A computational study (DFT, MP2, and GIAO-DFT) of substituent effects on protonation regioselectivity in β,β-disubstituted vinyldiazonium cations: formation of highly delocalized carbenium/ diazonium dications

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Protonation reactions were studied by quantum-chemical theoretical methods (DFT and MP2) for a series of β,β-disubstituted vinyldiazonium cations (1^+–14^+), bearing stabilizing electron-releasing groups (H_3CO-, $(H_3C)_2N-$, H_3C-, $(H_3C)_3Si-$, as well as halogens F, Cl). Taking into account the various mesomeric forms that these species can represent, protonations at C_α, at the β-substituent, and at N_β were considered. The energetically most favored pathway in all cases was C_α protonation, which formally corresponds to trapping of the mesomeric diazonium ylid. Based on the computed properties (optimized geometries, NPA-charge densities, and multinuclear GIAO-NMR chemical shifts), the resulting dications can best be viewed as carbenium/diazonium dications, in which the carbocation is further delocalized into the β-substituent. For the α-nitro derivative 15, protonation of the nitro group was predicted to be the most favored reaction, while C_α- and N_β-protonation resulted in the loss of the nitronium ion. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: delocalized carbenium/diazonium dications; DFT and GIAO-DFT; protonation; substituent effects; trapping of mesomeric diazonium ylid; vinyldiazonium cation

INTRODUCTION

A significant body of work has been published on alkenediazonium ions over the years, focusing on their generation, isolation, NMR measurements, X-ray analysis, and theoretical calculations.[1–8] The importance of vinyldiazonium salts as synthetic building blocks was highlighted in a recent feature article by Saalfrank and Maid.[9]

Stability of alkenediazonium ions toward dediazoniation varies greatly depending on their structure, ranging from those that can be isolated as salts and stored indefinitely at room temperature,[10–17] to those that require *in situ* generation and trapping,[18–20] to those that can be generated at low temperature under stable ion conditions for direct NMR studies.[21,22] In this way, generation of alkenediazonium salts has been accomplished, either as reactive intermediates or as isolable compounds, by diverse synthetic routes.[10–17] Stable ethenediazonium salts were generally synthesized by *O*-alkylation of alkyl diazoacetates or α-diazoacetamides with Meerwein salts, diazotization of vinyl isocyanates, or ionization of tosyl hydrazones.[10–17] For example, *O*-ethylation of ethyldiazoacetate generated stable 2,2-diethoxy-ethenyldiazonium salts.[16] These compounds can be represented by several limiting mesomeric structures (Eqn 1). Their behavior as alkylating agents toward typical nucleophiles has emphasized the importance of the oxonium mesomeric forms.[3]

(1)
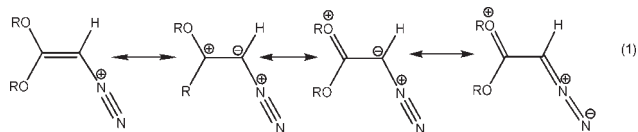
Vinyldiazonium ions are viable precursors to vinyl cations via the dediazoniation route.[23,24] Early progress on solvolytic generation of vinyl cations by deamination of suitable substituted

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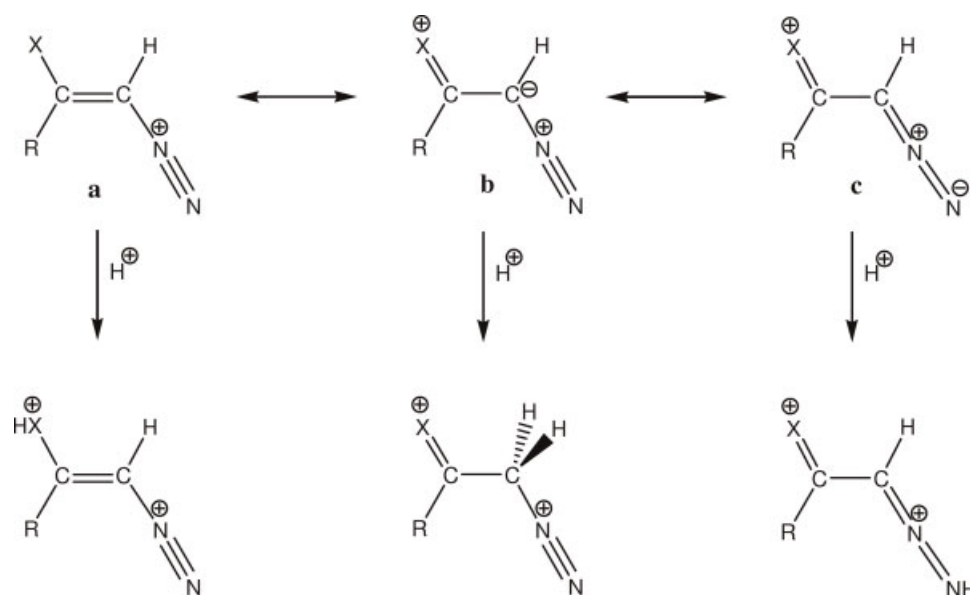
Figure 1. Mesomeric monocation structures and their protonation outcomes

vinyl amines, via the *in situ* generated vinyldiazonium ions, has been reviewed.[23] Introduction of electron-releasing substituents in the β-position or incorporation of vinylic bond into an appropriate ring system tends to suppress this fragmentation reaction.[10–17]

