

has the structure  $\begin{array}{c} \text{BH}_2 \\ \diagdown \quad \diagup \\ \text{B} \\ \diagup \quad \diagdown \\ \text{BH}_2 \end{array}$ — $\text{BH}_2$ , the fifth boron atom being coplanar with the square four-membered ring. The values found for interatomic distances are  $\text{B-B} = 1.76 \pm 0.02 \text{ \AA.}$  and  $\text{B-H} = 1.17 \pm 0.04 \text{ \AA.}$

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## The Molecular Structures of the 2-Butenes and the 2,3-Epoxybutanes

BY L. O. BROCKWAY AND PAUL C. CROSS

During an investigation of the reactions of the 2-butenes and some of their derivatives conducted in this Laboratory by Professor Howard J. Lucas<sup>1,2</sup> and his collaborators it was necessary to distinguish between the *cis* and *trans* forms of the 2-butenes and also of the 2,3-epoxybutanes. At the request of Professor Lucas these substances have been investigated by the electron diffraction method of determining the molecular structure of gas molecules. The experimental procedure has been described in detail.<sup>3</sup>

**2-Butenes.**—The two isomers of 2-butene have boiling points of 3.0 and 0.3°, respectively, at 745 mm. The compounds were photographed at a camera distance of 10.43 cm. with electrons having a wave length of about 0.06 Å. The photographs from each of the compounds show four maxima and in general are very similar in appearance. Two distinguishing features were observed, however. Photographs from the lower boiling butene show a pronounced inner maximum (preceding the first measured maximum at  $s = 5.67$  in Fig. 1) which does not appear on the other photographs. The fourth minimum in the photographs of this compound is broad and flat in comparison with the sharp, distinct fourth minimum in the photographs of the higher boiling compound.

Calculations of the theoretical diffraction curves were made with the aid of the formula,

(1) W. G. Young, R. T. Dillon and H. J. Lucas, *THIS JOURNAL*, **51**, 2528 (1929).

(2) C. E. Wilson and H. J. Lucas, *ibid.*, **58**, 2396 (1936).

(3) L. O. Brockway, *Rev. Modern Phys.*, **8**, 239 (1936).

$I = \sum_i \sum_j Z_i Z_j \frac{\sin sr_{ij}}{sr_{ij}}$ , in which  $r_{ij}$  is the distance between the  $i$ th and  $j$ th atoms; the summations extend over all of the atoms in the molecule. The curves for 2-butene in Fig. 1 are based on models in which the four carbon atoms are coplanar with a distance of 1.38 Å. between the two center atoms and 1.54 Å. for the bond distances connecting the outer atoms. The C-H distances are 1.06 Å.

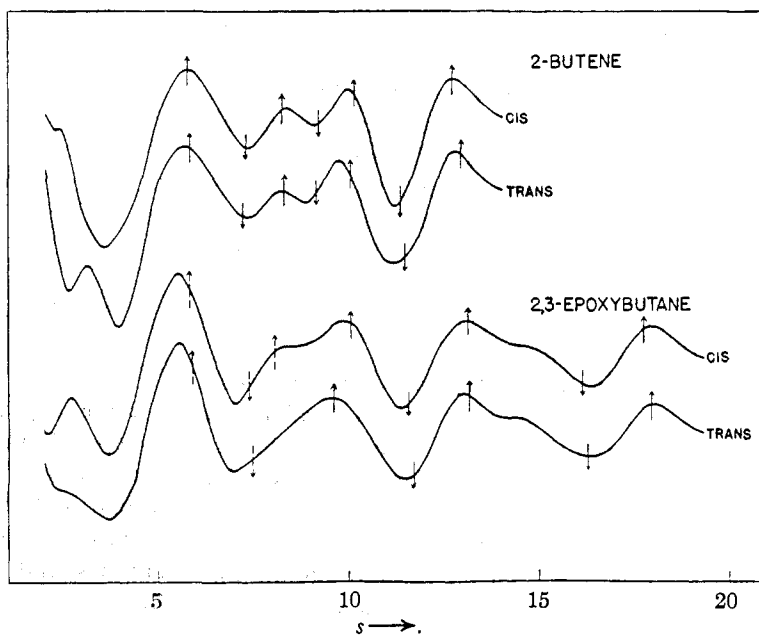


Fig. 1.—Theoretical electron diffraction curves for 2-butenes and 2,3-epoxybutanes. The arrows mark the positions of the observed maxima and minima.

