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On the planarity of styrene and its derivatives: the molecular structures of styrene and (Z)- β -bromostyrene as determined by ab initio calculations and gas-phase electron diffraction¹

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Abstract

The molecular structures of styrene and (Z)- β -bromostyrene have been studied in the gas phase at nozzle temperatures of 303 and 338 K respectively. For both molecules the electron diffraction data were consistent with the results from ab initio calculations which described the vinyl torsional motion, near the planar configurations, in terms of a double minimum potential function with barriers of 243 cal mol⁻¹ (styrene) and 430 cal mol⁻¹ (bromostyrene) at the planar form, and with the minimum energy forms 27° (styrene) and 39° (bromostyrene) away. The perpendicular barriers were calculated to 2.73 kcal mol⁻¹ (styrene) and 1.10 kcal mol⁻¹ (bromostyrene). The important distances (r_a) and angles (\angle_a) obtained from least squares refinements of the electron diffraction data are as follows: styrene, $r(C-H)_{Ax} = 1.102(7)$ A, r(C=C) = 1.355(16) A, r(C-C) = 1.399(2) Å, r(C-C=) = 1.475(23) Å, $\angle C=C-C = 126.9(24)^\circ$; and bromostyrene, $r(C-H)_{Ax} = 1.082(13)$ Å, r(C-C) = 1.331(20) Å, $r(C-C)_{Ph} = 1.400(2)$ Å, r(C-C=) = 1.465(20) Å, r(C-Br) = 1.893(8) Å, $\angle C=C-C = 132.8(23)^\circ$, $\angle Br-C=C = 125.7(15)^\circ$, $\angle C^2-C^1-C^7 = 123.9(33)$. © 1997 Elsevier Science B.V.

Keywords: Styrene; Structure; Conformation; Conjugation; Electron diffraction

1. Introduction

The question of the eventual planarity of styrene has been the subject of many spectroscopic [1-8] and theoretical [9-22] investigations. Carreira and Towns [1] analyzed low frequency Raman data of gaseous styrene in terms of a torsional potential with a minimum at the planar form and a high barrier

at the perpendicular configuration. These data, together with fluorescence data, were later reinterpreted by Hollas and Ridley [2] using a flat torsional potential with the minium at the planar form. The weak rotational spectrum of styrene was recorded by Caminati, Vogelsanger and Bauder [6] using pulsed microwave Fourier transform spectroscopy, and the small inertial defect obtained suggested the presence of a planar styrene. Theoretical calculations at the 3-21G level carried out by Bock, Trachtman and George [16], concluded that styrene has a flat torsional potential with a minimum at the

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planar form, supporting the conclusion drawn by Hollas and Ridley [2]. However, lower levels of theoretical calculations [9,11] had suggested a nonplanar minimum for styrene. No complete structure determination has been carried out on styrene.

Microwave spectroscopic studies of 3-iodo [3], 4-fluoro [4], and 4-chloro [5] styrenes were carried out, and the presence of planar forms was confirmed. However, 2-fluorostyrene was found by Villamanan, Lopez and Alonso [8] to have a rather large inertial defect and a zig-zag variation behavior of the rotational constants with the torsional quantum number, suggesting that the torsional motion of the vinyl group was governed by a double minimum potential function in the region of the trans form (where the vinyl group is cis to C^6) with a barrier of 16 cm⁻¹. This result is interesting in that the trans form of 2-fluorostyrene is sterically similar to styrene (Fig. 1), since one would expect that the interaction between the cis β -proton on the vinyl group and the phenyl ortho proton would be the major sterical factor influencing the planarity of the vinyl group. We therefore decided to initiate investigations on the gas-phase molecular structures and conformations of styrene and (Z)- β -bromostyrene (Fig. 1), using the techniques of electron diffraction and ab initio molecular orbital calculation, with the hope to shed some light on the preferred conformations of these two molecules.

2. Experimental

A commercial sample of styrene was obtained from Aldrich and was used without further purification. (Z)- β -Bromostyrene was prepared from (E)-cinnamic acid by the method of Cristol and Norris [23]. In a three-necked flask fitted with dropping funnel, reflux condenser, magnetic stirrer and ice-bath were placed 29.6 g (0.200 mol) of (E)-cinnamic acid in 200 mL of



Fig. 1. Models of styrene, 2-fluorostyrene and (Z)- β -bromostyrene, showing the numbering of atoms referred to in the text.

dry benzene. A solution of 32.0 g (0.200 mol) of bromine in 20 mL of dry benzene was added dropwise with rapid stirring. After 4 h the solid precipitate was collected on a Buchner funnel and dried in a vacuum desiccator. The yield was essentially quantitative. This dibromide, 54.4 g (0.177 mol) and sodium acetate, 44.6 g (0.531 mol) were dissolved in 1 L of dry acetone. This mixture was heated under reflux for 8 h. The acetone was then removed on a rotary evaporator and the residue dissolved in 600 mL of water. The aqueous mixture was extracted twice with ethyl ether, the ether dried over magnesium sulfate and removed on a rotary evaporator. The yield of (Z)- β -bromostyrene was 82%. The product was confirmed via NMR chemical shifts.

The electron diffraction patterns were collected on Kodak Electron Image plates using the Oslo apparatus for styrene and the Balzers Eldigraph KDG-2 instrument [24,25] for bromostyrene, at nozzle temperatures of 303–305 and 338–340 K, respectively. The voltage/distance calibration was done with benzene as reference. The nozzle-to-plate distances were as follows: 480.71 and 200.17 mm for styrene; 498.55 and 248.54 mm for bromostyrene. Six plates from each camera distance were selected for both molecules for use in the least squares analysis. The optical densities were measured with a Joyce Loebl microdensitometer.

