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On the Planarity of 2-Fluorostyrene

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Abstract: The microwave spectrum of 2-fluorostyrene has been analyzed in the frequency region 26.5–40.0 GHz. Only the trans form has been detected in the gas phase. Rotational transitions in the ground and three excited states of the vinyl group torsion vibration have been identified. The ground-state inertial defect value of -1.215 u Å^2 and the zig-zag variation behavior of the rotational constants with the torsional quantum number show that the vinyl group torsion in the region of the trans conformer is governed by a double minimum potential function with a very low barrier at the planar configuration. A reduced potential function $V(X) = 5.8(X^4 - 3.35X^2)$ cm^{-1} with a barrier to planarity of 16 ± 2 cm^{-1} has been determined from the variation of the rotational constants with torsional quantum number and the vibrational spacing between the $v = 0$ and $v = 1$ states of the torsional mode. Some structural considerations have also been made.

The question of the planarity in styrene and halostyrenes has been the subject of considerable discussion and controversy over the past few years.[1-9] The main origin of this controversy lies in the existence of destabilizing interactions, usually attributed to steric hindrance between hydrogens of the vinyl group and the ortho hydrogens or substituents, which could lead to nonplanar gauche structures being the more stable.[8] In this case the torsional potential energy curve in the region of two equivalent conformers may be approximated by a double minimum function.

Microwave spectroscopy is a reliable tool to analyze this problem on the basis of inertial defect values and the variation of the rotational constants with torsional quantum number. A recent microwave study of styrene[9] has shown the molecule to be planar with a very flat torsional potential function in the region close to the minimum. The same conclusion has been found for 4-fluoro-[4] and 4-chlorostyrene[5] from their microwave spectrum. No microwave study has yet been made on the 2-substituted halostyrenes.

The effects of ortho substitution on the potential function governing the vinyl group internal rotation may be expected to be considerable. Such effects have been analyzed in other aromatic derivatives such as 2-fluoronitrobenzene,[10,11] which was found to be nonplanar, and 2-fluorobenzaldehyde,[12] for which only the trans rotamer with a planar configuration was detected in the gas phase.

We have studied the microwave spectrum of 2-fluorostyrene (2-FS) in an attempt to find the stable conformations in the gas phase and to settle the question of its planarity.

Experimental Section

The sample of 2-FS was supplied by Ventron and was used without further purification. All Stark-modulated spectra were obtained with a

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(1) Ralowski, W. M.; Wettermark, G.; Ljunggren, S. *Acta Chem. Scand.* **1973**, *27*, 1565–1572.
(2) Ralowski, W. M.; Mjöberg, P. J.; Almlöf, J. E. *J. Chem. Soc., Faraday Trans.* **1975**, *71*, 1109–1113.
(3) Carreira, L. A.; Towns, T. G. *J. Chem. Phys.* **1975**, *63*, 5283–5286.
(4) Ralowski, W. M.; Mjöberg, P. J.; Ljunggren, S. O. *J. Mol. Struct.* **1976**, *30*, 1–11.
(5) Ralowski, W. M.; Mjöberg, P. J.; Ljunggren, S. O. *J. Mol. Struct.* **1976**, *31*, 169–176.
(6) Carreira, L. A.; Towns, T. G. *J. Mol. Struct.* **1977**, *37*, 85–92.
(7) Hollas, J. M.; Ridley, T. *Chem. Phys. Lett.* **1980**, *75*, 94–98.
(8) Bock, C. W.; Trachtman, M.; George, P. *Chem. Phys.* **1985**, *93*, 431–443.
(9) Caminati, W.; Vogelsanger, B.; Bauder, A. *J. Mol. Spectrosc.* **1988**, *128*, 384–398.
(10) Cornell, T.; Larsen, N. W.; Pedersen, T. *J. Mol. Struct.* **1979**, *65*, 43–49.
(11) Alonso, J. L.; Gonzalez, S.; Mulas, R., unpublished.
(12) Alonso, J. L.; Villamañân, R. M. *J. Chem. Soc., Faraday Trans.* **1989**, *85*, 137–149.

