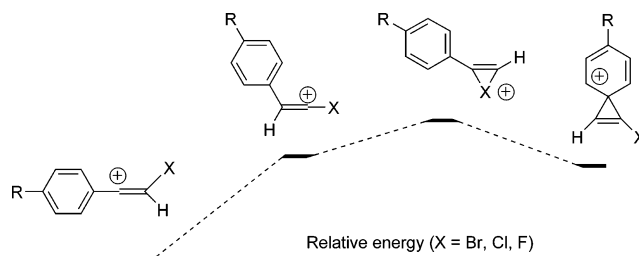# Intermediates of Halogen Addition to Phenylethynes and Protonation of Phenylethynyl Halides. Open Halovinyl Cations, Bridged Halonium, or Phenyl-Bridged Ions: A Substituent Effect Study by DFT and GIAO-DFT

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Relative energy (X = Br, Cl, F)

Formation of α-phenyl-β-halovinyl cation, β-phenyl-α-halovinyl cation, as well as the halogen-bridged and the spirocyclic phenyl-bridged cations as intermediates of protonation of phenylethynyl halides or by halogen addition to phenylethynes was evaluated by DFT at B3LYP/6-31+G(d) and, for comparison in representative cases, by B3LYP/6-311++G(d,p). Relative stabilities of the resulting minima were gauged as a function of substituents on the phenyl group with *p*-OH, *p*-OMe, *p*-H, *p*-CF₃, *p*-CN, and *p*-NO₂ and with *p*-OMeH⁺, *p*-NO₂H⁺, and *p*-N₂⁺. In the majority of cases, the α-aryl-β-halovinyl cations were identified as the most likely intermediates, irrespective of X and for most R groups. For R = *p*-N$_2^+$ (with X = Br and Cl), R = CNH⁺ (with X = Cl), and R = MeOH⁺ (with X = Br), the corresponding β-aryl-α-halovinyl cations become more stable than α-aryl-β-halovinyl cations (but in most cases with a relatively small stability difference). Whereas competitive formation of the spirocyclic aryl bridged cations via this route appears remote, with R = N$_2^+$ and R = NO₂H⁺ as substituents (with X = Br), cyclic halonium ions could intervene, since their relative stabilities are within ∼4 kcal/mol of the lowest energy vinyl cations. Geometrical features, GIAO NMR chemical shifts, and NPA-derived charges were used to gain insight into the structural/electronic features in the resulting mono and dications. The study provides a basis for stable ion and solvolytic/kinetic studies on a series of substituted phenylethynyl halides that are being synthesized.

Introduction

The optimized structure of α-phenylvinyl cation, formed via protonation of phenylacetylene, has a perpendicular conformation, allowing 2p(C⁺) overlap with the π-system, enabling significant conjugative stabilization.[1] The β-phenylvinyl cation (via ionization of β-bromostyrene) undergoes rapid 1,2-hydride shift to form the α-phenylvinyl cation.[1] The corresponding aryl-bridged ion was calculated in an early computational study to lie 16 kcal/mol higher than the α-phenylvinyl cation, and this relative energy difference did not change much in the corresponding *p*-Me and *p*-OH substituted analogues, although as pointed out by Apeloig and Müller in their authoritative review,[1] inclusion of polarization functions into the basis set and electron correlation could influence this outcome.

As elegantly demonstrated by Siehl and associates in their stable ion studies,[2] the presence of a bulky α-aryl substituent
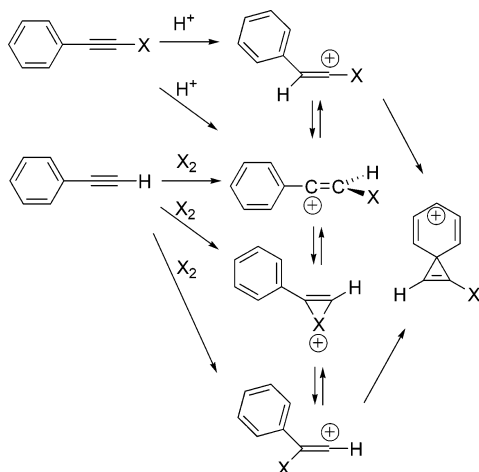

FIGURE 1. Intermediates of halogen addition to phenylethyne and protonation of phenylethynyl halides.

(such a mesityl group) and a β-silyl substituent created a perfect set of conditions for generation and direct NMR study of persistent α-phenylvinyl cations by protonation of phenylacetylenes in superacids. More recently, Müller and associates were able to take stable vinyl cation chemistry to the next level by synthesis and isolation of room-temperature stable vinyl cation salts.[3] In order to achieve this goal, their strategy combined π-delocalization via an α-aryl group bearing suitably stabilizing substituents and hyperconjugation involving β-silyl group(s), with the use of weakly coordinating counterions.

Parallel to experimental advances, the structures, relative energies, charge delocalization modes, and NMR parameters of a number of vinyl cations have been studied computationally via density functional methods.[2,3]

In comparison, however, much less is known concerning the reactive intermediates of halogen addition to phenylalkynes and the interplay among the possible intermediates, namely the α-halovinyl-, β-halovinyl-, the halogen-bridged-, or the spiro-cyclic phenyl-bridged cations, as a function of halogen and the substituents on the phenyl ring (Figure 1). In principle, the same intermediates could be accessible by protonation of phenyl-ethynyl halides. Insight into the relative energies, structures, charge delocalization modes, and NMR parameters of the resulting cations could serve as a guide to the synthesis of suitable precursors for solvolytic and stable ion studies.

