Vinyl Cations Substituted with β π-Donors Have Triplet Ground States

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Abstract: Computations at the CASPT2, CBS-QB3, and B3LYP levels of theory demonstrate that β-substitution of vinyl cations with π-donors switches the ground state of these ions from the familiar closed-shell singlet state to a carbene-like triplet state similar to the electronic state of triplet phenyl cations. Although the parent vinyl cation is a ground-state singlet species with a very large energy gap to the lowest energy triplet state, substituting the β hydrogens with just one strong π-donor (e.g., NH_2, NMe_2, OMe) or two moderate π-donors (e.g., F, OH, Ar, vinyl) makes the triplet state the computed ground electronic state. In many cases, the singlet states for these β π-donor-substituted vinyl cations are prone to rearrangements, although such rearrangements can be inhibited through incorporation of the π-donors into rings. For example, a vinyl cation based on 1,3-dimethyl-2-methylene imidazolidine (**32**) is predicted to show a substantial barrier to singlet state rearrangement as well as possess a triplet ground state with a large energy gap. In contrast to the singlet states, the stabilized triplet states appear to be well behaved and more immune to rearrangements. These triplet ions may exhibit substantially different properties and reaction chemistry than those seen for typical closed-shell vinyl cations.

1. Introduction

Vinyl cations are intermediates in many important industrial and commercial reactions, and they are typically formed from the solvolysis of leaving-group-substituted olefins, from the photolysis of vinyl halides, and from electrophilic addition reactions (including protonations) of allenes and alkynes.[1−6] Vinyl cations have been studied by laser flash photolysis,[7−11] mass spectrometry,[12−14] stable ion media NMR,[15−17] trapping studies and product analyses,[4,5,7,18] and, in one exceptional case, X-ray crystallography.[19]

Numerous theoretical and experimental studies have been reported on the effect of substituents on the stabilities of vinyl cations.[5,18,20] For example, in 1977, Apeloig, Schleyer, and Pople examined (RHF/4-31G) the effect of β-substituents on the thermodynamic stability of vinyl cations.[21] Other computational studies have appeared that compare the energies of bridged versus open geometries of β π-donor-substituted vinyl cations,[22,23] and two computational studies by Okazaki and Laali examined the geometries and computed NMR shifts of β-halogen- and β-aryl-substituted vinyl cations.[24−26] More recent computational[27,28] and experimental[29−31] studies examined the effect of α substituents on the stability of vinyl cations. Common

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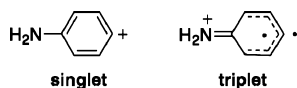(30) Kotani, M.; Kobayashi, S.; Mishima, M.; Hori, Y. *Chem. Lett.* **2003**, *32*, 294–295.

Figure 1. The *p*-aminophenyl cation: A ground-state triplet ion.

to all of these studies is that the computations were performed on the singlet states of the vinyl cations.

Given the structural similarity of vinyl cations to phenyl cations, we thought it possible that a triplet state might become the ground electronic state with appropriate substitutions of the vinyl cations. The phenyl cation (Ph$^+$) is an important member of the carbenium family of intermediates, having a formally empty hybrid σ-orbital on an unsaturated carbon.[4,5,32−34] One of the most interesting features of phenyl cations is that they are one of a few known classes of carbenium ion that can exist in either a singlet state or a triplet electronic state.[35−37] The unsubstituted phenyl cation is a ground-state singlet, but the triplet state becomes the lower-energy electronic state when the ortho or para positions of the phenyl ring are substituted with π-donors (e.g., OR, NR$_2$). To a reasonable approximation, the triplet state of a phenyl cation can be described as a triplet carbene[38] (see Figure 1 for an example).

Given that triplet phenyl cations can be exploited to undergo useful nucleophile-selective synthetic transformations,[39−43] and given the similarity of phenyl cations to vinyl cations, we thought it worthwhile to test whether similar π-donor group substitutions could lead to triplet ground state vinyl cations. Recently, triplet vinyl cations have been observed by laser flash photolysis as well as proposed as reactive intermediates in photolysis reactions.[44,45] In these cases the observed (or proposed) triplet vinyl cations were presumed to be in a high-energy triplet excited state. However, aside from an intriguing computational study of C$_2$H$_4$N$^+$ isomers by Würthwein[46] in 1984, the possibility that substituents might favor the triplet state has apparently not been investigated.

Computations, described below, demonstrate that β-substitution of vinyl cations with π-donors leads to ions with carbene- or diradical-like triplet states exhibiting an electronic structure similar to that of triplet phenyl cations. When the β-position is

substituted with a single moderate π-donor (e.g., F, OH, Ar), the singlet remains the ground state, but with a small gap to the lowest-energy triplet state. In cases where the β-position is substituted with one or two strong π-donor groups (e.g., OMe, NH$_2$, NMe$_2$) or two moderate π-donor groups (e.g., OH, F, Ar, Vinyl), the triplet state is the computed ground state. Many of the simplest β π-donor substituted systems were found to have very low barriers to isomerization, suggesting that experimental characterization of such species may be challenging. However DFT calculations have identified a family of vinyl cations having cyclic β-substituents. These latter species show substantial barriers to isomerization and are thus expected to be excellent targets for experimental studies.

2. Results and Discussion

2.1. Computational Methods. We computed the singlet−triplet state energy gaps (ΔE_{ST}) of the vinyl cations examined in this study by three computational methods: multireference second-order perturbation theory (CASPT2), the complete basis set (CBS-QB3) method of Petersson, and density functional theory (B3LYP). Here, the singlet−triplet energy gap, or ΔE_{ST}, refers to the gas phase energy difference between the lowest energy singlet and the lowest energy triplet state (including unscaled zero-point vibrational energies). A negative value for ΔE_{ST} indicates a singlet ground state.