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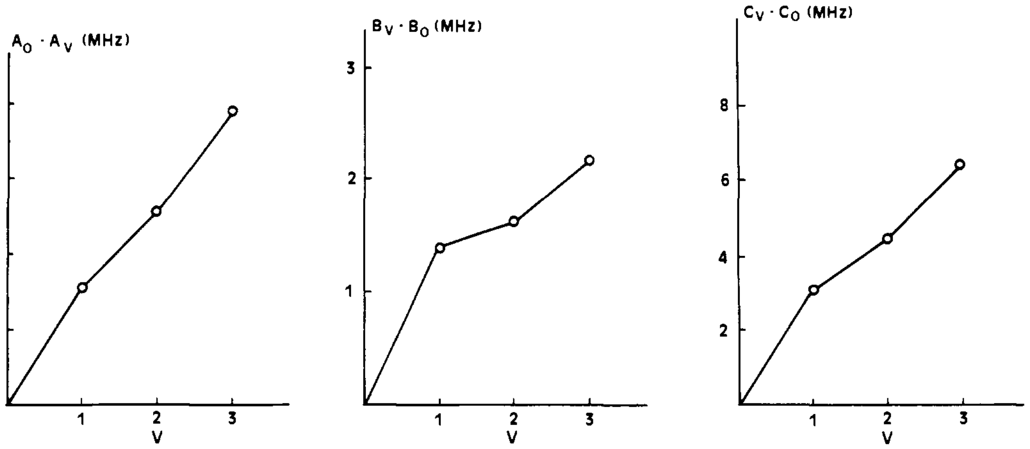

Figure 1. Variation of the rotational constants of 2-fluorostyrene with the vinyl group torsion quantum number.

computer-controlled spectrometer[13] operated in the 26.5–40-GHz region. Radiofrequency microwave double resonance experiments (RFMWDR)[14,15] were made for the assignment of the spectra. The waveguide sample cell was cooled to 260 K. The estimated accuracy of frequency measurements is 0.05 MHz.

Results

A. Rotational Spectra. Planar model calculations based on the related molecules styrene[8] and fluorobenzene[16] show that both the cis and trans conformers of 2-FS are prolate asymmetric rotors. The microwave spectrum has been observed to be fairly dense and complex. Using very low Stark modulation fields, it was possible to observe groups of closely spaced pairs of transitions occurring every ~3 GHz. These were identified as ^{b}Q-branch transitions $J_{K,J-K} \leftarrow J_{K-1,J-K+1}$ and $J_{K,J-K+1} \leftarrow J_{K-1,J-K+2}$ with $J = 17$ to 22 and $K_{-1} = 12$ to 15, consistent with the predictions for the trans conformer. These groups were assigned by their characteristic Stark effect pattern and their identification was confirmed by RFMWDR. At this point, $A-C$ and the asymmetry parameter κ for the molecule were accurately determined. Using this information $^{b}R_{11}$- and $^{a}R_{01}$-type transitions were assigned by RFMWDR.

Each ground-state line was accompanied by several vibrational satellites. The identification of transitions belonging to three vibrationally excited states was possible on the basis of their characteristic regular spacing and decreasing intensity. These vibrational satellites were assigned to the torsional mode of vibration of the vinyl group which is expected to be the lowest frequency mode. The 1 ← 0 vibrational spacing of this mode has been estimated from relative intensity measurements[17] to be 25 ± 6 cm^{-1}. This value is in good agreement with that of 22.1 cm^{-1} obtained by Hollas[18] from the single vibronic level fluorescence spectra.

All experimental frequencies for the ground and excited states have been fitted using an A-reduced semirigid Hamiltonian[19] in the I^r representation. The measured frequencies are given in Table I. The rotational and centrifugal distortion constants as well as the inertia defects $\Delta_c = I_c - I_a - I_b$ are given in Table II. The more negative inertia defect for successive excited states confirms that the satellite lines arise from an out-of-plane vibration.

Searches to detect transitions attributable to the cis conformer were unsuccessful. Therefore, this form could be present only in a very low proportion in the gas phase.