It was reported that whereas alkynes with alkyl substituents at the triple bond are more likely to undergo halogen addition via cyclic halonium ions, the open vinyl cations are the key intermediates in halogen addition to 1-phenylpropyne.[4] The tendency for the formation of the open vinyl cation increases as halogen bridging ability decreases in the sequence I > Br > Cl. Charge delocalization into the α-aryl ring confers increased stability to the open vinyl cation.[4] A more recent kinetic study of bromination of α-arylalkynes in ionic liquid solvents by Chiappe and co-workers[5a] pointed to an open vinyl cation in

the case of PhC≡CR and a bridged bromirenium ion with p-CF$_3$−C$_6$H$_4$−C≡CR. A related recent kinetic study on bromination of arylalkynes by Bianchini et al.,[5b] employing a diode-array stop-flow technique, provided evidence for π-complexes as reactive intermediates. A reaction profile for electrophilic addition of bromine to alkynes was postulated, involving exothermic formation of reactive 1:1, followed by a 1:2 alkyne/Br$_2$ complexes from which the open β-bromovinyl cation and the cyclic bromirenium ions are formed.[5b]

We previously reported a DFT study, focusing on the intermediates of halogen addition to alkynes by examining the resulting α-halovinyl cation, β-halovinyl cation, and the bridged halonium ions as a function of alkyne structure and the halogen and their NMR parameters by GIAO-DFT, GIAO-MP2, and by PCM-GIAO calculations.[6] The present study focuses on the intermediates that could be formed by halogen addition to phenylacetylenes or by protonation of phenylethynyl halides, with particular interest in the substituent effects on relative stabilities, in the charge delocalization in the resulting minima, and on the trends in their NMR chemical shifts. We have examined the influence of the substitutents p-OH, p-OMe, p-OMeH$^+$, p-NO$_2$, p-NO$_2$H$^+$, p-CF$_3$, p-CN, and p-N$_2$$^+$ on the relative stabilities of various possible cationic intermediates.

The present study forms the basis for stable ion and solvolytic/kinetic studies on HX addition to phenylethynyl halides and their corresponding para-substituted derivatives, whose syntheses are currently underway in a joint project with the Chiappe laboratory at Pisa.

Results and Discussion

Computational Protocols. Structures were optimized using molecular point groups shown in Tables S1−S7 (Supporting Information) by the density functional theory (DFT) method at B3LYP/6-31+G(d) level using the Gaussian 03 package.[7a] For comparative purposes, several structures (Figure 2) were re-optimized by B3LYP/6-311++G(d,p) (Table S1a), and in selected cases (for X = Br and Cl) by MP2/6-31+G(d) (Table S1b) (Supporting Information).[7b] Computed geometries were verified by frequency calculations. Furthermore, global minima were checked by manually changing initial geometries and by comparing the resulting optimized structures and their energies. NMR chemical shifts were calculated by the GIAO (gauge-including atomic orbital) method at B3LYP/6-31+G(d) level.[8,9] Natural population analysis (NPA)-derived charges were computed at the same level. In selected cases, and for comparison, the GIAO NMR shifts were computed with B3LYP/6-311++G-

(2) Siehl, H. U. In *Stable Carbocation Chemistry*; Prakash, G. K. S., Schleyer, P. v. R., Ed.; Wiley: New York, 1997; Chapter 5.

(3) Müller, T.; Margraf, D.; Syha, Y. *J. Am. Chem. Soc.* **2005**, *127*, 10852.

(4) Carroll, F. A. *Perspectives in Structure and Mechanism in Organic Chemistry*; Brooks/Cole: Pacific Grove, CA, 1998; Chapter 9.

(5) (a) Chiappe, C.; Conte, V.; Pieraccini, D. *Eur. J. Org. Chem.* **2002**, 2831. (b) Bianchini, R.; Chiappe, C.; Lo Moro, G.; Lenoir, D.; Lemmen, P.; Goldberg, N. *Chem. Eur. J.* **1999**, *5*, 1570.

(6) Okazaki, T.; Laali, K. K. *J. Org. Chem.* **2005**, *70*, 9139.

(7) (a) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision B.05; Gaussian, Inc.: Pittsburgh, PA, 2003. (b) Structures proved too large for successful optimization by MP2/6-311++G(d,p).
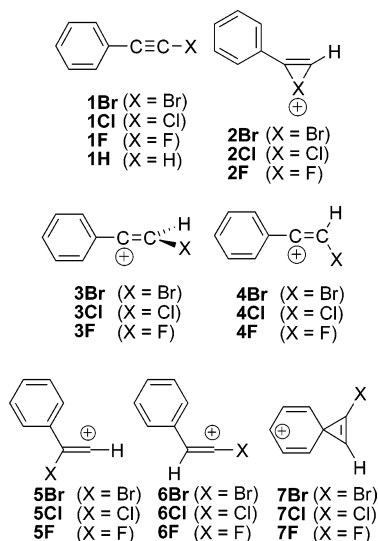
FIGURE 2. Computed phenylethynyl halides and their derived cations.

(d,p) and MP2/6-31+G(d) basis sets. NMR chemical shifts were referenced to CH_3F for $\delta^{13}C$ (71.6 ppm) and $\delta^{19}F$ (−271.9 ppm), calculated with a molecular symmetry of C_{3v} at the same level of theory.

Parent Phenylethyne and Phenylethynyl Halides. Phenylethynes (**1Br**, **1Cl**, **1F**, and **1H**), bridged halonium ions (**2Br**, **2Cl**, and **2F**), α-phenyl-β-halovinyl cations (**3Br**, **3Cl**, **3F**, **4Br**, **4Cl**, and **4F**), β-phenyl-β-halovinyl cation (via 1,2-halogen migration) (**5Br**, **5Cl**, and **5F**), α-halo-β-phenylvinyl cations (via 1,2-hydride shift) (**6Br**, **6Cl**, and **6F**), and the phenyl-bridged ions (**7Br**, **7Cl**, and **7F**) shown in Figure 2 were computed by DFT at the B3LYP/6-31+G(d) level.

Table S1 (Supporting Information) provides the electronic energies (*E*), zero-point energies (ZPE), Gibbs free energies (*G*), and relative Gibbs free energies (Δ*G*) for the optimized structures obtained as minima (no imaginary frequencies), along with their molecular symmetry.

Optimization starting from structures **4Br**, **5Br**, **2Cl**, **5Cl**, and **2F** afforded structures **2Br**, **2Br**, **4Cl**, **4Cl**, and **4F**, respectively. Frequency analysis indicated that vinyl cations **4Cl**, **4F**, **5F**, and **6F** were transition states (with one imaginary frequency).

Among the brominated intermediates, **2Br**, **3Br**, **6Br**, and **7Br** were obtained as minima. As shown in Table S1 (Supporting Information), the open vinyl cation **3Br** is more stable than the halogen-bridged ion **2Br** (by 23.2 kcal/mol). The **3Br** is also more stable than **6Br** and **7Br** (by 17.5 and 16.3 kcal/mol, respectively). The stability order **3Br** > **7Br** > **6Br** > **2Br** was, therefore, established among the four possible minima.

