

0.1 mL (0.7 mmol) of triethylamine at 0 °C. After TLC indicated complete reaction (45–75 min), ether was added. The organic phase was washed with aqueous sodium hydroxide, aqueous sodium bicarbonate, water, and brine. Chromatography (4:1 hexane/ethyl acetate) gave the titled product. Using 12.9 mg (16.2 μ mol) of diester ligand **10**, there was produced 31 mg (61% yield) of **36** of 74% ee. Using 12.2 mg (15.5 μ mol) of diamide ligand (+)-**11**, there was obtained 35 mg (71% yield) of **36** of 95% ee. Using 11.2 mg (16.2 μ mol) of diamide ligand **12**, there were obtained 37 mg (75% yield) of **35** of 73% ee and, in a second run, 42 mg (85% yield) of **35** of 78% ee.

The same procedure in an achiral experiment using 4.2 mg (4.06 μ mol) of (dba)₃Pd₂CHCl₃, 6.37 mg (24.3 μ mol) of triphenylphosphine, 51.1 μ L (0.358 mmol) of triethylamine, 50 mg (0.162 mmol) of dibenzoate **28**, and 41.8 μ L (0.324 mmol) of *N*-benzyl-*N*-methylamine in 1.6 mL of THF at 0 °C for 27 h gave 35 mg (70% yield) of racemic titled product: IR (neat) 3062, 2943, 1716, 1452, 1335, 1314 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 8.04 (m, 2 H), 7.59–7.28 (m, 8 H), 6.18 (m, 1 H), 6.07 (m, 1 H), 5.83 (m, 1 H), 3.99 (m, 1 H), 3.64 (d, *J* = 13.2 Hz, 1 H), 3.50 (d, *J* = 13.0 Hz, 1 H), 2.57 (m, 1 H), 2.23 (s, 3 H), 1.95 (dt, *J* = 14.5, 4.4 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 166.6, 139.5, 133.1, 131.7, 130.6, 129.8, 129.1, 128.6, 128.52, 128.48, 127.2, 78.4, 67.8, 58.3, 37.8, 30.2; HRMS calcd for C₂₀H₂₁NO₂, 307.1572, found 307.1573.

Preparation of (S)-O-Methylmandelate Esters of 1-Hydroxy-4-(N-benzyl-N-methylamino)cyclopent-2-ene (37 and 38). A mixture of 19.8 mg (64 μ mol) of the above amino benzoate and 8.1 mg (0.193 mmol) of lithium hydroxide monohydrate in 0.4 mL of ethanol and 0.1 mL of water was heated 7 h at 60–65 °C. After evaporation and chromatography (4:1 ether/acetone) of the residue, 12.2 mg (94% yield) of the alcohol was obtained: IR (neat) 3355 (br, OH), 3050, 2937, 2851, 2792, 1453, 1370, 1358 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.33–7.25 (m, 5 H), 6.02 (m, 1 H), 5.97 (m, 1 H), 4.73 (m, 1 H), 3.78 (m, 1 H), 3.60 (d, *J* = 13.1 Hz, 1 H), 3.46 (d, *J* = 13.1 Hz, 1 H), 2.41 (dt, *J* = 13.9, 7.6 Hz, 1 H), 2.18 (s, 3 H), 1.91 (br s, OH), 1.67 (dt, *J* = 13.7, 4.9 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 139.5, 135.83, 135.77, 129.1, 128.4, 127.1, 75.5, 68.0, 58.6, 38.06, 34.5; HRMS calcd for C₁₃H₁₇NO, 203.1310, found 203.1319.

A solution of 5 mg (24.5 μ mol) of the above alcohol in 0.6 mL of methylene chloride cooled to 0 °C was added to a neat mixture of 8 mg

(0.05 mmol) of (*S*)-*O*-methylmandelic acid, 8 mg (0.04 mmol) of DCC, and 0.1 mg (0.8 μ mol) of DMAP at 0 °C. After stirring 24 h at 0 °C and allowing the reaction to warm to room temperature, ether was added. The organic phase was washed with aqueous sodium hydroxide, aqueous sodium bicarbonate, water, and brine. After drying (MgSO₄), evaporating in vacuo, and chromatographing (2:1 hexane/ethyl acetate), there was obtained 7.1 mg (82% yield) of the titled ester. NMR analysis before and after chromatography revealed that the diastereomeric ratio was not altered by this purification.

37: IR (neat) 3030, 2940, 2828, 1746, 1455 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.45–7.22 (m, 10 H), 6.08 (m, 1 H), 5.92 (m, 1 H), 5.61 (m, 1 H), 4.74 (s, 1 H), 3.85 (m, 1 H), 3.43 (d, *J* = 13.0 Hz, 1 H), 3.41 (s, 3 H), 3.23 (d, *J* = 13.3 Hz, 1 H), 2.33 (dt, *J* = 14.8, 8.0 Hz, 1 H), 2.00 (s, 3 H), 1.51 (dt, *J* = 14.8, 4.1 Hz, 1 H); ¹³C NMR (50 MHz, CDCl₃) δ 170.6, 139.5, 138.6, 136.4, 130.9, 129.0, 128.9, 128.8, 128.4, 127.4, 127.1, 82.5, 78.6, 67.7, 58.0, 57.2, 37.7, 29.8; HRMS calcd for C₂₂H₂₅NO₃, 351.1834, found 351.1822.

38: IR (neat) 3030, 2934, 2828, 1745, 1454 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.44–7.25 (m, 10 H), 6.04 (m, 1 H), 5.82 (m, 1 H), 5.57 (m, 1 H), 4.75 (s, 1 H), 3.88 (m, 1 H), 3.47 (d, *J* = 13.2 Hz, 1 H), 3.41 (s, 3 H), 3.36 (d, *J* = 13.2 Hz, 1 H), 2.44 (dt, *J* = 14.7, 8.0 Hz, 1 H), 2.09 (s, 3 H), 1.76 (dt, *J* = 14.6, 4.1 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 170.8, 139.6, 138.5, 136.4, 130.9, 129.1, 128.8, 128.7, 128.4, 127.3, 127.1, 82.7, 78.8, 67.8, 58.1, 57.3, 37.8, 30.1; HRMS calcd for C₂₂H₂₅NO₃, 351.1835, found 351.1841. Anal. Calcd for C₂₂H₂₅NO₃: C, 75.19; H, 7.17; N, 3.99. Found: C, 74.93; H, 7.27; N, 3.77.

