si-substituted allenes, the regiochemistry of addition is controlled by the formation of a β-silyl-stabilized vinyl cation by attack at C_3.[14]

Protonation of *tert*-alkyl-substituted alkynes such as 3,3-dimethyl-1-butyne in $FSO_3H{\cdot}SbF_5$ (1 : 1) led to the observation of allyl cation *via* a transient vinyl cation (attack at C_1), followed by skeletal rearrangement (1,2-methyl shift). Similarly, *tert*-butyl cation reacted with 2-butyne to give allyl cation by initial attack at C_2 and subsequent methyl shifts.[15]

Given the importance of both allyl cations and vinyl cations as intermediates in electrophilic addition to allenes, protonation studies on allenediazonium ions seemed highly relevant. In principle, it might be possible to control the energy and relative stability of the allenyldiazonium ions, and possibly also the chemoselectivity of electrophile addition, depending on the choice of the substitutents on the allene moiety. It was also of interest to understand how the resulting allyl or vinyl cation formed by protonation at the allenyl moiety would interact with the -N_2^+ group. Geometrical features, computed charges and GIAO NMR data on the resulting minima were used to shed light on the structural/electronic features in the dications. It was hoped that the insights gained from the present DFT study could facilitate the design of experiments aimed at the synthesis of allenediazonium salts as energetic materials and as precursors to novel electrophiles.

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Results and discussion

Computational protocols

Geometry optimizations were performed employing standard techniques.[16] Optimized structures were subsequently checked by vibrational analyses with respect to being true minima on the potential energy surface, as shown by the absence of imaginary frequencies. Allenediazonium monocations were first calculated by at the B3LYP/6-31++G** level and then at the MP2/6-31++G** level. Since there were no notable differences in the optimized geometries, subsequent calculations were all performed at the B3LYP/6-31++G** level. NMR chemical shifts were computed by GIAO/B3LYP/6-31++G** and were referenced relative to the $Si(CH_3)_4$ (TMS) for ^{13}C, $CFCl_3$ for ^{19}F and to NH_3 for ^{15}N NMR. All energy differences correspond to enthalpy differences at 298 K and 1 atm, and take into account zero-point energy and thermal corrections. In all structures, charges at the atomic centers were calculated by fitting to a density-derived electrostatic potential by using the CHelpG scheme.[17,18] The calculations were performed with the Gaussian 03 package of programs.[19]

Rationale for the choice of the substituents

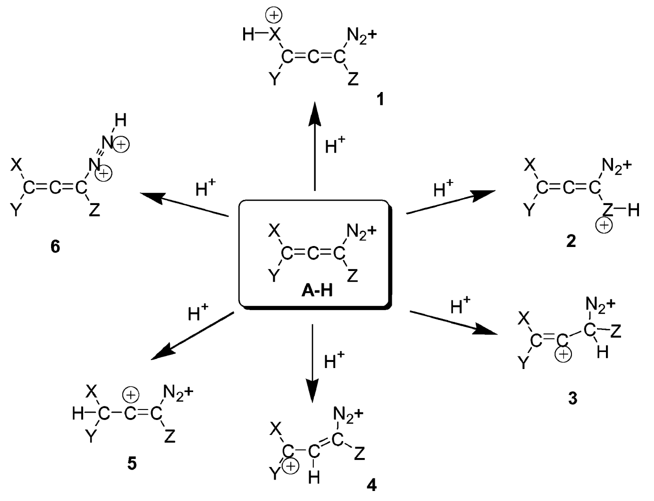
The allenediazonium cations $XYC{=}C{=}C(Z)N_2^+$ listed in Table 1, bearing electron-withdrawing substituents (monocations **B–G**), electron-donating and electron-withdrawing substituents (**H**), and electron-donating substituent(s) (**I–K**) were studied in this work, for which various modes of protonation (see Scheme 1) led to minima on the potential energy surface. The substituents were primarily chosen on the basis of the relative stability of the dications formed by protonation of allenediazonium cations.

Allenediazonium monocations (A–K)

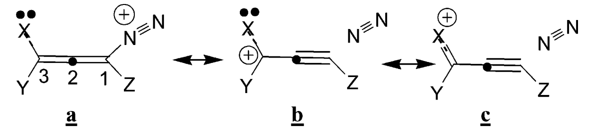
The optimized structures, geometric parameters and the GIAO NMR chemical shifts for the optimized allenyldiazonium monocations are summarized in Fig. 1. In accordance with the experimental NMR data reported for simple allenes,[20] GIAO ^{13}C shifts for the formally sp-hybridized carbon of the allenic moiety (C_2) are the most deshielded (**A**: 239 ppm; **B**: 181 ppm; **C**; 251 ppm; **D**: 204 ppm; **E**: 217 ppm; **F**: 239 ppm; **G**: 238 ppm and **H**: 255 ppm). For the MeO-substituted allenediazonium ions (**I** and **J**) C_3 is most downfield, suggesting a larger contribution by the “no-bond resonance” structure (see Scheme 2 and further discussion). This is consistent with the computed longer/weaker C–N bonds in these diazonium ions.