For X = Cl and X = F, the vinyl cations **3Cl**, **6Cl**, and **3F** and the phenyl-bridged cations **7Cl** and **7F** were characterized as minima by frequency analyses, but the cyclic halonium ions **2Cl** and **2F** were not minima. Vinyl cation **3Cl** is more stable than **6Cl** and **7Cl** (by 22.3 and 20.2 kcal/mol, respectively), and **3F** is more stable than **7F** (by 22.3 kcal/mol). Based on

relative energies, the stability orders **3Cl** > **7Cl** > **6Cl** and **3F** > **7F** were clearly established, showing that the α-phenyl-β-halovinyl cations in perpendicular conformation are the preferred intermediates, irrespective of X.

Optimized structures including bond lengths, GIAO-derived NMR chemical shifts, and the NPA-derived charges for cations **2Br**, **3Br**, **6Br**, **7Br**, **3Cl**, **6Cl**, **7Cl**, **3F**, and **7F** are gathered in Figure S1 (Supporting Information). Focusing first on the most favored α-phenyl-β-halovinyl cations, the GIAO chemical shifts for the cationic centers and for the vinylic carbon are progressively deshielded in the order Br < Cl < F, and charge delocalization into the α-phenyl group is clearly evident, with the para carbon becoming deshielded the most in the case of **3F**. The computed C_α chemical shift in **3Br** (δ 254 ppm) is in close range to the experimental value reported by Siehl for the Tol-C^+=CH_2 (δ 250.9 ppm).[2]

In the case of **3Br** and **3Cl**, significant positive charge resides on C_α and on the halogen, but for **3F** the C_α and C_β are both positive. There are no notable changes in bond lengths for the vinyl moiety Ph−C_α^+=$C_\beta HX$ as a function of X.

The less favored α-bromo-β-phenylvinyl cation **6Br** and α-chloro-β-phenylvinyl cation **6Cl** have highly deshielded C^+ carbons (see later comment). Their NPA-derived charges are consistent with strong halonium ion character in these vinyl cations (charge mainly residing on halogen and on C^+).

The halogen-bridged cation **2Br** is unsymmetrical (with C−Br bond lengths of 2.102 and 2.019 Å), with positive charge residing mainly on the bromine and on C_α. The GIAO ^{13}C shifts for **2Br** are at δ 119.5 and 83.7 ppm. Benzenium ion character of the aryl-bridged cations **7Br**, **7Cl**, and **7F** is clearly evident from their GIAO shifts, exhibiting quite deshielded *ortho/para* carbons. The NPA-derived charges indicate that the halogens in **7Br** and **7Cl** bear substantial positive charge. GIAO shifts for the spirocyclic carbons in **7Br**, **7Cl**, and **7F** (δ 73, 71, and 70 ppm) are in close range to the experimental value for this carbon in the parent phenonium ion (no double bond in the three-membered ring), reported at δ 68.8 ppm by Olah et al. in 1977.[10]

To assess the effect of basis set on relative stabilities, structures shown in Figure 2 were recalculated by B3LYP/6-311++G(d,p). Relative energies for the optimized structures are gathered in Table S1a (Supporting Information), showing that the derived stability orders: **3Br** > **7Br** > **6Br**, **3Cl** > **7Cl** > **6Cl**, and **3F** > **7F** remained unchanged.[11] A further assessment of the method dependency was made by re-optimization of the same structures (with X = Br and Cl) at the MP2/6-31+G(d) level (Table S1b, Supporting Information). Relative stability orders **3Br** > **7Br** > **2Br** > **6Br** and **3Cl** > **7Cl** > **6Cl** were established. Given the comparative nature of the present study, and to reduce computational costs, all subsequent calculations were performed by B3LYP/6-31+G-(d).

Substituent Effect Study on Relative Carbocation Stability: (a) 4-Hydroxyphenylacetylene and (4-Hydroxyphenyl)ethynyl Halides. Structures of parent *p*-hydroxyphenylethyne (**1aH**) and (4-hydroxyphenyl)ethynyl halides (**1aBr**, **1aCl**, and **1aF**), the bridged halonium ions (**2aBr**, **2bBr**, **2aCl**, **2bCl**, **2aF**,

(8) (a) Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251. (b) Dichfield, R. *Mol. Phys.* **1974**, *27*, 789.

(9) For representative recent GIAO NMR calculations on carbocations, see: (a) Siehl, H.-U.; Wrcek, V. In *Calculation of NMR and EPR Parameters. Theory and Applications*; Kaupp, M., Bühl, M., Malki, V. G., Ed.; Wiley-VCH: Weinheim, 2004; Chapter 23. (b) Siehl, H.-U.; Müller, T.; Gauss, J. *J. Phys. Org. Chem.* **2003**, *16*, 577. (c) Siehl, H.-U.; Brixner, S. *J. Phys. Org. Chem.* **2004**, *17*, 1039.

(10) Olah, G. A.; Spear, R. J.; Forsyth, D. A. *J. Am. Chem. Soc.* **1977**, *99*, 2615.

(11) (a) Cyclic bromonium ion **2Br**, characterized as a high energy (least favored) minimum by B3LYP/6-31+G(d), was found not to be a minimum by B3LYP/6-311++G(d,p).
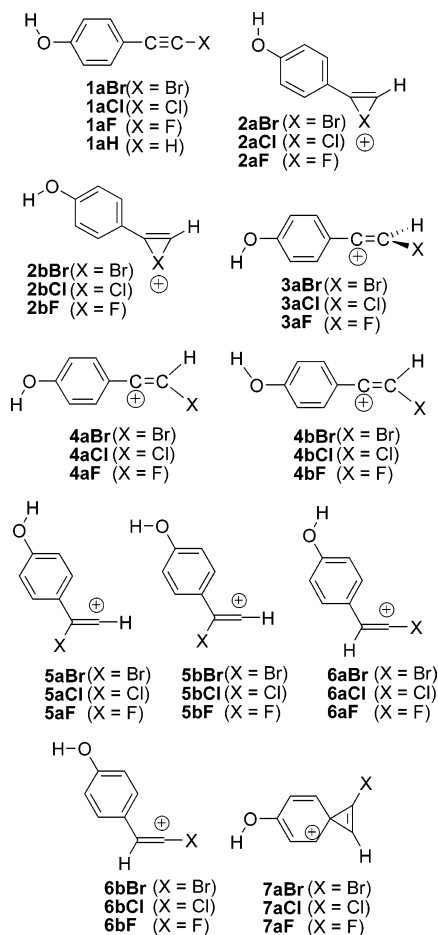
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FIGURE 3. Computed (4-hydroxyphenyl)ethynyl halides and their derived cations.

and **2bF**), open vinyl cations (**3–6**), and the phenyl-bridged cations (**7aBr**, **7aCl**, and **7aF**), shown in Figure 3, were optimized by DFT. Results of electronic energies (*E*), zero-point energies (ZPE), Gibbs free energies (*G*), and relative Gibbs free energies (Δ*G*) of their optimized structures computed as minima by frequency analysis along with their molecular symmetry are provided in Table S2 (Supporting Information).