Despite the fact that a number of stable alkenediazonium salts are synthetically accessible, no stable ion NMR study or computational work has been undertaken to examine their protonation behavior and study the structural features in the resulting dications. As a guiding tool in our planned experimental stable ion NMR studies, and in connection to an earlier computational study on allenediazonium ions,[25] we have used quantum-chemical calculations to probe a series of vinyldiazonium cations bearing different substituents at the β-carbon, and to study their protonated dications. Multinuclear GIAO-NMR data (^{13}C, ^{19}F, ^{15}N, and ^{29}Si) and the NPA charges were computed in order to understand the structural features in the energetically favored dications.
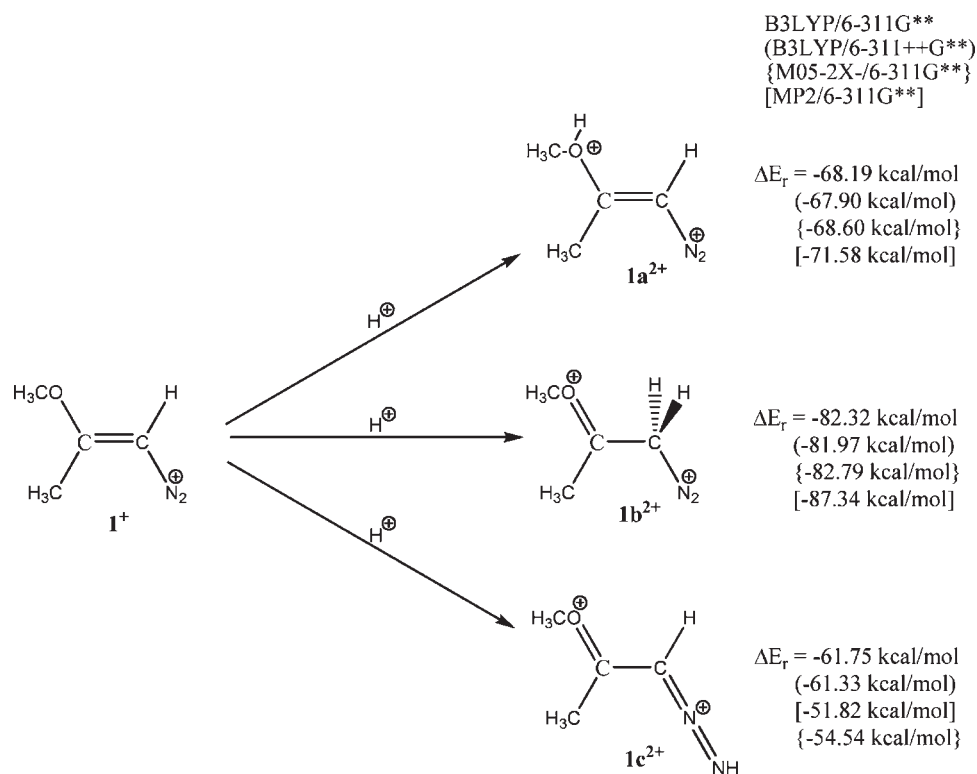

Figure 2. Comparison of protonation energies from different levels of theory

COMPUTATIONAL METHODS

All calculations were performed using standard techniques with the Gaussian 03 suite of programs.[26] For density functional theory (DFT) computations, the B3LYP[27–29] and the M05-2X[30] hybrid functionals were employed in conjunction with the 6-311G** and 6-311++G** basis sets. Optimizations at the MP2[31] level were also performed using the 6-311G** basis set. All geometries were fully optimized without imposing symmetry constraints. Optimized structures were subsequently checked with respect to being true minima on the respective potential energy surfaces (equilibrium structures, no imaginary frequencies) by harmonic vibrational frequency calculations at the same level and with the same basis set used for the optimization procedure. Natural population analysis (NPA)-derived charges were computed at the same level of theory by means of the NBO program.[32] NMR chemical shifts were calculated by the GIAO (gauge independent atomic orbitals)[33,34] method at the B3LYP/ 6-311G** level. NMR chemical shifts were referenced to TMS (GIAO isotropic shielding = 182.4656 ppm; this value is related to the GIAO isotropic magnetic susceptibility for ^{13}C; and GIAO isotropic shielding = 327.3890 ppm, value related to the GIAO isotropic magnetic susceptibility for $^{29}Si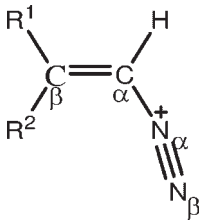$); to $CFCl_3$ (GIAO isotropic shielding = 179.0548 ppm, value related to the GIAO isotropic magnetic susceptibility for ^{19}F); and to NH_3 (GIAO isotropic shielding = 258.4000 ppm; value related to the GIAO isotropic magnetic susceptibility for ^{15}N).

RESULTS AND DISCUSSION

Protonation reactions for a series of β,β-disubstituted vinyldiazonium ions were examined by quantum-mechanical computations. Taking into account the limiting mesomeric forms for this type of compounds, protonation was considered at three possible sites (Fig. 1). In order to analyze the proper level of theory required, calculations were initially performed on model vinyldiazonium 1^+ with the B3LYP functional employing the 6-311G** and 6-311++G** basis. It has recently been reported that the M05-2X functional performs better than B3LYP,[35,36] therefore calculations with M05-2X/6-311G** were also performed for comparison purposes, as well as MP2/6-311G** optimizations. The results are shown in Fig. 2.