CASPT2 is an appropriate method to model these electron-deficient species because it explicitly accounts for the mixing of excited-state (or degenerate) determinants with the ground-state wave function. Additional dynamical correlation is then captured using second-order perturbation theory. While it is an expensive method and consequently can only be used for relatively small systems, results from CASPT2 are generally trustworthy because this method can handle even pathological cases for theory such as open-shell singlet diradicals and mixed excited states. When employed with a large, flexible basis set and an appropriate active space, this method typically gives good quantitative estimates of the ΔE_{ST} for related electron-deficient species like nitrenes, carbenes, and benzynes.[47−50] Included in these CASPT2 calculations is a level shift (IPEA shift = 0.25, level shift = 0.1) that reduces a systematic error in the method favoring high spin states.[51] Because analytical gradients of the CASPT2 energy are not currently available to us, molecular geometries were optimized at the CASSCF level with the cc-pVTZ basis set of Dunning.[52] For the CASSCF geometry optimizations, the active space was chosen to include all π-electrons (including π lone pairs) and all π-orbitals plus the empty σ orbital on the cationic vinylic carbon. For example, the geometry of the 2,2-difluorovinyl cation **21** was optimized at the CASSCF(6,5)/cc-pVTZ level. We note that in all cases we observe negligible changes in the molecular geometries on switching from CASSCF/cc-pVDZ to CASSCF/cc-pVTZ, suggesting that the geometries are well converged with respect to basis set size. The same active space was chosen for the CASPT2 single-point energy corrections, for which the flexible

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ANO-L basis set of Widmark et al. was used, which is of polarized valence triple-ζ quality.[53] The effect of increasing the active space size for the CASPT2 energy corrections was tested in select cases by increasing the active space to (12,12) for ions **8**, **10**, and **12−18**; this larger active space was found to have only a minimal effect on ΔE_{ST}, changing the values in most cases by less than 2 kcal/mol and in all cases by less than 4 kcal/mol (see Supporting Information). Thus, except where noted, the CASPT2 computations described in this paper refer to CASPT2 computations with the active space selected by the criteria outlined above.

We also examined the singlet−triplet splittings using the complete basis set (CBS-QB3) method of Petersson,[54,55] which employs a DFT (B3LYP) optimization, and a coupled cluster single-point energy calculation using an extrapolation procedure to find the electronic energy at the basis set limit (along with an empirically determined correction for spin contamination). Since the electronic energy is derived from a coupled cluster calculation, this method may perform poorly when an electronic state cannot be well described by a single reference wave function. However, we note that this is not a concern here since the CASSCF calculations show that all the singlet states in this study consist almost entirely of a single closed-shell determinant (reference weight >0.85 for all species). Open-shell singlet states were found to be significantly higher in energy and generally did not mix in any significant way with the ground-state closed-shell singlet wave function. For example, CASPT2(12,12)/pVTZ vertical gaps from the closed-shell singlet configuration ($^1A'$) to the open-shell singlet configuration ($^1A''$) for the 2-hydroxy vinyl cation **16** and 2-amino vinyl cation **20** were 37 and 39 kcal/mol, respectively (C_s symmetry).

Because CBS-QB3 is fairly new and has therefore not been benchmarked for a large number of similar systems, we provide some benchmarks here for ΔE_{ST} of hypovalent species with experimentally known ΔE_{ST} values or values obtained from converged *ab initio* methods. These include the parent carbene methylene (CBS-QB3 $\Delta E_{ST} = +8.6$ kcal/mol, experimental = +9 kcal/mol[56]), difluorocarbene (CBS-QB3 $\Delta E_{ST} = -56.1$ kcal/mol, experimental = −57 kcal/mol[57]), phenyl carbene (CBS-QB3 $\Delta E_{ST} = +4.5$ kcal/mol, experimental = +2.3 kcal/mol[58]), the parent nitrenium ion NH_2^+ (CBS-QB3 $\Delta E_{ST} = +28.6$ kcal/mol, experimental = +29.9 kcal/mol[59,60]), and the parent phenyl cation Ph^+ (CBS-QB3 $\Delta E_{ST} = -24.9$ kcal/mol, CAS-MP2/6-311+G(3df,2p) = −24.6 kcal/mol[32]). These minimal benchmarks computed for related species lead us to anticipate good quantitative accuracy from this method in the current study. In related studies, this method has also successfully predicted the ground states of simple nitrenes.[61-63] Given that the vinyl

Table 1. Computed Singlet-Triplet Energy Gaps (ΔE_{ST}, kcal/mol), Including Zero-Point Energies for Substituted Vinyl Cations

Compound Number	Z (β)	Y (β)	X (α)	B3LYP/ 6-31G(d,p)	CASPT2/pVTZ// CASSCF/cc-pVTZ	CBS-QB3
					ΔE_{ST}	
1	H	H	H	−41.9	−42.8[a]	−48.5
2	H	H	CH_3	−46.2	−53.2	−52.8
3	H	H	NH_2	−46.4	−51.6	−53.5
4	H	H	F	−31.6	−33.0	−38.5
5	H	H	CN	−30.4		−37.6
6	CF_3	H	H	−40.5		−46.6
7	H	H	CF_3	−39.9		−46.4
8	NH_2	H	CF_3	+5.6		+5.9
9	NH_2	CF_3	H	+7.4		+6.5
10	CF_3	H	NH_2	−45.3		−50.0
11	CH_3	CH_3	CH_3	−31.4	−36.8	−38.1
12	NH_2	NH_2	NH_2	−25.2	--	−30.5
13	CH_3	H	F	−20.2	−26.5	−28.4
14	F	H	CH_3	−19.2	−18.1	−25.5
15	F	F	CH_3	−7.8	--	−12.9
16	OH	H	H	−2.4[c]	−3.3	Nsm[d]
17	F	H	F	−3.1	−5.6	−10.2
18	F	F	F	+2.9	+3.1	−1.6
19	OMe	H	H	+3.8[c]	+0.3	Nsm
20	NH_2	H	H	+3.8[c]	+6.0	Nsm
21	F	F	H	+4.6	+5.8	+0.1
22	NH_2	H	F	+5.5	+9.9	+2.0
23	NMe_2	H	H	+11.1	+11.9[b]	+8.2
24	NH_2	NH_2	H	+17.1[c]	+14.1	Nsm