Among halogen-bridged structures, only the bromonium ions (**2aBr** and **2bBr**) are minima with very similar energies, but the bridged chloronium (**2aCl** and **2bCl**) and fluoronium ions (**2aF** and **2bF**) could not be obtained as final structures. Among the open vinyl cations, **3aBr**, **3aCl**, and **3aF** were calculated to be most favored. Thus, **3aBr** is more stable than **2aBr/2bBr** (by ~30 kcal/mol). The phenyl-bridged ion **7aBr** is ~18.0 kcal/mol less stable, **3aCl** is preferred over **7aCl** by ~22.0 kcal/mol, and **3aF** is 24.0 kcal/mol more stable than the halogen-bridged analog **7aF**.

GIAO-derived NMR chemical shifts, NPA-derived charges, and the optimized structures including bond lengths for **2bBr**, **3aBr**, **6bBr**, **7aBr**, **3aCl**, **7aCl**, **3aF**, and **7aF** are gathered in Figure S2 (Supporting Information). By comparing the GIAO-δ¹³C values and the NPA-derived charges in the series **3aBr**, **3aCl**, and **3aF** with those of **3Br**, **3Cl**, and **3F**, it can be seen that a *p*-OH substituent stabilizes the vinyl cation by enhancing positive charge delocalization into the phenyl ring. A similar effect could be deduced by comparing the GIAO and NPA data for **7aBr**, **7aCl**, and **7aF** with **7Br**, **7Cl**, and **7F**, respectively.
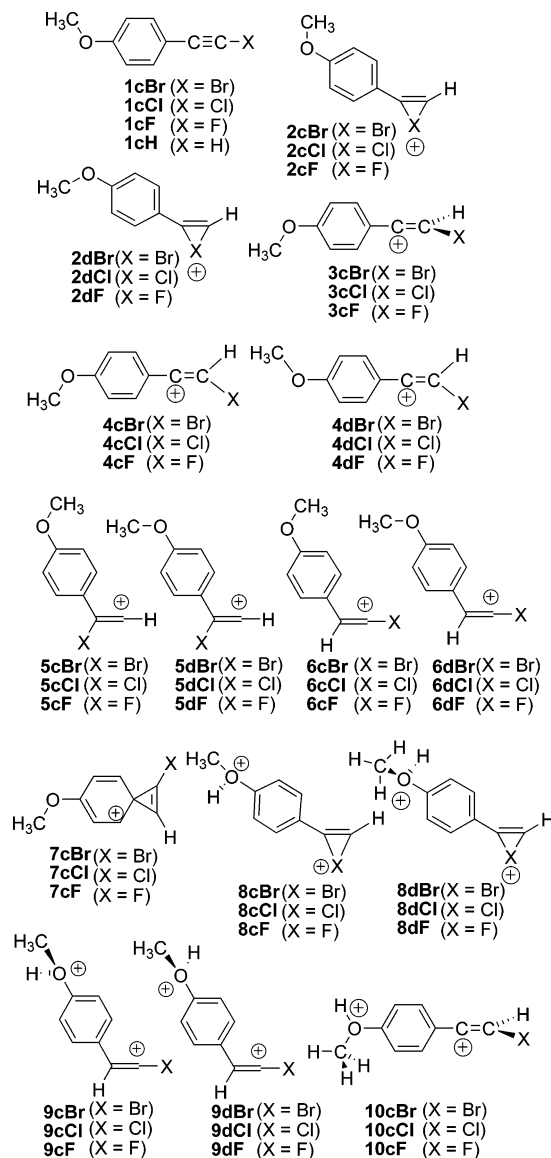

FIGURE 4. Computed (4-methoxyphenyl)ethynyl halides and their derived mono- and dications.

(b) *p*-Methoxyphenylacetylene, (4-Methoxyphenyl)ethynyl Halides, and Their O-Protonated Dications. Structures of anisylacetylenes (**1cBr**, **1cCl**, **1cF**, and **1cH**), halogen-bridged ions (**2cBr**, **2dBr**, **2cCl**, **2dCl**, **2cF**, and **2dF**), the corresponding open vinyl cations (**3–6**), and the anisyl-bridged ions (**7cBr**, **7cCl**, and **7cF**) shown in Figure 4 were optimized by the DFT method at the B3LYP/6-31+G(d) level. Results of the electronic energies (*E*), zero-point energies (ZPE), Gibbs free energies (*G*), and relative Gibbs free energies (Δ*G*) of their optimized structures computed as minima together with their molecular symmetry are gathered in Table S3 (Supporting Information). Structure optimization starting from structures **4cBr** and **4dBr** afforded **2dBr** and **2cBr** as final structures. The structures of **4cCl** and **4dCl** were found to be transition states, but **4cF** and **4dF** were minima (with identical energy) lying 47 kcal/mol higher than **3cF**.

As with the previous two series, among the bridged halonium ions, only **2cBr** and **2dBr** were found to be minima, whereas **2cCl**, **2dCl**, **2cF**, and **2dF** were not minima. Irrespective of X, the most stable monocation intermediates were the α-anisyl-β-

halovinyl cations **3cBr**, **3cCl**, and **3cF**. For X = Br, The anisyl-bridged cation **7cBr** is 18 kcal/mol less stable than **3cBr**, followed by the β-anisyl-α-halovinyl cations **6cBr**/**6dBr** (two conformations) which are an additional 10 kcal/mol less stable, with the bromine-bridged cations **2cBr**/**2dBr** being least favored. For X = Cl, **3cCl** is 22 kcal/mol lower than the anisyl-bridged cation **7cCl**. This preference is somewhat higher with X = F, where **3cF** is more stable than **7cF** by 24 kcal/mol.

