

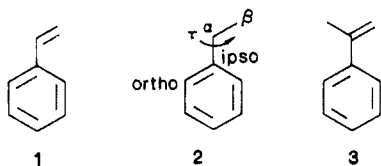
Observation and Geometry Assignment of Conformations of Styrenes in the Ground and First Excited Singlet State

Jeffrey I. Seeman,^{*,1a} V. H. Grassian,^{1b} and E. R. Bernstein^{*,1b}

Philip Morris Research Center
P.O. Box 26583, Richmond, Virginia 23261
Department of Chemistry, Colorado State University
Fort Collins, Colorado 80523

Received September 2, 1988

Despite considerable experimental and theoretical efforts expended over the last decade, the minimum energy conformations of styrene (1) and substituted styrenes have not been unambiguously determined.^{2,3} Though not proven, the planarity of 1 (i.e., $\tau = 0^\circ$ in 2) appears to be the best explanation for the available



data.⁴ The barrier to rotation about the $C_{\text{ipso}}-C_\alpha$ bond for styrene has been estimated to be 2-3 kcal mol⁻¹, too low to observe signals for specific conformations by dynamic nuclear magnetic resonance (DNMR).^{2c,3} Numerous hindered styrenes and 1-vinylnaphthalenes have been examined, and for sterically congested systems, nonplanar conformations have been observed and identified by DNMR studies.^{2a,b,d,4} Herein, we report the use of supersonic molecular jet laser spectroscopy (1) to establish the coplanarity of the vinyl and aromatic ring systems in both S_0 and S_1 in sterically unencumbered styrenes, (2) to observe two minimum energy conformations for an asymmetrically substituted styrene, (3) to demonstrate the nonplanarity ($\tau \approx 30^\circ$) of α -methylstyrene (3) in its ground electronic state S_0 , and (4) to demonstrate the planarity ($\tau \approx 0^\circ$) of 3 in its first excited singlet state S_1 .

Laser jet spectroscopy has two important features which facilitate conformational analysis: first, the molecules are at near absolute zero in the expansion; second, each stable conformation corresponding to a potential energy minimum generates its own spectroscopic 0₀⁰ (origin) transition.⁵ Laser jet spectroscopy has been used to observe spectroscopic features of stable conformations of various alkyl- and methoxy-substituted aromatic molecules and to assign geometries to these conformations.⁵ For example, in ethylbenzene and methoxybenzene, the orientations of the ethyl and methoxy groups, as defined in 2, are perpendicular ($\tau = 90^\circ$) and planar ($\tau = 0^\circ$), respectively.⁵

The time of flight mass spectrum (TOFMS) of styrene (Figure 1) shows a single intense feature, an origin at 34585.0 cm⁻¹. It

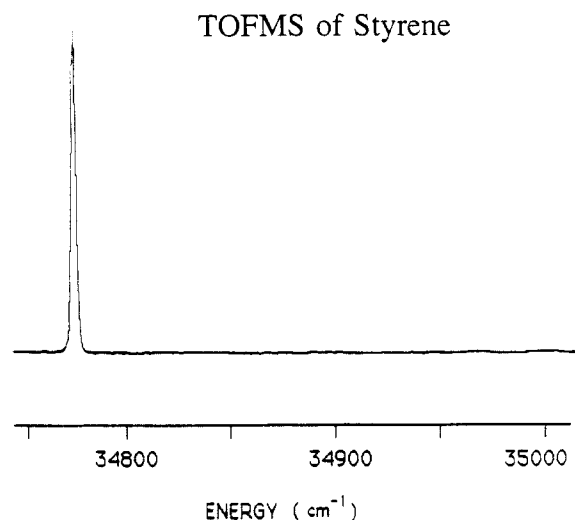


Figure 1. The one-color TOFMS of jet-cooled styrene (1). A single origin, at 34778.7 cm⁻¹, is present.

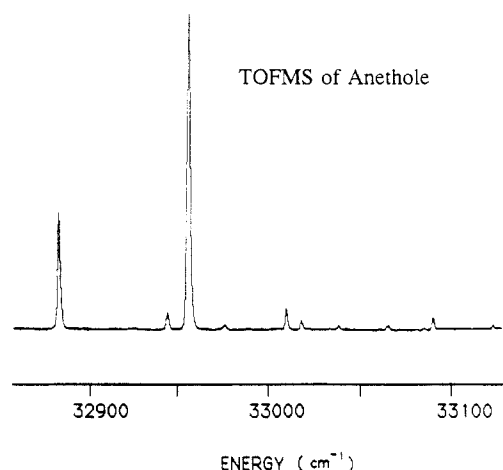


Figure 2. The TOFMS of jet-cooled anethole (5) exhibits two origins at 32889 and 32958 cm⁻¹.

