

## Comment on Broadband Microwave Investigations on Monobromostyrenes

LISE NYGAARD

Chemical Laboratory V, University of Copenhagen,  
The H. C. Ørsted Institute, DK-2100 Copenhagen,  
Denmark

The recent paper<sup>1</sup> on the possible molecular structure of monobromostyrenes based on broadband microwave spectra can be read as a serious overinterpretation of the experimental data. As stated in eqn. (1) of Ref. 1, one piece of evidence is found in a broadband spectrum of each molecular species, *i.e.* the sum of the two rotational constants B and C. It is therefore not to be expected, that more than one structural parameter can be extracted from the experiments, or maybe a set of two or three strongly correlated parameters, assuming values for all other parameters.

Since bromobenzene and a few of its isotopic species have been investigated by high resolution microwave spectroscopy<sup>2</sup> (a tentative molecular structure of bromobenzene was only proposed), an improved data treatment would be to use the *moments of inertia* of bromobenzene as a starting point for the *m*- and *p*-bromostyrenes *without discussing the structure of the C<sub>6</sub>H<sub>4</sub>Br fragment* and try to extract some values for the vinyl group with structural assumptions for that part only. It should be remembered, however, that this rather qualitative procedure will result in a partial *r<sub>0</sub>*-structure based on an insufficient amount of *I<sub>0</sub>*-values, and that nothing can be said about a possible deformation of the benzene ring here (or in bromobenzene) without data from the spectra of the <sup>13</sup>C-species.

The structure of the vinyl group in styrene can be described by the following parameters, two CC bond lengths, three CH bond lengths, two CCC angles, and three CCH angles. The dihedral angle between the vinyl group and the benzene ring will be ignored, since the present experimental results can give no information of this detail. High resolution experiments are needed to determine the three rotational constants separately and find the inertial defect, as *e.g.* in the microwave spectrum of benzaldehyde,<sup>3</sup> which was shown to be planar.

Assuming vinyl parameters in accordance with the structure of the planar *trans*-form of 1,3-butadiene<sup>4</sup> (CH 1.09 Å, C=C 1.34 Å, and C=C-H 122°), trial values of the three parameters marked in Fig. 1 in the range  $r = 1.49 \pm 0.03$  Å,  $\alpha = 123^\circ \pm 3^\circ$ , and  $\beta = 122^\circ \pm 2^\circ$  all give a satisfactory fit within  $\pm 20$  MHz of the measured (B+C)-value for *p*-<sup>79</sup>Br-styrene. The (B+C)-difference for the two Br-species is reproduced exactly, but is only slightly dependent on the model.

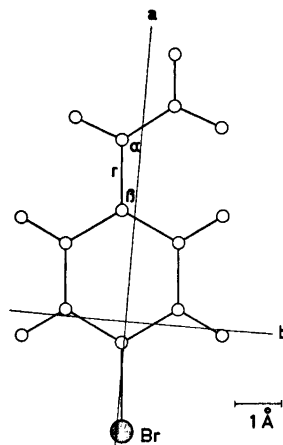


Fig. 1. Model of *p*-bromostyrene.

For *m*-<sup>79</sup>Br-styrene a similar treatment shows that the assigned broadband spectrum is probably that of the *cis*-form, since the calculated (B+C)-value for the *trans*-form is about 150 MHz smaller, and the model variations are less than 30 MHz from the experimental B+C. The (B+C)-difference for the two Br-species is calculated to be 11.2 and 9.7 MHz for the *cis*- and the *trans*-form, respectively. A high resolution experiment is needed to decide the possible presence of the spectrum of the *trans*-form or a non-planar form.

For *trans*- $\beta$ -bromostyrene model calculations with benzene as a starting point, assuming distances and angles for the vinyl part as shown above and using model values from *p*- and *m*-bromostyrene, agree with a C(vinyl)-Br distance of  $1.87 \pm 0.02$  Å. This compares favourably with the electron diffraction result for this molecule<sup>5</sup> and for *cis*-1,2-dibromoethylene,<sup>6</sup> and with the microwave substitution structure of vinyl bromide.<sup>7</sup>

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Received November 22, 1973.