3. Structural studies and results

3.1. Styrene

3.1.1. Theoretical calculations

The geometry of styrene was first studied by ab initio calculations at the HF/6-31G^{*} level using GAUSSIAN 92. The conformer with a torsional angle ϕ [C²-C¹-C⁷=C⁸] of 16.2° was found to have minimum energy. In order to study the C¹-C⁷ torsional potential more closely, similar optimizations were carried out also for other conformers, where the torsional angle ϕ varied continuously between 0° and 90°. A potential function with barriers of 0.020 kcal mol⁻¹ at 0° and 2.85 kcal mol⁻¹ at 90° was obtained. Similar calculations were later carried out by the GAUSSIAN 94 [26] program, using more sophisticated methods, including electron correlation.

φ(C1C7) (°)	ΔE (kcal mol ⁻¹)	∠C-C=C	$\angle C^2 - C^1 - C^7$	$\angle C^{1} - C^{2} - H$	$\angle C^{\perp} - C^{\circ} - H$
0	0.210	127.25	122.16	120.41	119.74
5	0.195	127.14	122.16	120.41	119.74
10	0.155	126,99	122.06	120.35	119.74
15	0.098	126,69	121.92	120.25	119.73
20	0.042	126.28	121.75	120.13	119.72
25	0.005	125.81	121.53	120.00	119.72
27.418	0	125.53	121.39	119.94	119.73
30	0.007	125.31	121.23	119.83	119.72
40	0.190	124.32	120.76	119.59	119.73
50	0.642	123.64	120.36	[19.42	119.73
60	1.278	123.26	120.21	119.38	119.70
90	2.556	123.13	120.03	119.49	119.58

Energies and some angle parameters (in degrees) for styrene conformers^a from MP2/6-31G* ab initio calculations

^aThe phenyl C–C and C–H bonds were assumed to be equal in the calculations.

Some relevant results from MP2/6-31G^{*} optimizations are tabulated in Table 1. The results are based on a model with equal C–C and C–H bonds, respectively, in the phenyl group. All other geometry parameters were relaxed, except the C^1-C^7 dihedral angle. The results from these more advanced calculations show a ten-fold increase in the planar torsional barrier, compared to that from the GAUSSIAN 92 HF/6-31G^{*} calculations (0.210 vs. 0.020 kcal mol⁻¹), while the barrier at the perpendicular conformation is somewhat reduced (2.556 vs. 2.850 kcal mol⁻¹). The C^1-C^7 torsion angle of the minimum energy conformer increased from 16.2 to 27.4°. The torsional potential energies corresponding to the data in Table 1 are shown in Fig. 2.

Table 1

In order to ascertain that the restrictions introduced above in the geometry of the phenyl ring do not significantly influence the position of the torsional potential minimum and the magnitudes of the torsional barriers, MP2/6-31G^{*} optimizations without any geometry restrictions were carried out for the minimum energy conformer and for the planar and perpendicular conformers corresponding to the torsional maxima. Table 2 shows the parameters obtained for the minimum energy conformer for the unrestricted model (IA) and for the one with equal C-C and C-H bonds in the phenyl ring (IB), as well as for the planar (II) and for the perpendicular (III) conformers. The calculated energy of the unrestricted model is 0.2538 kcal mol⁻¹ lower than that of the restricted model. The position of the torsion potential minimum is only negligibly influenced by

the phenyl ring restrictions $(27.21^{\circ} \text{ vs. } 27.42^{\circ})$, while the planar and perpendicular torsional barriers are both slightly increased (0.243 vs. 0.210 kcal mol⁻⁴ and 2.730 vs. 2.556 kcal mol⁻¹) when they are calculated from the fully relaxed structures presented in Table 2.

The frequencies of the minimum energy fully relaxed MP2/6-31G^{*} styrene structure (Table 2, IA) have been calculated and are listed in Table 3, I. Column II shows the frequencies multiplied by 0.9427, as recommended for MP2/6-31G^{*} frequencies



Fig. 2. Torsional potential functions for styrene (fully drawn) and (Z)- β -bromostyrene (dashed) for rotation around the C^1-C^2 bond, as calculated by ab initio MP2/6-31G⁻ and HF/6-31G⁻ optimization, respectively.

[27]. The calculated IR intensities are listed in column 3. Vibrational frequencies have been measured by several groups [28–31], and those reported by Condirston and Laposa [31] and by Mross and Zundel [30] are included in Table 3. The assignments and notations of the frequencies are those used by Condirston [31]. The agreement between calculated and experimental frequencies is far from perfect. Generally the deviations are smallest when the calculated frequencies are compared to those of Condirston et al. [31].

3.1.2. Gas electron diffraction study

The structural analysis was carried out after the ED data were interpolated to integral $q [(40/\pi)\sin(\theta/2)]$

units. A calculated background [32] was subtracted from the averaged long and short intensity data to obtain two averaged experimental molecular intensity curves. Least squares analyses were carried out simultaneously on these two intensity curves, following the procedure outlined by Gundersen and Hedberg [33]. The elastic scattering and phase shift factors used in all calculations were those tabulated by Schafer et al. [34].