[a] CASPT2(10,10)/pVTZ. [b] ZPVE added at CASSCF/cc-pVDZ level. [c] Single-point calculation at CASSCF/cc-pVTZ geometry (singlet rearranges spontaneously at DFT level; see discussion vide infra). Dashes indicate that we were unable to obtain a converged CASSCF solution for these ions. [d] Nsm = No singlet minimum energy structure was located. Negative values for the ΔE_{ST} indicate a singlet ground state.

cations in the following study are well-described using a single-reference wave function, this method may in fact yield better quantitative estimates of the ΔE_{ST} than even the CASPT2 method.

While both the CASSCF and CBS-QB3 models are rigorous computational methods, DFT has also shown to be quite robust for predicting relative energies of many hypovalent species that have wave functions consisting of primarily a single closed-shell determinant. Since DFT can be employed at a fraction of the computational cost of the CASPT2 and CBS-QB3 calculations, this method is applicable to larger systems of interest that are intractable at the higher levels of theory. Thus, we also chose to model these vinyl cations using DFT, employing the hybrid B3LYP functional along with the polarized valence double-ζ 6-31G(d,p) basis set, benchmarking the performance of this functional in smaller systems against the CBS-QB3 and CASPT2 results.

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Table 2. Key Geometric Parameters[a] for Singlet and Triplet State Vinyl Cations

|	Z (β)	Y (β)	X (α)	Singlet r_0	Singlet a_0	Singlet ω	Triplet r_0	Triplet a_0	Triplet ω
1	H	H	H	1.262 (1.270)	180.0 (179.9)	0.0 (0.0)	1.400 (1.385)	137.6 (133.8)	0.0 (0.0)
2	H	H	CH$_3$	1.274	178.2	0.3	1.396	141.1	0.01
3	H	H	NH$_2$	1.273	179.8	0.0	1.389	136.6	0.00
4	H	H	F	1.270	180.0	180.0	1.410	127.1	0.0
5	H	H	CN	1.276	180.0	0.0	1.362	179.0	0.0
6	CF$_3$	H	H	1.253	178.8	120.2	1.391	137.3	3.04
7	H	H	CF$_3$	1.267	175.8	179.7	1.396	133.9	1.60
8	NH$_2$	H	CF$_3$	1.343	135.2	92.4	1.391	133.4	180.0
9	NH$_2$	CF$_3$	H	1.330	145.9	85.1	1.387	136.9	180.0
10	CF$_3$	H	NH$_2$	1.289	178.9	18.7	1.390	136.0	0.0
11	CH$_3$	CH$_3$	CH$_3$	1.279	179.1	179.9	1.402	141.5	1.8
12	NH$_2$	NH$_2$	NH$_2$	1.446	120.4	93.4	1.435	125.7	0.0
13	CH$_3$	H	F	1.272	179.8	0.0	1.407	123.2	0.0
14	F	H	CH$_3$	1.306 (1.320)	179.8 (122.8)	0.0 (0.0)	1.392 (1.426)	141.9 (120.4)	0.0 (0.0)
15	F	F	CH$_3$	1.323	174.8	178.6	1.391	140.2	0.0
16	OH	H	H	-- (1.317)	-- (172.0)	-- (180.0)	1.394 (1.407)	138.3 (131.5)	0.0 (0.0)
17	F	H	F	1.304	173.1	0.00	1.414	125.1	0.0
18	F	F	F	1.439 (1.444)	127.4 (130.1)	103.1 (103.6)	1.416 (1.431)	125.2 (124.0)	0.0 (0.0)
19	OMe	H	H	-- (1.342)	-- (139.4)	-- (101.0)	1.389 (1.412)	138.3 (131.2)	0.0 (0.0)
20	NH$_2$	H	H	1.309 (1.338)	142.4 (137.1)	116.8 (105.6)	1.386 (1.411)	140.0 (132.3)	0.0 (0.0)
21	F	F	H	1.338 (1.344)	156.2 (177.5)	92.9 (90.3)	1.402 (1.409)	136.9 (129.9)	0.0 (0.0)
22	NH$_2$	H	F	1.421 (1.552)	123.9 (106.5)	−103.1 (−180.0)	1.392 (1.407)	126.4 (123.9)	180.0 (180.0)
23	NMe$_2$	H	H	1.359 (1.438)	126.7 (111.5)	114.4 (108.8)	1.371 (1.407)	143.7 (135.3)	0.0 (−1.3)
24	NH$_2$	NH$_2$	H	-- (1.471)	-- (109.0)	-- (109.8)	1.422 (1.445)	136.6 (130.0)	0.0 (0.0)

[a] The C=C bond distance is given as r_0 (Å), a_0 is the C−C−X bond angle (deg), and ω_0 is the Y−C−C−X torsional angle (deg). See Figure 4. [b] Values in parentheses are from CASSCF optimizations; dashes indicate that no geometric information is available by this method due to facile rearrangements.

