

Broadband Microwave Investigations on Monobromostyrenes

W. RALOWSKI, G. WETTERMARK and S. LJUNGGREN

Department of Physical Chemistry, Royal Institute of Technology, S-100 44 Stockholm 70, Sweden

Broadband microwave spectra of *p*-bromostyrene, *trans*- β -bromostyrene and *m*-bromostyrene are recorded and the sum of the rotational constants ($B+C$) are calculated. From the results obtained, the $C_b-C=C$ angle in *p*-bromostyrene and *cis*-*m*-bromostyrene is $127 \pm 4^\circ$.

High-resolution microwave spectroscopy cannot at present be successfully applied to the study of large molecules. Apart from the fact that the absorption intensities are rapidly diminished with increasing molecular weight, the spectra are usually complicated by the presence of a large number of low-lying vibrational satellites. A high-resolution spectrum often presents such an abundance of weak lines that the assignment becomes a problem of unwieldy complexity.

When the spectrum of a near-symmetric top molecule is scanned at a high sweep rate and detector time constant, a band spectrum is obtained, in which each band consists of the superposition of a large number of unresolved high K lines belonging to a particular $J \rightarrow J+1$ transition.

Neglecting the usually insignificant systematic errors, a band spectrum can be described by formula (1):

$$\nu = (B + C)(J + 1) \quad (1)$$

The constant ($B+C$) can thus be determined from the distances between the bands and their positions.

This work is one of the first attempts to obtain significant structural information from broadband microwave studies. In this paper, investigations of three monobromostyrenes are reported, *p*-bromostyrene, *m*-bromostyrene, and *trans*- β -bromostyrene. They have all high $|\mu|$ -values * large dipole moments along the a principal axis and possess no constituent at sterically hindering positions. Their vapour pressure at room temperature is

* Cf., e.g., C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy*, McGraw, New York 1955.

sufficiently high for microwave studies to be possible. There appears to be no reliable data available at present on the molecular geometry of styrene. The structure of only one styrene derivative has been studied experimentally so far, *trans*- β -bromostyrene, by electron diffraction.¹ Styrene is usually described as a planar molecule where π -electrons belonging to the vinyl group and the benzene ring conjugate. It is, however, conceivable that the vinyl group may rotate more or less freely or that a twisted conformation is the most stable one by analogy with biphenyl² and *N*-benzylideneaniline.³ *p*- and *trans*- β -Bromostyrene are near-symmetric rotors with κ -values around -0.98 . *m*-Bromostyrene, on the other hand, is less symmetric, although a band structure is still observed. The broadband microwave spectra of the three bromostyrenes are shown in Fig. 1. The natural abundances of the two bromine isotopes, ⁷⁹Br and ⁸¹Br, are approximately equal. The spectra thus consist of two superimposed sets of bands. Although this fact provides some possibility to check on different structural assumptions, it also complicates the assignment of the spectra to a considerable degree.

EXPERIMENTAL

Commercial samples of bromostyrenes were used. The sample of *m*-bromostyrene had to be purified by vacuum distillation, whereas *p*- and *trans*- β -bromostyrene were found to be sufficiently pure for our purpose. Microwave spectra in the frequency range 26 500 to 40 000 MHz (Mc/sec) were recorded at room temperature on a Hewlett-Packard 8460A spectrometer.

RESULTS

The frequencies of the band centres are listed in Tables 1–3. All frequencies are given in MHz. The position of any band is calculated as the average value of the frequencies obtained from two sweeps in opposite directions.

Table 1. *p*-Bromostyrene.

<i>J</i>	Observed frequencies	
	⁷⁹ Br	⁸¹ Br
29	26 915	26 665
30	27 802	27 545
31	28 698	28 420
32	29 597	29 310
33	30 500	30 205
34	31 393	31 098
35	32 295	31 988
36	33 195	32 873
37	34 090	33 765
38	34 990	34 645
39	35 888	35 528
40	36 785	36 417
41	37 680	37 308
42	38 580	38 202
43	39 480	39 093
44	—	39 980

Table 2. *trans*- β -Bromostyrene.