Table 1 Allenediazonium cations studied

$XYC{=}C{=}C(Z)N_2^+$	X	Y	Z
A	H	H	H
B	F	F	F
C	F	F	H
D	F	H	F
E	H	H	F
F	CF_3	H	H
G	CF_3	CF_3	H
H	Me	F	H
I	OMe	OMe	H
J	H	OMe	OMe
K	Me_2N	H	H

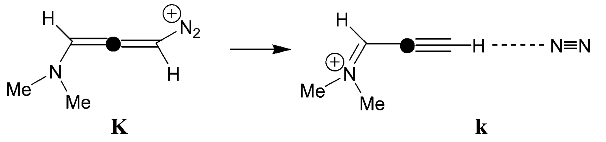


Scheme 1 Various protonation modes.



Scheme 2 Contributing resonance structures in allenediazonium cations.

Optimization of the Me_2N-substituted allenediazonium ion **K** resulted in the formation of a monocation–N_2 complex (**k**), whose cationic moiety has distinct characteristics of an iminium ion bonded to ethyne (Scheme 3). The complex is rather similar to that formed *via* propargyl cation–N_2.[11]



Scheme 3 Structure optimization on allenediazonium ion **K** leading to monocation–N_2 complex **k**.

Experimental NMR values reported for C_2 in parent allene, and various methyl-substituted derivatives, are typically in the 200–213 ppm range.[20] Comparing the experimental chemical shift data for the parent allene ($H_2\mathit{C}{=}C{=}\mathit{C}H_2$, 74 ppm; $H_2C{=}\mathit{C}{=}CH_2$, 213 ppm; $H_2C{=}C{=}C\mathit{H}_2$, 4.67 ppm) with the calculated values in this study ($H_2\mathit{C}{=}C{=}\mathit{C}H_2$, 76 ppm; $H_2C{=}\mathit{C}{=}CH_2$, 228 ppm; $H_2C{=}C{=}C\mathit{H}_2$, 4.84 ppm), shows reasonable agreement, with differences in the order of ~2 ppm for the methylene carbon, ~15 ppm for the quaternary carbon and ~0.17 ppm for the hydrogens. It is known that the NMR chemical shifts suffer from systematic error due to the approximations employed in the calculations.[21] Hence the calculated NMR chemical shift values for the other systems should have similar standard deviations as in the allene itself.

It is noteworthy that the chemical shift of the =C= moiety in allenediazonium cations does not change greatly relative to that in neutral allene. Whereas the GIAO ^{15}N shifts for the diazonium moiety in **A** are close to the reported values for PhN_2^+ (224 and 317 ppm),[22] they were generally found to be more deshielded in the other allenediazonium cations examined in the present study.

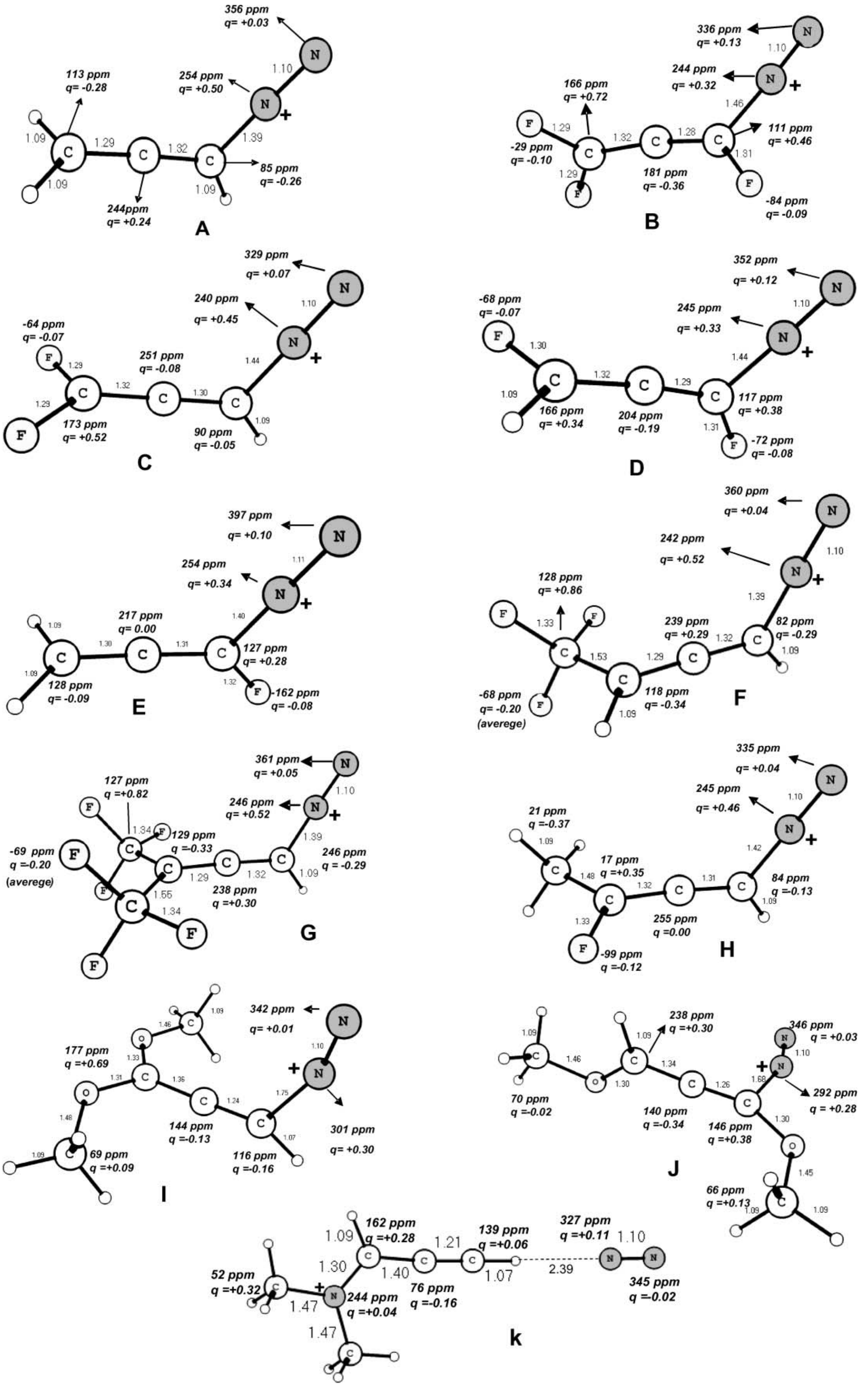
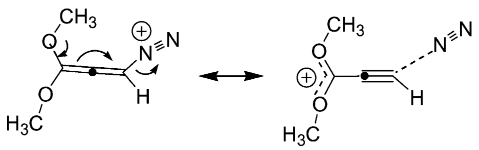