The amplitudes of vibration were calculated using a force field similar to the one used for benzil [35]. In the beginning of the study three assumptions were made in order to reduce the number of parameters needed to define the geometry of styrene. First, the \angle CCC and \angle CCH valence angles of the benzene ring

Table 2

Results obtained by fully optimized (IA, II and III) MP2/6-31G^{*} ab initio calculations for the minimum energy conformer of styrene (IA) and for the planar (II) and perpendicular (III) forms at the torsional barriers. The numbers in brackets show the deviations from average C-C and C-H distances in the phenyl ring. The results shown in IB are those obtained for a restricted model

	IA		IB	II(0°)	III(90°)
$\overline{C^1 - C^2}$	1.4046	(+0.0061)		1.4057	1.4021
$C^{2}-C^{3}$	1.3941	(-0.0041)		1.3930	1,3960
$C^{3}-C^{4}$	1.3974	(-0.0011)	1.3984(Av.)	1.3981	1.3965
$C^{4}-C^{5}$	1.3964	(-0.0021)		1.3955	1.3966
$C^{5}-C^{6}$	1.3947	(-0.0038)		1.3948	1.3959
C ⁶ -C ¹	1.4039	(+0.0054)		1.4043	1.4021
$C^{1}-C^{7}$	1.4718		1.4754	1.4713	1.4849
$C^{7}=C^{8}$	1.3429		1.3426	1.3433	1.3399
C^2-H	1.0877	(-0.0001)		1.0873	1.0881
C^3-H	1.0876	(-0.0002)		1.0876	1.0876
C ⁴ -H	1.0873	(-0.0005)	1.0876(Av.)	1.0873	1.0873
C ⁵ -H	1.0875	(0.0003)		1.0875	1.0876
C ⁶ -H	1.0889	(+0.0011)		1.0890	1.0881
C ⁷ -H	1.0903		1.0903	1.0904	1.0907
C ⁸ -H _{trans}	1.0849		1.0849	1.0848	1.0856
$C^8 - H_{cis}$	1.0858		1.0859	1.0854	1.0861
$C^{6}-C^{1}-C^{2}$	118.48		(120)	118.18	118.91
$C^{1}-C^{2}-C^{3}$	120.64		(120)	120.73	120.55
$C^{2}-C^{3}-C^{4}$	120.31		(120)	120.44	120.13
$C^{3}-C^{4}-C^{5}$	119.59		(120)	119.48	119.72
$C^{4}-C^{5}-C^{6}$	120.06		(120)	120.00	120.13
$C^{5}-C^{6}-C^{1}$	120.90		(120)	121.18	120.55
$C^{2}-C^{1}-C^{7}$	122.04		121.39	123.11	120.54
$C^{1} - C^{7} = C^{8}$	125.25		125.53	127.00	123.15
$C^{1}-C^{2}-H$	119.56		119.94	120.06	119.28
$C^{I}-C^{6}-H$	119.28		119.73	119.14	119.28
$C^{8}-C^{7}-H$	118.72		118.60	117.98	119.43
$C^7 - C^8 - H_{trans}$	121.17		121.15	120.70	121.53
$C^7 - C^8 - H_{cis}$	122.09		122.19	122.95	121.35
$\phi(-C^{1}-C^{7}-)$	27.21		27.42	0.(Fixed)	90.(Fixed)
E (hartree)	-308.5934390		-308.5930345	-308.593052	-308.5890887

Table 3

Calculated frequences (in cm⁻¹) from a MP2/6-31G^{*} optimized model of styrene (I, II), compared to experimentally obtained data for the molecule

I (calc)	II (x0.9427)48	Calc. IR Int.	Description ^a	Ref. [31]	Ref. [30]	
83	78	0.1	torsion	(76)		•
191	181	1.0	$X-s(\gamma C-CHCH_2)$	212	213	
235	221	1.0	$X-s(\beta C-CHCH_2)$	241	239	
397	374	0.1	φ CC	407	3.38	
409	386	1.7	$X-s(\phi C-C)$	433	400	
462	436	3.8	$X-s(\alpha C-C-C)$	442	500	
494	466	0.2	$\beta -C = C$	554	554	
570	562	3.8	α C-C-C	621	620	
633	597	0.1	$\gamma_{\rm as} = CH$,	640	679	
679	640	9.1	φ CC	699	698	
743	700	67.2	γC-H	776	772	
798	752	0.1	$X-s(\alpha C-C-C)$	776	776	
832	784	0.1	γ C-H	841	838	
862	813	0.3	$\gamma_{\rm v} = CH_{\rm v}$	909	909	
885	834	0.1	γ C-H	909	982	
891	840	0.3	ν C-H	970	1019	
918	865	38.2	, γ C-Η	985	1032	
1021	963	9.3	γ =CH-	992		
1024	966	12.2	ring	999		
1057	996	5.7	βČ-H	1019		
1076	1015	0.2	$\beta_{11} = CH_2$	1032	1081	
1132	1068	3.6	βC-H	1083	1108	
1215	1146	0.0	β C–H	1156	1156	
1234	1164	0.1	βC-H	1181	1182	
1259	1187	1.8	$X-s(\nu C-CHCH_3)$	1203	1245	
1347	1270	1.6	β C-H	1289	1315	
1376	1297	1.5	$\beta = CH_{-}$	1303	1386	
1462	1378	2.6	v C-C	1334	1413	
1490	1405	4,9	$\beta_{\rm c} = CH_{\rm c}$	1411	1446	
1510	1423	3.4	$\nu C-C$	1459	1492	
1556	1467	11.5	ν C-C	1494	1541	
1651	1557	2.0	νC-C	1575	1576	
1678	1582	1.7	νC-C	1603		
1715	1617	3.3	ν C=C	1630	1630	
3198	3015	11.5	$\nu_{\rm c} = CH_{\rm c}$	2981	2940	
3212	3028	7.4	$\nu = CH -$	3009	2979	
3217	3033	1.3	ν C-H	3029	3009	
3220	3036	1.5	ν C–H	3055	3029	
3229	3044	8.2	ν C–H	3061	3045	
3237	3051	26.3	ν C-H	3084	3059	
3246	3060	13.2	$v_{\rm m} = CH_2$	3091	3080	
3308	3119	11.6	ν C-H	3106	3087 ^a	