All DFT calculations were performed using the Gaussian03 software suite employing the B3LYP functional[69−71] along with the 6-31G(d,p) basis set. Geometries, energies, and analytical frequencies were calculated at this level of theory. In all cases, optimized geometries were found to have zero imaginary frequencies, and corrections for the zero-point vibrational energy were added unscaled. Computed transition state structures had one imaginary frequency that connected the starting structure and product. CASSCF optimizations were performed using Gaussian03,[72] but CASPT2 calculations were accomplished with the Molcas software.[73,74]

Given that the CASSCF calculations show that all the singlet states for these vinyl cations consist almost entirely of a closed-shell determinant (weights greater than 0.85 for the principal closed-shell determinant were observed for all singlet states computed at the CASSCF level) and that an open-shell configuration mixed negligibly with the ground-state wave function (often the open-shell configuration was of a different state symmetry), we elected to use restricted DFT energies and geometries for the singlet states (we performed unrestricted singlet computations in a few select cases; these can be found in the Supporting Information).

2.2. Computational Results. Studies of simple vinyl cations, for which the accurate CASPT2 and CBS methods could be applied, are summarized in Tables 1 and 2. Many obvious cases (e.g., 2-fluorovinyl cation, 2-methylvinyl cation, 2,2-bis(dimethylamino)vinyl cation) could not be included in these tables because we were unable to locate a singlet minimum corresponding to the desired vinyl cation structures. These rearrange-
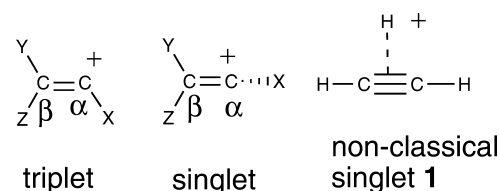
Figure 2. Approximate geometries of singlet and triplet states.
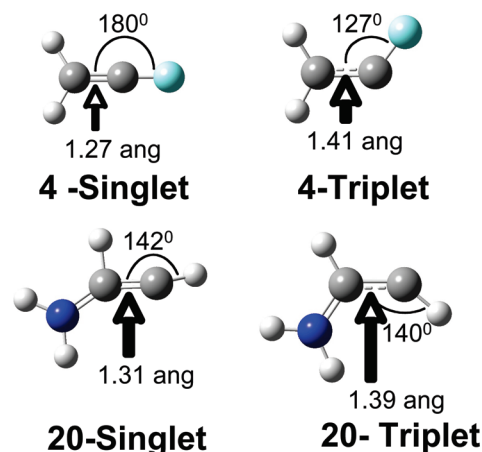
Figure 3. Equilibrium geometries for the singlet and triplet states 1-fluorovinyl cation (**4**) and 2 aminovinyl cation (**20**). With the exception of **20** singlet, each structure is planar. In the case of **20** singlet the α-H atom lies below the plane. (The bond orders depicted here do not denote a pentavalent carbon but rather derive from arbitrary bond distances used by the Gaussview program to generate a visual approximation of the bond order.)

ment processes are detailed in a subsequent section. Figures 2 and 3 illustrate geometries of vinyl cations for the general cases and selected examples, respectively. The parent cation (**1**), in particular, has been examined in some detail. For this simplest vinyl cation, both classical and nonclassical structures (Figure

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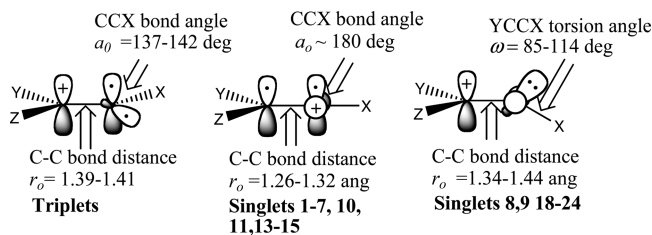
**Figure 4.** Approximate vinyl cation electron configurations.

2) are minima on the singlet surface, with the latter being slightly lower in energy. The calculations carried out in this study are generally in good agreement with previous results (see Supporting Information for a more detailed discussion). Other than **1**, only one minimum for each of the cations listed in Tables 1 and 2 was found on the singlet surface, each corresponding to a classical vinyl cation structure. Attempts to optimize the structures starting from nonclassical geometries resulted in either classical or rearranged structures. Inasmuch as our goal was to characterize the effect of substituents on ΔE_{ST}, we reasoned that the classical singlet structures would serve as an adequate reference for the comparison to the triplet energies and thus did not pursue the search for alternative nonclassical structures in further detail.

The most striking trend is the effect of substituents on ΔE_{ST}. Shown in Table 1 are ΔE_{ST} values for substituted vinyl cations computed using three levels of theory. The parent vinyl cation **1** is clearly a ground-state singlet, with a substantial energy gap. The α-substituted vinyl cations have received most of the experimental attention to date, presumably because substitution at that position is more effective at stabilizing them relative to nucleophilic addition or rearrangement processes. As exemplified by cations **2−5**, **7**, this substitution pattern also provides cations, which, like the parent system **1**, have singlet ground states with substantial energy gaps.

In contrast, switching the donor groups from the α- to the β-position causes a dramatic swing in the ΔE_{ST} in favor of the triplet. For example, α-amino vinyl cation **3** has a ΔE_{ST} of −51.6 kcal/mol; switching the amino group from the α- to the β-position leads to an ion **20** with a ΔE_{ST} of +6.0 kcal/mol—a swing of 57.6 kcal/mol in the ΔE_{ST}! Indeed, the change in the ΔE_{ST} in favor of the triplet for this vinyl cation is sufficiently large that the ground state is computed to be the triplet state for the ion **20**. A similar swing in the ΔE_{ST} in favor of the triplet is observed for the other vinyl cations upon switching the donor substituent from the α- to the β-position.