Addition of diffuse functions led to results that differed by less than 1 kcal/mol for the calculated reaction energies. Accordingly, the use of diffuse functions was not considered to be essential,

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Table 1. Changes in energy for protonation reactions in β,β-disubstituted vinyldiazonium cations

R^1	R^2	C$_\alpha$	R	N$_\beta$
			ΔE_r for protonation position (kcal/mol)	
1^+ OCH$_3$	CH$_3$	−82.32	−68.19[a]	−61.75
2^+ CH$_3$	OCH$_3$	−89.13	−68.59[a]	−59.70
3^+ OCH$_3$	OCH$_3$	−95.22	−70.86	−68.18
4^+ N(CH$_3$)$_2$	CH$_3$	−99.50	−94.64	−70.17
5^+ N(CH$_3$)$_2$	OCH$_3$	−106.63	−80.50 (OCH$_3$) −99.30 (N(CH$_3$)$_2$)	−82.42
6^+ N(CH$_3$)$_2$	N(CH$_3$)$_2$	−113.19	−113.78 (N(CH$_3$)$_2$ *anti*) −109.41 (N(CH$_3$)$_2$ *syn*)	−91.44
7^+ OCH$_3$	Si(CH$_3$)$_3$	−89.74	−86.55[a]	−69.05
8^+ Si(CH$_3$)$_3$	OCH$_3$	−90.57	−82.95[a]	−70.80
9^+ Si(CH$_3$)$_3$	CH$_3$	−75.94		−87.80[b]
10^+ OCH$_3$	F	−70.80	−50.63[a]	−50.24
11^+ OCH$_3$	Cl	−77.24	−59.04[a]	−56.33
12^+ N(CH$_3$)$_2$	F	−89.74	−67.80 (F)[c] −79.90 (N(CH$_3$)$_2$)	−69.86
13^+ N(CH$_3$)$_2$	Cl	−94.93	−66.85 (Cl)[c] −88.41 (N(CH$_3$)$_2$)	−74.70
14^+ F	Cl	−43.32	−14.90 (F) −18.90 (Cl)	−25.05

[a]OCH$_3$.
[b]Rearrangement.
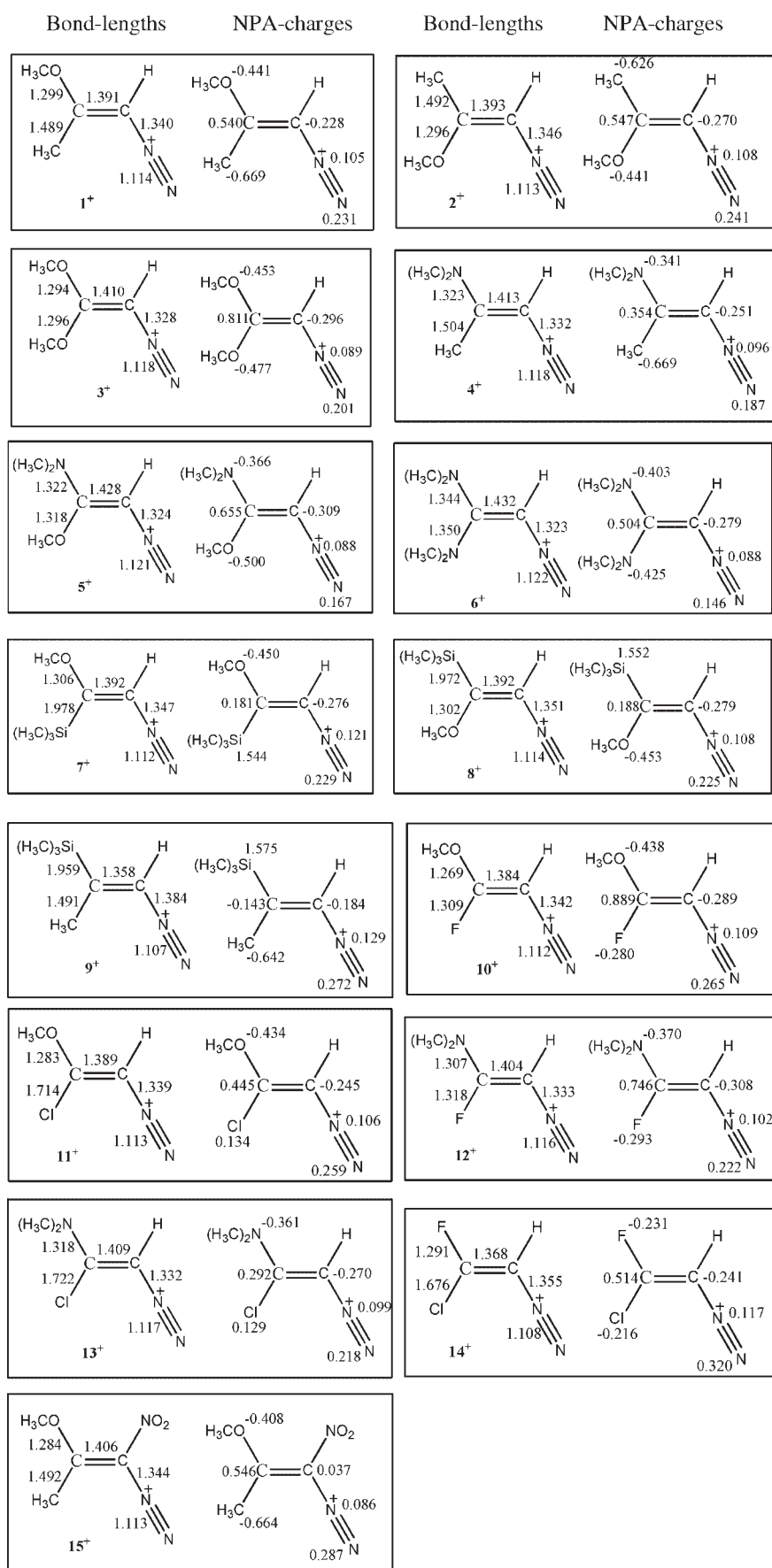[c]Dissociation.