^aSee Ref. [31] for an explanation of the symbols.

are assumed equal to 120°. Second, all the C–H bond lengths are assumed to be identical, and third, all C–C bond lengths in the benzene ring are assumed to be identical. The geometrical parameters chosen are: $r(C-H)_{Av}$, $r(C-C)_{Ph}$, r(=C-C), r(C=C), $\angle C=C-C$, ϕ [torsion angle $C^2-C^1-C^7=C^8$]. Preliminary RD curves showed that the experimental curve was not very sensitive to the value of ϕ . Best results were obtained for a nonplanar model with a torsion angle of 18°. The experimental uncertainty of this parameter was, however, large, and the other structure parameters were hardly influenced if the torsional angle

	Styrene		(Z)-β-Bromostyrene	
	Dynamic model ^b	Static model	Static model	
$r(C-H)_{Av}$	1.102(7)	1.100(7)	1.082(13)	
$r(C-C)_{Ph}$	1.398(2)	1.399(3) ^c	1.400(2)	
$(C^7 = C^8)$	1.346(20)	1.355(16)	1.331(20)	
$(\mathbf{C}^{\top} - \mathbf{C}^{7})$	1.486(22)	1.475(23)	1.465(20)	
(C-Br)			1.893(8)	
$(C^2 - C^1 - C^7)$	122.0(assumed)	122.0(assumed)	123.9(33)	
$\angle C^{1} - C^{7} = C^{8}$	126.5(24)	126.9(24)	132.8(23)	
∠C=C-Br			125.7(15)	
5		28(21)	29(14)	
⁴ ک	5.75%	5.69%	7.60%	

Table 4 Structural results from least squares analyses of electron diffraction data for styrene and (Z)-β-bromostyrene^a

^aDistances (r_a) in ångstroms and angles (\angle_{α}) in degrees.

^b $R = [\sum (I_{calc} - I_{obs})^2 / \sum (I_{obs})^2]^{1/2}$. ^cPotential function of the form $V = V_0 [1 - 2^* (\phi/\phi_0)^2 + (\phi/\phi_0)^4]; \phi_0 = 27.2^\circ; V_0 = 0.243 \text{ kcal mol}^{-1}$. ^dAverage value [(C¹-C²): 1.405(3); (C²-C³): 1.395(3); (C³-C⁴): 1.398(3)].



Fig. 3. Experimental and theoretical GED molecular intensities for styrene and their differences.

was fixed at 27.2° , corresponding to the minimum energy conformer from the MP2/6-31G^{*} calculations. In the final refinements of the static styrene model some constraints based on the MP2/6-31G^{*} optimization (Table 2, IIA) were introduced. These include the magnitude of the CCH valence angles and the differences between the CC bonds in the phenyl ring.

Refinements of the data using dynamic models with (a) a flat torsional potential about the planar form and (b) a double minimum potential function with a small barrier at the planar form were carried out. All these tests gave good agreement with the data and the structures obtained from the least squares refinements were virtually identical. A model with the vinyl group perpendicular to the benzene ring gave, however, a much poorer fit to the experimental data. Results from the least squares refinement are summarized in Table 4 and the intensity and radial distribution curves corresponding to the dynamic model are shown in Figs. 3 and 4 respectively.

3.2. (Z)- β -Bromostyrene

3.2.1. Theoretical calculations

The geometry of (Z)- β -bromostyrene was fully optimized at the ab initio HF/6-31G^{*} level using GAUSSIAN 94 [26]. The minimum energy conformer was found to have a torsional angle $\phi [C^2 - C^{\dagger} C^7 = C^8$ of 39.3°. In order to generate the torsional potential and the barriers of the potential function, full optimizations were also carried out for conformers with the torsional angle ϕ fixed at regular intervals in the region between 0° and 90° . Barriers of 0.43 kcal mol⁻¹ at 0° and 1.10 kcal mol⁻¹ at 90° were obtained. The results are tabulated in Table 5, and the torsional potential function is shown in Fig. 2. We made attempts to carry out MP2/6-31G^{*} optimizations also for this molecule, but the requirements regarding supercomputer memory and computing time were so demanding that we did not consider it worthwhile.



Fig. 4. Experimental and theoretical radial distribution curve for styrene and their differences.

				Styrene	
r(C7=C8)	1.3214	1.3154	1.3190	1.3220	
$r(C^{1}C^{7})$	1.4774	1.4901	1.4809	1.4808	
$r(C^{\dagger}C^{6})$	1.3959	1.3898	1.3916	1.3947	
$r(C^{5}C^{6})$	1.3832	1.3851	1.3851	1.3827	
$r(C^4C^5)$	1.3845	1.3856	1.3851	1.3876	
$r(C^{3}C^{4})$	1.3857	1.3853	1.3859	1.3836	
$r(\mathbf{C}^{2}\mathbf{C}^{3})$	1.3838	1.3854	1.3833	1.3855	
$r(\mathbf{C}^{T}\mathbf{C}^{2})$	1.3956	1.3897	1.3935	1.3919	
r(C-Br)	1.8887	1.8879	1.8889		
$\angle C^2 - C^1 - C^6$	117.96	119.10	118.62	118.17	
$\angle C^1 - C^6 - C^5$	121.44	120.44	120.46	121.14	
$\angle C^4 - C^5 - C^6$	119.87	120.15	120.40	120.05	
$\angle C^3 - C^4 - C^5$	119.44	119.71	119.63	119.45	
$\angle C^2 - C^3 - C^4$	120.69	120.14	119.96	120.39	
$\angle C^1 - C^2 - C^3$	120.58	120.46	120.92	120.79	
$\angle C^7 - C^1 - C^6$	116.51	120.45	118.17	118.17	
$\angle C^7 - C^1 - C^2$	125.53	120.45	123.21	121.39	
$\angle C^1 - C^7 = C^8$	134.87	127.45	131.21	127.2	
$\angle C^7 = C^8 - Br$	129.00	124.71	126.99		
φ	0°	90°	39.28°	27.42°	
E	0.43	1.10	0.0		