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NMR Spectroscopic and Computational Characterization of 1-(*p*-Anisyl)vinyl Cations. Methoxy Group Rotation as a Probe of C _{β} -Si, C _{β} -C, and C _{β} -H Hyperconjugation

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Abstract: The 1-(*p*-anisyl)-2-(triisopropylsilyl)vinyl cation **1** and the 1-(*p*-anisyl)vinyl cation **2** were generated in solution and characterized by NMR spectroscopy. Ab initio molecular orbital calculations using the 6-31G basis set were performed for cation **2**, the 1-(*p*-anisyl)-2-methylvinyl cation **3**, and the 1-(*p*-anisyl)-2-silylvinyl cation **4**, serving as a model cation for **1**, to elucidate the importance of α - π aryl stabilization and β - σ bond stabilization in 1-(*p*-anisyl)vinyl cations with various β substituents. For comparison, the *p*-anisylmethyl cation **5** was also calculated. The para carbon chemical shifts, the experimentally determined and calculated torsional barriers around the phenyl-methoxy C–O bond, and the computed geometrical parameters and charges are used to determine the contributions of conjugative and hyperconjugative stabilization effects in 1-(*p*-anisyl)vinyl cations. The ability of β substituents to hyperconjugatively donate electrons to the empty cationic orbital follows the order silyl > methyl > H.

1-Arylvinyl cations, first postulated in 1964,¹ can be regarded as the prototype of vinyl cations. They have been generated as transient intermediates in solution in the course of solvolysis reactions, electrophilic addition reactions, and photolysis reactions

from various progenitors and have been investigated intensively using mainly indirect techniques like kinetic measurements and product analyses.² Gas-phase investigations³ and several com-

† Yamaguchi University.

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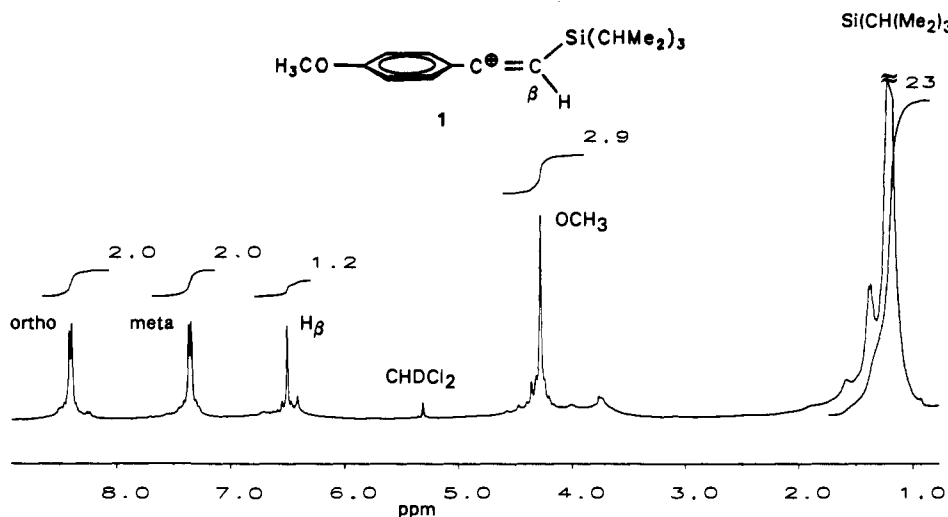


Figure 1. 400-MHz ^1H NMR spectrum of cation **1** at $-120\text{ }^\circ\text{C}$.

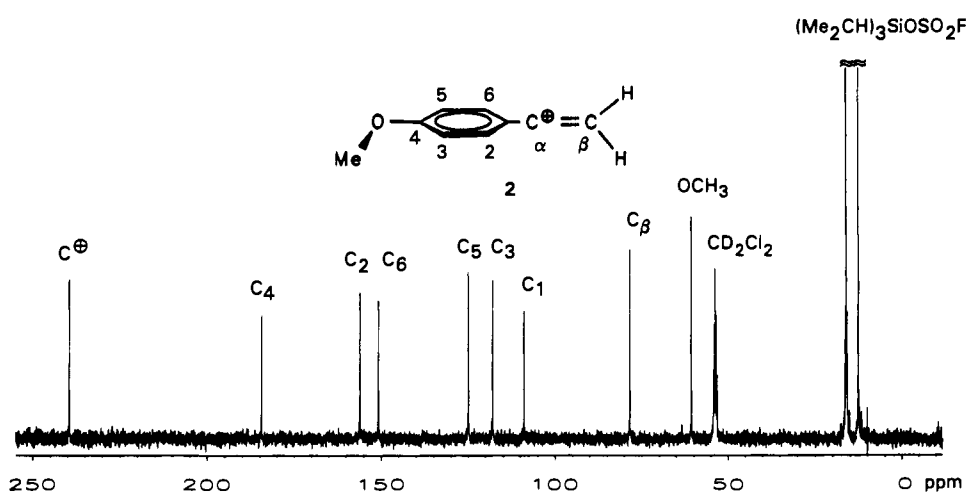


Figure 2. 100.6-MHz ^{13}C NMR spectrum of cation **2** at $-102\text{ }^\circ\text{C}$.

putational investigations^{3,4} of substituted vinyl cations have also been reported. Thus, vinyl cations are by now well-established reaction intermediates. Despite extensive efforts, however, until recently, 1-arylvinyl cations were rather elusive toward NMR spectroscopic observations. Hitherto, only a few other types of vinyl cations could be generated in permanent concentration in solution.⁵ Early attempts to generate persistent 1-(*p*-anisyl)vinyl cations failed.⁶ A claim for having observed 1-phenylvinyl cations⁷ has been disproven by a systematic NMR spectroscopic investigation of the reaction of SbF_6^- with 1-arylvinyl halides in non-nucleophilic media which has shown that heterolytic cleavage of sp^2C -halogen bonds in 1-arylvinyl halides was not achieved under superacid conditions.⁸

Protonation of allenes⁹ or alkynes,¹⁰ except for 1-ferrocenyl-alkynes,¹¹ has also been unsuccessful in yielding stable vinyl cations in solution. Only very recently were persistent vinyl cations, generated by protonation of sterically congested mesitylalkynes with large β -alkyl or β -silyl substituents¹² and from protonation of tetrakis(trimethylsilyl)allene,¹³ characterized by NMR spectroscopy.¹⁴

We report here the first NMR spectroscopic characterization of the so far elusive 1-(*p*-anisyl)vinyl cations in solution and the results of a comparative ab initio structural study which provides