Figure 3. Selected bond-lengths and the NPA-charges for the vinyldiazonium cations
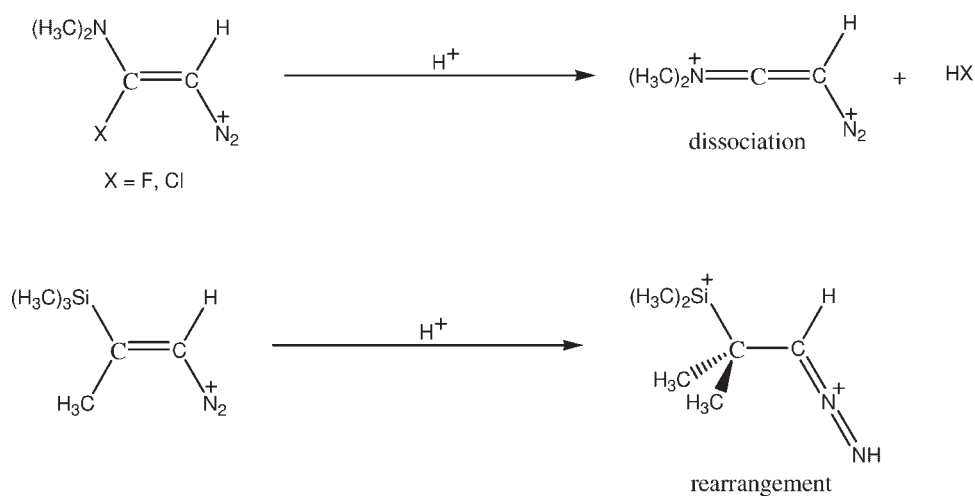
Figure 4. Alternative reaction paths

and the 6-311++G** basis was not further employed in subsequent calculations. The M05-2X functional afforded nearly equal results to B3LYP. Moreover, the MP2/6-311G** optimizations afforded the same trend in regioselectivity as that derived from DFT, although protonation reactions were more exothermic. This could be attributed to the lower DFT performance for π electron systems, which led to the suggestion that DFT overestimates the conjugation energy.[37] Given that our

intention was to estimate *relative* protonation energies rather than to compute absolute proton affinities, we employed the less costly DFT level of theory for the rest of the study, utilizing the B3LYP/6-311G** methodology.

Protonation reactions were then examined for β,β-disubstituted vinyldiazonium cations $\mathbf{1^+}$ through $\mathbf{14^+}$, presenting stabilizing electron-releasing groups (H$_3$CO−, (H$_3$C)$_2$N−, H$_3$C−, (H$_3$C)$_3$Si−) as well as halogens (F, Cl). Reaction energies for protonation of the
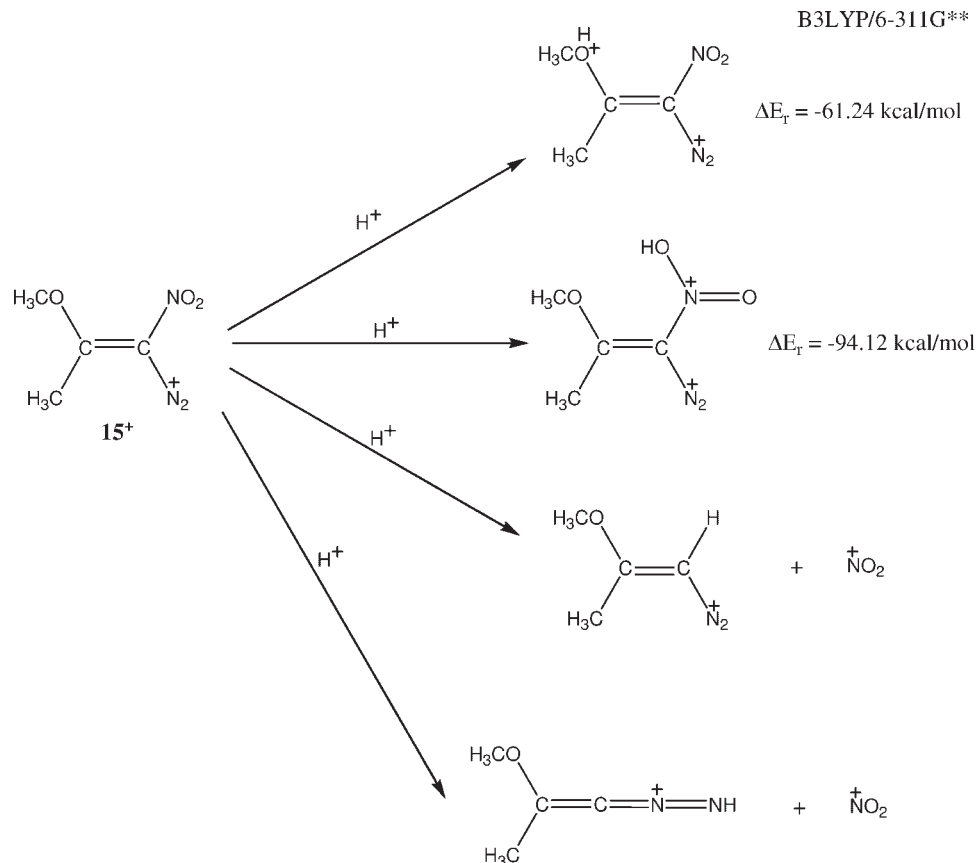

Figure 5. Protonation reactions for the α-nitro derivative

vinyldiazonium monocations are displayed in Table 1. Selected bond-lengths and the NPA-charges for the monocations are collected in Fig. 3.