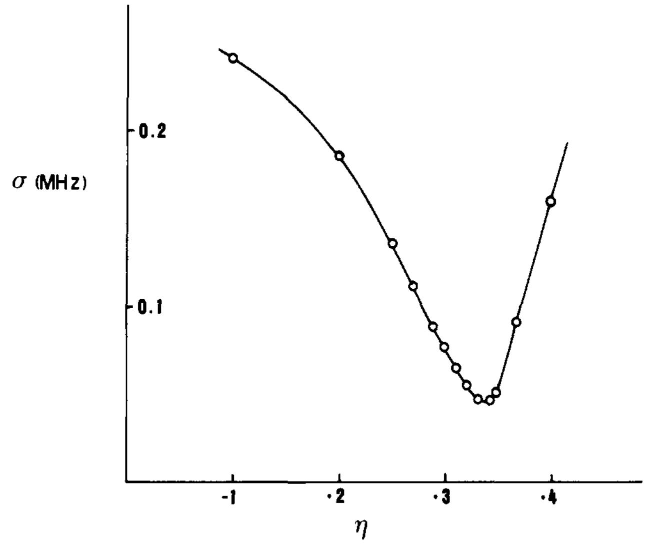

Figure 2. Dependence of the standard deviation on η for the simultaneous fitting of the rotational constants of 2-fluorostyrene to eq 2.

B. Equilibrium Conformation and Torsional Potential Function. The ground-state inertial defect value ($\Delta_c = -1.215$ u Å^2) is large compared to that of related molecules such as styrene ($\Delta_c = -0.6958$ u Å^2), 4-fluorostyrene ($\Delta_c = -0.775$ u Å^2), and 4-chlorostyrene ($\Delta_c = -0.801$ u Å^2). Furthermore, a zig-zag behavior in the variation of the rotational constants with the torsional quantum number has been observed as Figure 1 shows. Both facts indicate that the potential energy function governing the torsional motion at the trans configuration could be of the double-minimum type with a very low barrier at the planar configuration.

A reduced[20] quadratic–quartic potential function model of the form

$$V(X) = \nu_0(X^4 - \eta X^2) \tag{1}$$

can be used to analyze the potential curve for the rotation of the vinyl group in the region of the minima. The torsional potential function can be derived from the vibrational dependence of the rotational constants g_v using the expansion[21]

$$g_v = g(0) + g(2)\langle X_v^2\rangle + g(4)\langle X_v^4\rangle \tag{2}$$

where the $g(0)$ constants refer to the planar molecule; $\langle X_v^2\rangle$ and $\langle X_v^4\rangle$ are the average values of X^2 and X^4 for the torsional state with vibrational quantum number v. By a numerical fitting of the observed rotational constants to expression 2 it is possible to

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(13) López, J. C.; Alonso, J. L.; Peláez, F. J. *J. Mol. Spectrosc.* **1988**, *131*, 9–20.

(14) Wodarczyk, F. J.; Wilson, E. B. *J. Mol. Spectrosc.* **1971**, *37*, 445–463.

(15) Peláez, F. J.; Alonso, J. L.; Muñoz, J. M. *Opt. Pura Apl.* **1983**, *16*, 83–89.

(16) Bak, B.; Christensen, D.; Hansen Nygard, L.; Tannenbaum, E. *J. Chem. Phys.* **1957**, *26*, 134–137.

(17) Esbitt, A. S.; Wilson, E. B. *Rev. Sci. Instrum.* **1963**, *34*, 901–907.

(18) Hollas, J. M., personal communication.

(19) Watson, J. K. G. *Vibrational Spectra and Structure*; Elsevier: Amsterdam, 1977; Vol. 6, pp 1–89.

(20) Chan, S. I.; Stelman, D. *J. Mol. Spectrosc.* **1973**, *10*, 278–299.

(21) Chan, S. I.; Zinn, J.; Fernández, J.; Gwinn, W. D. *J. Chem. Phys.* **1960**, *33*, 1643–1655.

Table I. Observed Rotational Transitions for the Trans Conformer of 2-Fluorostyrene in the Ground and Excited States (MHz)