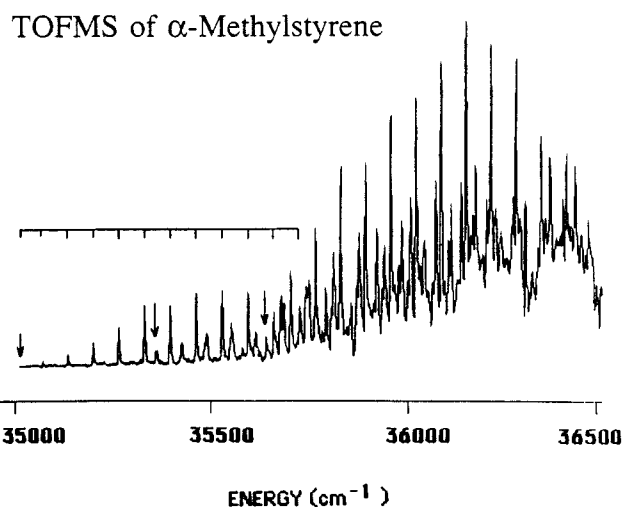


Figure 3. The TOFMS of jet-cooled α -methylstyrene (3) from 35 000 to 36 500 cm⁻¹. The weak origin and two other higher vibrational features are marked by arrows. A low-frequency torsional motion is built on the origin, with an energy level spacing of 69 cm⁻¹.

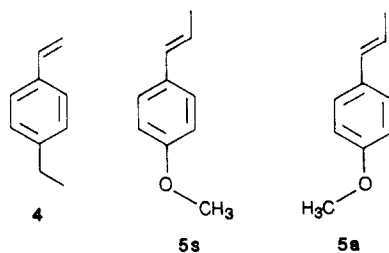
then follows that styrene exists in a single conformation [planar ($\tau = 0^\circ$), gauche ($0^\circ < \tau < 90^\circ$), or perpendicular ($\tau = 90^\circ$)]. The TOFMS of 4-ethylstyrene (4) also has a single intense origin transition at 34388.0 cm⁻¹. Since the ethyl group of 4 is perpendicular to the plane of the aromatic ring,^{5a,d} the observation

(1) (a) Philip Morris Research Center. (b) Colorado State University.
(2) For experimental studies, see: (a) Ōki, M. *Applications of Dynamic NMR Spectroscopy to Organic Chemistry*. VCH Publishers: Deerfield Beach, FL, 1985. (b) Jackman, L. M.; Cotton, F. A. *Dynamic NMR Spectroscopy*. Wiley: New York, 1975. (c) Hollas, J. M.; Musa, H.; Ridley, T.; Turner, P. H.; Weissenberger, J. H.; Fawcett, V. *J. Mol. Spectrosc.* **1982**, *94*, 437. (d) Anderson, J. E. *Tetrahedron* **1987**, *43*, 3041 and references cited therein. (e) Hemley, R. J.; Dinur, U.; Vaida, V.; Karplus, M. *J. Am. Chem. Soc.* **1985**, *107*, 836. (f) Hollas, J. M.; Ridley, R. *Chem. Phys. Lett.* **1980**, *75*, 94.

(3) For theoretical studies, see ref 1e and (a) Fabian, W. M. F. *J. Comput. Chem.* **1988**, *9*, 369. (b) Leister, D.; Kao, J. J. *Mol. Struct.* **1988**, *168*, 105.

(4) Anderson, J. E.; Barkel, D. J. D.; Parkin, J. E. *J. Chem. Soc., Perkin Trans. 2* **1987**, 955 (cf. in particular, footnote 1).