Protonation at C_α was the preferred reaction path (two exceptions will be discussed below), leading to the most stable dications. This process formally corresponds to trapping of the mesomeric diazonium ylid structure **b** (in Fig. 1). The resulting dications can be viewed as carbenium/diazonium dications in which the carbocation is further delocalized onto the

β-substituent, thus taking either ammonium, oxonium, or halonium ion character in the case of the amino, methoxy, and the fluoro analogs. These observations were also reflected in the geometrical features of the dications, presenting relatively long C_α–C_β and short C_β–OCH_3 bonds (Fig. 3), and in the NPA-charge densities, which were negative for C_α and positive for C_β. It could be noted that C_α protonation was increasingly favored, as the C_α–C_β bond became longer, i.e., as the ylid form became more stabilized by conjugation with the β-substituent. In
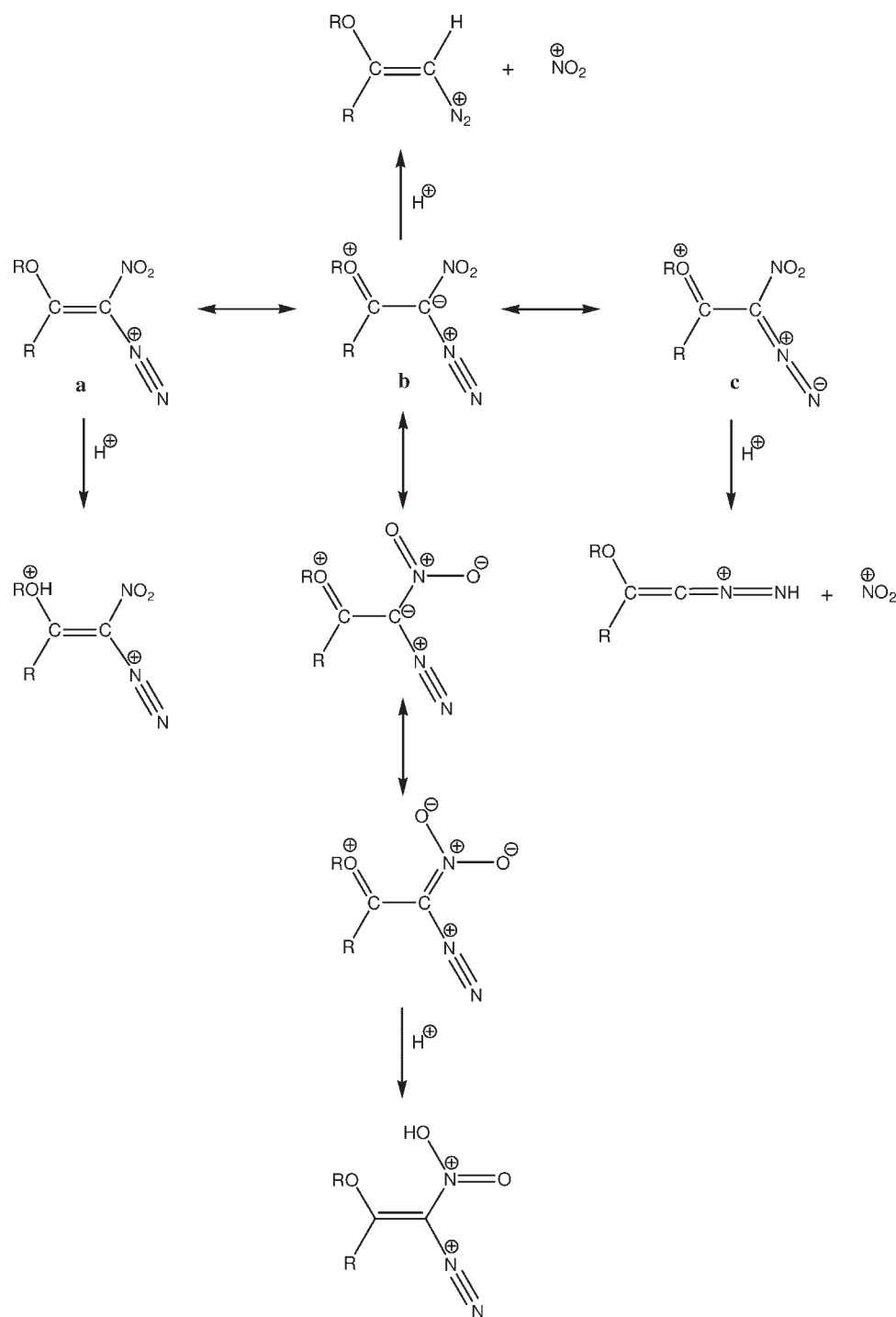