transition						ground state		$v = 1$		$v = 2$		$v = 3$	
						obsd	$\Delta\nu$[a]	obsd	$\Delta\nu$[a]	obsd	$\Delta\nu$[a]	obsd	$\Delta\nu$[a]
6	5	2	5	4	1	26 971.49	−0.03	26 963.98	−0.09			26 948.46	−0.01
6	6	0	5	5	1	29 594.72	0.02	29 579.81	0.10	29 569.36	0.03	29 555.56	0.03
6	6	1	5	5	0	29 593.57	0.03			29 568.17	0.00	29 554.36	−0.02
7	6	1	6	5	2	32 164.24	0.06	32 153.47	−0.01	32 144.38	0.04	32 132.82	−0.03
7	6	2	6	5	1	32 151.43	−0.03	32 140.79	−0.01	32 131.69	−0.01	32 120.19	−0.07
8	7	1	7	6	2	37 308.66	0.03	37 294.85	0.03	37 283.69	−0.01	37 269.52	0.03
8	7	2	7	6	1	37 306.41	−0.04	37 292.55	−0.10	37 281.45	−0.08	37 267.39	0.06
9	7	2	8	6	3	39 870.17	0.02	39 860.66	0.02	39 850.84	0.06	39 838.91	0.02
9	7	3	8	6	2	39 855.20	−0.02	39 845.75	−0.01	39 835.93	−0.02	39 824.13	0.00
13	1	12	12	2	11	28 009.32	−0.04			28 106.40	−0.01		
13	2	11	12	3	10	29 943.00	0.01	30 008.72	−0.06	30 031.59	0.02	30 071.73	0.09
13	2	12	12	1	11	28 010.37	−0.03	28 081.80	0.03	28 107.43	−0.01	28 151.90	−0.03
13	3	10	12	4	9	31 725.39	−0.03	31 786.05	0.01	31 805.77	0.00	31 841.19	0.01
13	3	11	12	2	10	29 974.66	0.02	30 040.35	0.01	30 063.18	0.01	30 103.30	0.02
13	4	9	12	5	8	32 112.01	0.00	32 171.37	−0.03	32 187.81	−0.05		
13	4	10	12	3	9	32 226.26	0.02	32 285.52	0.05	32 305.59	0.02	32 341.37	0.03
13	5	9	12	4	8	36 080.09	0.00	36 128.26	−0.05	36 145.19	−0.01	36 175.54	−0.05
13	9	4	12	9	3	33 887.29	−0.04	33 941.78	0.12	33 957.00	0.08	33 985.43	−0.07
13	9	5	12	9	4	33 885.42	−0.01	33 939.81	0.05	33 954.92	−0.11	33 983.55	−0.07
14	0	14	13	1	13	28 013.71	0.03	28 096.79	0.02	28 127.59	0.00	28 180.40	0.02
14	1	14	13	0	13	28 013.71	0.03	28 096.79	0.02	28 127.59	0.00	28 180.40	0.02
15	0	15	14	1	14	29 945.86	0.00	30 035.09	0.00	30 068.18	−0.02	30 124.90	−0.02
15	1	15	14	0	14	29 945.86	0.00	30 035.09	0.00	30 068.18	−0.02	30 124.90	−0.02
15	10	5	14	10	4	39 181.05	0.02	39 243.39	−0.09	39 260.96	−0.01		
15	10	6	14	10	5	39 179.37	0.01	39 241.82	0.01	39 259.36	0.05	39 292.07	0.09
16	0	16	15	1	15	31 878.03	−0.01	31 973.42	0.00	32 008.84	0.02	32 069.46	−0.01
16	1	15	16	0	16	29 501.02	−0.01	29 415.85	−0.03			29 304.78	0.02
16	1	16	15	0	15	31 878.03	−0.01	31 973.42	0.00	32 008.84	0.02	32 069.46	−0.01
16	2	15	16	1	16	29 501.02	−0.01	29 415.85	−0.03			29 304.78	0.01
17	1	16	17	0	17	31 426.56	0.01	31 335.85	0.03			31 217.47	−0.02
17	2	16	17	1	17	31 426.56	0.01	31 335.85	0.03			31 217.47	−0.02
17	12	5	17	11	6	28 786.90	−0.05	28 704.28	0.06	28 668.73	0.00	28 613.22	−0.02
17	12	6	17	11	7	28 788.73	0.02	28 705.99	0.02	28 670.46	−0.02	28 614.99	0.01
18	12	6	18	11	7	28 512.36	−0.01	28 430.45	0.02	28 395.56	0.01	28 340.87	−0.02
18	12	7	18	11	8	28 519.07	−0.03	28 437.16	0.01	28 402.23	−0.01	28 347.49	−0.03
19	12	7	19	11	8	28 172.70	−0.02	28 091.82	0.05	28 057.66	0.00	28 004.06	0.01
19	12	8	19	11	9	28 195.69	0.02	28 114.64	−0.02	28 080.41	−0.03	28 026.67	0.01
19	13	6	19	12	7	31 171.25	−0.09	31 081.72	−0.02	31 043.41	−0.02	30 983.43	−0.02
19	13	7	19	12	8	31 172.87	0.06	31 083.21	0.00	31 044.92	0.03	30 984.99	0.09
20	13	7	20	12	8	30 876.46	−0.01	30 787.71	−0.02	30 750.07	−0.01	30 690.97	−0.01
20	13	8	20	12	9	30 881.91	0.01	30 793.12	−0.02	30 755.43	−0.03	30 696.29	−0.03
21	13	8	21	12	9	30 519.09	−0.02	30 431.41	0.01	30 394.57	0.01	30 336.59	0.01
21	13	9	21	12	10	30 537.20	0.02	30 449.40	−0.02	30 412.45	−0.03	30 354.35	−0.01
21	14	7	21	13	8	33 546.76	−0.08	33 450.37	−0.02	33 409.28	−0.01	33 344.83	0.00
21	14	8	21	13	9	33 548.15	0.10	33 451.60	0.01	33 410.51	0.03	33 346.05	0.03
22	14	8	22	13	9	33 233.49	0.01	33 137.95	0.02	33 097.55	0.02	33 034.00	−0.02
22	14	9	22	13	10	33 237.81	0.02	33 142.24	0.00	33 101.87	0.06	33 038.25	−0.01
23	14	9	23	13	10	32 859.95	−0.02	32 765.53	0.01	32 725.97	0.00	32 663.62	0.01
23	14	10	23	13	11	32 874.09	0.04			32 739.91	−0.01	32 677.46	0.01
23	15	8	23	14	9			35 811.45	−0.01	35 767.61	0.02	35 698.66	−0.02
23	15	9	23	14	10			35 812.41	−0.02	35 768.56	0.01	35 699.65	0.01
24	15	9	24	14	10	35 584.47	0.03	35 482.09	−0.03	35 438.92	−0.07	35 370.99	−0.08
24	15	10	24	14	11	35 587.81	−0.02	35 485.52	0.02	35 442.39	0.04	35 374.43	0.04
25	15	10	25	14	11	35 196.21	0.06	35 094.92	−0.03	35 052.68	−0.02	34 985.98	−0.01
25	15	11	25	14	12	35 206.95	−0.07	35 105.82	0.03	35 063.48	0.00	34 996.67	0.00
26	15	11	26	14	12	34 734.78	0.01			34 593.76	0.01	34 528.57	0.03
26	15	12	26	14	13	34 767.05	−0.02			34 625.78	0.01	34 560.30	0.01