Results from ab initio HF/6-31G^{*} calculations for (Z)-β-bromostyrene^a Similar data for the minimum energy form of styrene are included

^aDistances in angles in degrees. E = relative energies in kcal mol⁻¹.

The CC and CH bond lengths of styrene, see Table 2, are not compatible with those of bromostyrene in Table 5. It is well known that unsaturated CC bond lengths obtained from HF optimizations are generally too short, while those from MP2 calculations mostly agree fairly well with experimentally obtained data. In order to facilitate the comparison of the calculated structure parameters of styrene and bromostyrene, the results from the HF/6-31G^{*} optimization of the former are included in Table 5.

3.2.2. Gas electron diffraction study

Electron diffraction data reduction was carried out in the usual way [33] and a calculated background [32] was subtracted from the averaged long and averaged short camera data in order to obtain experimental molecular intensity curves. The average experimental intensity curves for the two camera distances are shown in Fig. 5. Scattering amplitudes and phase shifts for all calculations were obtained from values tabulated by Schafer et al. [34].

The amplitudes of vibration were calculated from the same force field as that used for styrene, with the addition of the following parameters: $k_{\text{str}}(\text{C-Br}) = 3.5 \text{ mdyn } \text{\AA}^{-1}, \ k_{\text{b}}(\text{C=C-Br}) = 0.65 \text{ mdyn } \text{\AA} \text{ rad}^{-2}, \ k_{\text{b}}(\text{Br-C-H}) = 0.50 \text{ mdyn } \text{\AA} \text{ rad}^{-2}.$

In order to simplify the model and to reduce the number of parameters necessary to define the structures of this molecule, the following assumptions, guided by the results obtained from ab initio calculations, were made: (1) all \angle CCC and \angle HCC valence angles of the benzene ring equal 120°, (2) $\angle C^1 - C^7 - H = 114.7^\circ$ and (3) $\angle C^7 = C^8 - H = 121.4^\circ$. The structure of bromostyrene was defined by the following geometrical parameters: $r(C-H)_{Av}$, $r(C-C)_{Ph}$, $r(C^1-C^7)$, $r(C^7 = C^8)$, $r(C^8 - Br)$, $\angle Br - C^8 = C^7$, $\angle C^8 = C^7 - C^1$, $\angle C^7 - C^1 - C^2$, $\phi [C^2 - C^1 - C^7 = C^8$ torsional angle].

Preliminary tests using models with ϕ values of 0°, 45° and 90° showed that the 45° model gave the best agreement with the experimental RD curve. The 0° and 90° models gave distances in the 4–6 Å region not compatible with the experimental curve. In later refinements, the value of ϕ was allowed to refine simultaneously with other geometrical and amplitude parameters. The results from the final least squares refinement are summarized in Table 4. The RD and intensity curves corresponding to this model are shown in Figs. 6, and 5.

Table 5



Fig. 5. Experimental and theoretical GED molecular intensities for (Z)- β -bromostyrene and their differences.

A dynamic model with a double minimum potential with a barrier at the planar form was also tested. Test refinements using different barrier heights showed that the data were not sensitive to this parameter. The location of minimum of the potential function was tested at 60°, 40° and 20°. The 40° model gave better agreement ($\approx 0.5\%$) with the experimental data than the 20° model, while the 60° model failed to converge. The dynamic model gave a larger value for ϕ than the static model because the static model ϕ value represented a weighted averaged value between 0° and 50° along the potential function. Values for the other geometrical parameter were essentially the same as those obtained for the static model.

4. Discussion

The results from the gas electron diffraction studies of styrene and (Z)- β -bromostyrene are summarized in

Table 4. Table 6 presents some of the structural results for these and related molecules [36–39]. The experimental C=C bond length for all six molecules are in the range of 1.33 to 1.35 Å. Substitutions by Cl, Br, Ph or both Br and Ph did not change the C=C bond length significantly. Calculations at the HF/6-31G^{*} level gave the following results: (1) there is a decrease of the ethylene C=C bond due to Cl and Br substitutions, (2) there is an increase in the ethylene C=C bond length due to phenyl substitution and (3) there is a decrease in the styrene C=C bond upon bromine substitution. Unfortunately all of the calculated bond length differences due to substitutions are in the range of 0.005 Å, which is well within the error limits of electron diffraction studies.

