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Effect of Substituents on the Structure of the Vinyl Radical: Calculations and Experiments

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Literature reports indicate either a linear or a bent configuration for α-substituted vinyl radicals. In order to get a better insight into this structural question, calculations of the structure of some α-substituted vinyl radicals were conducted by the DFT approach [BLYP/6-31G(d,p) and B3LYP/6-311G(2d,2p)]. For vinyl radicals bearing σ-type substituents (Me, SH, Cl, OH, F), the bent form is found to be the minimum energy structure; the inversion barrier of the *E* and *Z* forms is found to markedly increase as the electronegativity of the group increases. Vinyl radicals bearing π-type substituents ($CH{=}CH_2$, CHO, CN, C_6H_5) are found to be linear. The effect of β-substituents is much lower, and the β-fluoro- and β-ethenylvinyl radicals, representative of σ- and π-type substituents, are calculated to be bent. Comparison with other literature calculations, obtained by different methods for some similar vinylic radicals, supports our computational results. Experimental support was also sought, with particular regards to the inversion barrier of the bent radicals. Since a very high barrier is calculated for the α-fluorovinyl radical, its inversion rate could be slower than the “sampling” time of a proper chemical reaction. Indeed, the α-fluorovinyl radicals, generated from $PhCH{=}C(F)Br$ by reaction with Bu_3SnH/AIBN, retained the configuration of their precursors in the overall hydrodebromination process.

In a recent investigation on the $S_{RN}1(V)$ reaction,[1] as we have dubbed the vinylic counterpart of the $S_{RN}1$ process of aryl halides[2] (Scheme 1, where RX is the vinyl or aryl substrate, and Y^- is a suitable nucleophile), definite evidence has been gathered for the intermediacy of vinyl radicals in the propagation cycle.

Scheme 1

$$RX \xrightarrow{h\nu/Y^-} RX^{\bullet-} \text{ (initiation)} \qquad (1)$$

$$RX^{\bullet-} \rightarrow R^\bullet + X^- \qquad (2)$$

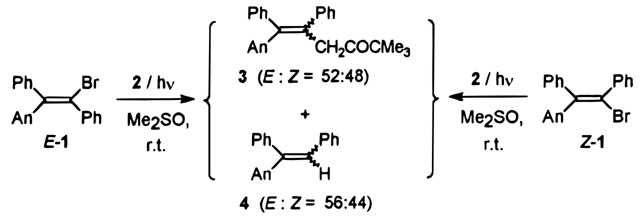
$$R^\bullet + Y^- \rightarrow RY^{\bullet-} \qquad (3)$$

$$RY^{\bullet-} + RX \rightarrow RY + RX^{\bullet-} \qquad (4)$$

$$R^\bullet + SH \rightarrow RH + S^\bullet \qquad (5)$$

As for the stereochemical course of the $S_{RN}1(V)$ process, investigation of the photostimulated reaction of the *E* and *Z* isomers of a suitable vinyl halide (i.e., **1**) with pinacolone enolate ion ($Me_3CCOCH_2^-$; **2**) as the nucleophile revealed complete loss of the original stereochemistry of (*E*)-**1** and (*Z*)-**1** in the substituted (**3**) and hydrodehalogenated (**4**) products (Scheme 2, where An is anisyl).[1]

Scheme 2



This outcome has been attributed to the intermediacy of a substituted α-phenylvinyl radical [$AnC(Ph){=}C(Ph)^\bullet$, **5**], which partitions between hydrogen atom abstraction from the solvent (SH, in eq 5), to give the hydrodehalogenated product, and combination with the nucleophile, to eventually afford the substitution product (eqs 3 and 4). The stereoconvergence observed indicates that intermediate radical **5** has either a linear sp structure or an “average linear” structure due to a rapidly interconverting *E*,*Z* mixture of sp^2 bent radicals. From our results it was difficult to decide between the two structural hypotheses.[1]

If we remember that the structures of the “close neighbors” of the vinyl radical, *viz.* the vinyl anion and the vinyl cation, are bent and configurationally stable for the former,[3] while linear or bridged for the latter,[4] an intermediate structure for the vinyl radical seems reasonable.[5,6]