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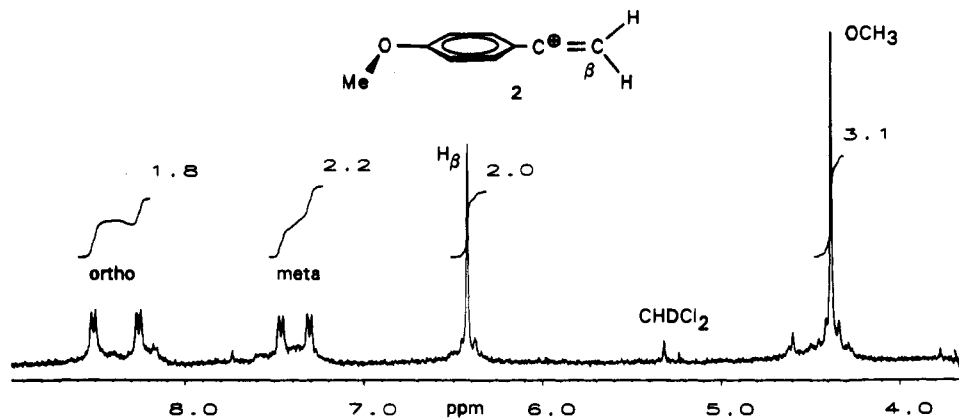
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(14) (a) Earlier attempts at observing β -silyl-substituted carbocations by NMR spectroscopy have failed.^{14b} In contrast to our findings,^{12,13} a recent NMR study^{14c} of 1-adamantyl-2-(trimethylsilyl)allyl cation inferred no stabilizing but some destabilizing effect of a β -silyl substituent. This is due to the orthogonal alignment of the C_β -Si bond and the $2p$ orbital on C^+ and to steric perturbation of allyl resonance in this cation. (b) Olah, G. A.; Berrier, A. L.; Field, L. D.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1975**, *97*, 1845. (c) Prakash, G. K. S.; Reddy, V. P.; Rasul, G.; Casanova, J.; Olah, G. A. *J. Am. Chem. Soc.* **1992**, *114*, 3076.

Table I. ¹H and ¹³C NMR Spectral Data (ppm) for Cations 1 and 2^{a,b}

	C _α	C _β	C ₁	C ₂ /C ₆		C ₃ /C ₅		C ₄	OCH ₃	other
1	209.82	75.94 (179) [6.52]	106.83	151.31 (172) [8.42]		119.69 (172) [7.37]		176.96	59.87 (152) [4.29]	CH 13.18 (115) [1.18] C-Me 17.58 (128) [1.20]
2	239.67	78.37 (176) [6.42]	108.90	156.06 (147) [8.51]	150.85 (173) [8.26]	117.97 (174) [7.30]	124.90 (173) [7.46]	184.39	60.67 (150) [4.37]	c

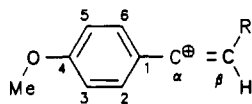
^a δ₁₃C (±0.02 ppm) at -115 °C, in SO₂Cl/SO₂F₂/CDCl₂ at 100.6 MHz; internal reference δ = 53.8 (CD₂Cl₂), ¹J_{CH} coupling constants (±1.8 Hz) in parentheses. ^b ¹H data in square brackets, δ_H (±0.01 ppm) at -120 °C, in SO₂ClF/SO₂F₂/CDCl₂ at 400 MHz; internal reference δ = 5.32 (CHDCI₂). ^c (Si(CH(Me)₂)₃OSO₂F, CH 12.60 (127) [1.60], Me 16.12 (127) [1.24].

Figure 3. 400-MHz ¹H NMR spectrum of cation 2 at -102 °C.

information on the importance of conjugative and hyperconjugative stabilization in β-substituted 1-(*p*-anisyl)vinyl cations. The torsional barrier for methoxy group rotation is used as a probe for the relative charge delocalizing ability of C_β-H, C_β-C, and C_β-Si σ bonds. The experimental and computational results obtained allow for a comparison of the hyperconjugational stabilizing effect of β-silyl, β-methyl, and β-H substituents in this type of carbocation.

Results and Discussion

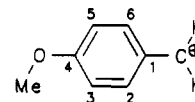
Protonation of 1-(*p*-anisyl)-2-(triisopropylsilyl)alkyne with FSO₃H/SbF₅ at -130 °C using contemporary experimental techniques¹⁵ yields a yellow-green solution in SO₂ClF/SO₂F₂/CD₂Cl₂. The ¹H NMR spectrum initially measured at -120 °C (Figure 1, Table I) shows the clean formation of the 1-(*p*-anisyl)-2-(triisopropylsilyl)vinyl cation 1. When the temperature was raised to approximately 115 °C, a second set of signals appeared which increased in intensity after prolonged time. The ¹³C NMR spectrum measured at -115 °C shows that a mixture of the 1-(*p*-anisyl)vinyl cation 2 and 1 had formed at that temperature. At approximately -100 °C, complete conversion of 1 had taken place, and clean ¹H and ¹³C NMR spectra of 2 were obtained (Figures 2 and 3).



- 1, R = Si(CH(Me)₂)₃
- 2, R = H
- 3, R = CH₃
- 4, R = SiH₃

The vinyl cations 1 and 2 were characterized by their ¹H and ¹³C NMR chemical shifts and coupling constants (Table I). Assignments were done by taking into account the gradually decreasing and increasing intensities of the signals for 1 and 2

in the spectra taken between -120 and -100 °C, using specific ¹H-decoupled ¹³C NMR spectra and by comparing these with the spectra of other vinyl cations.^{5,11-13} The specific assignments of the nonequivalent C₂ and C₆ ortho and C₃ and C₅ meta positions in 2 (Figure 2, Table I) was done analogously to the assignments of cation 5¹⁶ and was confirmed by quantum chemical calculations on model cations (see below).



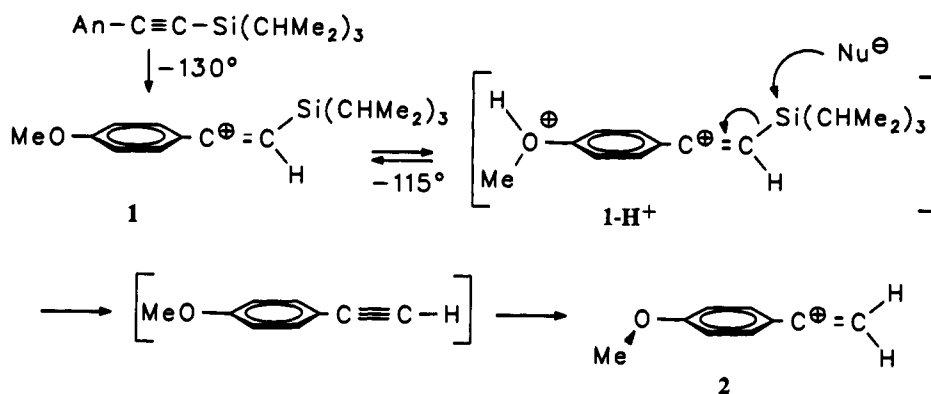
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The generation of persistent silyl-substituted carbocations, like 1, is severely hampered by the reactivity of the silicon center.¹²⁻¹⁴ Due to the high affinity of silicon to oxygen or fluorine, the facile formation of five-coordinated Si intermediates or transition states and the polar nature of the carbon-silicon bond (C^{δ-}-Si^{δ+}), which is further enhanced in β-silyl-substituted carbocations if C_β-Si hyperconjugation is important, the silicon center is prone to attack even by weakly nucleophilic anions of superacids, with subsequent cleavage of the C_β-Si bond. Recently, we showed for the first time that the C_β-Si bond cleavage in carbocations in superacid media can be prevented under appropriate conditions and that direct observation of β-silyl-substituted carbocations by NMR spectroscopy in solution is possible.^{12,13} In a series of β-(tri-alkylsilyl)-substituted 1-mesitylvinyl cations, with alkyl groups of different sizes at silicon, the α-π conjugative stabilization by the aryl group and, thus, also the electron demand, which is put on the silicon by the hyperconjugational electron donation of the C_β-Si σ bond to the formally vacant 2p(C⁺) orbital, is approximately constant. We have demonstrated that in such cases, steric control at the silicon center plays the major role in preventing the S_N2(Si)/C_β-Si bond cleavage reaction.¹² β-Silyl-substituted vinyl cations with more hindered silyl groups are persistent at relatively higher temperatures, and the fragmentation to silicon-free vinyl cations is significantly slowed down compared to that of cations