Figure 6. Vinyldiazonium mesomeric structures and protonated dications for the α-nitro derivative
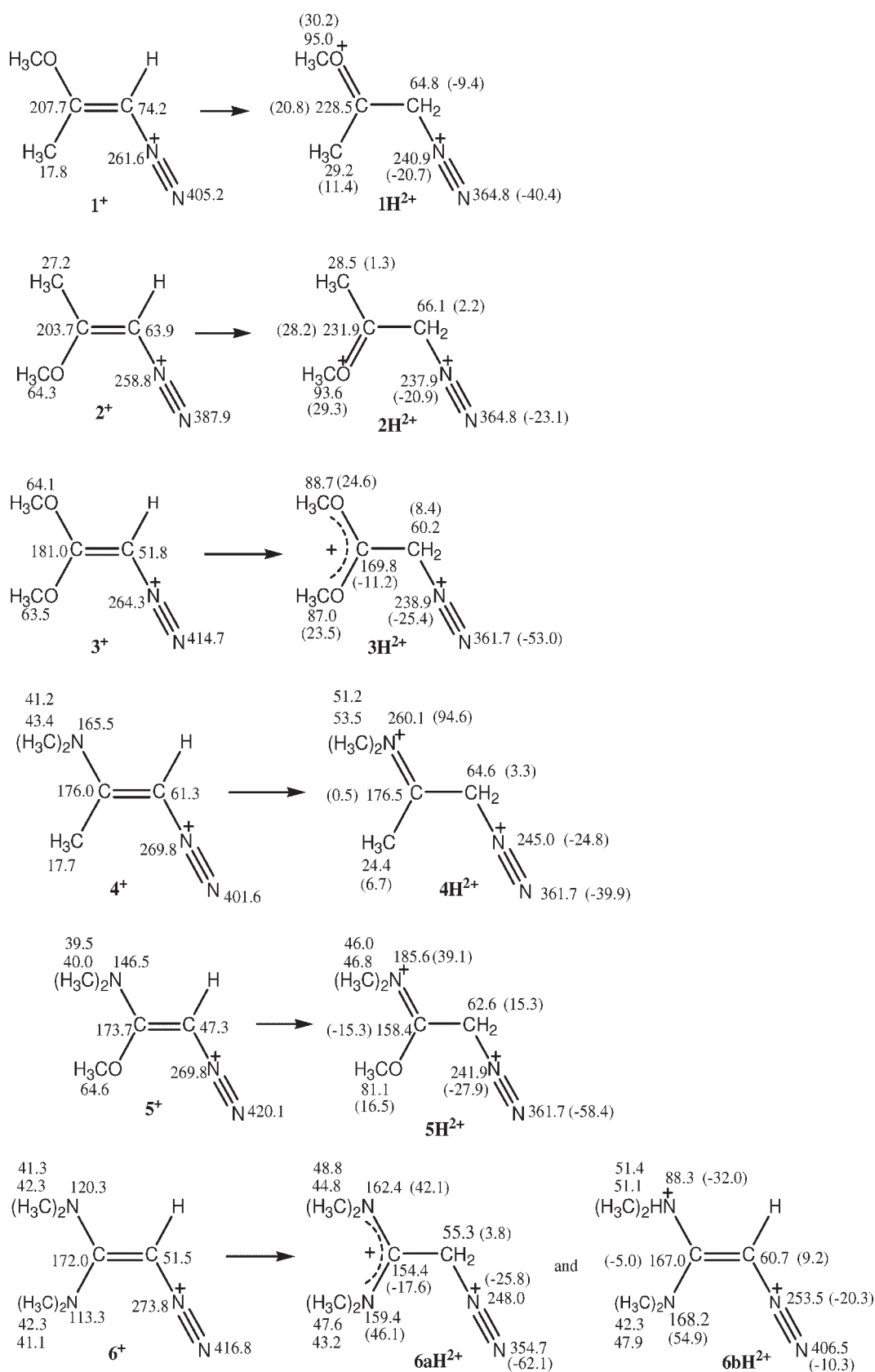
Figure 7. Multinuclear GIAO-NMR chemical shifts (changes in chemical shifts in parenthesis)
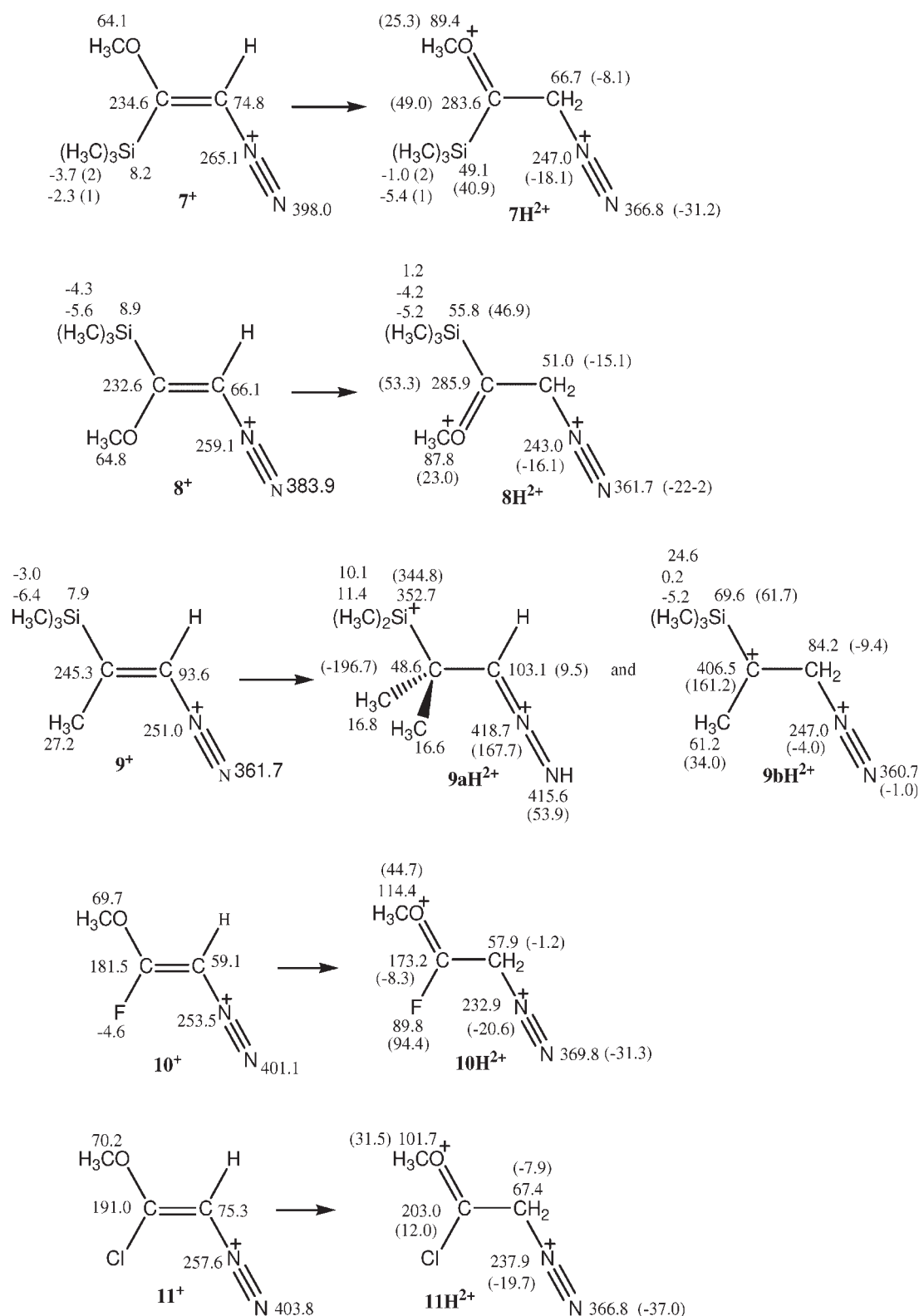
Figure 7. (Continued)

accord with Olah's definition,[38–40] the resulting charge separated carbenium/diazonium dications represent new examples of distonic superelectrophiles.