Fig. 1 Optimized structures for the allenediazonium cations **A–K**, obtained at B3LYP/6-31++G** with selected geometric parameters, CHelpg charges (*q*) and GIAO NMR chemical shifts.

Parent allenediazonium ion $H_2C{=}C{=}CH(N_2^+)$ **A** has a linear allenyl moiety with near-equivalent allenyl C–C bond-lengths, and with the positive charge residing primarily on N_α and on C_2. Based on GIAO NMR, the most deshielded carbon resonance is C_2 (at 244 ppm) followed by C_3 (113 ppm).

Fluorine substitution at C_1 and/or C_3 (as in allenediazoniums **B**–**E**) shortens the attached allenic C–C bonds. It also exerts a deshielding effect at C_1/C_3. In the bis-CF_3 derivative (**G**), positive charge resides mainly on C_2, on N_α and on the fluorines.

Allenediazonium cation **I**, with two methoxy-substituents at C_3, has an interesting optimized structure, exhibiting a short C_1–C_2 and a long C_2–C_3 bond, two relatively short C–O bonds (with near identical bond-lengths), and with the positive charge localized mainly at C_3. These features taken together with the GIAO NMR data (deshielded OMe groups, a relatively deshielded C_3 and a deshielded N_α) underscore the importance of the carboxonium-mesomeric structure (Scheme 4).



Scheme 4 Mesomeric structures for **I**.

Protonation studies on allenyldiazonium cations

Protonations at the allenyl moiety, at C_1 (mode 3), C_2 (mode 4), and C_3 (mode 5), as well as *N*-protonation (mode 6) (see Scheme 1) were considered in all cases. Mode 1 protonation was included only with OMe, F, and Me_2N as substituents, and mode 2 protonation was only considered as a possibility when Z = F or OMe. Relative energies, geometrical features, charge delocalization modes and computed NMR chemical shifts of the resulting dications were examined. Table 2 contains the relative energies for the studied protonated allenyldiazonium dications. As the following discussion details, in the majority of cases, the most stable dications were derived by protonation in mode 4, *i.e.* by attack at the central allene carbon.

Parent allenyldiazonium ion A

Fig. 2 shows the structures obtained after geometry optimization by protonation of $H_2C{=}C{=}CH(N_2^+)$ *via* modes 3–6. Among various doubly-charged minima, dication **A4** (in the *E*-configuration) formed by C_2-protonation is the most stable, followed by **A3** (protonated at C_1) which is 4.8 kcal mol^{-1} higher in energy (Table 2). Competitive formation of dication **A5** by protonation at C_3 should not be considered likely, as it is ~17 kcal mol^{-1} less stable. Dication **A6**, formed by protonation at N_β, was not a minimum.

The allylic nature of **A4** and the vinylic nature of **A3** and **A5** can be clearly deduced, taking into account the computed bond-lengths, charges and the GIAO NMR shifts. Hence **A4** is best viewed as an allyl–N_2^+ hybrid dication, whereas **A3** and **A5** are best viewed as vinyl–N_2^+ hybrid dications.

Protonation studies on the fluorinated allenediazonium ions B–E and H

Fig. 3 shows the structures obtained after geometry optimization by protonation of $F_2C{=}C{=}CF(N_2^+)$. Among various protonation modes, **B4** (protonation at the central allenic carbon) is most

Table 2 Relative enthalpies (at 298 K and 1 atm) of the protonated allenediazonium dications and their related/derived structures