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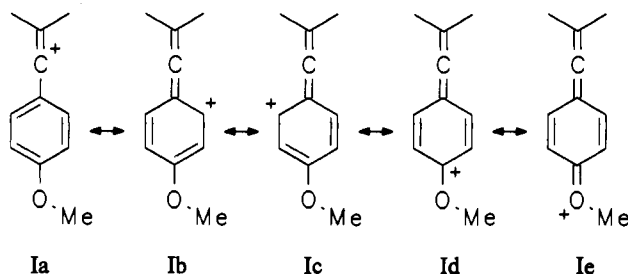
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Scheme I

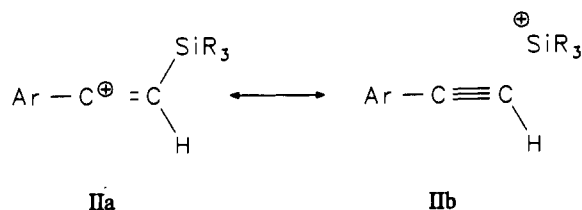


with less bulky alkyl groups at silicon. This shows that the initial attack of the nucleophile is the rate-determining step in the $S_N2(\text{Si})$ reaction in superacids and that this reaction can be controlled by the steric crowding caused by the alkyl groups at silicon.

The easy C_β -Si bond cleavage in the 1-(*p*-anisyl)-2-(triisopropylsilyl)vinyl cation **1** at temperatures at which the corresponding β -(triisopropylsilyl)-substituted 1-mesityl-,¹² 1-(*p*-tolyl)-, and 1-phenylvinyl cations are perfectly stable¹⁷ shows, however, that steric hindrance at silicon is not the only factor controlling the stability of β -silyl-substituted carbocations toward Si_β -C bond cleavage in superacids. The facile formation of **2** from **1** can be explained as follows (Scheme I). The highly sterically hindered alkyne precursor is protonated at -130°C to form the β -silyl-substituted vinyl cation **1** without any apparent formation of side products. At temperatures above approximately -115°C , the large excess of superacid leads to a reversible protonation at the oxygen of the methoxy group to form a double-charged carbo and oxonium cation (**1-H⁺**). This cation is not observed spectroscopically and presumably is only a minor species in equilibrium with **1**. The protonated *p*-OCH₃ group is not a good electron-releasing group. Therefore, resonance structures like **Ia** and **Ie**,



which contribute significantly to delocalizing the positive charge in **1**, are less important for **1-H⁺**. As α - π stabilization of the carbocation center in **1-H⁺** is lower, the demand for charge delocalization by C_β -Si hyperconjugation is higher. Thus, the formal *no-bond* hyperconjugative resonance structure **IIb** gains more



importance, and the partial positive charge at silicon is increased. The silicon therefore becomes more susceptible to nucleophilic attack by the gegenion to form an $S_N2(\text{Si})$ transition state (Scheme I). The subsequent fast cleavage of the C_β -Si bond is facile because the strongly electron-withdrawing vinyl cation moiety is acting as a good leaving group for the formation of the substitution

product $(\text{Me}_2\text{CH})_3\text{SiOSO}_3\text{F}$. The intermediate alkyne, formed in situ, is immediately protonated by the excess superacid to form the silicon-free vinyl cation **2**. The NMR spectra indicate (Figures 2 and 3) that the cleavage reaction proceeds without significant formation of side products. On the other hand, all attempts to generate 1 arylvinyl cations without β substituents by direct protonation of 1-arylalkynes with superacids at low temperatures have led only to rather complex mixtures and partial polymerization, as is evident from NMR spectra. β -Alkyl-substituted 1-(*p*-anisyl)vinyl cations, like **3**, and β -silyl-substituted vinyl cations, such as **1**, but with less bulky alkyl groups at silicon, also could not be obtained from the corresponding alkynes under the experimental conditions used for the generation of **1**. The indirect route to generate α -substituted vinyl cations without β substituents, like **2**, from protonation of 1-aryl-2-silylalkynes, yielding initially α,β -disubstituted vinyl cations, such as **1**, which has a bulky β substituent (thus preventing the otherwise facile electrophilic attack of gegenions at the C^+ carbon), is a favorable pathway for the clean generation of the so far elusive α -arylvinyl cations. The slow cleavage of the C_β -Si bond in **1** at low temperatures leads to the gradual formation of low local concentrations of monosubstituted arylalkyne, preventing cationic polymerization of the alkyne in the highly acidic media. These findings demonstrate, similar to results reported earlier,¹² that the generation of β -silyl-substituted cations in superacids at very low temperatures, followed by controlled β -silyl fragmentation at somewhat higher temperatures, is a new and advantageous method for generating persistent carbocations which otherwise are not accessible.

Discussion of NMR Spectroscopic Results. The ¹³C NMR chemical shifts of the positively charged carbons in **1** (209.8 ppm) and **2** (239.7 ppm) are comparable with the C^+ carbon shift in 1-mesitylvinyl cations with analogous β substituents (207.8 and 238.5 ppm, respectively¹²). The signals for the sp^2 -hybridized β -carbon in **1** (76.0 ppm) and **2** (78.4 ppm) show a doublet ($^1J_{\text{CH}} = 179$ Hz) or a triplet ($^1J_{\text{CH}} = 176$ Hz), respectively, in the proton-coupled ¹³C NMR spectrum. The assignment was confirmed by specific decoupling of the vinylic protons at 6.52 and 6.42 ppm, respectively (see Table I for other ¹H NMR data). The chemical shift of the signals for C_β is in accord with that in other vinyl cations and with IGLO calculations of model vinyl cations.^{5,11-13} A shielding of 5–4 ppm is observed, as compared to the corresponding C_β signals of analogous 1-mesitylvinyl cations (81.1 and 82.3 ppm¹²).