<i>J</i>	Observed frequencies	
	⁷⁹ Br	⁸¹ Br
36	27 090	26 802
37	27 808	27 518
38	28 550	28 250
39	29 285	28 985
40	30 010	29 700
41	30 737	30 422
42	31 472	31 145
43	32 208	31 880
44	32 938	32 600
45	33 673	33 315
46	34 405	34 045
47	35 130	34 770
48	35 853	35 493
49	36 595	36 210
50	37 320	36 940
51	38 065	37 660
52	38 790	38 385
53	39 505	39 105
54	—	39 825

Table 3. *m*-Bromostyrene.^a

<i>J</i>	Observed frequencies	
	⁷⁹ Br	⁸¹ Br
23	27 360	27 100
24	28 510	28 230
25	29 660	29 390
26	30 785	30 500
27	31 925	31 630
28	33 070	32 730
29	34 190	33 895
30	35 345	34 995
31	36 495	36 125
32	37 640	37 295
33	38 770	38 380
34	39 905	39 505

^a There are also strong bands at 27 580, 31 400, 33 410, 34 450, 34 740, 36 800 and 37 850 MHz. The band corresponding to the transition $J=27\leftarrow 26$ is weak.

Values of $(B+C)$ were obtained by a least-squares method based on eqn. (1). The obtained values of $(B+C)$ are listed in Table 4. The error in the values of $(B+C)$ was estimated to be ± 2 MHz.

Table 4.

Molecule	Bromine isotope	($B+C$)
<i>p</i> -Bromostyrene	79	897.1
	81	888.4
<i>m</i> -Bromostyrene	79	1141.0
	81	1130.0
<i>trans</i> - β -Bromostyrene	79	731.9
	81	724.3

DISCUSSION

The structure of each molecule was analyzed in the following way.

- (i) An initial structure was assumed.
- (ii) The parameters with the largest influence on ($B+C$) were found.
- (iii) Agreement with experimental data could be achieved by reasonable changes of the parameters.
- (iv) The refined structure was finally checked by computing the value of ($B+C$) for the other isotopic isomer and comparing it with the experimental data. The initial structure was based upon the assumption of hexagonal symmetry of the benzene ring and the following bond lengths (see Fig. 2): $r_b =$

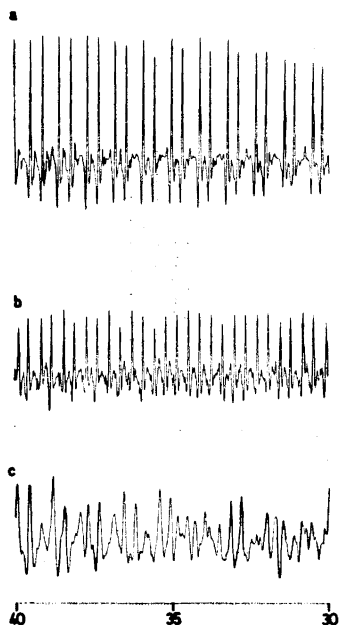


Fig. 1. Broadband microwave spectra of *p*-bromostyrene (a), *trans*- β -bromostyrene (b) and *m*-bromostyrene (c) in the frequency range 30–40 GHz.

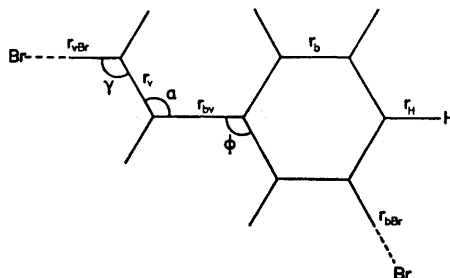


Fig. 2. Structural parameters of bromostyrene type molecules.

1.40 Å, $r_v = 1.34$ Å, $r_{bv} = 1.48$ Å, all $r_H = 1.08$ Å, $r_{bBr} = 1.87$ Å, $r_{vBr} = 1.89$ Å, and all the angles 120° .

Point (ii) above requires some comments. All the parameters were varied in calculations for the three molecules in order to determine their relative effects on the value of $(B+C)$. It was thus shown that the positions of the hydrogen atoms had no significant effect on $(B+C)$. The r_b , r_b , r_{Br} and r_{bv} bond lengths were far more important, but reasonable changes in these parameters did not lead to agreement with experiment. The values of r_b , r_v and r_{Br} were thus taken to be the same as those from many different investigations on similar systems.⁴ The error caused by this assumption was assumed to be negligible.

The bond length r_{bv} was taken from the one existing experimental work on a styrene derivative, *trans*- β -bromostyrene.¹ The effect of the choice of r_{bv} will be discussed in connection with *p*-bromostyrene.

In addition to the bond length, r_{bv} , the following angles were the most essential parameters:

α : the $C_b - C = C$ angle.

γ : the $Br - C = C$ angle.

θ : the dihedral angle between the benzene ring and the plane of the vinyl group.

ϕ : the $C_b - C_b' - C$ angle.

Keeping the α and γ angles equal to 120° , the ϕ angle was varied in calculations for *p*-bromostyrene and *m*-bromostyrene. The experimental values of $(B+C)$ could only be reproduced for $\phi = 124^\circ$ in *p*-bromostyrene and $\phi = 132^\circ$ in *m*-bromostyrene. The very different values obtained for the two isomers appear quite unreasonable. Thus, in the subsequent calculations, the angle α is taken as 120° in agreement with the first assumed structure.