The results from the experimental GED study of styrene indicate that the equilibrium conformer of the molecule might be nonplanar, in agreement with the theoretical MP2/6-31G^{*} optimized structure. Due to the insensitivity of the styrene GED scattering data



to the $-C^1-C^7$ - torsion angle, the GED results do not, however, verify beyond doubt that the equilibrium styrene conformer is nonplanar. A structurally related molecule, 2-*tert*-butyl-1,3-butadiene, was, however, recently studied by gas electron diffraction [40], and in this case it was possible to determine the preferred nonplanar conformation with confidence, because this molecule contains many CC distances that are sensitive to the magnitude of the C=C-C=C torsion

angle. The minimum energy conformers of 2-*tert*butyl-1,3-butadiene and styrene are expected to be governed by the same two factors, namely the π -electron conjugation, favoring a planar conformer on one side, and the nonbonded repulsion between the cis β vinyl proton and the ortho phenyl protons (analogous for 2-*tert*-butyl-1,3-butadiene), favoring a nonplanar form, on the other side.

In Fig. 7 structural details of the MP2/6-31G*

	H ₂ C=CH ₂	H ₂ C=CHCl	H ₂ C=CHBr	CIHC=CHCI	PhHC=CH ₂	PhHC=CHBr
r(C=C)	1.3391(13)	1.342(4)	1.348(8)	1.345(6)	1.346(20)	1.331(20)
	1.3169	1.3116	1.3118		1.322	1.319
r(C-X)		1.730(4)	1.881(7)	1.718(4)		1.893(8)
			1.889			1.889
∠X-C=C		122.5(3)	122.8(3)	123.8(2)		125.7(15)
Ref.	[36]	[37]	[38]	[39]	this work	this work

Table 6 Structural parameters of styrene, (Z)- β -bromostyrene and related molecules^a

^aDistances in angles in degrees. Values without error limits are from ab initio HF/6-31G^{*} calculations.

 ${}^{b}X = Br and Cl.$





.343 Å

.485

3.033

2.44

1.347

Fig. 7. Details of structure results for styrene (from MP2/6-31G^{*} optimizations) and 2-*tert*-butyl-1,3-butadiene (from an experimental GED study [40]).

optimized minimum energy conformer of styrene are compared to analogous data obtained experimentally for 2-*tert*-butyl-1,3-butadiene [40]. The structure details in the two systems are strikingly similar. According to the data presented for these two molecules they do both prefer nonplanar equilibrium conformations. The observed deviation from planarity in 2-*tert*-butyl-1,3-butadiene, $\phi = 32.1^{\circ}$, is somewhat larger than that calculated for styrene, $\phi = 27.2^{\circ}$. This seems reasonable, considering that the C¹=C² bond in 2-*tert*-butyl-1,3-butadiene is substantially shorter than the corresponding bond in styrene (1.347 vs. 1.405 Å).

Nearly all valence angles in the regions of interest are remarkable similar in the two molecules, and their absolute magnitudes reflect the problems connected to internal nonbonded repulsions between atoms in close proximity. The ab initio calculations show that the valence angles $C^2-C^1-C^7$, $C^1-C^7=C^8$, $C^7=C^8-H^{14}$ of the minimum energy conformer of styrene are enlarged by 1.5° , 2.1° and 0.7° , respectively, relative to the "strainless" perpendicular conformer. These geometry changes do all contribute to reduction of the nonbonded repulsion. $\angle \beta_1$ is considerably larger in 2-tert-butyl-1,3-butadiene than in styrene. This is, however, not surprising as it seems reasonable that it will be easier to adjust $\angle \beta_1$ in 2-tert-butyl-1,3-butadiene in a manner that reduces the HH nonbonded repulsion (i.e. by enlargement), than what is the case for styrene. For the latter molecule, an increase in $\angle \beta_1$ will obviously imply stereochemical changes in the phenyl ring as well, and the total effect on the energy might be disadvantageous.

For (Z)- β -bromostyrene the nonplanar equilibrium conformation has been established from electron diffraction data, as well as from ab initio calculations. Fig. 2 shows that the calculated torsional potentials of (Z)- β -bromostyrene and styrene have similar shapes, with maxima for the planar and the perpendicular forms, and with syn energy minima ((Z)- β -bromostyrene: 39°; styrene: 27°). There are, however, also significant differences between the two torsional potentials. The perpendicular potential for (Z)- β bromostyrene is less than half that for styrene (1.1 vs. 2.7 kcal mol⁻¹), while the situation for the planar barrier is reversed (0.4 vs. 0.2 kcal mol⁻¹). These differences are probably primarily due to larger nonbonded repulsions in (Z)- β -bromostyrene conformers over the entire syn region. The lower perpendicular barrier in(Z)- β -bromostyrene is therefore probably not due to stabilization of this conformer, but to destabilization of the reference minimum energy conformer. It can not, however, be ruled out that positive interaction between the bromine atom and the π electrons of the phenyl ring might contribute somewhat toward stabilizing the perpendicular conformer.

The explanation of the torsional potential of (Z)- β bromostyrene suggested above is supported by the angle parameters obtained from the experimental as well as from the theoretical studies. The observed values for $\angle C^1 - C^7 = C^8$ and $\angle C = C - Br$ (132.8° and 125.7°), which are crucial for the distance between Br and the ortho H atom, are both very large. The calculated values for these angles are of similar magnitude. For a planar conformer of (Z)- β -bromostyrene $\angle C^1 - C^7 = C^8$ is calculated to be 135°. This effect is, therefore, probably also responsible for the magnitude of the planar barrier of (Z)- β -bromostyrene, relative to that of styrene.