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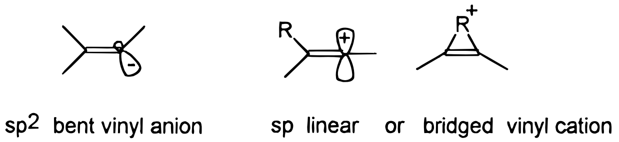
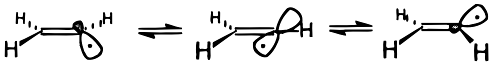


There exists circumstantial esr evidence[7] that the parent vinyl radical has two sp^2 bent structures that are rapidly interconverting (4×10^{10} s^{-1} at 300 K), due to an inversion barrier as low as 3 kcal/mol.[7a] The sp linear structure could be the transition structure for this inversion, instead of a real intermediate.



It is reported that α-substituents can modify this situation to a major extent. For example, the $R_2C{=}C(R')^{\bullet}$ radical, where R′ = Ph, appears linear by esr investigation[8] and by muon spin rotation spectroscopy,[9] whereas when R′ = Cl or Br, the evidence favors a bent stable structure.[10] Analysis of the stereochemistry of the olefinic products formed in a radical addition to 1-alkynes, where an α-substituted alkenyl radical is the reactive intermediate, supports[11] a bent, stable structure for the α-MeO-alkenyl radical and points[8f] to a linear structure for the α-CO_2Me and α-$SiMe_3$ vinyl radicals. However, stereochemical results suggest[11] that the α-CN and the α-Ph vinyl radicals could be bent and rapidly equilibrating at elevated temperatures (240−260 °C), but are more likely to be linear at lower temperatures. In the case of α-alkylvinyl radicals, a bent and fast equilibrating structure was corroborated,[8f,11] thereby confirming the structure deduced from esr investigation.[7]

Conflicting literature reports appear to afflict mostly π-type substituents, such as the phenyl or carbonyl groups. These substituents, which could allow stabilization of the adjacent vinyl radical by delocalization of the unpaired electron, are likely to impose a linear structure at the radical center in order to achieve maximum orbital overlap, as it is shown for the α-CN group.

This expectation appeared to be confirmed by an old esr study on the pertinent radicals generated in solid matrices.[8a,b] However, a more recent esr investigation of these radicals, generated in solution by UV photolysis of suitable peroxide precursors,[12] questions this structure, for at least the α-carbomethoxyvinyl and α-cyanovinyl radicals, which seem to have a bent structure characterized by a very small inversion barrier. The latter would make the two intrinsically nonequivalent vinylic β-hydrogens appear equivalent, similar to a linear structure. Indeed it was this "apparent" equivalence of the β-hydrogens on the esr timescale that suggested the linear structure in the earlier esr studies.[8a,b] Very recently, a new esr investigation confirmed a linear structure for an α-phenylvinyl radical intermediate.[8f] Consequently, the structural description of the α-substituted vinyl radicals appears elusive and certainly difficult to determine by experimental methods. A computational approach may be easier for settling the question. The desirable goal of such a computational endeavor would be to explore the potential energy surface for a number of substituted vinyl radicals, in order to ascertain if a linear or bent structure represents the energy minimum and, whenever appropriate, to calculate the energy barrier to inversion between the bent isomeric forms.

In spite of the importance of vinyl radicals among the fundamental intermediates of organic chemistry, it was surprising to find, when we started this investigation, that there was only a thorough study of the potential energy surface of the parent ethenyl radical by post Hartree−Fock *ab initio* methods.[13] However, there was no computational information about the relative energy of the linear and bent forms of α-substituted vinyl radicals. Likewise, no evaluation was available for the energy barrier to interconversion of isomeric *E,Z* bent vinyl radicals as a function of the substituent. A knowledge of the barrier could allow the investigation of the inversion rate, which is important for interpreting the stereochemical outcome of reactions involving vinyl radicals as intermediates.