In the cases of *p*-bromostyrene and *m*-bromostyrene the possible influence of a deformation of the benzene ring was studied by carrying out parallel calculations for the hexagonally symmetric ring and the bromine-distorted ring structure. As a result of the above assumptions the only remaining parameters to be considered are the angles α , θ and γ .

p-Bromostyrene. The molecule is very nearly symmetric with $\kappa \approx -0.98$. If r_{bBr} is assumed to be 1.87 Å, α and r_{bv} are the two remaining parameters with the largest influence on the value of $(B+C)$. If we assumed that $\alpha = 120^\circ$ and $(B+C) = 888.4$ MHz, the bond length r_{bv} would have to be 1.546 Å.

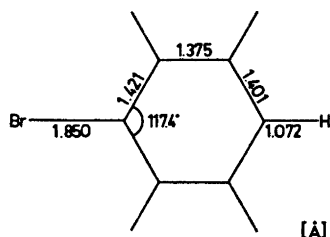


Fig. 3. Distorted structure of bromobenzene.

This value appears unreasonable, since even the single C–C bond in ethane is shorter than this. Igarashi *et al.*¹ determined r_{bv} in *trans*- β -bromostyrene as 1.48 Å. For this bond length the calculated value of α would be 126.3°. Unfortunately, these two parameters appear to be correlated and cannot be separated. This implies that for each pair of parameters which gives $(B+C) = 888.4$ MHz, the value of $(B+C)$ for the isotopic isomer $C_6H_4^{79}Br-CH=CH_2$ is equal to the experimental value 897.1 MHz. A rotation of the benzene ring has only a small effect on the value of $(B+C)$. Thus, when the benzene ring is twisted from the planar to the perpendicular conformation, the value of $(B+C)$ decreases by no more than 0.7 MHz. This corresponds to a decrease of α or r_{bv} by 0.4° and 0.004 Å, respectively.

Parallel calculations were made in order to estimate the effect of the deformation of the benzene ring on the value of $(B+C)$. Bromobenzene has previously been investigated by high resolution microwave spectroscopy.⁵ Rotational constants for several isotopic species have been obtained. The complete r_s structure was not reported, but a structure consistent with the experimental data has been proposed and is reproduced with minor modifications in Fig. 3.

The three rotational constants belonging to this structure are reproduced in Table 5.

Table 5.

	Measured ^a	Calculated ^b
$C_6^{79}H_5Br$		
A	5667.47 ± 1.05	5668.19
B	994.894 ± 0.006	994.87
C	846.250 ± 0.006	846.33
$C_6H_5^{81}Br$		
A	5668.87 ± 1.18	5668.19
B	984.704 ± 0.006	984.69
C	838.858 ± 0.006	838.95

^a From Ref. 5. ^b Cf. Fig. 3.

The rotational constant A should be equal for both isotopic isomers and can be estimated as an average of the two measured constants. It seems reasonable to assume that the bromine atom will cause a stronger deformation of the benzene ring than the vinyl group. Hence, if we let the structure above represent the true ring structure of *p*-bromostyrene, the results are approximately the same as above, *i.e.* $\alpha = 126.9^\circ$. A CNDO/2 calculation⁶ on styrene gave an energy minimum for $\alpha = 130^\circ$. The corresponding angle in butadiene has been experimentally determined to be 123° .⁷

trans- β -Bromostyrene. *trans- β -Bromostyrene* is the only styrene derivative whose structure has so far been experimentally investigated.¹ The molecule was found to have a planar configuration with the r_{bv} bond length equal to 1.48 ± 0.03 Å. Using the parameters suggested by Igarashi *et al.*, the value of $(B+C)$ was calculated to 739.8 MHz, which is about 15 MHz larger than the $(B+C)$ value obtained from the band spectrum.

The molecule is very nearly symmetric with $\kappa \approx -0.99$. The two most important parameters are the angles α and γ . For example, changing the angle α by 1° causes a change of 2.5 MHz in $(B+C)$. In contrast, a rotation of the benzene ring by 90° from the planar conformation increases the value of $(B+C)$ by merely 0.2 MHz. Unfortunately, the influences of the two angles could not be separated and, in consequence, it can only be concluded that $\alpha = 120^\circ$ corresponds to $\gamma = 128.2^\circ$, and $\alpha = 124.5^\circ$ to $\gamma = 120^\circ$. The value $\alpha = 126.3^\circ$, which was obtained for *p*-bromostyrene, gives $\gamma = 118.1^\circ$. Igarashi *et al.* state that the γ angle is $119 \pm 2^\circ$.