The large upfield shift of about 24–32 ppm for the aromatic C_1 position in **1** (106.8 ppm) and **2** (108.9 ppm) relative to *p*-anisylmethyl (139.7 ppm), 1-(*p*-anisyl)ethyl (136.2 ppm), and 1-methyl-1-(*p*-anisyl)ethyl cations (133.3 ppm),¹⁶ which have an sp^2 -hybridized C^+ carbon, shows the shielding influence of the sp -hybridized C^+ carbon on the shift of the C_1 signals in the vinyl cations **1** and **2**. The shieldings of both signals, that for the olefinic C_β carbon and that for the aromatic C_1 carbon, are characteristic for vinyl cations and, taken together, can be used as a diagnostic tool to prove vinyl cation structures.

The shift of the C^+ carbon signal is not a good choice for use in monitoring the electron demand of the carbocation center in

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1 and **2** and evaluating the effect of a β -silyl group on the positive charge. The chemical shift of the C^+ carbon resonance, aside from the local charge, is also influenced by a substituent effect from the different substitution at C_β . It is well established, however, that the para carbon chemical shift in benzylic-type carbocations is a reliable monitor of the electron demand of the carbocation center and thus should serve as a suitable probe for evaluating the effect of a β -silyl group on a positive charge in 1-arylvinylium cations. The para carbon chemical shifts in the 1-(*p*-anisyl)vinyl cation **2** (184.4 ppm) and in the 1-(*p*-anisyl)ethyl cation (185.6 ppm¹⁶) are similar, suggesting that both cations are stabilized by the β substituents, $=CH_2$ and $-CH_3$, respectively, as compared to the *p*-anisylmethyl cation **5** (188.1 ppm¹⁶), which lacks a β substituent. The signal for the para carbon in the β -silyl-substituted (1-*p*-anisyl)vinyl cation **1** (177.0 ppm) appears approximately 7 ppm upfield compared to the signal in the silicon-free cation **2** (184.4 ppm), indicating a lower demand for charge delocalization onto the aryl ring when the β substituent is changed from β -H to a β -silyl group. This is clear evidence that the β -silyl stabilization effect is operative even in highly conjugatively stabilized carbocations with α -anisyl substituents. The para carbon shift in **1** may be compared with those in 1-phenyl- or 1-cyclopropyl-substituted *p*-anisylmethyl or 1-(*p*-anisyl)ethyl cations (176–181 ppm¹⁶). The similar shifts suggest that the β -silyl stabilization in the vinyl cation **1** is about as efficient in dispersing the positive charge as π conjugation of an additional α -phenyl ring or C–C σ bond hyperconjugation of an additional α -cyclopropyl group in 1-(*p*-anisyl)-substituted carbocations with an sp^2 -hybridized C^+ carbon.

The most pronounced difference between **1** and **2** is that the NMR spectra for **2** show magnetically nonequivalent signals for the C_2 and C_6 ortho and C_3 and C_5 meta carbon and proton signals (Figures 2 and 3), whereas these positions remain equivalent in the 1H and ^{13}C NMR spectra of **1**, even at the lowest accessible temperatures in solution. In 1-(*p*-anisyl)-substituted carbocations exists a torsional barrier for methoxy group rotation around the phenyl- C_4 -oxygen bond which is due to delocalization of positive charge onto the methoxy group, resulting in a partial double-bond character of the C_4 -O bond. This rotational barrier is lower in energy than the other barrier around the C_1 - C^+ bond, which is also present in **1** and **2** as well as in other α -benzyl-substituted cations lacking a C_4 -OCH₃ group. The C_4 -oxygen rotational barrier in sp^2 -hybridized 1-(*p*-anisyl) carbocations has been used to determine the relative electron-releasing properties of α substituents¹⁶ and is used here as a probe for determining the hyperconjugating ability of β substituents in vinyl cations.

The demand for delocalizing positive charge into the aryl moiety is higher in **2** than in **1**, as is evident from the para carbon chemical shifts. In **2**, the enhanced participation of the *p*-methoxy group in delocalizing the positive charge results in higher double-bond character of the phenyl- C_4 -oxygen bond as compared to that of **1**. The contribution of resonance structure **1e** is higher in **2** than in **1**. In the minimum energy conformation of **2**, the O-methyl bond is coplanar with the aryl ring for maximum n - π overlap (see calculational results below). This conformation gives rise to different environments for the ortho and meta positions which are syn (C_2 and C_3) or anti (C_6 and C_5) relative to the orientation of the O-methyl group. In **2**, the rotation of the methoxy group around the C_4 -O bond is slow relative to the NMR timescale, and four distinct resonance lines originating from the two ortho and two meta position are observed (Figures 2 and 3). Above -85 °C, decomposition of the cation occurs, preventing further measurements at higher temperatures. The shift difference for the two ortho and the two meta carbon signals at -116 °C is 5.2 ppm for C_2 and C_6 , and 6.9 ppm for C_3 and C_5 . Kinetic line broadening is observed at temperatures above -116 °C. Rate constants were determined by fitting calculated and experimental spectra using an interactive line shape analysis program.¹⁸ At -100 °C, the energy of activation is $\Delta G^\ddagger = 9.0 \pm 1$ kcal mol⁻¹.

(18) Petillo, P.; Nelsen, S., University of Madison, Wisconsin, private communication.

Table II. Calculated Total Energies and Rotational Energy Barriers (6-31G) of Cation Structures 2–5 and 2-TS–5-TS

	total energy (hartrees)	barrier (kcal mol ⁻¹)
2	-420.461 80	
2-TS	-420.448 57	8.3
3	-459.490 18	
3-TS	-459.477 52	7.9
4	-710.504 51	
4-TS	-710.492 74	7.4
5	-382.638 69	
5-TS	-382.624 06	9.2

Table III. Bond Lengths (Å) of the Aromatic Ring C–C Bonds in 2–5 and 2-TS–5-TS

	C_1 - C_2 / C_1 - C_6		C_2 - C_3 / C_5 - C_6		C_3 - C_4 / C_4 - C_5		
4	1.428	1.433	1.362	1.355	1.411	1.414	
4-TS	1.426	1.426	1.365	1.365	1.405	1.405	
3	1.434	1.439	1.359	1.353	1.415	1.417	1.417
3-TS	1.432	1.432	1.363	1.363	1.407	1.407	
2	1.436	1.441	1.358	1.352	1.417	1.418	
2-TS	1.435	1.435	1.361	1.361	1.409	1.409	
5	1.444	1.447	1.354	1.349	1.422	1.424	1.424
5-TS	1.442	1.442	1.357	1.357	1.414	1.414	