As a mimic for superacid protonation chemistry, further O-protonation of the resulting monocations was also considered. Thus, O-protonation of **3cBr**, **3cCl** and **3cF** resulted in dications **10cBr**, **10cCl**, and **10cF** as minima. O-Protonation was also studied in the case of halogen-bridged cations and for other optimized vinyl cations, resulting in dications **8cBr**/**8dBr** and **9cBr**/**9dBr** as minima. It can be seen in Table S3 (Supporting Information) that whereas dications **10cBr** and **9cBr**/**9dBr** are almost equally preferred, the halogen-bridged bromonium/oxonium dications **8cBr**/**8dBr** are clearly less favored. GIAO-derived NMR chemical shifts, NPA-derived charges, and the optimized structures including bond lengths for the mono- and dications **2cBr**, **3cBr**, **6dBr**, **7cBr**, **8dBr**, **9cBr**, **9dBr**, **10cBr**, **3cCl**, **7cCl**, **9cCl**, **9dCl**, **10cCl**, **3cF**, **4cF**, **7cF**, **9cF**, **9dF**, and **10cF** are gathered in Figure S3 (Supporting Information) for comparison.

Computed shifts for the C$^+$ carbons and the para carbons in the α-anisyl-β-halovinyl cations (**3cBr**, **3cCl**, and **3cF**) are at δ 238 and 176 (for X = Br), δ 247 and 177 (for X = Cl), and δ 265 and 178 ppm (for X = F), respectively. These values compare remarkably well with the experimental values for α-anisyl vinyl cation (X = H) reported by Siehl at 239.7 and 184.4 ppm respectively.[2] Charge delocalization into the α-anisyl group is effectively shut down by methoxy protonation. This is nicely manifested in the GIAO shifts, showing that the C$^+$ moves much more downfield while the *para* carbon becomes shielded. The C$^+$ and the *para* carbon chemical shifts for **10cBr**, **10cCl**, and **10cF** are computed at δ 278 and 161 (for X = Br), δ 309 and 162 (for X = Cl), and δ 352 and 165 ppm (for X = F) respectively. The NPA charge maps reinforce this feature, exhibiting greatly increased positive charge at C$^+$ and at halogen and decreased positive charge at the *para* carbon. For **10cF**, positive charge increases at C$^+$, at the *para* carbon and at the vinylic carbon, while negative charge decreases at fluorine, suggesting that O-protonation not only shuts down π-participation, but also decreases fluorine back-bonding. This trend is further reinforced by comparing R = NO$_2$ versus NO$_2$H$^+$ and R = CN versus CNH$^+$ (see further). It is noteworthy though that the computed GIAO-^{19}F shifts, show a shielding effect in going from **3cF** (δ −177) to **10cF** (δ −196)! Given that π-delocalization via the anisyl group is less significant in the halogen bridged cation **2cBr**, as compared to the open vinyl cations, methoxy protonation did not greatly impact the GIAO shifts in this case.

In comparing the computed shifts in the β-aryl-α-halovinyl cations (with X = Br, and Cl), it is quite obvious that GIAO greatly overestimates the C$^+$ chemical shift, and this trend is consistently observed in the series throughout this study (with various para substituents). Kaupp et al.[12] have discussed the importance of spin−orbit (SO) coupling and electron correlation effects on NMR chemical shifts in halomethyl cations CX$_3^+$. They found that SO correction that needed to be applied for X

(12) Kaupp, M.; Malkina, O. L.; Malkin, V. G. *Chem. Phys. Lett.* **1997**, *265*, 55.

= Br was quite considerable. In our previous study of α-halovinyl cations[6] such large overestimations were not found, for example in BrC$^+$=CH$_2$ the computed chemical shift at the cation center varied between δ 311 and δ 288 ppm, as the basis set was augmented systematically from B3LYP/6-31+G(d) to MP2/6-311++G(3df,3dp). It is also noteworthy that the large overestimations, found in the present study in the monocations, disappeared in the dications (compare for example, GIAO C$^+$ between **6dBr** with **9dBr** and between **6Cl** and **9cCl**). For these systems, comparison of the NPA-derived charges seems to be more instructive, clearly showing that a *p*-OMeH$^+$ substituent increases the positive charge at C$^+$ and at halogen.

In a test study (Figure S8, Supporting Information), GIAO shifts were computed by B3LYP/6-311++G(d,p) for several representative open halovinyl cations (**3Br**, **3Cl**, **3F**, **6Br**, **6Cl**, **6bBr**, and **6dBr**) and for the phenyl-bridged cation **7Cl**, identified as minima in this study. Comparison at the two levels indicated limited variations, with the computed values for the C$^+$ in **6Br** and **6Cl** still remaining unusually large! As a final test, GIAO shifts for **3Cl**, **6Cl**, and **7Cl** were computed by MP2/6-31+G(d).[7b] Whereas the computed shift for C$^+$ and for the vinylic carbon in **3Cl** (a representative α-aryl-β-halovinyl cation) by MP2 (δ 255 and 93 ppm) were rather close to those computed by DFT with the same basis set (δ 270 and 103 ppm), a considerably less deshielded value was obtained for the C$^+$ in **6Cl** (a representative α-halo-β-phenylvinyl cation) (δ 316 and 74 ppm). Taken together, the MP2-derived GIAO values appear more realistic, but given that α-aryl-β-halo-vinyl cations are identified as the most likely intermediates (for which DFT and MP2-derived GIAO values were similar in representative cases), considering the comparative nature of this study, and in an effort to reduce computational costs, the bulk of the NMR shift calculations were performed with GIAO-DFT.

As a model for quenching experiments, ease of proton transfer to benzene by dications **10cBr** and **9cBr** was examined via the isodesmic reactions shown in Scheme 1. Whereas proton transfer from the dications to benzene to form benzenium ion and the corresponding halovinyl cations (**3cBr** and **6dBr**) was favorable in both cases, this was more facile with **10cBr**, consistent with the higher stability of **3cBr** relative to **6dBr**.