For these reasons, and as an implementation of our previous stereochemical investigation,[1] we have undertaken a theoretical scrutiny of the following α-substituted vinyl radicals:

6 R = H ; **7** R = CH_3 ; **8** R = SH **16** R = F ; **17** R = $CH{=}CH_2$
9 R = Cl ; **10** R = OH ; **11** R = F
12 R = $CH{=}CH_2$; **13** R = CH=O
14 R = CN ; **15** R = C_6H_5

These radicals were chosen in order to investigate the effect of σ-type substituents (structures **6**−**11**) and of π-type substituents (structures **12**−**15**) and bear some resemblance with those experimentally examined by us.[1,14] Two β-substituted vinyl radicals (structures **16** and **17**) were also studied. The results of the calculations, carried out by using the DFT approach on these structures, are presented below. In order to compare calculations and experiment, the stereochemistry and products of a reaction leading to the formation of one of these α-substituted vinyl radical intermediates was investigated, and we present the results along with other experimental literature data.[15]

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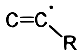
Results

Computational Details. Since it is known that the electron correlation should be taken into account when dealing with inversion barriers in vinyl radicals,[13] and with the aim of keeping the computational effort within reasonable limits, we have chosen the DFT approach as a theoretical method. It is known that this method may achieve a greater accuracy than the Hartree–Fock (HF) theory, at a modest increase in cost. The DFT approach overcomes the major limitation of the HF theory, i.e. the neglect of electron correlation, by including some of the electron correlation effects. Its results may be compared to the post HF MP2 method.[16] The DFT approach has been already used as a theoretical tool for the investigation of fluoro-substituted vinyl radicals.[17] While our study was in progress, a paper appeared where *ab initio* calculations for a certain number of α-substituted vinyl radicals, but neither including the phenyl and ethenyl groups nor the formyl group, were reported.[18] Some results of this paper are in agreement with ours, but others, in the case of the π-type substituents, are in contrast with ours and with previous[8] findings. Since our approach differs from that employed in the paper quoted above,[18] it is interesting to compare the results of the two approaches.

All the calculations were carried out by using either the Gaussian 92/DFT[19] or the Gaussian 94 packages.[20] The Density Functional approach (DFT) was used with the Becke's 1988 exchange functional, which includes the Slater exchange along with corrections involving the gradient of the density,[21] and with the correlation functional of Lee, Yang and Parr, which includes both local and nonlocal terms[22,23] (BLYP). A 6-31G(d,p) basis set, a split valence basis set supplemented with polarization p-functions on hydrogens and d-functions on heavy atoms, was used. For each radical, starting both from a linear structure and a bent structure, a full optimization was carried out in order to find the nearest stationary point. For all the structures obtained, the spin contamination due to states of multiplicity higher than the doublet state was negligible, in that the $\langle S^2 \rangle$ parameter was, in all cases, well within the 10% of the expectation value for a doublet (0.75). The stationary points found were characterized by a frequency calculation. For the linear structure featuring one imaginary frequency, and therefore found to be a saddle point, the normal mode, corresponding to the imaginary frequency, was animated by using the visualization program *MolWin*.[24] In this way it was verified that the displacements that compose the mode lead to the two isomeric bent forms, thus confirming that the linear form is indeed the transition state for the inversion. For the radicals found to be bent, the barrier of inversion was obtained as the difference between the total energies of the bent and the linear form. This energy difference was then corrected for the differences in the zero point energies. In order to check the reliability of the BLYP/6-31G(d,p) model used here, the calculations for radicals **6**, **9**, and **11** have been repeated at a higher level of theory by using the Becke's three-parameter functional, with the correlation functional of Lee, Yang, and Parr (B3LYP). A triple ζ (zeta) basis set with polarization 2p-function on hydrogen and 2d-function on heavy atoms was used [6-311G(2d,2p)].

Table 1. Inversion Energy Barriers and Bond Angles Found for Bent Radicals 6–11, 16, and 17 As Obtained from DFT Calculations (BLYP/6-31G(d,p)//BLYP/6-31G(d,p). For Radicals 6, 9, and 11 the Corresponding Values Obtained at a Higher Level of Theory (B3LYP/6-311G(2d,2p)//B3LYP/6-311G(2d,2p)) Are Reported in Parentheses

radical	energy barrier,[a] *kcal/mol*	 bond angle, °
6 (α-H)	3.3 (3.2)	138.0 (137.9)
7 (α-CH$_3$)	3.1	141.0
8 (α-SH)	4.7	134.3
9 (α-Cl)	11.1 (10.6)	134.3 (134.5)
10 (α-OH)	13.3	130.3
11 (α-F)	19.5 (20.8)	129.9 (130.0)
16 (β-F)	1.4 (*E* → *Z*)	138.3 (*E*)
	1.5 (*Z* → *E*)	143.0 (*Z*)
17 (β-CH=CH$_2$)	3.7 (*E* → *Z*)	137.3 (*E*)
	3.2 (*Z* → *E*)	137.7 (*Z*)

[a] Corrected for the zero point energies.