Table 7 shows experimentally obtained conformation results of styrene derivatives, other than those that are studied in the present work. Most of these molecules are reported to be planar, but in several of the references it is stated that it is difficult to distinguish between a planar equilibrium conformer and a nonplanar one, where the torsional potential in the

Table 7			
Conformations of styrene derivative	s obtained by	experimental	methods

Molecule	$\angle \phi$ (°) ^a	Method	Ref.	
$\overline{\bigcirc}$	0	MW	[2]	
\bigcirc	0	MW	[6]	
$\bigcirc \sim$	0	MW	[41]	
\bigcirc	0	MW	[3]	
	0	MW	[4]	
.0	0	SJFS ^b	[42]	
	0	MW	[5]	
	0	SJFS ^b	[43]	
Ŷ, Ŷ,	nonplanar	MW	[8]	
, ,				
\otimes	25	SJFS ^b	[44]	
Q L	45	SJFS ^b	[44]	
(O) V	50	SJFS ^b	[44]	
$\bigcirc \bigcirc \bigcirc \bigcirc$				
	18	NMR	[45]	
	0	NMR	[47]	
	O-cis: 38 O-trans: 45 129.6	NMR	[48]	

^aTorsion angle between the phenyl and vinyl groups.

^bSJFS: Supersonic Jet Fluorescence Spectroscopy.

nearby region is characterized by a double minimum, separated by a small barrier in the planar form.

A series of molecules of special interest regarding the question of nonplanarity of styrene derivatives was recently studied by Manea and Cable [44]. They recorded the electronic spectrum of the styrene derivative, benzylidenecyclobutane, seeded in a supersonic jet expansion, using resonantly enhanced two-photon ionization spectroscopy [44]. Analysis of the observed torsional levels revealed an exited state with planar equilibrium geometry undergoing largeamplitude motion, and a nonplanar ground state having an energy minimum at a torsional angle of 25° between the phenyl and vinyl groups. Two other β -cycloalkane derivatives, benzylidenecyclopentane and benzylidenecyclohexane, are estimated to have ground state torsional angles of 45° and 50°, respectively [44]. The latter two β -cycloalkane derivatives are obviously sterically more hindered than styrene, but in the cyclobutyl derivative the β -Z substituent is forced away from the ortho hydrogen because of the angle requirements in the four-membered ring. It is, therefore, not unlikely that the torsional potentials of benzylidenecyclobutane and styrene are similar in the *syn* region close to the planar form.

There are also some recently published NMR

studies that are of great interest in relation to the present investigation. High-resolution deuterium NMR spectra of 2-vinylanthracene- α -d were studied by Ni et al. [45]. The observed quadrupolar splitting was used to calculate the torsional angle between the vinyl and anthracene planes (18°). It is hard to see why the minimum energy conformation in 2-vinylanthracene should differ from that of styrene. Ni et al. have also studied torsional angles in a series of alkenylarenes by semiempirical MO methods [46]. These results are, however, less convincing, as they differ dramatically, depending on the choice of calculation method.

Two other molecules listed in Table 7 have been studied by NMR, namely phenylallene [47] and formylstyrene [48]. Both studies are by Schaefer et al., and the results are of great interest in relation to the material presented in this contribution. Formylstyrene might assume different conformations, depending on the orientation of the formyl group. In the O-cis form, with the carbonyl group cis oriented relative to the vinyl group, the vinyl group is found to be rotated 38° out-of-plane, while the torsional potential of the O-trans form shows two minima, one at 45° (lowest) and another at 129.6° .

In the NMR study of phenylallene [47], it is concluded that this molecule is planar. This seem reasonable considering that this molecule has no β substituent that might interact with the ortho proton. The torsional potential was also studied by ab initio HF/6-31G^{*} calculations [47], which gave minimum energy for the planar form, and a torsional barrier for the perpendicular form equal to $3.86 \text{ kcal mol}^{-1}$. This should be compared with our similar calculations for styrene, which gave a double minimum potential at $\pm 16.2^{\circ}$ and a perpendicular barrier of 2.85 kcal mol⁻¹. Schaefer [47] did also give results from MP2/6-31G^{*} calculations for the planar and perpendicular forms of phenylallene (PA), and the geometric parameters from these calculations are almost identical to similar parameters calculated for the minimum and maximum energy forms of styrene in the present study (Table 2, IA and III), with the following exceptions:

	$IA(\phi = 27)$	′.2°) II(0°)	PA(0°)	III(90°)	PA(90°)
$C^{2}-C^{1}-C^{7}$	122.0	123.1	121.9	120.5	120.4
$C^{1}-C^{7}=C^{8}$	125.3	127.0	124.8	123.2	122.5
$C^{1}-C^{2}-H$	119.6	120.1	119.3	119.3	119.3

The increased sterical repulsion in styrene compared to that of phenylallene is reflected in a torsional barrier in the planar form and in enlarged angles in the critical region.

The larger perpendicular barrier calculated for phenylallene, relative to that of styrene (MP2/6-31G^{*}: styrene, 2.73 kcal mol⁻¹; phenylallene, 3.83 kcal mol⁻¹) is probably to a large extent due to the nonbonded HH repulsion present in the *syn* form of styrene, but not in that of phenylallene.