(c)　　*p*-Nitrophenylacetylene,　　(4-Nitrophenyl)ethynyl Halides, and Their NO$_2$-Protonated Analogues. Structures of *p*-nitrophenylacetylenes, bridged halonium ions, open vinyl cations, and aryl-bridged ions shown in Figure 5 were optimized by the DFT method at the B3LYP/6-31+G(d) level. As a model for superacid protonation of (4-nitrophenyl)ethynyl halides, the derived nitro-protonated dications were also computed (included in Figure 5). Gathered in Table S4 (Supporting Information) are the results of electronic energies (*E*), zero-point energies (ZPE), Gibbs free energies (*G*), and relative Gibbs free energies (ΔG) of their optimized structures computed as minima by frequency analysis along with their molecular symmetry.

GIAO-derived NMR chemical shifts, NPA-derived charges, and the optimized structures including bond lengths for **2eBr**, **3eBr**, **6eBr**, **6fBr**, **8eBr**, **8fBr**, **9eBr**, **9fBr**, **10eBr**, **3eCl**, **6eCl**, **6fCl**, **9eCl**, **9fCl**, **10eCl**, **3eF**, **7eF**, **9eF**, **9fF**, and **10eF** are summarized in Figure S4 (Supporting Information).

As in the earlier cases, the corresponding α-aryl-β-halovinyl cations (**3eBr**, **3eCl** and **3eF**) are most favored. For X = Br, the α-halo-β-arylvinyl cation (**6eBr**) and the bridged halonium ion (**2eBr**) are, respectively, 13 kcal/mol and 20 kcal/mol less stable relative to **3eBr**. The **6eBr** and **6eCl** cations (with C_s

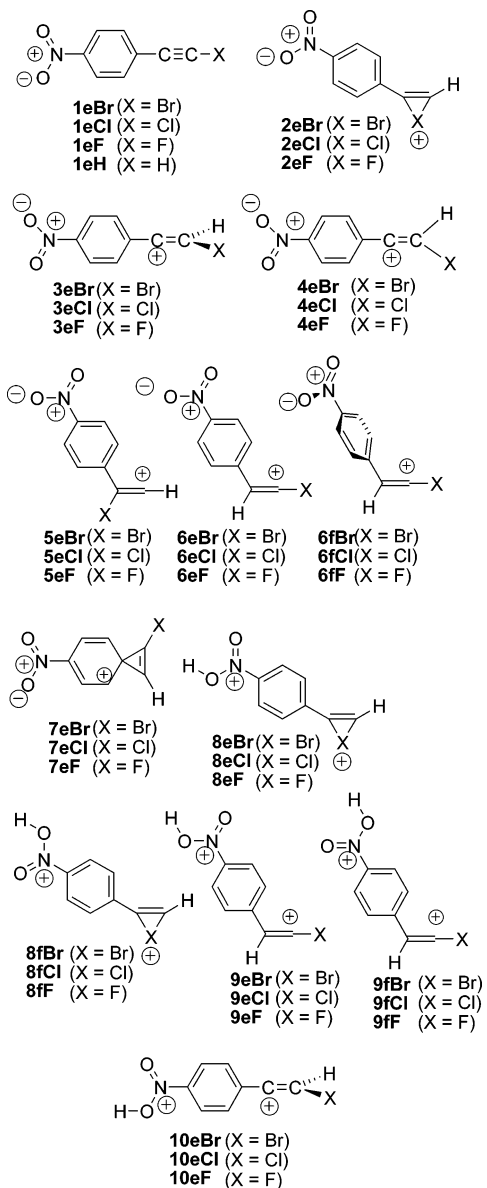**FIGURE 5.** Computed (4-nitrophenyl)ethynyl halides and their derived mono- and dications.

symmetry) are modestly preferable (by 1 kcal/mol) over **6fBr** and **6fCl** (with C_1 symmetry) respectively. For X = Cl, **3eCl** is preferred over **6eCl/6fCl** (by 17 kcal/mol). With X = F, the aryl-bridged cation **7eF** is a minimum, but it is less stable (by 21 kcal/mol) relative to **3eF**.
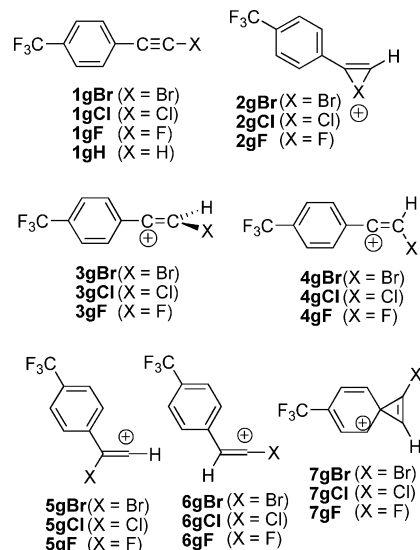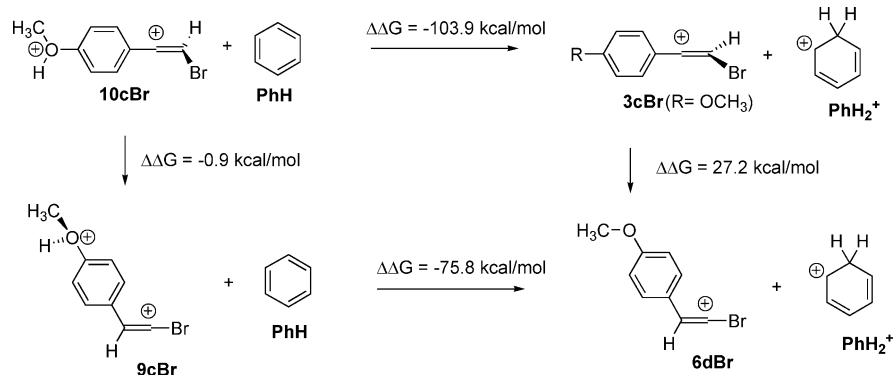
SCHEME 1. Isodesmic Cycle for Proton Transfer to Benzene

FIGURE 6. Computed (4-trifluoromethylphenyl)ethynyl halides and their derived cations.

Whereas nitro substitution seems to have a minimal effect on the GIAO shifts at C^+ in α-aryl-β-halovinyl cations (compare **3Br** with **3eBr** and **3Cl** with **3eCl**), it does induce notable changes when nitro group is protonated. For example, in comparing **3eBr** with **10eBr**, the C^+ is somewhat shielded (δ 261 → 250), but an opposite effect is observed in comparing **10eCl** with **3eCl** (C^+ goes from 280 to 355) and **10eF** with **3eF** (C^+ changes from δ 311 to δ 411). The NPA-derived charges provide a more consistent trend of increased positive charge at C^+ and at halogen (decreased negative charge in the case of X = F) and decreased positive charge at the *para* carbon upon nitro protonation.