Computational Results. Radicals **6–11**, bearing σ-type substituents, were found to be *bent*. The corresponding linear forms were characterized as the transition state for the inversion between the two isomeric bent forms. The values of the energy barrier to the inversion, together with the bond angles at the radical center (namely, the angle between the double bond and the substituent bond) found for the minimum-energy structures, are reported in Table 1. The nature of the substituent greatly affects the inversion barrier and, to a lesser extent, the bond angle at the radical center. In Figures 1 and 2 the height of the barrier and the bond angle values, respectively, are plotted against the electronegativity[25] of the α-substituent. It is evident from both Table 1 and Figures 1 and 2 that the results from the B3LYP/6-311G(2d,2p) calculations strictly follow those obtained from the BLYP/6-31G(d,p) model.

Radicals **12–15**, bearing π-type substituents, were found to be *linear*. For all of them the π system of the substituent is orthogonal to the π system of the double bond and coplanar with the p orbital at the radical center.

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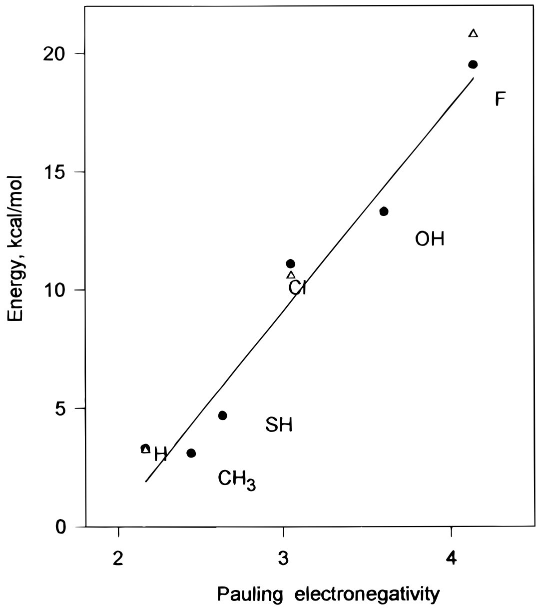

Figure 1. Inversion barrier *vs* electronegativity of the α-substituent as obtained from DFT calculations: (●) BLYP/6-31G(d,p)//BLYP/6-31G(d,p); (△) B3LYP/6-311G (2d,2p)//B3LYP/6-311G(2d,2p).

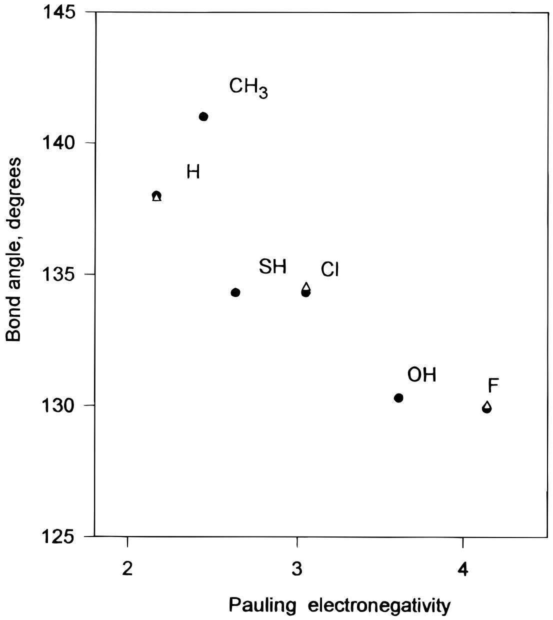

Figure 2. Bond angle at the radical centre *vs* electronegativity of the α-substituent as obtained from DFT calculations: (●) BLYP/6-31G(d,p); (△) B3LYP/6-311G(2d,2p).