2.2.1. Comparing the Energies of α- versus β-Substituted Vinyl Cations. Because the α- and β-substituted vinyl cations are isomeric, it is possible to compare the absolute energies of these isomers to ascertain the origin of this change in the ΔE_{ST} upon changing the location of the substituent. Inspection of these absolute energies shows that the swing in the ΔE_{ST} derives *not* from a stabilization of the triplet state upon changing the donor from the α-position to the β-position but rather from a large destabilization of the singlet state. For example, moving an amino substituent from the α-position (**3**) to the β-position (**20**) results in a +58 kcal/mol destabilization of the singlet state. Similar effects are seen with the dimethylamino and methoxy substituents. Singlet β-dimethylaminovinyl cation **23** is +60 kcal/mol (B3LYP) less stable than singlet α-dimethylaminovinyl cation, and singlet β-methoxyvinyl cation **19** is +52 kcal/mol less stable than its isomer α-methoxyvinyl cation. This effect on the singlet states can be rationalized by loss of the resonance

Scheme 1. Comparison of Singlet Stability between α- and β-Substituted Vinyl Cations
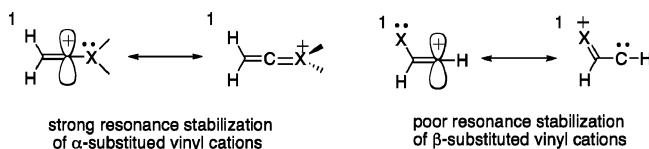
Scheme 2. Comparison of the Triplet States between α- and β-Substituted Vinyl Cations Explains Why These Isomers Exhibit Similar Energies
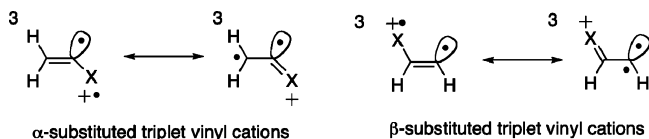
delocalization of the charge onto the substituent that is present in **3**, while requiring **20** to adopt a high-energy singlet carbene configuration. See Scheme 1.

In contrast, the triplet states are relatively insensitive to the location of substituents. The triplet states of the isomeric β-aminovinyl cation **20** and α-aminovinyl cation **3** differ by only 0.1 kcal/mol; likewise, the triplet states of methoxy-substituted **19** and dimethylamino-substituted **23** are, respectively, only 8 and 1 kcal/mol less stable than their α-substituted isomers. The insensitivity of the energy of the triplet species to the location of the substituent can be explained by inspection of the electronic structures of the two triplet isomers (Scheme 2). Irrespective of whether the substituent is located in the α- or β-position, there is a favorable allylic resonance stabilization of these triplet ions. This similar stabilization of both the α- and β-substituted triplet vinyl cations explains why there is so little difference in the energies of these isomeric triplet species.

Unfortunately, a comprehensive study of the energy differences between the α- and β-substituted vinyl cations is hindered by rearrangement processes of some of the singlet cations (described in detail *vide infra*); however, from these examples of vinyl cations that do not rearrange, it seems clear that the large swing in ΔE_{ST} on going from α-substituted vinyl cations to the β-substituted vinyl cations is almost entirely due to the difference in *singlet* stability between the two isomers and is not significantly effected by a change in the triplet state energy.

In fact, with the strongest β π-donors seen in ions **19−24**, the ground state is the triplet state. It is important to note that this conclusion is supported by both single reference B3LYP/ CBS-QB3 calculations and multireference CASPT2 calculations. Notably, there is quite reasonable, albeit imperfect, quantitative agreement among these three methods. Further, adding two donors to the β-position increases the magnitude of this substituent effect. While the β-aminovinyl cation **20** has a ΔE_{ST} of +6.0 kcal/mol, adding a second β-amino substituent **24** increases the ΔE_{ST} to +14.1 kcal/mol. Moreover, while α-substituents have only a modest effect on the ΔE_{ST}, α-electron-withdrawing groups, such as CF_3 (**5**) and CN (**7**), slightly increase the ΔE_{ST} in favor of the triplet, presumably by lowering the energy of the LUMO. In combination with β-donors this effect can be used to further increase the singlet−triplet gap in favor of the triplet. Thus, while β-amino vinyl cation **20** has a ΔE_{ST} of +3.8 kcal/mol, 2-amino-1-trifluoromethyl vinyl cation **8** has a ΔE_{ST} of +5.6 kcal/mol (B3LYP).

In examples **11−15** it is seen that ions that have donors in both the α- and β-positions generally possess singlet ground

states but feature smaller energy gaps between the singlet and triplet states than the parent system **1**. Ions **16**−**18** are predicted to have singlet and triplet states that are nearly degenerate. In these cases, **16** has only a weakly π-donating OH group and **17** and **18** have donors in both positions.

2.3. Molecular Geometries and Electronic Structure. Table 2 summarizes key geometrical parameters for all of the simple vinyl cations in this study. Representative examples are provided in Figure 3. The triplet states all show qualitatively similar geometries. In all cases the vinyl group is exactly or nearly coplanar with its three substituents. With the exception of β-amino derivatives **12**, **23**, and **24**, the C=C bond distances fall between typical single (1.54 Å) and double (1.32 Å) bond lengths and are thus consistent with the view of formation of a triplet by promoting one electron from the C=C π-orbital into the in-plane nonbonding orbital (Figure 4). The C=C−X bond angles (where X is the α substituent) also support this picture. These values fall into two groups—those vinyl cations with α-fluorine substituents and those without. Those lacking α-fluoro substituents fall into the range 137°−142°. This is similar to the 138° bond angle computed for the vinyl radical (CH$_2$=CH$^\bullet$ UB3LYP/6-31G(d.p)). Fluoro substituents are well-known to increase the degree of p character in their bonding orbitals. Consequently, the bond angles where X = F are 123°−127°, closer to the sp^2 norm of 120°. Indeed, UB3LYP/6-31G(d,p) optimization of the fluorovinyl radical provides a value of 129° for the corresponding bond angle.