(d) *p*-Trifluoromethylphenylacetylene and (4-Trifluoromethylphenyl)ethynyl Halides. Structures of *p*-trifluoromethylphenylethynes, bridged halonium ions, open vinyl cations, and aryl-bridged cations shown in Figure 6 were optimized by the DFT method at B3LYP/6-31+G(d) level. Table S5 (Supporting Information) summarizes the results of electronic energies (*E*), zero-point energies (ZPE), Gibbs free energies (*G*), and relative Gibbs free energies (Δ*G*) of the optimized structures computed as minima along with their molecular symmetry. The GIAO-derived NMR chemical shifts, NPA-derived charges, and optimized structures including bond lengths for **2gBr**, **3gBr**, **6gBr**, **7gBr**, **3gCl**, **6gCl**, **7gCl**, **3gF**, and **7gF** are gathered in Figure S5 (Supporting Information).
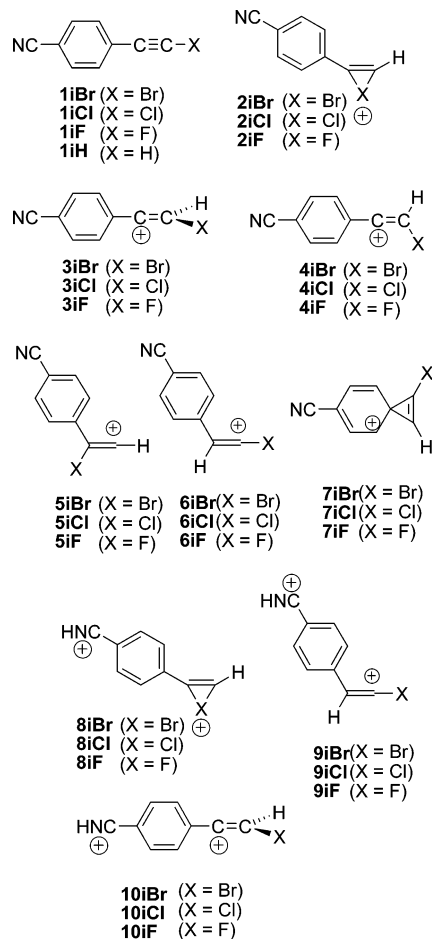
FIGURE 7. (4-Cyanophenyl)ethynyl halides and their derived mono- and dications.

As in earlier cases, the most preferred species, irrespective of X, are the α-aryl-β-halovinyl cations (**3gBr**, **3gCl**, and **3gF**). For X = Br, the β-aryl-α-halovinyl cation **6gBr** and the aryl-bridged cation **7gBr** are 14 kcal/mol and 15 kcal/mol less stable, respectively. For X = Cl, the β-aryl-α-halovinyl cations **6gCl** and the aryl-bridged cation **7gCl** are very close in energy, but are 20 kcal/mol above the vinyl cation **3gCl**. For X = F, the vinyl cation **3gF** is 22 kcal/mol lower in energy relative to the aryl-bridged cation **7gF**.

For X = Cl and X = F, introduction of a *p*-CF$_3$ substituent (**3gCl** versus **3Cl** and **3gF** versus **3F**) slightly deshields the C$^+$ (from δ 270 to 275, and from δ 299 to 307 ppm respectively). This trend is consistent with decreased π-participation. The effect is less pronounced in comparing the GIAO chemical shift for the C$^+$ in **3gBr** and **3Br**. A similar trend is reflected when comparing the NPA-derived charges, showing a more positive C$^+$ in the case of *p*-CF$_3$ analogues.

(e) *p*-Cyanophenylacetylene and (4-Cyanophenyl)ethynyl Halides and Their CN-Protonated Dications. Structures of *p*-cyanophenylethynes, bridged halonium ions, open vinyl cations, and the aryl-bridged ions shown in Figure 7 were optimized by the DFT method at B3LYP/6-31+G(d) level. Results of electronic energies (*E*), zero-point energies (ZPE), Gibbs free energies (*G*), and relative Gibbs free energies (Δ*G*) for the optimized structures computed as minima are gathered in Table S6 (Supporting Information) along with their molecular symmetry.
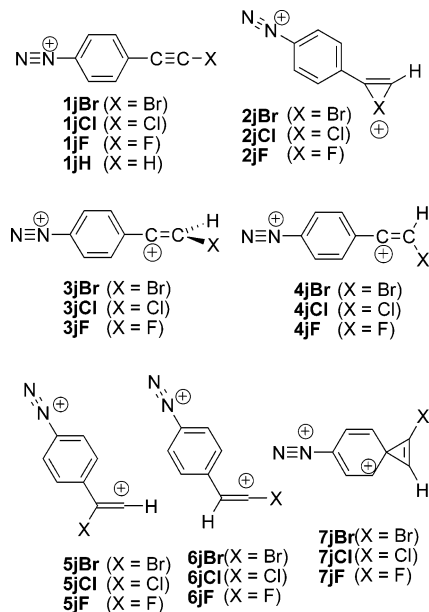

FIGURE 8. Computed *p*-diazoniophenylacetylenes and their derived cations.

In line with the already emerging trend, the corresponding α-aryl-β-halovinyl cations (**3iBr**, **3iCl**, and **3iF**) are favored relative to α-halo-β-arylvinyl cations (**6iBr** and **6iCl**) or to the aryl-bridged cations (**7iBr**, **7iCl**, and **7iF**). Thus, **3iBr** is favored by 16 kcal/mol as compared to **6iBr** and **7iBr** (these have rather close energies), and **3iCl** is 20 kcal/mol more stable than **6iCl** and **7iCl** (these have almost the same energies). For X = F, **6iF** is a transition state to the formation of **7iF**, which is 22 kcal/mol less stable than **3iF**. The GIAO-derived NMR data, NPA-derived charges, and optimized structures including bond lengths for **2iBr**, **3iBr**, **6iBr**, **7iBr**, **3iCl**, **6iCl**, **7iCl**, **3iF**, and **7iF** are sketched in Figure S6 (Supporting Information).