Table IV. Selected Bond Lengths (Å) and Angles (deg) of the Alkyl Part and the OCH₃ Group in 2–5 and 2-TS–5-TS

	C^+ - C_1	C^+ - C_β	C_β -R	C_4 -O	O-CH ₃	C_4 -O-Me
4	1.355	1.275	1.959	1.318	1.455	125.5
4-TS	1.363	1.272	1.956	1.343	1.466	123.2
3	1.346	1.288	1.512	1.314	1.457	125.7
3-TS	1.353	1.286	1.513	1.339	1.468	123.9
2	1.342	1.285	1.075	1.311	1.459	126.0
2-TS	1.348	1.284	1.076	1.336	1.471	124.4
5	1.350			1.305	1.463	126.5
5-TS	1.354			1.329	1.476	125.9

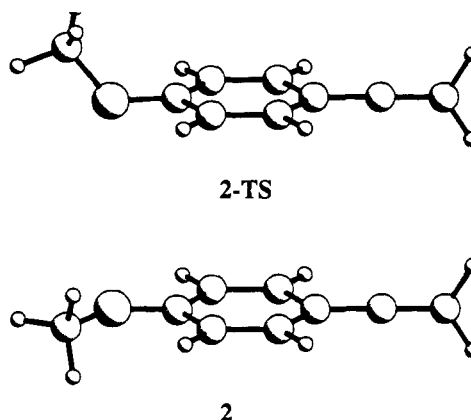


Figure 4. Calculated geometry for cation structures **2** and **2-TS**.

Due to decomposition of the carbocation at higher temperatures, kinetic data could be obtained only over a limited temperature range, thus preventing the determination of the thermodynamic parameters ΔH^\ddagger and ΔS^\ddagger with sufficient accuracy.¹⁹ The fact that the rotation around the C_4 -O bond in **2** is frozen out but is fast in **1** clearly demonstrates that **1** is stabilized by the β -silyl effect as compared to **2**.

Computational Results. In order to confirm the experimental results, we have performed ab initio molecular orbital calculations for cation **2**, the 1-(*p*-anisyl)-2-methylvinyl cation **3**, and the 1-(*p*-anisyl)-2-silylvinyl cation **4**, which served as a model structure for **1**. For comparison, calculations were also performed for the *p*-anisylmethyl cation **5**, which has an sp^2 -hybridized C^+ carbon. The ab initio MO calculations were performed with the Gaussian series of programs using the 6-31G basis set.^{20,21} The geometries

(19) (a) The entropy of activation is expected to be close to zero. (b) Reference 16 and references cited therein.

Table V. Selected Mulliken Charges (Hydrogens Summed into Heavy Atoms) in the Cation Structures 2–5

	4	3	2	5
aryl part	0.693	0.739	0.760	0.724
alkyl part	0.307	0.261	0.240	0.276
ortho (C ₂)	0.248	0.256	0.263	0.214
ortho (C ₆)	0.244	0.251	0.258	0.207
meta (C ₃)	0.010	0.010	0.015	0.029
meta (C ₅)	0.047	0.048	0.052	0.067
para (C ₄)	0.508	0.514	0.518	0.519
methoxy CH ₃	0.489	0.496	0.501	0.514

for structures 2–5 and for the transition-state structures 2-TS–5-TS for the rotation of the methoxy group around the C₄–oxygen bond were both optimized using the energy gradient method and verified by vibration frequency calculations to be minima or transition states, respectively.

The energies for 2–5 and 2-TS–5-TS are listed in Table II, and selected geometrical parameters are in Tables III and IV. Figure 4 shows, as an example, the calculated geometries for 2 and 2-TS. In the vinyl cations 2–4, the C_β–R bond is confined in the same plane with the formally vacant 2p(C⁺) orbital, allowing optimum overlap with the p orbitals of the aromatic π system as well as with the C_β–R σ bond. The torsion angle (R_β–C⁺–C₁–C₂) between the C_β–R bond and the plane of the aryl ring is calculated to be 90° in 2 and 3 and 87° in 4. The bonds to the C⁺ carbon in 2–4 are calculated to be colinear, except for very small deviations from linearity in 3 and 4 (most noticeable in 4 (~1°)), which are due to lower symmetry caused by the β-monosubstitution. The calculations show that in the most stable conformation for the vinyl cations 2–4 and also for 5, the O–methyl bond of the C₄–OCH₃ group is coplanar with the aryl ring (torsion angle C₃–C₄–O–CH₃ = 0°) because of the contributions of resonance forms Ie. The decrease of the C₄–OMe bond distance in 4 (1.318 Å), 3 (1.314 Å), 2 (1.311 Å), and 5 (1.304 Å), and a concomitant increase

in the C₄–O–Me bond angles and lengthening of the O–Me bonds demonstrate that charge dispersal to the *p*-methoxy group becomes more important as hyperconjugative interaction of the formally vacant 2p(C⁺) orbital with the β–σ bond is decreasing in the order 4, 3, and 2, where the β substituent changes from β–SiH₃ to β–CH₃ and β–H, and is most pronounced in the *p*-anisylmethyl cation 5, which lacks β–σ stabilization. This confirms the interpretation of the experimental data that even in highly π-stabilized α-anisyl carbocations, β–σ bond hyperconjugation contributes to the dispersal of positive charge. The calculated data also confirm the relative order of the hyperconjugational electron-donor ability of β–σ bonds to be C–Si > C–C > C–H. A corresponding shortening of the C₁–C⁺ bond length is found for the vinyl cations in the order 4 (1.355 Å), 3 (1.346 Å), and 2 (1.342 Å), due to more charge delocalization onto the aryl ring and, thus, an increasing double-bond character of the C₁–C⁺ bond. The C₁–C⁺ bond length in cation 5 (1.350 Å) cannot be directly compared, since the C⁺ carbon is sp² hybridized.

The calculated bond lengths for the aromatic C–C bonds in the optimized structures 2–5 show the nonequivalence of the bonds in syn and anti orientation to the OCH₃ group. The anti bonds C₁–C₆ and C₄–C₅ are slightly longer than the syn-oriented bonds C₁–C₂ and C₃–C₄, and the anti C₅–C₆ bonds are slightly shorter than the syn C₂–C₃ bonds. Bond alternation for the aromatic C–C bonds indicates major contributions of resonance structures Id and Ie due to significant charge delocalization to the para position. Similar to the geometric changes observed for the OCH₃ group, the bond alternation effect is more pronounced if the demand for α–π stabilization is higher because of decreasing β–σ stabilization in the cations in the order 4, 3, 2, and 5. Compared to a normal aromatic bond and most pronounced for 5, the C₁–C₂/C₁–C₆ bonds and C₃–C₄/C₄–C₅ bonds are elongated, up to 1.444/1.447 and 1.422/1.424 Å, respectively, in 5, and the C₂–C₃/C₅–C₆ bonds are shortened, up to 1.354/1.349 Å in 5.