The singlet states show a much more diverse range of structures. The parent system **1** and indeed most of the singlet ground state vinyl cations **1**−**7** and **13**−**17** have equilibrium geometries that feature linear or nearly linear C=C−X bond angles, expected from a simple picture of a classical, sp-hybridized vinyl cation. In contrast, those with strong β-donors, **18**−**24**, as well as **8**, **9**, and **12** show more acute bond angles. More interestingly, the X group in these examples with strong β-donors is rotated out of the plane containing C=C, Y, and Z. On the basis of these geometrical considerations, the latter vinyl cations can be regarded as carbenes with cationic substituents, as illustrated in Figure 4. In this case, the out-of-plane geometry maximizes the overlap of the filled carbenoid NMBO with the vacant p-orbital associated with the Z−C−Y bond. This picture is further supported by the C−C bond distances that fall in the range 1.26−1.34 Å for the singlet ground state vinyl cations (**1**−**17**, excluding **12**). The carbene-like vinyl cations include **18** and **22**−**24**. In addition to the nonplanar geometry, these species also have longer C−C bond distances of ca. 1.4 Å.

Several vinyl cations do not conform to these trends. For example, the triamino derivative, **12**, is a ground state singlet, but its singlet state shows geometric characteristics of a ground state triplet vinyl cation. That is, this ion possesses a nonplanar geometry and a long (1.45 Å) C=C bond distance. In this case, the singlet state is probably well described as a carbene. We note that amino-carbene is a ground state singlet due to electron donation from the filled NH$_2$ NBMO into the unfilled carbene p orbital. Cation **12** can thus be regarded as a carbene, wherein the singlet state is stabilized through interaction with the α-amino group.

Of the triplet structures, the β-amino derivatives, **23** and **24**, have the most distinct geometries. The former has a C−C bond length that is shorter (1.37 Å) than that of the other triplets, and the corresponding bond length of the latter is longer (1.42 Å). It appears that **23** represents a cation with more diradical character, and therefore, the C−C bond length is closer to the double bond norm. Indeed, analysis of the Mulliken atomic spin

densities reveals a significant amount of spin on the nitrogen substituent (0.48). In contrast, the diamino cation **24** derivative has significantly less spin density on the two nitrogen substituents (0.13 on each) and, in fact, appears to be more carbene-like with a spin density of 1.85 on the α-carbon. Thus, the C−C bond distance in **24** is close to the single bond norm.

2.4. Facile Unimolecular Singlet Rearrangement Processes. While the discovery of vinyl cations that adopt high-spin ground states is interesting from a fundamental point of view, it is also useful to consider the kinetic stability of these ions. Any species subject to rapid unimolecular decay processes will be difficult to characterize experimentally and even less likely to find use in any materials or synthetic applications. In this regard, two sources of kinetic instability need to be considered: that of the triplet state itself as well as the stability of the higher energy singlet state. The former is obviously relevant as these would be the target state for any materials application. The latter is important for two reasons. First, most experimental methods for generating vinyl cations involve ground state reactions of singlet state precursors (e.g., solvolysis of vinyl halides). Such conditions are expected to initially form the singlet vinyl cation, even in cases where this state is higher in energy than the triplet. Thus a highly reactive singlet state could prevent successful generation and application of what would be a stable ground state triplet vinyl cation. Second, even assuming that a triplet vinyl cation can be generated, the presence of an unbound singlet excited state that is relatively close in energy to the triplet ground state could provide an additional pathway for triplet decay via a conical intersection with the singlet surface. While a complete dynamical study of such processes are beyond the scope of this investigation, a computational evaluation of the driving force for the triplet to rearranged singlet state is reported.

2.4.1. Singlet State Stability. As noted in previous studies,[4,5,64] many singlet vinyl cations are unstable to rearrangement processes. A number of vinyl cations are not included in Tables 1 and 2 because it was not possible to identify stationary points on the singlet surface that corresponded to vinyl cation geometries. Figure 5 shows the singlet state input geometries and the optimized minima for several examples. In examples **25** and **26**, a shift of a hydride from the β- to the α-position occurs without a detectable barrier. In contrast, both electron-donating amines (**27** and **28**) as well as electron-withdrawing cyano groups (**29**) minimize to an isomer wherein the β-substituent bridges the two (nominally) vinylic carbons. Finally the 2,2-bis(dimethylamino)vinyl cation (**30**) rearranges by a carbene-like insertion of the α-carbon into the C−H bond of the dimethylamino substituent.