The β-substituted vinyl radicals **16** and **17**, bearing a σ-type and a π-type substituent, respectively, were found to be *bent*. The minimum energy structures for radicals **11** and **15** are drawn in Figure 3.

Discussion

σ-Substituted Vinyl Radicals. The calculations concerning the vinyl radicals **6**−**11** indicate that they exist as two isomeric *bent* forms, which interconvert through the linear structure. The bond angle values at the radical center range from 130° to 141°, which are values larger than expected from an sp^2 hybridization and suggest a structure "intermediate" between a bent (120°) and a linear (180°) one for these radical centers. The double bond-to-substituent angle gradually approaches the "normal" sp^2 angle on increasing the electronegativity of the α-substituent (Figure 2). The height of the barrier to inversion also depends strongly on the electronic effect of the α-substituent, and a quasilinear relationship is observed between the former and the electronegativity of the α-substituent (Figure 1). In comparison with the effect of the α-substituent, it can be verified that the β-substituent effect (structures **16** and **17**) is greatly diminished, as the case of the fluorine substituent demonstrates, and the related radicals are bent, regardless of the σ- or π-character of the substituent.

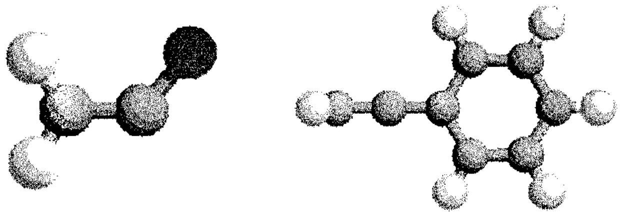

Figure 3. Minimum energy structures calculated (BLYP/6-31G(d,p)) for radicals **11** (left) and **15** (right).

The computational results for the structure of vinylic radicals substituted with α-σ-substituents are in accord with available spectroscopic evidence,[7,10] and also with results of recent *ab initio* calculations.[18] The barriers calculated by us are ca. 2−4 kcal/mol lower than those from reference 18. However, whereas our values are corrected for the differences in the zero point energies, such correction was not mentioned in reference 18.

The results obtained by our calculations for the inversion barrier of the bent radicals lend themselves to experimental corroboration. For example, given that the rate constant of H-atom abstraction by a vinyl radical from Bu_3SnH is ca. 10^8 M^{-1} s^{-1} at 30 °C,[26] bent vinyl radicals endowed with an inversion barrier greater than 6−7 kcal/mol should behave as configurationally stable toward this reaction. The case of α-fluorovinyl radical was investigated since, in view of its very high calculated inversion barrier (19.5 kcal/mol), it was expected to give retention of configuration in reaction with Bu_3SnH. We note that inversion barriers comparable in height, and of the order of 25−27 kcal/mol, are indeed reported for configurationally stable vinyl anions.[3a,d]

Experimental Support. Retention of configuration in the case of the α-MeO and α-Cl groups (our calculated barriers 13.3 and 11.1 kcal/mol, Table 1) has indeed been reported previously[10] and attributed to a *slower* inversion rate of the substituted vinyl radical, as controlled by the electronegativity of the substituent, than the rate of the "sampling" chemical reaction (hydrogen atom abstraction, in general). A check of the computational prediction for the inversion barrier of the α-fluorovinyl radical was carried out with precursor PhCH=C(Br)F (**19**). It was synthesized as an *E*,*Z*-mixture (ca. 80:20),[27] and the two diastereoisomers were separated by preparative GC. Proton NMR showed that the more abundant geometric isomer of **19** was the *E*, as judged from the J_{HF} coupling constant of 33 Hz, which has a typical value for a *trans*