The calculated charge distribution for the aromatic carbons in 2–5 (Table V) is in accord with the bond alternation, the geometrical changes for the C₄–OCH₃ group, and the ¹³C NMR chemical shift data. The charge distribution shows that most of the positive charge in 1-(*p*-anisyl)vinyl cations is delocalized to the aryl fragment, in contrast to the calculated charge distribution in the 1-phenylvinyl cation, where the charge is more evenly distributed between the vinyl (0.463) and the phenyl (0.537) parts.^{4b,c} The total charge of the vinyl fragment in 2, 3, and 4 is 0.240, 0.261, and 0.307 and of the complementary aryl fragment is 0.760, 0.739, and 0.693, respectively. This order is in accord with the interpretation of the geometry changes and confirms the increasing hyperconjugative stabilizing effect of β–H < β–CH₃ < β–SiH₃ substituents accommodating more charge in the vinyl fragment of 2, 3, and 4. Cation 5 has a smaller carbon framework, and the charge distribution between the aryl (0.724) and alkyl (0.276) part is not directly comparable with that in 2–4.

The charge at the para carbon is gradually increasing in 4 (0.508), 3 (0.514), and 2 (0.518), with decreasing σ-donor strength of the β substituent. This is consistent both with the bond alternation for the aromatic C–C bonds and also with the observed ¹³C NMR chemical shifts for the para carbon of 1 (177 ppm) and 2 (184 ppm). The charge calculated for the C₄ carbon in the *p*-anisylmethyl cation 5 (0.519) is about the same as for 2, while the chemical shift for C₄ in 5 (188 ppm¹⁶) differs by 4 ppm from that in 2, stressing the limited comparability of charges at specific aromatic positions in 5 and 2. The calculated total charge for the methoxy CH₃ group in 4 (0.489), 3 (0.495), 2 (0.501), and 5 (0.514) increases with decreasing β–σ stabilization in the same order as the ¹³C chemical shift for the OCH₃ signal observed for 4 (59.9 ppm), 2 (60.7 ppm), and 5 (61.5 ppm). The charges calculated for the syn and anti ortho (C₂ and C₆) and meta (C₃ and C₅) positions in 2 and 5 support the assignment of the corresponding signals in the ¹³C NMR spectra of 2 and 5.

The energy differences between the transition-state structures 2-TS–5-TS and the minimum structures 2–5 (Table II) are a measure for the barrier for methoxy group rotation around the C₄–oxygen bond. The structures 2-TS–5-TS are calculated to be

(20) (a) The size of the molecules and the computational resources available to us made calculations of 2–5 and 2-TS–5-TS at higher levels than 6-31G not generally feasible. Computational experience¹³ with more electron-deficient smaller vinyl cations lacking π-conjugative stabilizing substituents indicate, however, that although the effects of σ stabilization by β–σ C–H, C–C, and C–Si bonds are more pronounced at higher level of calculations, including electron correlation, the relative order for hyperconjugation of β substituents is not changed. The α-arylvinylium cations 2–5 have an inherently lower demand for β–σ hyperconjugative stabilization than vinyl cations lacking α–π-conjugating substituents, and the level of the calculation is not as crucial. Model calculations for 2 at 6-31G* and for 4 using the 6-31G level with inclusion of d orbitals at silicon^{20b} show that the data obtained for 2–5 using the 6-31G basis set are qualitatively reliable and thus adequate to allow comparison of a consistent set of calculated data with the experimental NMR results. The results are also in accord with our earlier conclusions.^{12,13} (b) Calculations of 2 and 2-TS, using the 6-31G* instead of the 6-31G basis set, showed only minor geometry differences. The largest difference for 2 is seen around the OCH₃ group. The C₄–O–CH₃ bond angle is 2.6° smaller, and the C₄–O and the O–CH₃ bonds are shortened by 0.025 and 0.028 Å, respectively. The Mulliken charge analysis indicates that somewhat more charge is localized at the alkyl fragment, with less charge at the complementary aryl fragment. The inclusion of d orbitals on all heavy atoms stabilizes 2 more than 2-TS, and the activation barrier for the methoxy group rotation is estimated to be larger by 1.0 kcal mol⁻¹ at 6-31G* than at the 6-31G level. A 6-31G calculation for 4 and 4-TS including d orbitals only at silicon, using the same exponents as the 6-31G* basis set, showed only marginal differences compared to the 6-31G results. The largest change in bond length is 0.03 Å (C_β–Si bond), and the bond angle changes are <1°. The relative energy difference between 4 and 4-Ts increases by only 0.1 kcal mol⁻¹.

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Table VI. Selected Mulliken Charges (Hydrogen Summed into Heavy Atoms) in the Transition-State Structures 2-TS-5-TS

	4	3	2	5
aryl part	0.658	0.708	0.729	0.691
alkyl part	0.342	0.292	0.271	0.309
ortho (C ₂)	0.238	0.249	0.257	0.211
ortho (C ₆)	0.238	0.249	0.257	0.210
meta (C ₃)	0.046	0.045	0.048	0.060
meta (C ₅)	0.046	0.045	0.048	0.060
para (C ₄)	0.478	0.489	0.496	0.506
methoxy CH ₃	0.472	0.481	0.489	0.506

higher in energy by 7.4 kcal mol⁻¹ (4-TS), 7.9 kcal mol⁻¹ (3-TS), 8.3 kcal mol⁻¹ (2-TS), and 9.2 kcal mol⁻¹ (5-TS) relative to the corresponding minimum structures 4, 3, 2, and 5. Although the differences are small, the order obtained is in agreement with the other calculated data, as well as with the observed chemical shifts for 1 and 2. Experimentally determined energy barriers ΔG^\ddagger for the methoxy group rotation have been reported for 5 (12 kcal mol⁻¹), the 1-(*p*-anisyl)ethyl cation (10.5 kcal mol⁻¹), and the 1-methyl-1-(*p*-anisyl)ethyl cation (9.1 kcal mol⁻¹).¹⁶ Comparing the experimentally measured and the calculated (9.2 kcal mol⁻¹) energy barriers for 5, the agreement between the experimentally determined (9 kcal mol⁻¹) and the calculated (8.3 kcal mol⁻¹) barrier for the vinyl cation 2 is good and gives confidence in the computational results obtained.²⁰