For vinyldiazonium cations bearing a methoxy and a methyl group as β-substituents ($\mathbf{1^+}$ and $\mathbf{2^+}$), C_α-protonation of the

Z-isomer was favored by almost 7 kcal/mol in comparison to the E-isomer. Lower stability of the protonated E-isomer seems to originate from restricted conjugation caused by repulsive interaction between the methyl and the $-N_2^+$ group, as inferred by the deformation observed in the sp^2 trigonal angles. For the
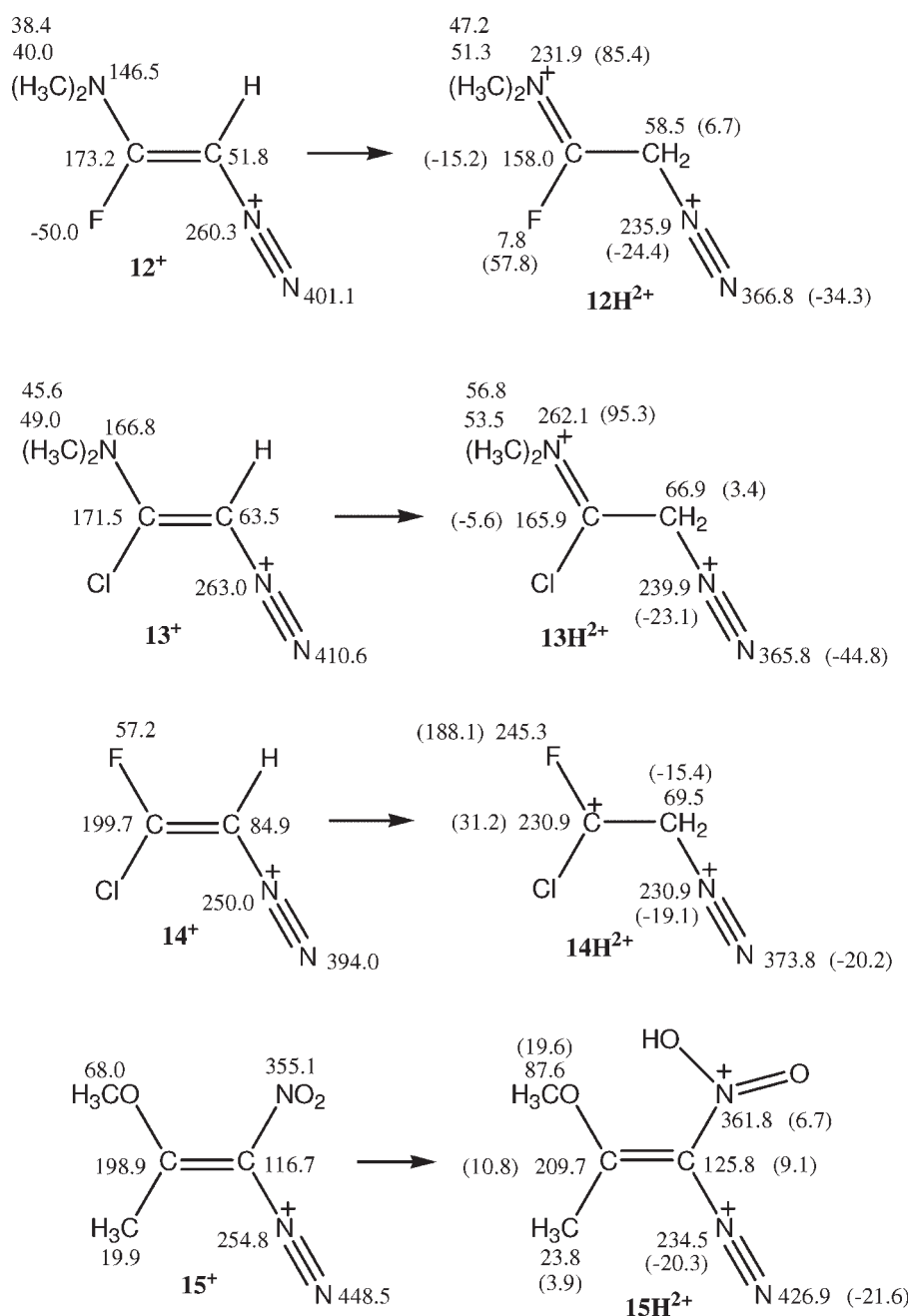
Figure 7. (Continued)

other two protonation modes (on oxygen and at N$_\beta$), no significant differences were observed. On the other hand, for the pair of isomers bearing a methoxy and a trimethylsilyl group as β-substituents (**7**[+] and **8**[+]), no important differences in reaction energies for the three different protonation modes were noticed. Furthermore, no relevant changes in bond lengths were observed by comparing both pairs of isomers (**1**[+]/**2**[+] and **7**[+]/**8**[+]). Hence, relative orientation of the methoxy lone-pairs did not appear to influence the relative stability of the mesomeric forms.