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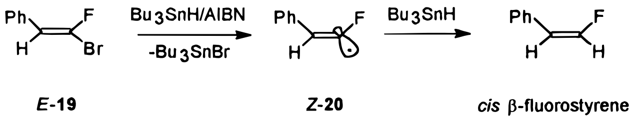
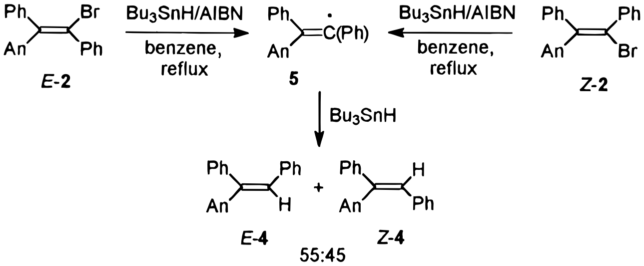
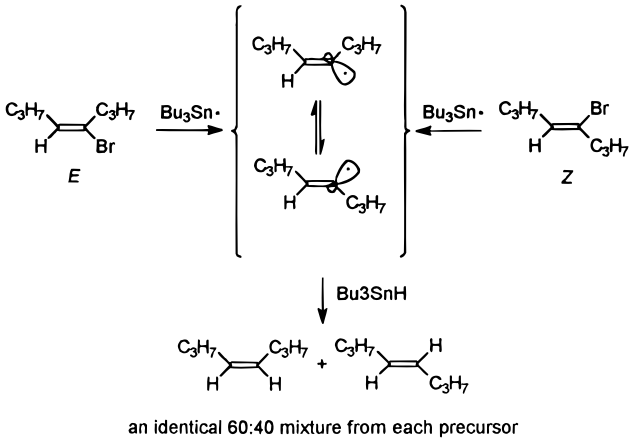
Scheme 3



Scheme 4



Scheme 5



H−F relationship in an unsaturated system.[28] Consistently, (*Z*)-**19** had a smaller J_{HF} coupling constant (15 Hz). Reaction of pure (*E*)-**19** with Bu_3SnH/AIBN in refluxing benzene gave a *single* hydrodebrominated product (i.e., β-fluorostyrene), presenting GC and GC-MS retention times significantly different (ca. 0.2 min, on capillary columns) from that of the *single* hydrodebrominated isomer resulting from the analogous reaction with (*Z*)-**19**. Proton NMR of the crude reaction product from (*E*)-**19** showed the expected large (60 Hz) J_{HF} coupling constant due to the *geminal* H−F relationship[28] and the small (9 Hz) J_{HH} coupling constant due to the *cis* H−H relationship. This spectral evidence is in keeping with the formation of *cis* β-fluorostyrene from (*E*)-**19** (Scheme 3). Retention of configuration in the bent α-fluorovinyl radical (*Z*)-**20** and (*E*)-**20** is therefore substantiated; it supports the result of the calculations, and confirms previous experimental findings with α-halovinyl radicals.[10]

One might wonder what would have been the possible stereochemical outcome of a reaction similar to that reported in Scheme 3 if the α-fluorovinyl radical intermediate were instead linear. Our previous investigation of the stereochemical behavior of the α-phenylvinyl radical intermediate, which is calculated to be linear, in reaction with Bu_3SnH has demonstrated loss of the configuration of the vinyl halide precursors (Scheme 4).[1]

Hence, either stereoconvergence or at least obtaining a *cis,trans* mixture of β-fluorostyrenes would appear as a likely outcome of the Bu_3SnH/AIBN reaction of (*E*)-**19** and (*Z*)-**19** through a *linear* radical intermediate. Obtaining an unbalanced diastereomeric mixture is indeed reported[29] even for an α-phenylvinyl radical (i.e., a linear radical) featuring a steric hindrance of the β-substituents more similar to that in **20** than to that in **5**. Thus, the hypothesis of an α-fluorovinyl radical being linear may be safely disregarded, on the basis of the different stereochemical outcome that linear radicals do induce.

Support from the literature can also be found for other cases of substituents investigated with our calculations. For example, the α-methylvinyl radical intermediate, with the very small calculated inversion barrier of 3.1 kcal/mol, is predicted to give rise to products that have lost the original configuration of a suitable *E*- or *Z*-parent precursor. Indeed, as shown in Scheme 5, the hydrodehalogenation of either *E*- or *Z*-α-propylvinyl halides with Bu_3SnH/AIBN is reported as leading to stereoconvergence.[30]

Comparable results are reported for other chemical trapping studies with α-alkylvinyl radicals.[11,15] This experimental behavior is in keeping with the bent fast-equilibrating structure predicted by the calculations for the α-alkylvinyl radical intermediate.