[a] Observed minus calculated frequency from rotational constants of Table II.

Table II. Rotational Constants, Inertia Defect ($\Delta = I_c - I_a - I_b$), and Centrifugal Distortion Constants for 2-Fluorostyrene in the Ground and Excited States

	ground state	$v = 1$	$v = 2$	$v = 3$
A/MHz	2573.6259 (12)[a]	2572.0694 (14)	2571.0684 (12)	2569.7103 (12)
B/MHz	1541.0978 (18)	1542.502 (2)	1542.7122 (18)	1543.261 (2)
C/MHz	966.1452 (16)	969.2092 (18)	970.363 (3)	972.3260 (17)
Δ/u Å^2	−1.215	−2.689	−3.341	−4.380
Δ_J/kHz	0.055 (4)	0.052 (5)	0.045 (4)	0.061 (4)
Δ_{JK}/kHz	0.141 (5)	0.156 (7)	0.128 (15)	0.146 (5)
Δ_K/kHz	0.127 (10)	0.131 (11)	0.160 (15)	0.142 (9)
δ_J/kHz	0.0183 (15)	0.0206 (18)	0.014 (3)	0.0223 (16)
δ_K/kHz	0.162 (8)	0.147 (10)	0.12 (3)	0.176 (9)
σ[b]/MHz	0.037	0.043	0.036	0.038
N[c]	56	54	53	55

[a] Standard errors in units of the last digit. [b] Standard deviation of the fit. [c] Number of frequencies fitted. Conversion factor 505 379.1 MHz u Å^2.