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References

- L.A. Carreira and T.G. Towns, J. Chem. Phys., 63 (1975) 5283.
- [2] J.M. Hollas and T. Ridley, Chem. Phys. Lett., 75 (1980) 94.
- [3] W.M. Ralowski, P.J. Mjoberg and J.E. Almlof, J. Chem. Soc. Faraday Trans., 71 (1975) 1109.
- [4] W.M. Ralowski, P.J. Mjoberg and S.O. Ljungren, J. Mol. Struct., 30 (1976) 1.
- [5] W.M. Ralowski, P.J. Mjoberg and S.O. Ljungren, J. Mol. Struct., 31 (1976) 169.
- [6] W. Caminatti, B. Vogelsanger and A. Bauder, J. Mol. Spectrosc., 128 (1988) 384.
- [7] J.M. Holas, H. Musa, T. Ridley, P.H. Turner, K.H. Weisenberger and V. Fawcett, J. Mol. Spectrosc., 94 (1982) 437.
- [8] R.M. Villamanan, J.C. Lopez and J.L. Alonso, J. Am. Chem. Soc., 111 (1989) 6487.
- [9] G. Favini and M. Simonetta, Theor. Chim. Acta., 1 (1963) 294.
- [10] P.L. Britton, C.L. Cheng, R.J.W. LeFevre, L. Radom, G.L.D. Ritchie, J. Chem. Soc. (London) B, (1971) 2100.
- [11] N.L. Allinger and J.T. Sprague, J. Am. Chem. Soc., 95 (1973) 3893.
- [12] J.E. Almløf, P.U. Isacsson, P.J. Mjoberg, W.M. Ralowski, Chem. Phys. Lett., 26 (1974) 215.
- [13] J. Sühnel and K. Gustav, Z. Chem., 17 (1977) 342.
- [14] W.F. Reynolds, P.G. Mezey and G.K. Hamer, Can. J. Chem., 55 (1977) 522.
- [15] F. Mommicchioli, I. Baraldi and M.C. Bruni, Chem. Phys., 70 (1982) 161.
- [16] C.W. Bock, M. Trachtman and P. George, Chem. Phys., 93 (1985) 431.

- [17] T. Schaefer, R. Sebastian and G.H. Penner, Can. J. Chem., 66 (1988) 584.
- [18] K.L. Facchine, S.W. Staley, P.C.M. van Zijl, P.K. Mishra and A.A. Bothner-By, J. Am. Chem. Soc., 110 (1988) 4900.
- [19] T. Schaefer and G.H. Penner, Chem. Phys. Lett., 114 (1985) 526.
- [20] S. Tsuzuki, K. Tanabe and E. Osawa, J. Phys. Chem., 94 (1990) 6175.
- [21] M. Head-Gordon and J.A. Pople, J. Phys. Chem., 97 (1993) 1147.
- [22] R. Hargitai, P.G. Szaly, G. Pongor and G. Fogorasi, J. Mol. Struct. (Theochem), 306 (1994) 293.
- [23] S.J. Cristol and W.P. Norris, J. Am. Chem. Soc., 75 (1975) 2645.
- [24] W. Zeil, J. Hasse and L.Z. Wegmann, Instrumentenkd., 64 (1966) 84.
- [25] O. Bastiansen, R. Graber and L. Wegmann, Balzers High Vac. Rep., 25 (1969) 1.
- [26] M.J Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Ciosłowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez and J.A. Pople, GAUSSIAN 94, Rev. B.1, Gaussian Inc., Pittsburgh PA, 1995.
- [27] J.B. Foresman and Æ. Frisch, Exploring Chemistry with Electronic Structure Methods., 2nd ed., Gaussian Inc., Pittsburgh, PA, 1996, p. 63.
- [28] K.S. Pitzer, L. Guttman and E.F. Westrum, J. Am. Chem. Soc., 68 (1946) 2209.
- [29] W.G. Fateley, G.C. Carlson and F.E. Dickson, Appl. Spectrosc., 22 (1968) 650.

- [30] W.D. Mross and G. Zundel, Spectrochim. Acta Part A. 26 (1970) 1109.
- [31] D.A. Condirston and J.D. Laposa, J. Mol. Spectrosc., 63 (1976) 466.
- [32] L. Hedberg, Abstract of Papers, 5th Austin Symposium on Gas Phase Molecular Structure, Austin, TX, March 1974, p. 37.
- [33] G. Gundersen and K. Hedberg, J. Chem. Phys., 51 (1969) 2500.
- [34] L. Schafer, A.C. Yates and R.A. Bonham, J. Chem. Phys., 56 (1971) 3056.
- [35] Q. Shen and K. Hagen, J. Phys. Chem., 91 (1987) 1357.
- [36] E. Hirota, Y. Endo and S. Saito, J. Mol. Spectrosc., 89 (1981) 223.
- [37] P.A.G. Huismen and F.C.J. Mijhoff, Mol. Struct., 54 (1979) 145.
- [38] P.A.G. Huismen and F.C. Mijhoff, J. Mol. Struct., 57 (1979) 83.
- [39] K. Hagen and R. Stolevik, J. Mol.Struct., 147 (1986) 341.
- [40] M. Traetteberg, H. Hopf, H. Lipka, R. Hänel, Chem. Ber., 127 (1994) 1459.
- [41] W.E. Sinclair, H. Yu, D. Phillips, R.D. Gordon, J.M. Hollas, S. Klee and G. Mellau, J. Phys. Chem., 99 (1995) 4386.
- [42] J.M. Hollas and M.Z. Bin Hussein, J. Mol. Spectrosc., 145 (1991) 89.
- [43] J.M. Hollas and P.F. Taday, J. Chem. Soc. Faraday Trans., 87 (1991) 3585.
- [44] V.P. Manea and J.R. Cable, J. Chem. Phys., 105 (1996) 5687.
- [45] Y. Ni, J.S. Siegel, V.L. Hsu and S. Kearns, J. Phys. Chem., 95 (1991) 9211.
- [46] Y. Ni, J.S. Siegel and D.R. Kearns, J. Phys. Chem., 95 (1991) 9208.
- [47] T. Schaefer, S. Krocker and D.M. McKinnon, Can. J. Chem., 73 (1995) 1478.
- [48] T. Schaefer, S. Krocker and D.M. McKinnon, Can. J. Chem., 73 (1995) 2208.