For some of the vinyl cations listed in Tables 1 and 2, minima were found for the singlet states at the CASSCF/cc-pVTZ level but rearrangements were found to occur apparently without a barrier at the DFT level of theory (since CBS-QB3 employs a B3LYP optimization, any structures that rearrange at the B3LYP level likewise rearrange when employing CBS-QB3). This was the case for the hydroxy- **16**, methoxy- **19**, and diamino- **24** substituted vinyl cations. Given that CASSCF is likely a more rigorous model theory than current DFT functionals, and given the propensity of DFT to underestimate reaction barriers, these structures probably have minima on their singlet potential energy surfaces, but with a barrier for rearrangement that is very small. In other cases, such as with the amino- **20** and dimethylamino- **23** substituted vinyl cations, minima were found for the singlets at the DFT level, but the barriers for 1,2-hydride shifts were predicted to be smaller than the zero-point vibrational energy
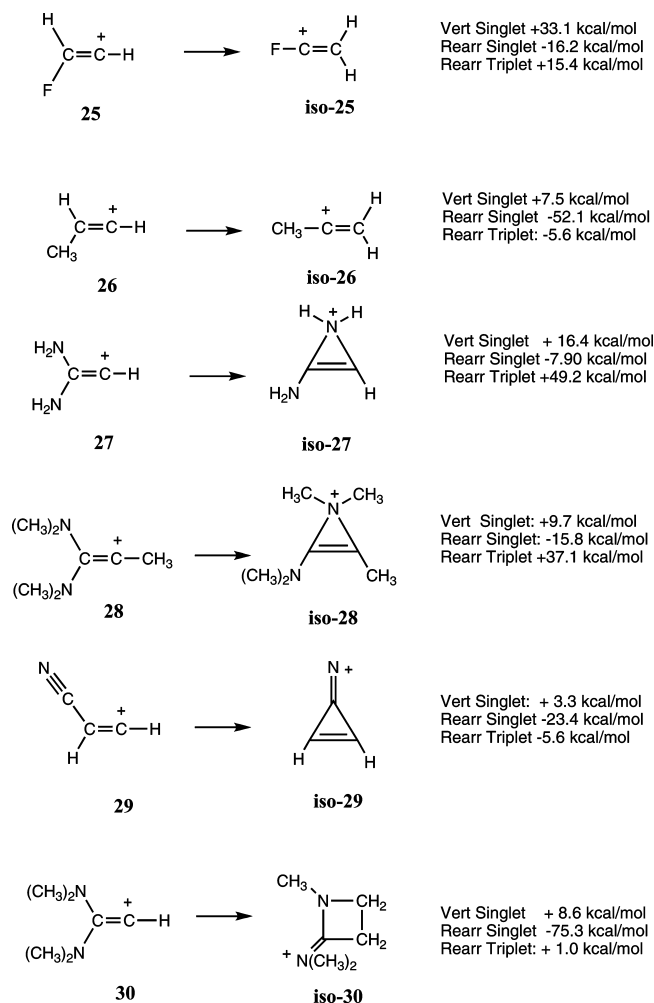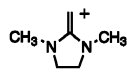
Vert Singlet +33.1 kcal/mol
Rearr Singlet -16.2 kcal/mol
Rearr Triplet +15.4 kcal/mol

25 → **iso-25**

Vert Singlet +7.5 kcal/mol
Rearr Singlet -52.1 kcal/mol
Rearr Triplet: -5.6 kcal/mol

26 → **iso-26**

Vert Singlet + 16.4 kcal/mol
Rearr Singlet -7.90 kcal/mol
Rearr Triplet +49.2 kcal/mol

27 → **iso-27**

Vert Singlet: +9.7 kcal/mol
Rearr Singlet: -15.8 kcal/mol
Rearr Triplet +37.1 kcal/mol

28 → **iso-28**

Vert Singlet: + 3.3 kcal/mol
Rearr Singlet -23.4 kcal/mol
Rearr Triplet -5.6 kcal/mol

29 → **iso-29**

Vert Singlet + 8.6 kcal/mol
Rearr Singlet -75.3 kcal/mol
Rearr Triplet: + 1.0 kcal/mol
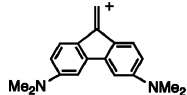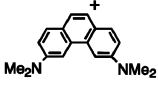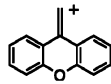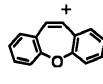
30 → **iso-30**

Figure 5. Driving forces for rearrangement for vinyl cations with no locatable singlet minimum energy structures (triplet vinyl cation minima were found for all species). Vert singlet indicates the vertical singlet−triplet gap from the equilibrium vinyl cation triplet geometry. Rearr singlet refers to the energy difference between the triplet vinyl cation and the rearranged singlet product (iso-X). Rearr triplet refers to the energy gap between the triplet vinyl cation and the rearranged triplet product (iso-X).

(a barrier of 0.1 kcal/mol for **20** and 0.8 kcal/mol for **23**). For those species that were found to rearrange at the DFT level but had minima at the CASSCF level of theory, DFT single-point energy differences were computed at the CASSCF geometries to aid in benchmarking the performance of DFT versus the higher-level methods.

2.4.2. Triplet State Stability. Also shown in Figure 5 are the calculated energy differences for the conversion of the vinyl cation triplet state to the rearranged singlet state. In each case, these rearrangements are found to be exothermic by as much as 75 kcal/mol, although smaller driving forces are seen in other examples. In such situations, it is likely that the lifetime of the desired cation would be very short, creating technical challenges to their characterization.

In contrast, the triplet states are unlikely to rearrange. For example, the adiabatic triplet state hydride shift rearrangement for **20** and **23** are predicted to be slightly exothermic by 0.4 kcal/mol for **20** and 1.0 kcal/mol for **23**, but with very large energy barriers of 56.4 and 54.8 kcal/mol, respectively. Thus, the triplet states are not anticipated to be prone to rearrangements by hydride shifts.