Table III. Fits of the Rotational Constants of 2-Fluorostyrene in the Ground and Three Excited States of the Torsional Mode to Eq 2 for η = 3.35 and $g(0)$, $g(2)$, and $g(4)$ Constants Obtained

	A_v/MHz		B_v/MHz		C_v/MHz	
v	obs	obs − calc	obs	obs − calc	obs	obs − calc
0	2573.6259	−0.0457	1541.098	−0.030	966.145	−0.018
1	2572.0694	0.0433	1542.502	0.019	969.209	0.015
2	2571.0684	−0.0176	1542.712	0.008	970.363	−0.003
3	2569.7103	−0.0012	1543.261	−0.008	972.326	−0.001
σ^a (MHz)		0.065		0.037		0.023
$g(0)$ (MHz)		2575.1 (2)[b]		1539.6 (1)		963.21 (6)
$g(2)$ (MHz)		−0.9 (2)		1.7 (1)		2.69 (7)
$g(4)$ (MHz)		−0.20 (3)		−0.08 (2)		0.12 (1)
σ^c (MHz)		0.045				

[a] Standard deviation of the fit for each rotational constant. [b] Standard errors in parentheses in units of the last digit. [c] Total standard deviation of the fit.

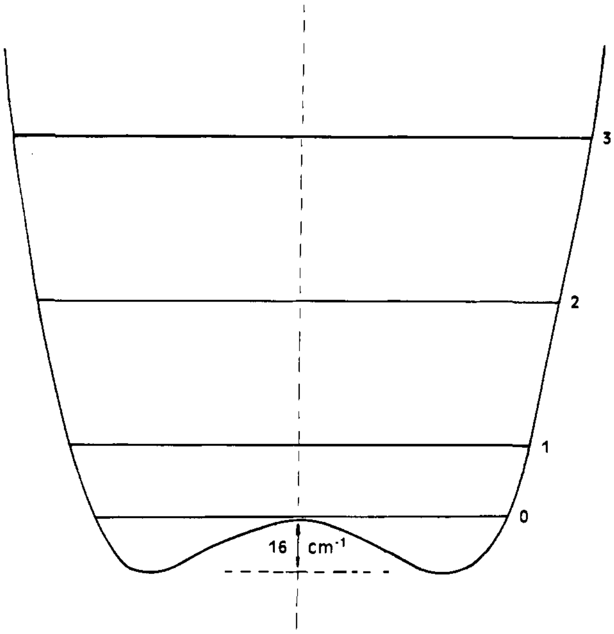

Figure 3. The experimentally determined potential function $V(X) = 5.8(X^4 - 3.5X^2)$, associated energy levels, and barrier to planarity. X is a reduced coordinate.

find a pausible potential function. The coefficients $g(0)$, $g(2)$, and $g(4)$ are treated as empirical parameters. A series of simultaneous fits of the rotational constants has been made for a wide range of η using a basis set of 80 harmonic oscillator eigenfunctions. Figure 2 shows the variation of the standard deviation of the fit in the interval where the best fitting was found. The minimum was obtained close to $\eta = 3.35$. The results for this value are collected in Table III. A confidence interval of $\eta = 3.25\text{–}3.50$ has been estimated in the same way as described elsewhere.[22] Using the energy separation[18] $E_{01} = 22.1$ cm^{-1}, a potential function

$$V(X) = 5.8(2)[X^4 - 3.35(13)X^2] \qquad (3)$$

with a barrier to planarity of 16 ± 2 cm^{-1} has been obtained (see Figure 3).

C. Structural Calculations. The microwave spectrum of only one conformer of 2-FS has been analyzed. Using reasonable structural parameters transferred from related molecules such as fluorobenzene[16] and styrene[8] it can be easily shown that the experimental data are only consistent with the trans conformer. However, these data are insufficient to perform a complete structural analysis of the molecule. In this way only the $C_2C_1C_\alpha$ and $C_1C_\alpha C_\beta$ angles (see Figure 4) have been refined to obtain a good fit between observed and calculated rotational constants. The values for these angles as well as the assumed structural parameters are given in Table IV.

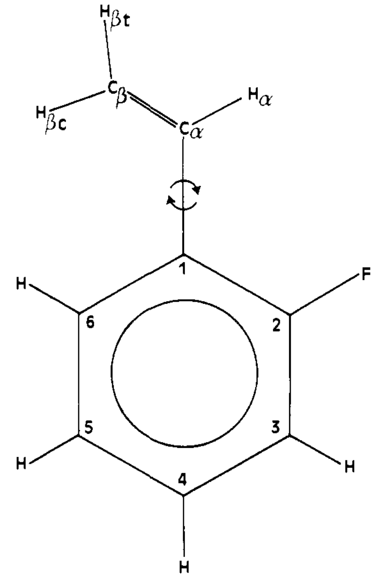

Figure 4. Ring atom numbering scheme for 2-fluorostyrene.