As a model for superacid protonation of the neutral precursors, the nitrile-protonated dications (**8iX−10iX**) were also considered (included in Figure 7 and Figure S6 and Table S6, Supporting Information).

Introduction of the *p*-CN group reduces aryl π-participation and increases the chemical shift of the vinyl cation. Magnitude of this deshielding increases in the sequence F > Cl > Br. Protonation of the nitrile group deshields the C$^+$, and this effect is most pronounced for X = F (compare **3iBr** with **10iBr**, **3iCl** with **10iCl**, and **3iF** with **10iF**). The corresponding NPA-derived charges also indicate significant increase in the positive charge at C$^+$ and on X (Br, Cl) upon CN protonation. With X = F, fluorine bears negative charge, and this decreases in going from **3iF** to **10iF**.

(e) *p*-Diazoniophenylethynes and (4-Diazoniophenyl)ethynyl Halides. Structures of *p*-diazoniophenylacetylenes, bridged halonium ions, and the open vinyl cations shown in Figure 8 were optimized by the DFT method at B3LYP/6-31+G(d) level. Table S7 (Supporting Information) summarizes the data on electronic energies (*E*), zero-point energies (ZPE), Gibbs free energies (*G*), and relative Gibbs free energies (Δ*G*) for the optimized structures computed as minima along with their molecular symmetry. The aryl-bridged dications (**7jBr**, **7jCl**, and **7jF**) were found not to be minima. The GIAO-derived NMR chemical shifts, NPA-derived charges, and optimized structures including bond lengths for dications **2jBr**, **3jBr**, **6jBr**, **3jCl**,

6jCl, **3jF**, and **6jF** are collected in Figure S7 (Supporting Information).

Remarkably, in this case (with X = Br and Cl), the corresponding α-halo-β-arylvinyl cations **6jBr** and **6jCl** become more stable than the α-aryl-β-halovinyl cations **3jBr** and **3jCl** (by 9.0 and 5.0 kcal/mol, respectively), whereas with X = F, the opposite relative stability order is seen, i.e., **3jF** > **6jF** (by 7 kcal/mol). For this class of dications, the corresponding bridged halonium ion **2jBr** is minimum but is 14 kcal (X = Br) less stable relative to the most favored dication. Increased stability of the α-halo-β-arylvinyl cation in this case is probably related to the powerful mesomeric electron-withdrawing effect of the $-N_2^+$ substituent. Comparing the NPA-derived charges between **3X** and **3jX** (X = Br, Cl, F) indicates that the $-N_2^+$ group causes significant increase in the positive charge at C^+ and at Br and Cl (with X = F negative charge at fluorine decreases).

Comparative Discussion

In the present study, the formation of four possible classes of carbocations namely the α-aryl-β-halovinyl-, β-aryl-α-halovinyl- the halogen-bridged, and the spirocyclic aryl-bridged cations was considered as intermediates via protonation of phenylethynyl halides. The resulting minima were characterized and their relative energies were compared as a function of the para substituents and the halogen.

Chart S1 (Supporting Information) provides a compilation summary of the $\Delta\Delta G$ values for all species characterized as minima in this study. It can be seen that the corresponding α-aryl-β-halovinyl cations are most preferred, usually by a significant margin relative to alternatives, except in a few cases (discussed further), and this feature is observed irrespective of X and the substituents.

With R = $p\text{-}N_2^+$ (with X = Br and Cl), the corresponding β-aryl-α-halovinyl cations become more stable. A similar effect was observed with $p\text{-}CNH^+$ (with X = Cl) and with $p\text{-}MeOH^+$ (with X = Br), but in these cases the β-aryl-α-halovinyl cations are only marginally more stable. This leads to the conclusion that the most plausible persistent cations to be formed via protonation of p-substituted phenylethynyl halides are the α-aryl-β-halovinyl cations, barring any unusual solvation effects that could possibly interchange relative stabilities. Preference for the formation of β-aryl-α-halovinyl cations in the observed cases, likely stems from very powerful electron withdrawing effects of these substituents ($-N_2^+$, $-CNH^+$, $-OMeH^+$), destabilizing the α-vinyl cation. It is noteworthy that with powerful electron withdrawing substituents (when X = Br), the energy difference relative to the corresponding halonium ions is relatively small, and this could be taken as an indication for onset of halogen participation with increasing electron demand.

Comparative trends, monitored via GIAO NMR chemical

shifts and via changes in the NPA charges, are in agreement with variation in the electronic effect of the aryl group. Chart S2 (Supporting Information) was generated to focus attention on the GIAO NMR trends as a function of the substituents, showing for the most part, the expected trend of shielding of C^+ with electron-donating groups and deshielding by electron-withdrawing substituents. It is notable that for a given halogen, the vinylic carbon exhibits limited sensitivity to substituent effects (for example: 6 ppm deshielding in going from R = OMe to R = $OMeH^+$). Also notable are substituent effects on the fluorine shifts. Introduction of electron donating groups, i.e., increased π-participation resulted in fluorine deshielding, whereas strongly electron withdrawing groups caused fluorine shielding (see Chart S2, Supporting Information).

An opposite trend emerges by considering the NPA charges, showing that fluorine becomes more positive (less negative) with highly electron withdrawing substituents. This implies that fluorine back-bonding increases with increasing electron-demand at the vinyl cation. Consideration of the C−F bond lengths reinforces this argument, showing shorter C−F bond with increasing electron-withdrawing power of the substituent (with $-OMeH^+$, NO_2H^+ and $-N_2^+$ as substituents, the vinyl cations computed to have the shortest CF bonds). Similar arguments could be made with X = Br and X = Cl, where the positive charge on halogen increases with increasing electron demand, but in these case, the accompanying C−X bond length variations are less noticeable.

Chart S3 (Supporting Information) is designed to focus attention on the structures of spirocyclic aryl-bridged cations as a function of the substituent and halogen. It is noteworthy that the three-membered ring becomes more unsymmetrical and the Ph−CX bond (b bond in Chart S3, Supporting Information) becomes longer/weaker, in going from electron-donating to electron-withdrawing substituents, this trend is most pronounced for X = Br and Cl (not so with X = F). This finding is consistent with diminished aryl participation with decreasing π-electron density. Judging from the computed relative energies, formation of these species by protonation of arylethynyl halides seems unlikely.