The angle between adjacent carbon-carbon bonds is 125° and the  $\text{H}_3\text{C-C-H}$  bond 110°. In the *cis* model the two methyl groups lie on the same side of the line joining the center atoms and on opposite sides in the *trans* model. All of the interatomic interactions were included in the calculation with the exception of those with small coefficients corresponding to the H-H separations.

The curves are very much alike because most of the interatomic distances are the same in the *cis* and the *trans* models. Comparison of the coefficients of the terms in the scattering formulas shows that 80% of the total scattering is represented by terms which are identical for the two models. For this reason there are only small differences by which the *cis* and *trans* compounds can be distinguished. One such difference is the maximum at  $x = 3.13$  which occurs only in the *trans* curve. Accordingly we conclude that the lower boiling compound has the *trans* configuration. The comparison of the fourth minima for the two compounds supports this assignment. As mentioned above the photographs of the lower boiling compound have a fourth minimum which is less sharp and distinct than the corresponding minimum from the higher boiling compound. The difference between the theoretical curves at this point is not marked but the *trans* curve definitely has the broader fourth minimum. The compound boiling at  $0.3^\circ$  (745 mm.) is, therefore, the *trans* isomer and the compound boiling at  $3.0^\circ$  (745 mm.) is the *cis* isomer.

G. B. Kistiakowsky and co-workers<sup>4</sup> have made the same assignment of the molecular configurations of the 2-butenes on the basis of their heats of hydrogenation. The compound whose heat of hydrogenation is nearly the same as that of cyclohexene was chosen as the *cis* isomer. These authors report *cis*-2-butene, b. p.  $3.73^\circ$  (759.8 mm.), f. p.  $-139.3^\circ$ ; and *trans*-2-butene, b. p.  $0.96^\circ$  (760 mm.), f. p.  $-105.8^\circ$ .

The determination of the size of the molecule is given in Table I. The observed  $s$  values are defined by  $4\pi(\sin \theta/2)/\lambda$ , in which  $\theta$  is the observed angle of scattering for the successive maxima and minima and  $\lambda$  is the effective wave length of the bombarding electrons. The calculated  $s$  values depend on the interatomic distances assumed in the molecular model described above. The general agreement between the observed points and the maxima and minima on the theoretical curves indicates that the model is probably the correct one. The final column in Table I shows the measured values of the carbon-carbon single bond distance for all of the observed points. The average value in the *cis* modification is  $1.54 \pm 0.03 \text{ \AA.}$ , and the double bond distance is accordingly  $1.38 \pm 0.03 \text{ \AA.}$

(4) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *THIS JOURNAL*, **57**, 879 (1935).

The final values for the *trans* modification are 1.56 and 1.40  $\text{\AA.}$ , respectively, but an extra uncertainty in the accelerating potential during the exposures allows a somewhat larger error than in the results from the *cis* compound; the deviations from the accepted value, 1.54  $\text{\AA.}$ , for the single carbon-carbon bond is not significant.

TABLE I  
2-BUTENES

<i>Cis</i> b. p. = $3.0^\circ$ (746 mm.)				
Max.	Min.	$s$ , obsd.	$s$ , calcd. <sup>a</sup>	C-C. $\text{\AA.}$
1		5.67	5.72	1.527
	2	7.22	7.33	1.517
2		8.16	8.32	1.511
	3	9.13	9.06	1.556
3		10.08	9.93	1.565
	4	11.30	11.15	1.560
4		12.62	12.70	1.531
				Average 1.538
				Av. dev. 0.019

<sup>a</sup> See text for description of model.

Final result: C—C =  $1.54 \pm 0.03 \text{ \AA.}$ ; C=C =  $1.38 \pm 0.03 \text{ \AA.}$

<i>Trans</i> b. p. = $0.3^\circ$ (744 mm.)				
Max.	Min.	$s$ , obsd.	$s$ , calcd. <sup>a</sup>	C-C. $\text{\AA.}$
1		5.77	5.67	1.566
	2	7.18	7.29	1.516
2		8.27	8.23	1.547
	3	9.11	8.83	1.588
3		10.02	9.72	1.588
	4	11.42	11.16	1.578
4		12.89	12.75	1.556
				Average 1.563
				Av. dev. 0.019

<sup>a</sup> See text for description of model.