Table IV. Molecular Structure of 2-Fluorostyrene (See Figure 4 for Nomenclature of Atoms)

angles (deg)		bond lengths (Å)	
Assumed Structural Parameters[a]			
$\angle C_1C_2C_3$	121.7	$C_1—C_2$	1.397
$\angle C_2C_3C_4$	118.7	$C_2—C_3$	1.397
$\angle C_3C_4C_5$	120.5	$C_3—C_4$	1.395
$\angle C_4C_5C_6$	120.0	$C_4—C_5$	1.396
$\angle C_5C_6C_1$	120.5	$C_5—C_6$	1.396
$\angle C_6C_1C_2$	118.7	$C_6—C_1$	1.395
$\angle C_2C_3H_3$	118.9	$C_2—F$	1.332
$\angle C_3C_4H_4$	119.4	$C_3—H_3$	1.080
$\angle C_4C_5H_5$	120.0	$C_4—H_4$	1.081
$\angle C_1C_6H_6$	119.4	$C_5—H_5$	1.080
$\angle C_1C_2F$	119.2	$C_6—H_6$	1.081
$\angle C_\beta C_\alpha H_\alpha$	118.1*	$C_1—C_\alpha$	1.475*
$\angle C_\alpha C_\beta H_{\beta c}$	123.1*	$C_\alpha{=}C_\beta$	1.340*
$\angle C_\alpha C_\beta H_{\beta t}$	121.1*	$C_\alpha—H_\alpha$	1.092*
		$C_\beta—H_{\beta c}$	1.089*
		$C_\beta—H_{\beta t}$	1.088*
Fitted Structural Parameters			
$\angle C_1C_\alpha C_\beta$	130		
$\angle C_2C_1C_\alpha$	121		

[a] Parameters are quoted from ref 16; those with an asterisk (*) are from ref 8.

The above structure has been used in order to derive the dihedral angle, τ, from both inertial data and the potential function (3). An internal rotation about the C_α–C_1 bond in which both the top

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(22) Villamañán, R. M.; López, J. C.; Alonso, J. L. *Chem. Phys.* **1987**, *115*, 103–108.

(vinyl group) and the frame behave as rigid units has been assumed as a model for the vinyl group torsion. It is therefore appropriate to use the dihedral angle τ as an internal coordinate for this motion. In order to estimate τ from inertial data, the vinyl group was rotated until the value of Δ_c for the ground state was reproduced. This occurs for $\tau = 13.6°$.

The normal coordinate Q for the vinyl torsion and the dihedral angle τ are related by:

$$Q = (G_{\tau\tau}^{-1})^{1/2}\tau \qquad (4)$$

where $(G_{\tau\tau}^{-1})$ is the inverse G matrix element for the coordinate τ.[23] $G^{-1}_{\tau\tau}$ has been calculated for several values of τ and has very little dependence on the angular coordinate. An average value of 10.98 u Å^2 has been used to calculate the value of τ corresponding to the value $\langle\tau_0^2\rangle^{1/2} = 14.7°$.

Using the value of $\tau = 13.6°$ and the assumed structure (see Table IV), the ground-state rotational constants are reproduced with discrepancies of less than 0.3%.

Discussion

The analysis of the microwave spectrum of 2-FS shows the trans form to be the most stable conformer in the gas phase. Careful searches for the microwave spectrum of the cis rotamer were made without success. On this basis the presence of this rotamer cannot be excluded, but if it exists it must be in a very low concentration with respect to the trans form.

Molecules with low-frequency skeletal vibrations often exhibit very anharmonic potential functions. In these cases it is more realistic to give the potential energy function and the corresponding path of motion rather than definite structural parameters. This may be the case of 2-FS for which the microwave data are consistent with a double minimum function contour for the vinyl torsion potential function in the region of the trans rotamer. Moreover, the small barrier to planarity of 16 cm^{-1} separating the two minima corresponding to nonplanar gauche configurations is very close to the lowest vibrational level. In this situation the molecule might be considered vibrating about the planar form even for this vibrational level. We have not sufficient data to perform a complete structural analysis for the path of the vinyl group torsional motion, and so we have only carried out some estimations using a rigid model.

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(23) Polo, S. R. *J. Chem. Phys.* **1956**, *24*, 1133–1138.