Structure[a]	Relative energy/kcal mol^{-1}	Structure	Relative energy/kcal mol^{-1}	Structure	Relative energy/kcal mol^{-1}	Structure	Relative energy/kcal mol^{-1}
A + H$^+$	39.5	**B** + H$^+$	65.9	**C** + H$^+$	50.0	**D** + H$^+$	55.8
A1	N/A	**B1** HF complexed	48.5	**C1**	48.8	**D1**	25.9
A2	N/A	**B2** HF lost	32.3	**C2**	N/A	**D2** HF lost	29.5
A3	4.8	**B3**	69.2	**C3**	55.5	**D3**	51.8
A4 (*E*)	0.0 (*E*), 5.6 (*Z*)	**B4** (*E*)	0.0 (*E*), 4.9 (*Z*)	**C4** (*Z*)	5.1	**D4**	0.00
A5	16.9	**B5**	23.2 (*E*)/28.7 (*Z*)	**C5** → **C4** (*E*)	0.0	**D5**	0.004
A6	[b]	**B6**	[b]	**C6**	66.6	**D6**	54.7
E + H$^+$	41.0	**F** + H$^+$	83.4	**G** + H$^+$	35.5	**H** + H$^+$	80.5
E1	N/A	**F1**	N/A	**G1**	N/A	**H1**	[b]
E2	[b]	**F2**	N/A	**G2**	N/A	**H2**	N/A
E3	17.2	**F3** rearranged	0.0	**G3**	3.3	**H3**	45.3
E4	0.0	**F4**	44.7	**G4**	0.0 (*E*), 5.4 (*Z*)	**H4** (*E*)	0.0 (*E*), 7.3 (*Z*)
E5	→ **E4**	**F5**	[b]	**G5**	→ **F** + CF_3^+	**H5**	→ **H4**(*Z*)
E6	28.2	**F6**	68.3	**G6**	24.6	**H6**	65.2
I + H$^+$	55.1	**J** + H$^+$	57.6	**K** + H$^+$	[b]		
I1	53.0	**J1**	53.0	**K1**	24.9		
I2	N/A	**J2**	48.1	**K2**	N/A		
I3	40.5	**J3** N_2 lost	0.8	**K3** rearranged	56.8		
I4	0.0	**J4** N_2 lost	0.0	**K4**	0.0		
I5	[b]	**J5**	17.3	**K5** rearranged	40.2		
I6	[b]	**J6** rearranged	65.6	**K6** rearranged	66.8		

[a] **A1** means mode 1 protonation for allenediazonium **A**. [b] Not a minimum.

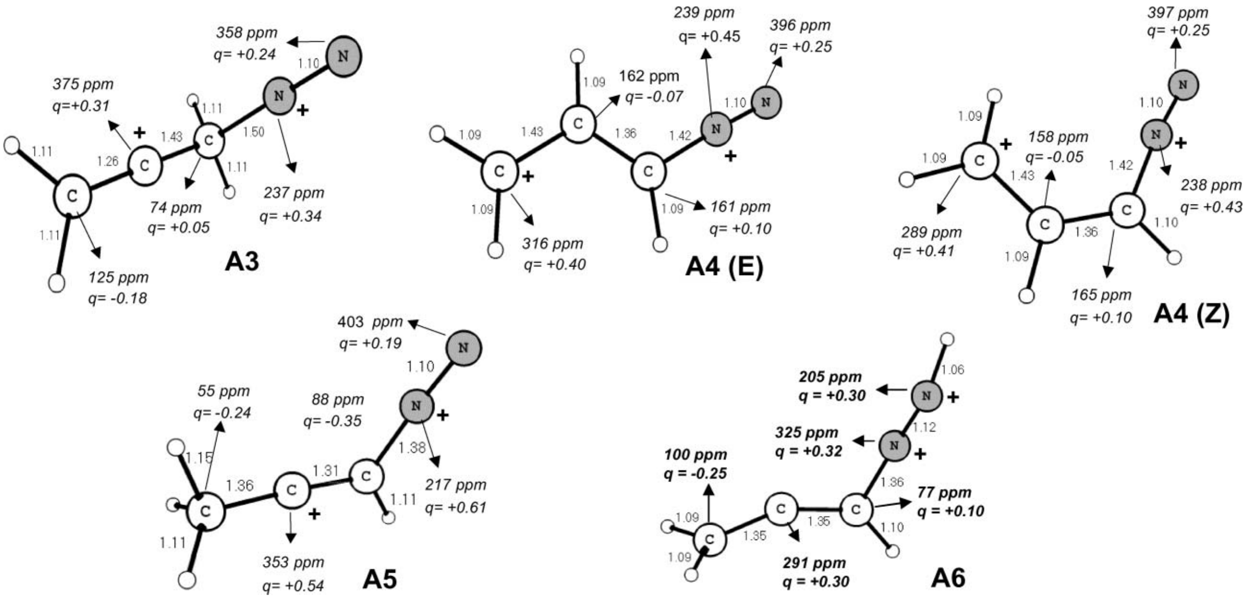


Fig. 2 Optimized structures for protonated allenediazonium cation **A**, with selected geometric parameters, CHelpg charges (q) and GIAO NMR chemical shifts.

favored (with the E-configuration being more stable than Z). Comparing **B4** with **A4**, it can be seen that fluorine substitution at C_1/C_3 causes very little change in the bond-lengths, but the computed charges at C_1/C_3 increase in **B4**. The computed GIAO shifts at C_1 are similar in the two dications, but C_3 is noticeably less deshielded in **B4**. This, taken together with fluorine deshielding at C_3, points to fluoronium ion character in dication **B4**. The resulting dication is best viewed as a fluoroallyl–N_2^+ hybrid dication. Initial protonation at C_3 (mode 5) forms a vinyl cation–N_2^+ species, which is not a stable structure, rearranging *via* fluorine shift to dications **B5** (E) and **B5** (Z) that are at least 23 kcal mol^{-1} less favored relative to **B4** (see Table 2). Considering the bond-lengths, computed charges and the GIAO shifts, the resulting rearranged dications have the characteristics of fluoroallyl cation–N_2^+ hybrids. Protonation at N_β (which should lead to dication **B6**) affords the coulombic (charge–charge) explosion products, $F{-}C^+{=}C{=}CF_2$ + HN_2^+. This likely stems from stabilization of the allenyl cation by p–π back-bonding to fluorine. Other protonation modes, despite being minima, were considerably less stable, and their competitive formation is considered unlikely.