Final result: C—C =  $1.56 \pm 0.04 \text{ \AA.}$ ; C=C =  $1.40 \pm 0.04 \text{ \AA.}$

**2,3-Epoxybutanes.**—The photographs of the 2,3-epoxybutanes show an extra maximum beyond those observed for the butenes. The second and third maxima of the butene photographs are only partly resolved in one of the epoxybutanes and not at all resolved in the other. Photographs of the two modifications are very similar but they are distinguishable by the partial resolution of the second maximum and the appearance of a marked inner maximum (preceding the first measured maximum at  $s = 5.80$ ) in the photographs of the lower boiling modification.

The molecular models for which theoretical curves were drawn consist of a chain of four carbon atoms separated by distances of 1.54  $\text{\AA.}$  and with angles of  $109^\circ 28'$ . An oxygen atom is connected to the two center atoms by bonds 1.43  $\text{\AA.}$  in length. The two center carbon atoms also

have a hydrogen atom attached to each at 1.06 Å. and angles of 109°28' and the end carbon atoms each hold three hydrogen atoms. The CCO plane bisects the H-C-CH<sub>3</sub> angles on each of the center carbons and the two models differ in having the methyl groups on the same or opposite sides of the CCO planes. Terms for all interactions were included in the calculation with the exception of the H-H terms.

TABLE II  
2,3-EPOXYBUTANES  
*Cis* b. p. = 54° (747 mm.)

Max.	Min.	s, obsd.	s, calcd. <sup>a</sup>	C-C, Å.
1		5.80	5.52	(1.467)
	2	7.37	7.04	(1.471)
2a		8.02	8.42	(1.617)
2b		10.06	9.86	1.508
	3	11.54	11.35	1.516
3		13.10	13.08	1.538
	4	16.09	16.33	1.563
4		17.68	17.91	1.560
				Average 1.537
				Av. dev. 0.020

<sup>a</sup> See text for description of model.

Final result: C-C = 1.54 ± 0.03 Å.; C-O = 1.43 ± 0.03 Å.

Max.	Min.	s, obsd.	s, calcd. <sup>a</sup>	C-C, Å.
1		5.89	5.55	(1.451)
	2	7.46	6.98	(1.442)
2		9.59	9.58	1.538
	3	11.69	11.47	1.513
3		13.16	13.05	1.526
	4	16.25	16.32	1.547
4		17.89	18.07	1.556
				Average 1.536
				Av. dev. 0.013

<sup>a</sup> See text for description of model.

Final result: C-C = 1.54 ± 0.03 Å.; C-O = 1.43 ± 0.03 Å.

The curve in Fig. 1 corresponding to the *cis* modification shows the inner maximum (at *s* equals about 3.0) and the slightly resolved second maximum. Accordingly, the correct assignment of the isomers of 2,3-epoxybutane is the following: *cis*-b. p. 54° (747 mm.); *trans*-b. p. 60° (747 mm.). In the work reported in reference 2 the same identification of these isomers was made by a study of the optical activity of the glycols obtained on hydrolysis of the epoxybutanes.

The results of the quantitative comparison of the photographs and the curves are contained in Table II. The observed distances from the first two points are much smaller than the average from the remaining points because of the contrast effect of the dense central image on the measurement of heavy photographs taken at short distances. The averages for each compound lead to the values: C-C = 1.54 ± 0.03 Å. and C-O = 1.43 ± 0.03 Å.

### Summary

The direct determination of the molecular structures by electron diffraction of the vapors has led to the following identification of the isomeric forms and molecular sizes of *cis* and *trans* 2-butene and *cis* and *trans*-2,3-epoxybutane:

	B. p., °C.	Mm.	C-C, Å.	C=C, Å.
2-Butene				
<i>Cis</i>	3.0	746	1.54 ± 0.03	1.38 ± 0.03
<i>Trans</i>	0.3	744	1.56 ± .04	1.40 ± .04
2,3-Epoxybutane				
				C-O, Å.
<i>Cis</i>	54	747	1.54 ± .03	1.43 ± .03
<i>Trans</i>	60	747	1.54 ± .03	1.43 ± .03

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