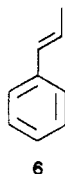
(5) (a) Breen, P. J.; Warren, J. A.; Bernstein, E. R.; Seeman, J. I. *J. Am. Chem. Soc.* **1987**, *109*, 3453. (b) Breen, P. J.; Warren, J. A.; Bernstein, E. R.; Seeman, J. I. *J. Chem. Phys.* **1987**, *87*, 1917. (c) Breen, P. J.; Warren, J. A.; Bernstein, E. R.; Seeman, J. I. *J. Chem. Phys.* **1987**, *87*, 1927. (d) Breen, P. J.; Bernstein, E. R.; Seeman, J. I. *J. Chem. Phys.* **1987**, *87*, 3269. (e) Seeman, J. I.; Secor, H. V.; Breen, P. J.; Bernstein, E. R. *J. Chem. Soc., Chem. Commun.* **1988**, 393. (f) Breen, P. J.; Bernstein, E. R.; Secor, H. V.; Seeman, J. I. *J. Am. Chem. Soc.*, in press.



of only one origin transition for **4** proves that the vinyl group must be in the plane of the ring. This conclusion is further confirmed by the number of spectroscopic origins in the TOFMS of anethole (Figure 2): two 0_0^0 transitions are observed, one each for the syn **5s** and anti **5a** conformations. Thus, for styrene and other sterically unhindered styrene derivatives, a planar conformation ($\tau = 0^\circ$) in both S_0 and S_1 obtains.

The TOFMS of α -methylstyrene (**3**), shown in Figure 3, is considerably more complex than the simple spectrum obtained for styrene and its sterically unhindered derivatives. In contrast to the intense 0_0^0 transition observed for styrene, α -methylstyrene exhibits a weak origin transition at 35063.7 cm^{-1} , blue-shifted with respect to the styrene origin. In addition, a progression in a low-frequency mode ($\approx 69\text{ cm}^{-1}$) is built on this origin. This low-frequency mode is due to the torsional motion about the $C_{\text{ipso}}-C_\alpha$ bond, described by the coordinate τ in **2**,^{5e,f} since this mode undergoes a significant shift, from 69 to 64 cm^{-1} , in the TOFMS of the deuteriated analogue of **3**, namely $\text{PhC}(\text{CD}_3)=\text{CD}_2$.

Alkyl group substitution generally causes a red-shift in the $S_1 \leftarrow S_0$ transition if the presence of the substituent causes no change in molecular conformation; for example, the 0_0^0 transition of *trans*- β -methylstyrene (**6**) is red-shifted by 193.7 cm^{-1} from



that of styrene. The blue-shift of the α -methylstyrene origin transition with respect to that of styrene by 285 cm^{-1} suggests that **3** is nonplanar in S_0 . By using the molecular orbital approach developed and employed by Suzuki,⁶ we find that $\tau \approx 31^\circ$ for **3** in S_0 .⁷

A Franck-Condon intensity analysis of the $S_1 \leftarrow S_0$ torsional progression for **3** results in a displacement of the angle τ of $30 \pm 5^\circ$ in S_1 relative to that in S_0 .⁷ The uncertainty in τ is due to approximations used for the ground-state potential and the uncertainty in the position of the maximum intensity peak in Figure 3 (8 ± 1). Similar torsional progressions have been observed for 9-phenylanthracene,⁸ 9-(2-naphthyl)anthracene,⁹ and biphenyl.¹⁰ In these cases of nonrigid aromatics, Franck-Condon analysis has led to the suggestion that a displacement occurs between S_0 and S_1 along a torsional coordinate.⁸⁻¹⁰ In analogy to biphenyl¹⁰ which is nonplanar in S_0 and planar in S_1 , we suggest that α -methylstyrene is twisted by ca. 30° in S_0 and is planar in S_1 .

In conclusion, this work has demonstrated that the vinyl moiety in sterically unhindered styrenes lies in the plane of the aromatic ring in both S_0 and S_1 . Addition of a single methyl group onto the α -vinyl carbon of **1** can significantly upset the delicate balance between π -conjugation and steric destabilization. Nonplanar S_0

but planar S_1 conformations are the minimum energy geometries for α -methylstyrene: π -conjugation dictates the S_1 geometry, whereas steric destabilization dictates the S_0 geometry.

Registry No. **1**, 100-42-5; **3**, 98-83-9; **4**, 3454-07-7; **5**, 104-46-1; **6**, 873-66-5.

Synthesis and Chemistry of a Dinuclear Iridium Bis- μ -oxo Complex: Observation of Oxygen Transfer and Phosphorus-Carbon Bond Cleavage

William D. McGhee, Thomas Foo, Frederick J. Hollander, and Robert G. Bergman*

Department of Chemistry, University of California, and the Materials and Chemical Sciences Division Lawrence Berkeley Laboratory Berkeley, California 94720

Received July 25, 1988

We wish to report the synthesis and chemistry of dinuclear iridium μ -oxo complexes capable of oxygen atom transfer and reaction with C-H bonds.