Dicationic structures obtained after geometry optimization by protonation of $F_2C{=}C{=}CH(N_2^+)$ in various modes are sketched in Fig. S1† along with their geometric parameters, charges and GIAO NMR shifts. Based on relative energy data for the dications (Table 2), the C_2-protonated species is by far the best possibility, resulting in dication **C4** (in the Z-configuration). The C_3-protonated dication **C5** rearranges *via* a formal hydride shift to dication **C4** (in the E-configuration). This species is the global minimum (**C4** lies 5.1 kcal mol^{-1} higher) (Table 2). Preference for the E-configuration is likely because positive charges are more distant (interatomic distance $N_\alpha \cdots C_{(CF_2)} = 3.725$ Å, as opposed to $N_\alpha \cdots C_{(CF_2)} = 3.043$ Å for the Z configuration).

Fig. S2† summarizes the structures obtained after geometry optimization in various protonation modes for the difluoroallenyldiazonium cation $FHC{=}C{=}CF(N_2^+)$. Relative energy data for the resulting minima indicate that the most viable protonation mode is **D4** *i.e.* by C-protonation at the central allenic carbon. The same dication is formed by initial protonation at C_3 followed by a formal hydride shift. Fluorine protonation at C_3 resulted in the formation of a fluoroallyl–N_2^+/HF complex (dication **D1**), while fluorine protonation at C_1 led to HF loss and formation of a monofluoroallyl cation–N_2^+ species (dication **D2**). These dications are at least 26 kcal mol^{-1} less stable than **D4**. The product of protonation at C_1 (dication **D3**) lies ~52 kcal mol^{-1} above **D4**. Considering the bond-lengths, computed charges and the GIAO shifts, **D4** is best viewed as a fluoroallyl cation–N_2^+ hybrid having significant fluoronium ion character, whereas the much less favored **D3** is a vinyl cation–N_2^+ hybrid.

Dicationic structures obtained after geometry optimization by protonation of $H_2C{=}C{=}CF(N_2^+)$ in various modes are sketched in Fig. S3†, along with their geometric parameters, charges and GIAO NMR shifts. Once again, protonation at the central allenic carbon (C_2) leads to the most viable dication (**E4**). The same species is formed by initial C_3-protonation by a formal hydride shift. As with **D4**, dication **E4** has clear characteristics of a fluoroallyl cation–N_2^+ species. The vinyl cation–N_2^+ species formed *via* C_1-protonation (dication **E3**) is the next best possibility (17 kcal mol^{-1} less stable).

Fig. 4 illustrates the structures obtained after geometry optimization for various protonation modes in the case of $H_3C(F)C{=}C{=}CH(N_2)^+$. Protonation at C_2 (central allenic moiety) gives rise to the most stable dication **H4**. The Z-configuration of this dication is the most stable. Protonation at C_3 (dication **H5**) as an initial structure gave rise to dication **H4** as the final structure by a formal hydride shift. Protonation at C_1 generates dication **H3** as a minimum, but given the relative energy data (Table 2), competitive formation of this dication is unlikely. Taking into account the geometrical features, charges and the GIAO shifts, dication **H4** is