m-Bromostyrene. *m-Bromostyrene* is the only bromostyrene which can be expected to exist in two stable conformations. For the planar molecule these are *trans*- and *cis-m*-bromostyrene. The difference in the calculated value of $(B+C)$ between the *trans* ($\theta = 0^\circ$) and the *cis* ($\theta = 180^\circ$) form is 130 MHz (as compared to 0.2 MHz for *trans- β -bromostyrene*). The *cis* isomer should have a slightly lower energy according to our calculations using a modified CNDO-method.⁸ The *trans* isomer is more symmetric than the *cis* isomer. The $|\kappa|$ -values are -0.93 and -0.80 , respectively. A simulated spectrum for a model of *cis-m-bromostyrene* shows that a band structure can be obtained even for such low values of κ . The spectrum, however, becomes more complicated, the bands broaden and may become split. Even a quasi-band structure may arise. If all the parameters are assumed equal in *p*- and *m*-bromostyrene, the resulting values of $(B+C)$ obtained for the bromine distorted structure are listed in Table 6.

Table 6. *m*-Bromostyrene.

Bromine isotope θ	^{79}Br	$(B+C)$	^{81}Br
0°	1010.2		1000.6 (<i>trans</i>)
90°	1073.7		1063.5
180°	1144.4		1133.4 (<i>cis</i>)

The spectrum consists of two series of bands with $(B+C)_{81} = 1130.0$ MHz and $(B+C)_{79} = 1141.0$ MHz. Most probably, these values may be assigned to the *cis* isomer. It should be observed that $\Delta(B+C)_{180} = 1144.4 - 1133.4 = 11.0$ MHz is equal to the difference between the values obtained from the measurements, cf. Table 4. For $\theta = 180^\circ$, $(B+C)$ becomes equal to 1130.0 and 1141.0, respectively, when $\alpha = 127.8^\circ$.

For the bromine distorted structure, $\alpha = 128.0^\circ$ is obtained. Attempts to localize the two remaining series of bands were unsuccessful, even when recording the spectra at other Stark voltages and sweep rates.

In order to establish whether it is possible to neglect the *trans* isomer signals in such a complicated spectrum, the band spectra of mixtures of *p*- and *trans*- β -bromostyrene in different concentrations were recorded. It was often found to be extremely difficult to identify the four band series, even though the exact band positions were known in advance. The Stark lobes are very strong and completely mask many of the bands. The discrepancy between the observed and expected pattern being very large, *trans*- β -bromostyrene was easily detected only in those mixtures where its relative concentration was high. It was even difficult to observe all of the bands of *p*-bromostyrene in mixtures with *m*-bromostyrene. It appears that especially the more closely lying bands are easily concealed.

The results of this study neither confirm nor exclude the existence of two conformers of *m*-bromostyrene — a conclusion similar to the results of one of the recent IR-investigations on this molecule.⁹ The hypothesis about the two conformers can probably be verified if a microwave band spectrum of *m*-bromostyrene, including only one of the two bromine isotopes, is studied.

Conclusions. The $C_b - C = C$ angle (α) in the molecules *cis*-*m*-bromostyrene and *p*-bromostyrene was found to be $127 \pm 4^\circ$. The uncertainty in the angle α is rather large because of the inherent assumptions in its calculation. This value $\alpha = 127 \pm 4^\circ$ is consistent with the $(B+C)$ value of *trans*- β -bromostyrene.

Acknowledgments. We thank Dipl. ing. J. Lewandowska for helping to purify the sample of *m*-bromostyrene and Miss A.-C. Blom for typing the manuscript.

REFERENCES

1. Igarashi, M., Cho, S. and Someno, K. *Nippon Kagaku Zasshi* **81** (1960) 23.
2. Bastiansen, O. and Smedvid, L. *Acta Chem. Scand.* **8** (1954) 1539.
3. Trættemberg, M. *Private communication*.
4. *Tables of Interatomic Distances and Configurations in Molecules and Ions*, Chem. Soc. Spec. Publ. **1965** No. 18.
5. Rosenthal, E. and Dailey, B. P. *J. Chem. Phys.* **43** (1965) 2093.
6. Hamer, G. K. and Reynolds, W. F. *Chem. Commun.* **19** (1971) 1218.
7. Haugen, W. and Trættemberg, M. *Selected Topics in Structure Chemistry*, Universitetsforlaget, Oslo 1967.
8. Höjer, G. *Diss.*, University of Stockholm 1971.
9. Fatelay, W. G., Carlson, G. L. and Dickson, F. E. *Appl. Spectry.* **22** (1968) 650.

Received December 2, 1972.