Treatment of the known,¹ air-stable (trishydroxy)diiridium cation **1** (as its acetate salt **1a**; cf. Scheme I) with lithium diisopropylamide (LDA)² in toluene at 25°C leads to the formation of an extremely air- and moisture-sensitive brick red solid. This material can be isolated in pure form in 30-50% yield. It was identified as the dinuclear bis- μ -oxo complex **2** on the basis of its very simple ^1H NMR (δ 1.67 (s) ppm) and $^{13}\text{C}\{^1\text{H}\}$ (δ 84.6 (s), 11.0 (s) ppm) spectra as well as MS, IR, UV-vis, and elemental analysis properties.³ Further evidence for the assigned structure was obtained by the rapid reaction of **2** with H_2O to regenerate the starting trihydroxy cation, in this case as the hydroxide salt **1b**.

The bis- μ -oxo complex rapidly transfers oxygen to CO, isocyanates, and phosphines. For example, addition of 4 equiv of CO to a rapidly stirred solution of complex **2** in toluene caused a color change from brick red to yellow-brown after 30 min at ambient temperature, due to the formation of $[\text{Cp}^*\text{Ir}(\mu\text{-CO})_2]_2$ (**3**)⁴ (80% NMR yield) and $\text{Cp}^*\text{Ir}(\text{CO})_2$ ⁵ (5% by NMR) along with the conversion of 2 equiv of CO to CO_2 .⁶ The dinuclear dicarbonyl complex **3** was isolated in 33% yield by crystallization from hexane at -40°C . Addition of CO to **3** did not lead to the dicarbonyl monomer $\text{Cp}^*\text{Ir}(\text{CO})_2$; instead, complex **3** was cleanly

(1) Nutton, A.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton, Trans.* **1981**, 1997.

(2) Strong amide bases such as LDA and $(\text{Me}_2\text{Si})_2\text{NLi}$ have been used extensively to prepare sensitive molecules (e.g., ester enolates and other reactive anions) in organic synthesis (see (a) Fieser, M.; Fieser, L. F. *Reagents for Organic Synthesis*; Wiley-Interscience: New York, Vol. 11, p 296 and references cited therein). Sharp and his co-workers have utilized this method in the synthesis of μ -oxo complexes in the rhodium series related to the ones described here ((b) Sharp, P. R.; Flynn, J. R. *Inorg. Chem.* **1987**, *26*, 3231), and we have employed it in an organometallic ring closure leading to oxo- and azametallacycles ((c) Klein, D. P.; Hayes, J. C.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 3704).

(3) Complexes **2**, **3**, **5a**, **b**, **6a**-**c**, **7a**, **b**, **8a** have been characterized by ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR, $^{31}\text{P}\{^1\text{H}\}$ NMR (where applicable), IR, and mass spectrometry and elemental analysis. Complex **4** has been characterized by ^1H NMR, IR, and mass spectrometry. Details are provided as Supplementary Material.

(4) Chetcuti, P. A.; Hawthorne, F. M. *J. Am. Chem. Soc.* **1987**, *109*, 942. Although the dicarbonyl dimer **3** has been previously reported, no details of its synthesis or spectral data beyond a ^1H NMR spectrum have appeared. Consequently, its full spectroscopic and analytical characterization is provided in the Supplementary Material. A more efficient synthesis of complex **3** has been reported: Graham, W. A. G.; Heinekey, D. H., private communication.

(5) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970.

(6) The conversion of CO to CO_2 by a bridging transition-metal oxo complex has appeared in only one other account: Herrmann, W. A.; Serrano, R.; Schafer, A.; Kusthardt, U. *J. Organomet. Chem.* **1984**, *272*, 55.

(6) Suzuki, H. *Electronic Absorption Spectra and Geometry of Organic Molecules*. Academic Press: New York, 1976; Chapter 13.

(7) Complete details of these calculations will appear in the full paper.

(8) Werst, D. W.; Gentry, W. R.; Barbara, P. F. *J. Phys. Chem.* **1985**, *89*, 729.

(9) Werst, D. W.; Brearley, A. M.; Gentry, W. R.; Barbara, P. F. *J. Am. Chem. Soc.* **1987**, *109*, 32.

(10) (a) Im, H.-S.; Bernstein, E. R. *J. Chem. Phys.* **1988**, *88*, 7337. (b) Murakami, J.; Ito, M.; Kaya, K. *J. Chem. Phys.* **1981**, *74*, 6505.