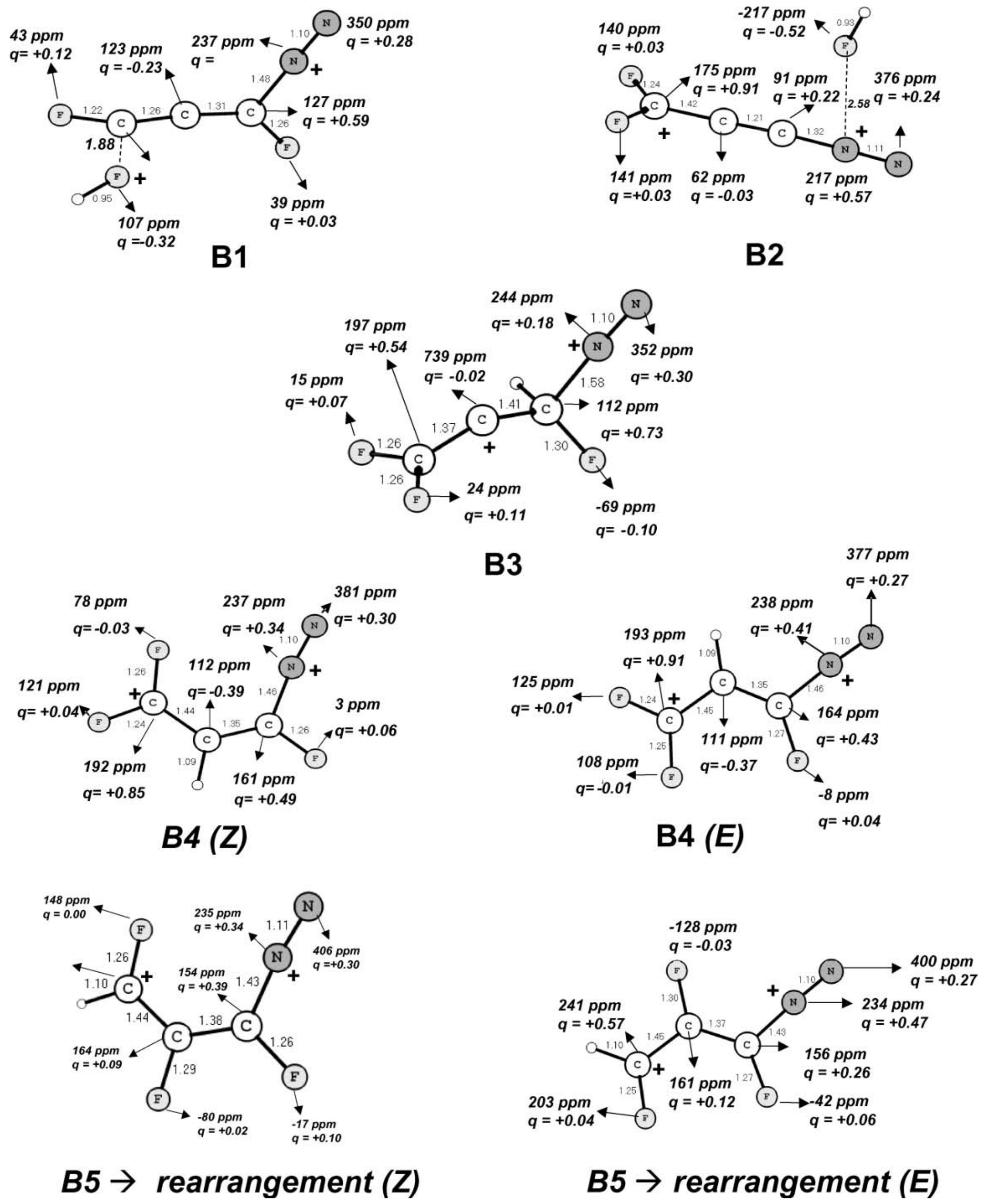


Fig. 3 Optimized structures for protonated allenediazonium cation **B**, with selected geometric parameters, CHelpg charges (q) and GIAO NMR chemical shifts.

best considered as a fluoroallyl cation–N_2^+ hybrid with fluoronium ion character, whereas **H3** is best viewed as a fluorovinyl cation linked to a $CH_2N_2^+$ moiety.

Protonation studies on the trifluoromethylated allenediazonium ions F and G

Optimized structures for the dications formed *via* protonation of the CF_3-substituted allenediazonium cation $(F_3C)HC{=}C{=}CH(N_2)^+$ are shown in Fig. 5, along with their computed bond-lengths, charges and GIAO NMR data. Although the dication resulting from protonation at the central allenic carbon (dication **F4**) is a minimum, based on relative energy data its formation is unfavorable. This can be understood given the destabilizing effect of α-CF_3 on an allyl cation (see later). In this instance, protonation at C_1 as a starting structure afforded **F3** (rearranged), skeletally rearranged by a formal 1,3-fluorine shift, as the most viable structure. Dication **F4** has clear characteristics of a (trifluoromethyl)allyl cation–N_2^+ species, in which the C_3 carbon of the allylic moiety is strongly deshielded by CF_3. The rearranged

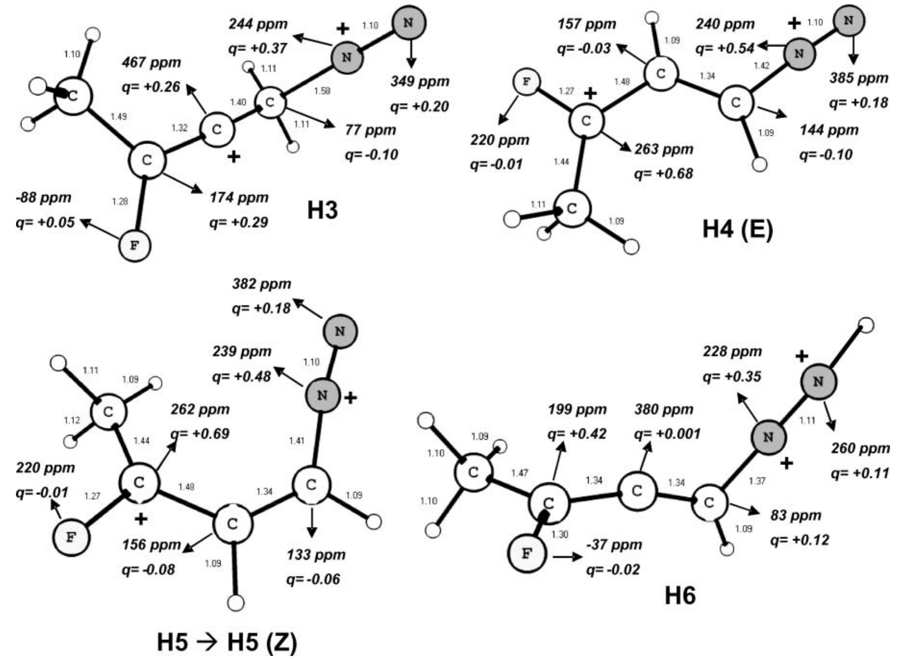


Fig. 4 Optimized structures for protonated allenediazonium cation **H**, with selected geometric parameters, CHelpg charges (*q*) and GIAO NMR chemical shifts.