π-Substituted Vinyl Radicals. The calculations of vinyl radicals **12**−**15** indicate that they exist in the *linear* forms, with substituent-to-double bond angles of 180°. The equilibrium geometry found shows that the π-system of the substituent is orthogonal to the π-system of the double bond and is coplanar with the p orbital at the radical center, thus suggesting a delocalization of the unpaired electron by the adiacent π-system of the substituent. These findings deserve some comments with respect to the experimental information already available for π-substituted radicals, and also to the *ab initio* results recently published.[18]

First, most experimental evidence points toward a linear structure for these radicals,[8,19] even though contrasting reports can also be found. For example, kinetic results[11] point toward a bent structure for radical **14** and **15**, while spectroscopic results[8] suggest a linear one. One should concede that, when the inversion barrier of the bent structure is only few kcal/mol, it may be difficult to experimentally distinguish between the two possibilities. This was our conclusion in the previous paper, where the stereoconvergence in the $S_{RN}1(V)$ reaction (Scheme 2), which is caused by the intermediacy of the α-phenylvinyl radical **5**, could be ascribed either to the linear radical or to a fast equilibrating pair of bent radicals. Second, among the three π-substituents examined earlier,[18] namely, $C\equiv CH$, CN, and COOH, only the cyano group is in common with ours (structure **14**). We calculate this radical to be linear, whereas the UMP4(SDQ) results indicate a bent structure with a barrier to inversion of 1.4 kcal/mol.[18] Such a value, which is probably not corrected for the zero point energy, is very small, thus indicating a very flat surface. Moreover, as noted,[18] such calculation may be affected by spin contamination, whereas our results should not be affected by such a problem. Incidentally, preliminary results concerning the structure of a vinyl radical α-substituted with a 2,4,6-

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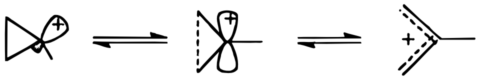
trimethylphenyl group[31] indicate that at a lower level of theory (ROHF/3-21G) this radical is more likely to be bent (bond angle: 144.1°), but it becomes linear, as our α-phenylvinyl radical **15**, when calculated by the DFT approach.

We conclude that the DFT approach employed here provides an overall picture which is consistent with the experimental body of evidence concerning vinyl radicals and as such can be viewed as a promising method for dealing with organic structures.

Vinyl *vs* Cyclopropyl and Other Radicals. The bonds in a cyclopropane ring bear *some* resemblance to π-bonds.[32] It is therefore interesting to compare information[33] on the structures of the cyclopropyl anion, radical, and cation, with that on their vinylic counterparts. The cyclopropyl anion is a bent configurationally stable species, while the cyclopropyl radical is a bent, rapidly inverting species,[33] with k_{inv} of 10^8 s^{-1} at −175 °C and 10^{11} s^{-1} at 71 °C,[34,35] due to a 3.9 kcal/mol inversion barrier.[36] Angular strain causes the cyclopropyl cation to be best viewed as an *open* allyl structure,[33] even though a *closed* bent cyclopropyl cation has been substantiated in the presence of some specific structural features.[37]



Calculations (MP3/6-31G*//6-31G*) for an α-chlorocyclopropyl radical[36] gives a barrier to *cis,trans* isomerization (i.e., 7.9 kcal/mol) that is 3.2 kcal/mol smaller than that for the corresponding α-chlorovinyl radical (i.e., **9**). More generally, the effect of α-substituents on the inversion rate (k_{inv}) of a cyclopropyl σ-radical had suggested a decrease of k_{inv} on increasing the electronegativity of the substituent.[38] This is in agreement with the trend for substituted vinyl σ-radicals obtained from our and Guerra's calculations.[18] An analogous correlation between inversion barriers and electronegativity was found for symmetrically α-substituted methyl ($Y_3C^\bullet$)[39] and silyl radicals ($Y_3Si^\bullet$),[40] and it therefore appears to be a common feature of radicals endowed with small-to-medium inversion barriers. The reason for the correlation between electronegativity of the substituent and effects that it causes on the geometry of a radical center, has been debated.[6,33,41] Our preferred explanation is that of Pauling,[41b] which suggests changes of the s character of the orbital occupied by the odd electron in response to a partially ionic character of the C-substituent bond(s). The more electronegative the substituent X, the more polar the C−X bond and the higher its p character (smaller bond angle, in Figure 2); as a consequence, the higher will become the s character of the orbital occupied by the odd electron. Conversely, radicals endowed with higher inversion barriers (E_{inv} > 30 kcal/mol), such as the acyl[42] $Y{-}C(^\bullet){=}O$ and phosphonyl[43] $Y_3P(^\bullet){=}O$, are firmly bent, and therefore not significantly influenced by the nature of the α-substituent(s) Y.