Gas-Phase Proton Transfer from Toluenes to Benzyl Anions

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Abstract: Gas-phase proton-transfer kinetics of PhCH$_2^-$ + ArCH$_3$ → ArCH$_2^-$ + PhCH$_3$ were studied for reactions having $\Delta H°_{rxn}$ = 0 to −20 kcal/mol. These reactions are very slow in the absence of thermodynamic driving force; their reaction efficiencies range from 0.004 to 0.7. RRKM theory was applied to obtain energy differences between the proton-transfer transition state and the loose orbiting transition state from reaction efficiencies. Marcus theory provides a general model for a rate–equilibrium relationship with a constant intrinsic energy barrier of 7 kcal/mol for the degenerate proton transfer from toluene to benzyl anion. The barrier is inferred from an RRKM fit to the energy difference of −5 kcal/mol between the proton-transfer transition state and the energy of the reactants and an estimated −12 kcal/mol for the energy of the collision complex relative to the reactants. In the reaction involving 3-nitrotoluene, electron transfer, which is some 11–12 kcal/mol less favorable than proton transfer, dominates almost exclusively.

Proton transfers are among the most thoroughly studied reactions. The most widely used free energy relationship, the Hammett equation, is based on acidities of benzoic acids. Rates of exothermic proton transfer reactions in solution vary from diffusion controlled, when the transfer occurs between oxygen and/or nitrogen substrates, to much slower than the diffusion rate, when the reaction involves carbon acids that form delocalized conjugate bases upon deprotonation. Because of the important role of proton transfer in solution chemistry, gas-phase and theoretical studies, particularly thermodynamic properties and reaction dynamics, have vigorously expanded over the past decade in the hope of understanding the intrinsic reactivity and the role of solvent molecules by comparing the behavior to the two phases. Gas-phase kinetic studies have led to conclusions similar to those made for the solution reactions. That is, proton transfers between charge-localized anions proceed with high efficiency[1,2] (close to collision rates) whereas those involving charge-delocalized anions can be slow even when energetically favorable.[1c,3] When only charge-localized anions are involved, it has been observed that some endothermic proton-transfer reactions dominate in the presence of competing exothermic reaction channels if reactant translational energy is enough to overcome the thermodynamic barrier.[4c] On the other hand, although proton-transfer reactions involving charge-delocalized carbon anions have generally been found to be significantly slower than collision rates,[3] they can still be facile enough to be competitive with other exothermic reaction

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(1) (a) Bohme, D. K. In *Interactions Between Ions and Molecules*; Ausloos, P., Ed.; Plenum: New York, 1975; p 489. (b) Mackay, G. I.; Payzant, L. D.; Schiff, H. I.; Bohme, D. K. *J. Phys. Chem.* **1976**, *80*, 2919. (c) Nicol, G.; Sunner, J.; Kebarle, J. *Int. J. Mass Spectrom. Ion Processes* **1988**, *84*, 135.

(2) Grabowski, J. J.; DePuy, C. H.; Van Doren, J. M.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1985**, *107*, 7384, and references therein.

(3) (a) Brauman, J. I.; Lieder, C. A.; White, M. J. *J. Am. Chem. Soc.* **1973**, *95*, 927. (b) Farneth, W. E.; Brauman, J. I. *J. Am. Chem. Soc.* **1976**, *98*, 7891. (c) Meyer, F. K.; Pellerite, M. J.; Brauman, J. I. *Helv. Chim. Acta* **1981**, *64*, 1058. (d) Also, see: Bohme, D. K.; Lee-Ruff, E.; Young, L. B. *J. Am. Chem. Soc.* **1972**, *94*, 5153.

(4) (a) Bohme, D. K.; Rakshit, A. B.; Mackay, G. I. *J. Am. Chem. Soc.* **1982**, *104*, 1100. (b) Hierl, P. M.; Ahrens, A. F.; Henchmen, M.; Viggiano, A. A.; Paulson, J. F.; Clary, D. C. *J. Am. Chem. Soc.* **1986**, *108*, 3140. (c) Henchmen, M.; Hierl, P. M.; Paulson, J. F. *J. Am. Chem. Soc.* **1985**, *107*, 2812. (d) Bohme, D. K. In *Ionic Processes in the Gas Phase*; Ferriera, M. A. A., Ed.; Reidel: Boston, 1984; p 111.

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