The differences for the syn/anti aryl C-C bond lengths present in 2-5 are absent in the transition-state structures 2-TS-5-TS due to symmetry. The O-Me group is oriented perpendicular to the plane of the aryl ring and cannot conjugate. The bond alternation scheme for the aromatic C-C bonds also changes characteristically in the structures 2-TS-5-TS, because delocalization of positive charge into the para position is not as favorable as in 2-5. In the transition-state structures 2-TS-5-TS, the C₃-C₄/C₄-C₅ distances are significantly shorter, the C₁-C₂/C₁-C₆ distances decrease only slightly, and the C₂-C₃/C₅-C₆ distances are longer compared to the corresponding minimum structures 2-5. The geometries calculated for 2-TS-5-TS indicate less contribution of resonance structures of type Id and Ie with a positive charge at the C₄ carbon and at the C₄-OCH₃ group compared to 2-5. As a consequence of overall less π resonance stabilization in 2-TS-5-TS, the C⁺-C₁ bonds are longer than those in 2-5. In accord with the hyperconjugational concept of IIa \leftrightarrow IIb no-bond resonance structures, the C⁺-C _{β} bond is shorter in 4 than in 3 and is further shortened in 4-TS and 3-TS, where resonance structures of type IIb gain more importance. A concomitant elongation of the C _{β} -R bond lengths compared to those of 2-4 is found in 2-TS-4-TS.

The diminished π resonance stabilization in 2-TS-5-TS is also evident from the calculated charge distributions (Table VI). Compared to 2-5, the charge at the para position and for the whole aryl fragment is lower, but it is higher for the alkyl fragment. The order 4-TS, 3-TS, 2-TS, to 5-TS, obtained for the relative changes of the aromatic C-C bond lengths and for the relative changes of the charges of the aryl and alkyl fragments, is the same as for 4, 3, 2, and 5, monitoring again the decreasing β - σ stabilization in the order β -SiH₃, β -CH₃, and β -H.

Conclusion

For the first time 1-(*p*-anisyl)vinyl cations are observed as persistent species in solution and are fully characterized by ¹H and ¹³C NMR spectroscopy. The initial generation of β -silyl-substituted carbocations, followed by temperature-controlled

cleavage of the β -carbon-silicon bond in superacid media, is an advantageous method for obtaining carbocations which hitherto have been inaccessible. It is demonstrated that, aside from a π -conjugative stabilization, β - σ hyperconjugative stabilization is operating in 1-aryl-substituted carbocations, even if the aryl group is a very good electron donor, like the *p*-anisyl group. The combined application of experimental and theoretical methods used in this study reveals that the para C₄ carbon chemical shifts and the barrier to C₄-O rotation, determined experimentally and computationally, as well as the computed geometrical parameters and charges, are useful tools for investigating the competition between π resonance stabilization and hyperconjugative stabilization by β - σ bonds in this type of carbocation.

Experimental Section

p-Anisylacetylene was prepared using a slightly modified literature procedure.²² ¹³C NMR (100.6 MHz, CDCl₃, 27 °C): δ 83.64 (²J_{CH} = 49.6 Hz, d, C_a), 75.74 (¹J_{CH} = 250.8 Hz, d, C _{β}), 114.16 (C₁), 113.91 (¹J_{CH} = 162.7 Hz, d, C_{3,5}), 133.54 (¹J_{CH} = 162.1, d, C_{2,6}), 159.92 (C₄), 55.21 (¹J_{CH} = 144.0, q, OCH₃). ¹H NMR (400 MHz, CDCl₃, 27 °C): δ 6.86 (³J_{HH} = 9 Hz, H_{3,5}), 7.42 (³J_{HH} = 9.0 Hz, H_{2,6}), 2.99 (H _{β}), 3.79 (OCH₃).

1-(*p*-Anisyl)-2-(triisopropylsilyl)acetylene was prepared by reacting *p*-anisylacetylene with methylolithium (5% in diethyl ether) at 4 °C, and subsequently, after the mixture was stirred 30 min at room temperature, an excess of triisopropylchlorosilane was added. Workup after stirring for 12 h at room temperature yielded 73% product, bp 125 °C (2.5 \times 10⁻² mbar). MS (70 eV): M⁺ *m/z* 288 (25), 175 (100). ¹³C NMR (100.6 MHz, CDCl₃, 27 °C): δ 107.13 (C_a), 88.61 (C _{β}), 115.80 (C₁), 113.77 (¹J_{CH} = 160.2 Hz, d, C_{3,5}), 133.48 (¹J_{CH} = 162.1, d, C_{2,6}), 159.61 (C₄), 55.26 (¹J_{CH} = 144.0 Hz, q, OCH₃), 11.38 (¹J_{CH} = 119.2 Hz, d, Si-CH₃), 18.67 (¹J_{CH} = 125.9 Hz, q, CH₃). ¹H NMR (400 MHz, CDCl₃, 27 °C): δ 6.81 (³J_{HH} = 8.6 Hz, H_{3,5}), 7.41 (³J_{HH} = 8.6 Hz, d, H_{2,6}), 3.79 (OCH₃), 1.12 (Si-CH₃), 1.12 (CH₃).

Preparation of Carbocations. The general experimental technique for the generation of carbocations has been described.¹⁴ In a special apparatus,¹⁴ 0.4 mmol of the acetylene precursor was distilled at 10⁻⁶ mbar onto the surface of a homogeneous matrix at -196 °C made of 7.6 mmol of FSO₃H, 1.6 mmol of SbF₅, 2.1 mL of SO₂ClF, 0.7 mL of SO₂F₂, and 0.3 mL of CD₂Cl₂. Warming the solution to -130 °C yields a yellow-green solution of 1. The solution was transferred under high vacuum at -130 °C into 10-mm NMR tubes, which were then sealed under vacuum and stored at -196 °C. Warming the solution to -100 °C leads to complete formation of cation 2.

¹H and ¹³C NMR spectra of the carbocation solutions were measured on a Bruker AMX 400 NMR spectrometer equipped with a variable frequency fluorine lock channel and a 10-mm ¹³C/¹H/¹⁹F probe, using the fluorine resonance of either SO₂ClF or SO₂F₂ as an internal lock. CD₂Cl₂ was used as internal standard (¹H NMR, CHDCl₂, δ = 5.32 ppm, ¹³C NMR, δ = 53.8 ppm). The probe temperature was calibrated with a ¹³C chemical shift thermometer using neat 2-chlorobutane²³ in a capillary in an NMR tube filled with SO₂ClF admixed with variable other solvents.

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Supplementary Material Available: Tables of optimized structures (RHF/6-31G) for cations 2-5 and 2-TS-5-TS (12 pages). Ordering information is given on any current masthead page.

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