Experimental Section

Calculations and Instrumentation. Calculations were conducted on a DEC Alpha AXP 3000/500. GC and GC-MS analyses were performed on methyl silicone gum capillary columns.[1] Preparative GC separation of the *E,Z*-mixture of **19** was executed on a Carlo Erba Fractovap ATC/f gas chromatograph. ^{1}H NMR spectra were taken in $CDCl_3$ at 300 MHz on a Bruker AC 300 instrument.

Synthesis of *β*-Bromo-*β*-fluorostyrene (19). A dry 500 mL three-neck roundbottom flask with reflux condenser, thermometer, septum, and a Tru-bore stirrer was flushed with N_2 prior to adding 26.0 g (99 mmol) of Ph_3P and 150 mL of freshly distilled anhydrous diglyme. The contents of the flask were heated to 70 °C prior to the injection of 12.7 g (47 mmol) of $CFBr_3$. The solution turned from clear to yellow with a precipitate forming. At 90 °C, 5.0 g (47 mmol) of PhCHO was injected and the mixture heated for 3 h at 120 °C. The dark solution was cooled and the product codistilled with water. The lower layer of the distillate was washed with water to remove diglyme, dried ($MgSO_4$), and vacuum distilled, bp 80−82 °C (at 11 Torr), to give 7.1 g (35 mmol; 75% yield) of a *E,Z* mixture of **19** (>97% pure by gas chromatography).[27] ^{1}H NMR δ 5.9 (J_{HF} = 33 Hz: *E* isomer; 88%), 6.6 (J_{HF} = 15 Hz: *Z* isomer; 12%). ^{19}F NMR δ −68.3 (*E*), −65.7 (*Z*).[28] The two diastereomers of **19** were separated (> 99% pure) by means of preparative gas chromatography on a 4 m × 4 mm methyl silicone fluid (550/SF) packed column at 170 °C.

Hydrodebromination of 19 with Bu_3SnH. A solution of 50 mg of (*E*)-**19** (0.25 mmol), 8 mg AIBN (0.05 mmol), and 330 μL Bu_3SnH (1.24 mmol) in 0.6 mL benzene was irradiated[1] at 350 nm for 3 h.[14b] Direct GC-MS analysis (no workup) of the reaction mixture revealed formation of fluorostyrene (retention time: 5.7 min). The reaction mixture was eluted on a short hand-made chromatographic column (a Pasteur pipette filled with silica gel) with the aid of a little C_6D_6 as the eluent, in order to remove tin−containing compounds. A fraction containing the reaction product was analyzed by ^{1}H NMR (no suppression of C_6H_6 was needed), and the vinylic pattern (J_{HH} 9 Hz), along with the J_{HF} geminal coupling constant (60 Hz, see text), allowed the assignment of the structure of *cis*-β-fluorostyrene to this product. Similarly, (*Z*)-**19** gave *trans*-β-fluorostyrene (GC-MS retention time: 5.9 min), as judged by its ^{1}H NMR (J_{HH} 15 Hz). The contamination of either one of the β-fluorostyrene isomers in the other isomer was lower than the detection limit of <0.1%.

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Supporting Information Available: Coordinates, total energies, zero-point vibrational energies, and unscaled vibrational frequencies of the stationary points obtained from BLYP/6-31G(d,p)//BLYP/6-31G(d,p) calculations for radicals **6**−**17** and from B3LYP/6-311G(2d,2p)//B3LYP/6-311G(2d,2p) calculations for radicals **6**, **9**, and **11** (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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