Table 3. Singlet-Triplet Energy Gaps (ΔE_{ST}, kcal/mol, including ZPVE), Singlet State Isomerization Driving Forces (ΔE_{SS}), and Singlet State Barriers for Isomerization ($\Delta E^{\ddagger}$) of Selected 2,2 Cyclic Cations (B3LYP/6-31G**)

Vinyl Cation	Rearranged Isomer	Vinyl Cation ΔE_{ST} B3LYP/6-31G** (CBS-QB3)	ΔE_{SS}	$\Delta E^{\ddagger}$
31		+13.5 (+9.2)	-10.7	+14.9
32		+15.4 (+11.2)	-41.7	+33.5
33		+7.1	-18.5	+23.3
34		+14.3 (+10.0)	-29.6	+2.3
35		+4.6	-16.6	+2.9
36		+17.0	-21.8	+3.2
37		+11.8	-16.3	+2.6

2.5. Incorporating the π-Donors into Rings Discourages Spontaneous Singlet-State Rearrangements. We next turned our attention to vinyl cations having both β-substituents incorporated into a ring. Rearrangement of such species would be expected to provide either a highly strained bicyclic structure or a 1,2-disubstituted cyclic vinyl cation. It was expected that the ring strain associated with these product structures would reduce the driving force for these reactions and, as a consequence, increase the barrier to rearrangement.

Table 3 shows seven examples of 2,2-cyclic vinyl cations along with the corresponding ΔE_{ST} values and associated barriers and driving forces for rearrangement. As seen with the smaller systems in Table 1 adding two heteroatoms to the β-position suffices to make the species a ground state triplet (**31−33**). Methylenecycloheptatrienyl cation **34** was examined because it was assumed that the triplet would be stabilized through delocalization of the positive charge into the cycloheptatrienyl ring. This would create a triplet carbene species with an aromatic cycloheptatrienyl cation substituent (Figure 6).

The calculations confirm these intuitions. In fact, the triplet state of **34** has a vinylic C−C bond distance of 1.39 Å, close to that of a typical single bond. Likewise, the α-carbon shows a spin density of 1.68, which implies a carbenoid structure. The
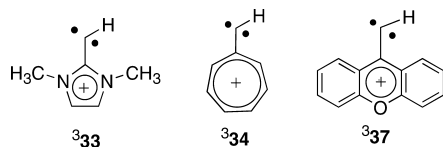
Figure 6. Triplet ions **33**, **34**, and **37** have electronic structures resembling Ar$^+$-substituted triplet carbenes.

fluorenyl vinylidene ion **35** was examined as a counterpoint to the cycloheptatrienyl example—delocalization of the charge into the ring would presumably be disfavored as it would form an antiaromatic ring system. To our surprise, this, too, was computed to be a ground state triplet, although given its lower ΔE_{ST} value and the tendency for DFT to underestimate the singlet stability, it is likely that in this case the singlet and triplet states are nearly degenerate. Analysis of the geometric parameters for the triplet state of this species revealed that this does not form the typical carbenoid triplet structure. Instead, the spin density on the α-carbon is 1.2 and the C–C bond length is 1.33 Å, making it more similar to a delocalized triplet diradical structure. Indeed, substituting this structure with two dimethylamino groups substantially stabilizes the triplet as seen in example **36**.

Example **37** represents an alternative approach to triplet stabilization where the donor substituent is located as part of a xanthyl ring system. It appears that, like the cycloheptatrienyl system, this system, too, experiences stabilization of a carbenoid triplet state. Again, the vinylic C=C distance is 1.38 Å and the α-carbon spin density is 1.59.

For each of the examples in Table 3, there is a significant, though not always large, activation barrier to the rearrangement, $\Delta E^{\ddagger}$. However given the known tendency of DFT methods to underestimate activation barriers, it is likely that these values represent lower limits to $\Delta E^{\ddagger}$.[75] The β-heteroatom-substituted systems **31** and **32** show fairly high barriers to singlet state ring expansion and are thus good candidates for characterization. The vinylic cations **34**−**37**, on the other hand, possess barriers of <4 kcal/mol, suggesting that experimental characterization of the vinyl cations may be difficult, although not impossible.

3. Conclusions

In conclusion, substitution of vinyl cations with β π-donors leads to ions that exhibit a carbene-like triplet state similar to the electronic state of triplet phenyl cations. Should many of

the simple cations **2**−**24** be experimentally generated in the singlet state, spontaneous rearrangements are likely to occur prior to intersystem crossing, although triplet sensitization methods may allow selective generation of the triplet vinyl cations. Vinyl cations with the π-donors incorporated into rings are particularly inviting for experimental studies because these species display fewer obvious singlet rearrangement pathways; these structures may be less prone to rearrangements from the singlet state prior to intersystem crossing to the ground-state triplet surface. Moreover, benchmarks for DFT against the accurate CASPT2 and CBS-QB3 methods show good quantitative agreement and bode well for the use of DFT to compute singlet−triplet gaps in new and/or larger vinyl cations of interest.

A natural question arising from this study is whether the reactions of triplet vinyl cations have unknowingly been observed before. The fluorenylidene vinyl cation **35** is one possible example.[4,66] Attempts to generate **35** via diazotization of the corresponding vinyl amine gave a cyclopropanation product that was attributed to reactions of a vinylidene carbene. Given the significant carbene character that we observe for the triplet vinyl cations in these computations, it seems reasonable that such a triplet vinyl cation intermediate could also account for the observed product. There may be other examples of β-substituted vinyl cations in the literature that may reward re-examination in light of the current study.

While an implicit assumption in the discussion of most intermediate carbocations is that these species adopt closed-shell singlet configurations, recent computational studies performed in our lab[36,67] and others[42,68] have caused us to re-examine this assumption, particularly for charged systems where substitutions with π-donors have been shown to cause dramatic swings in the electronic state orderings. The overriding conclusion from these studies is that a very large singlet−triplet energy gap for the parent system is no guarantee that even simple substituted analogues will remain closed-shell singlet ground state species.

Supporting Information Available: Cartesian coordinates and absolute energies. Unrestricted singlet energies for select ions. Discussion of the nonclassical bridged versus open geometry for **1**. Full citations for refs 72 and 73. This material is available free of charge via the Internet at http://pubs.acs.org.

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