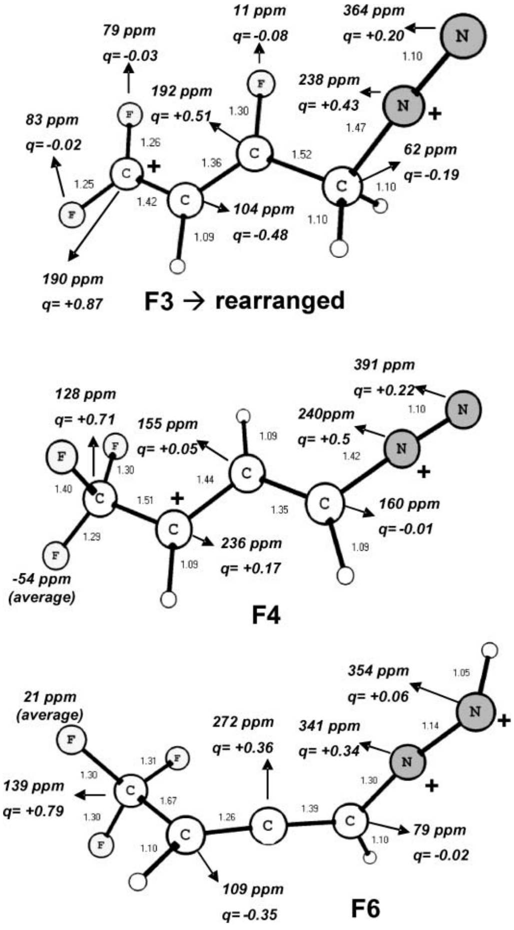


Fig. 5 Optimized structures for protonated allenediazonium cation **F**, with selected geometric parameters, CHelpg charges (*q*) and GIAO NMR chemical shifts.

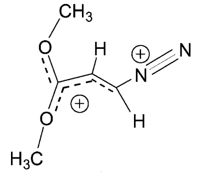
dication represents a 1,3,3-trifluoroallyl cation moiety linked to the diazonium group *via* a methylene spacer. The FC–$CH_2N_2^+$ bond is significantly longer than the other allylic C–C bonds.

Dicationic structures obtained after geometry optimization by protonation of the bis(trifluoromethyl)allenediazonium ion $(CF_3)_2C{=}C{=}CH(N_2)^+$ in various modes are sketched in Fig. S4† along with their geometric parameters, charges and GIAO NMR shifts

Surprisingly in this case, dication **G4** formed by protonation at C_2 (central allenic carbon) is most favored, despite the presence of two α-CF_3 groups on the allylic moiety! Dication **G3**, formed by C_1 protonation, is only 3.3 kcal mol^{-1} higher in energy and represents a reasonable possibility. Comparing the GIAO shifts in **G4** and **F4**, it can be seen that the second CF_3 group exerts additional deshielding at C_3. As with **F4**, dication **G4** represents a polyfluorinated allyl cation–N_2^+ hybrid dication. The *E*-configuration of this dication is the most stable. Comparison of the geometrical features, charges and the GIAO data in **G3** and **F3** (rearranged), provides evidence that **G3** is best viewed as $(CF_3)_2C{=}C^+{-}CH_2N_2^+$ *i.e.* a bis(CF_3)-substituted vinyl cation joined to a -$CH_2N_2^+$ moiety, rather than a polyfluoroallyl cation–N_2^+ species. Initial protonation at C_3 led to columbic explosion, forming the monocation **F** and CF_3^+. This is understandable considering internal charge–charge repulsion and the stability of CF_3^+.

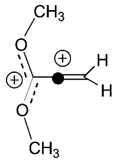
Protonation studies on allenediazonium ions I, J and K, with OMe or NMe_2 substituents

Optimized structures for the dications formed by protonation of $(MeO)_2C{=}C{=}CH(N_2)^+$ are shown in Fig. S5†, along with their computed bond-lengths, charges and GIAO NMR data. Formation of dication **I4**, resulting from protonation at the central allenic moiety, is most favored. The same dication is formed by initial protonation at C_3 (**I5**), followed by hydride shift. This structure reflects the distonic character of the dication and the ability of the oxygen to stabilize positive charge (see below).



I4

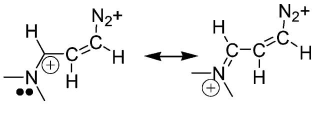
Distinct carboxonium ion character in **I4** is revealed by considering the geometrical features, charges and the GIAO shifts. *O*-Protonation gave rise to dication **I1**, as a high energy minimum. Protonation at C_1 resulted in "dediazonation" (see Fig. S5†). The resulting dication (see below) may be best viewed as a carboxonium moiety linked to a vinyl cation.