Protonation regioselectivity in the case of a β-substituent with nonbonding electron pairs, was preferred in the order N(CH$_3$)$_2$ > OCH$_3$ > Cl > F. For the vinyldiazonium cations bearing F and N(CH$_3$)$_2$ as well as Cl and N(CH$_3$)$_2$ (**12**[+] and **13**[+]), halogen

protonation led to loss of HX (Fig. 4). For the bis-dialkylamino-derivative **6**[+], protonation at the amino nitrogen *anti* to the diazo moiety was favored by around 4 kcal/mol over protonation of the *syn* amino group. By comparing the geometries and the computed NPA-charges for the monocation of the dimethylamino derivative **6**[+] (Fig. 3), and the corresponding C$_\alpha$- and N$_\beta$-protonated dications, it can be concluded that both –N(CH$_3$)$_2$ groups participate in charge delocalization.

Although protonation at N$_\beta$ was generally the least favored mode, it became more exothermic as N$_\alpha$–N$_\beta$ bond-length became longer. This fact showed the incremental importance of the ylid mesomeric form **c**, especially for the β-amino compounds (ammonium/diazonium ylid mesomeric form). For

the derivative bearing CH_3 and $Si(CH_3)_3$ groups (9^+), N_β-protonation was the energetically preferred pathway, resulting in methyl migration from the trimethylsilyl group to C_β (Fig. 4).

Recent reports on the synthesis and chemistry of α-nitro-α-diazocarbonyl derivatives,[41,42] prompted the inclusion of α-nitro-vinyldiazonium cation 15^+ in this study. The protonation modes considered are shown in Fig. 5, and the geometries and NPA-charge densities are included in Fig. 3. In this case, nitro protonation was the preferred reaction, while C_α- and N_β-protonation brought about the loss of the nitronium ion. Reaction energies in Fig. 5 and geometry and charge density in Fig. 3 also underscore the ylid form **b** as the major contributor to the structure of 15^+, with further delocalization into the nitro group, as shown in Fig. 6. This fact explains the preferred formation of the nitro-protonated dication.

Computed GIAO ^{13}C, ^{15}N, ^{19}F, and ^{29}Si NMR chemical shifts for the vinyldiazonium cations (1^+ through 15^+) are shown in Fig. 7, along with GIAO-NMR chemical shifts and changes in chemical shifts for the most stable dication for each derivative ($1H^{2+}$ through $15H^{2+}$). The charge delocalization patterns gauged, based on magnitude of $\Delta\delta$ values, are in general agreement with the trends from calculated geometries and the NPA-charge densities, reflecting the importance of the mesomeric ylid form **b**. No ^{15}N NMR data on vinyldiazonium salts have been reported in the literature. The ^{15}N data reported for substituted PhN_2^+ X^- salts show that N_β is always more deshielded than N_α,[3,43] and this is in concert with the NPA charges and the GIAO-NMR data in this work.

Strong oxonium ion character is evident in $1H^{2+}$, $2H^{2+}$, and $3H^{2+}$ dications, leading to limited deshielding at C_β and shielding at N_β. This is particularly noteworthy in the case of $3H^{2+}$. Strong ^{15}N deshielding at the NMe_2 group and shielding at N_β imply strong azonium ion character in dications $4H^{2+}$, $5H^{2+}$, and $6aH^{2+}$. Development of silylium ion character is evident (from $\Delta\delta^{29}Si$) in the skeletally intact $9bH^{2+}$. Skeletal rearrangement in $9aH^{2+}$ (methyl shift from Si to C_β) resulted in the formation of a silylium ion (very large $\Delta\delta^{29}Si$). The fluoronium ion character in fluorinated dications $10H^{2+}$, $12H^{2+}$, and $14H^{2+}$ (as gauged through $\Delta\delta^{19}F$) is modulated by the other β-substituent. Whereas electron demand for fluorine back-bonding diminishes in the presence of $-OMe$ and $-NMe_2$ substituents ($10H^{2+}$, $12H^{2+}$), it greatly increases in $14H^{2+}$.

COMPARATIVE SUMMARY

Protonation reactions for a series of β,β-disubstituted vinyldiazonium cations bearing stabilizing electron-releasing groups (H_3CO-, $(H_3C)_2N-$, H_3C-, $(H_3C)_3Si-$, and halogens F, Cl) were examined by DFT and MP2 computations. Considering the various mesomeric forms in these vinyldiazonium cations, protonations at three possible sites were considered. Protonation at C_α was the preferred reaction path, underscoring the importance of the mesomeric ylid form **b**. The resulting dications can best be viewed as superelectrophilic distonic carbenium/diazonium dications, in which the carbocation is delocalized into the β-substituent. Among various β-substituents, C_α protonation was preferred in the order $N(CH_3)_2 > OCH_3 > Cl > F$. Whereas protonation at N_β was generally the least favored process, the mesomeric form **c** became more important in the β-amino compounds (ammonium/diazonium ylid mesomeric form).

For the α-nitro derivative, protonation of the NO_2 group was the preferred reaction, while C_α- and N_β-protonation led to loss of nitronium ion. The nitro-protonated dication is best represented as the ylid form **b**, with further delocalization into the nitro group. The calculated geometries, NPA-charge densities, and the computed GIAO-NMR chemical shifts were correspondingly indicative of mesomeric ylid **b** as the major contributor to the overall structure of vinyldiazonium cations. Delocalization into the β-substituents was apparent in ^{15}N deshielding in the dialkylamino compounds, and the fluoronium ion character was reflected in ^{19}F deshielding in the fluoro-derivatives.

The multinuclear GIAO-NMR data (^{13}C, ^{15}N, ^{19}F, and ^{29}Si) obtained from this work constitute a starting point for stable ion protonation studies on kinetically stable vinyldiazonium salts.

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