Finally, *N*-protonation (dication **I6**) led to the formation of coulombic explosion products, *i.e.* $(MeO)_2C{=}C{=}C^+{-}H + N_2H^+$.

Dicationic structures obtained after geometry optimization by protonation of the 1,3-dimethoxy-substituted allenediazonium cation $(MeO)H{-}C{=}C{=}C{-}OMe(N_2)^+$ (**J**) are sketched in Fig. S6†, along with their geometric parameters, charges and GIAO NMR shifts. The most reasonable skeletally intact dication is formed by protonation at C_2 (dication **J5**). But this species is less stable (by 17 kcal mol^{-1}) relative to structures **J3** (rearranged) and to **J4** (rearranged), derived from initial protonation at C_1 or C_2 followed by H-migration and C–N bond cleavage. As with several earlier discussed dicationic structures, dication **J5** is best viewed as a delocalized allyl cation–N_2^+ species. Tendency for skeletal rearrangement and nitrogen cleavage in protonation of **J** is likely due to additional stability gained by the bis(carboxonium) dication mesomeric structures. The oxonium–azonium dication formed by mode 1 protonation (**J1**) was considerably less stable. Initial *N*-protonation (mode 6) resulted in cyclization to generate **J6** (rearranged) as a high energy minimum.

Optimized structures for the dications formed by protonation of the dimethylamino-substituted allenediazonium cation $(Me_2N)HC{=}C{=}CH(N_2)^+$ are shown in Fig. S7†, along with their computed bond-lengths, charges and GIAO NMR data. Unlike its precursor (**K**) which was not a minimum and converged to monocation–N_2 complex **k** on optimization (see earlier), a skeletally intact dication was formed by protonation at C_2 as the most viable dication (**K4**). This species can best be viewed as an iminium–vinyldiazonium dication (Scheme 5).



Scheme 5

The *N*-protonated ammonium–diazonium dication **K1** is a minimum, but lies 25 kcal mol^{-1} higher. Initial protonation at C_1 and C_3 resulted in the formation of cyclized azirinium–diazonium dications **K3** and **K5**. Formation of these unusual cyclized species reflects neighboring group participation by the Me_2N group on the incipient vinyl cations. However, given their significantly higher relative energies, their competitive formation is unfavorable.

Comparative discussion

Protonation at C_2 (formally the sp-hybridized carbon of the allenyl moiety) (mode 4) leads to the formation of an allyl cation–diazonium species with the general formula $X(Y)C^+{-}CH{=}C(Z){-}N_2^+$. Preference for C_2-protonation is consistently observed throughout this study.

Focusing on the relationship between the computed carbon charges in allenediazonium ions and the preferred protonation sites, agreement is found only in limited cases, as substituent effects play a dominant role in controlling the protonation outcomes. Therefore, in several cases, initial protonation at a seemingly favorable site (judging only based on computed carbon charges), resulted in rearrangement to the energetically more favored dication.

Protonation at C_1 resulted in the formation of vinyl cations bonded to a $\text{-}CH(Z){-}N_2^+$ group with general structure $X(Y)C{=}C^+{-}CH(Z){-}N_2^+$. For allenediazonium **F** ($X = CF_3$), skeletal rearrangement (*via* a formal 1,3-F shift) generated a delocalized fluorinated allyl cation bonded to a $\text{-}CH(Z){-}N_2^+$ group. For the C_3-fluorinated allenediazonium cations (**C**, **D**, and **E**), initial protonation at C_3 (mode 5), to form a vinyl cation–diazonium species of general structure $X(Y)HC{-}C^+{=}C(Z){-}N_2^+$, was accompanied by rearrangement *via* a formal hydride shift to generate $X(Y)C^+{-}CH{=}C(Z){-}N_2^+$, thus leading to the same dication as that formed by C_2 protonation. Protonation at the diazonium group did produce stable minima in several cases, but the resulting dications were considerably less stable than those resulting from attack at C_2. Preference for C_2-protonation is also noted in the case of $(MeO)_2C{=}C{=}CH(N_2^+)$, generating a delocalized carboxonium cation–N_2^+ species. With **J**, protonation at C_1 and at C_2 resulted in stable dications with loss of nitrogen, while protonation at C_3 led to a skeletally intact dication that was energetically less favored. With the intact NMe_2 derivative **K** (itself not a minimum), the most favored dication was the skeletally intact **K4**, formed by C_2 protonation, with the dication exhibiting iminium–diazonium character. For allenediazonium cations **I**, **J**, and **K** (with OMe or Me_2N as substituents), mode 1 protonation (on the heteroatom substituent) generated stable oxonium–diazonium or ammonium–diazonium structures, but with considerably higher energies than those resulting from C_2-protonation. Likewise, protonation of the $\text{-}N_2^+$ group in several cases resulted in minima, but with considerably higher energies.

In conclusion, the present model computational study has given some encouraging indications as to the feasibility of generating allenediazonium ions experimentally (either under stable ion conditions or *in situ*), and as to their potential to yield a host of novel dications. Given the growing interest in allenes as building blocks in organic synthesis,[22,23] and the availability of synthetic routes to numerous substituted allenes, including the fluorinated, methoxy- and amino-substituted derivatives,[24] experimental studies along these lines appear to be an attainable goal.

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