

## An Electron Diffraction Investigation of the Molecular Structure of Butatriene

A. ALMENNINGEN, O. BASTIANSEN and M. TRÆTTEBERG

*Universitetets kjemiske institutt, Blindern - Oslo;  
Institutt for teoretisk kjemi, Norges tekniske høgskole, Trondheim, Norway*

The electron diffraction sector method was used to determine the structure of the butatriene molecule in the vapour phase. The molecular parameters are determined to be the following: C-H 1.083 Å ( $u = 0.080$  Å), C<sub>1</sub> = C<sub>2</sub> 1.318 Å ( $u = 0.040$  Å), and C<sub>2</sub> = C<sub>3</sub> 1.283 Å ( $u = 0.039$  Å). The error limits of all the parameters are approximately  $\pm 0.005$  Å. As in several other molecules with linear equilibrium conformation, a "shrinkage effect" is observed; *i.e.* the observed non-bonded CC distances are a trifle shorter than that calculated from the sum of the individual bond distances. The effect is explained by out-of-linearity vibrations.

The present work is a part of our endeavour to collect more precise information of CC bond lengths, particularly in conjugated and cumulated systems. The molecular structure of butatriene has been studied by Stoicheff<sup>1</sup> in 1957, using the Raman spectroscopic method. Assuming the end C=C double bond length to be the same as he found for allene<sup>2</sup>, namely 1.309 Å, he determined the central C=C double bond length to be 1.284 Å.

The electron diffraction method has the advantage that each individual bond length in principle can be determined independently. The central C=C double bond in butatriene with an *sp-sp*  $\sigma$ -bond, is of particular interest. The length of this bond has so far not been determined independently with particularly great accuracy.

### PREPARATION OF BUTATRIENE

Butatriene was prepared by Dr. Else Kloster-Jensen by a 2-stage synthesis<sup>3</sup> from 2-butyne-1,4-diol. This compound was converted to 1,4-dibromobutyne-2, and treated with zinc powder to give butatriene.

*1,4-Dibromobutyne-2.* After recrystallization of 2-butyne-1,4-diol, 700 ml of dry benzene was added to 111 g of the diol. The solution was stirred and cooled with ice as 500 g of phosphorus tribromide were added slowly during 3 h. The reaction mixture was stirred overnight at room temperature. The mixture was then transferred to 1 000 ml ice water

and the benzene layer isolated. After extraction of the water phase with  $4 \times 250$  ml ether, the organic extract was washed with  $4 \times 100$  ml 10 % sodium hydrogen carbonate solution and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure, and fractionated distillation gave 127.4 g colourless liquid at  $66-75^\circ\text{C}/1.5-2.5$  mm Hg.  $n_D^{21} = 1.5898$ .

*Butatriene.* 7.5 g zinc powder was suspended in 25 ml diethyl carbitol (distilled over metallic sodium). After evacuating the flask which was coupled to vacuum (1 mm) through a reflux cooler, 12.5 g 1,4-dibromobutynes-2 were dropped into the suspension which was stirred and heated to  $80^\circ\text{C}$ . A manometer showed that gas was developed. The crude distillate, collected in a liquid nitrogen cold trap, amounted to a few ml colourless solid. The redistilled product gave an infrared spectrum which was in good agreement with that published by Schubert <sup>4</sup>.

### ELECTRON DIFFRACTION STUDY

The electron diffraction diagrams were taken at the three usual distances between the scattering point and the photographic plate (approximately 48 cm, 19 cm, and 12 cm). A modified  $s^3$  sector was used. Photometer traces of the plates were read off at intervals of  $\Delta s = 1/4 \text{ \AA}^{-1}$  and transferred into intensity values in the usual way <sup>5</sup>.

The background scattering was subtracted by adjusting to the total intensity curve a theoretical background consisting of the atomic and incoherent scattering. After averaging the overlap regions an experimental molecular intensity curve ranging from  $s = 1.25 \text{ \AA}^{-1}$  to  $s = 63.5 \text{ \AA}^{-1}$  was obtained. Fig. 1 shows the theoretical (A) and experimental (B) molecular intensity curves. The theoretical curve is based on the final molecular model described later in this article.

It is usually difficult to obtain satisfactory correspondence between the theoretical background and the total experimental intensity curve for  $s$  values less than  $5 \text{ \AA}^{-1}$  and for very large  $s$  values. An empirical correction is usually

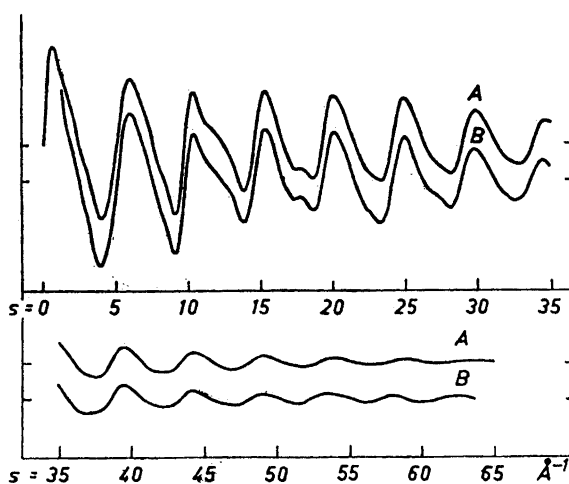


Fig. 1. Butatriene. Theoretical (A) and experimental (B) intensity curves.

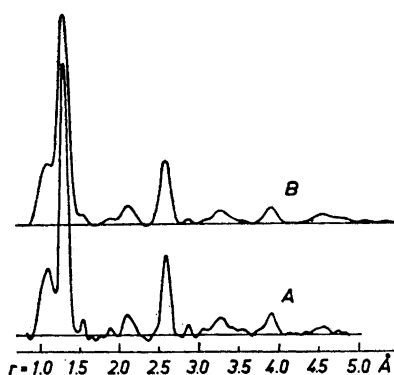


Fig. 2. Butatriene. Radial distribution curves with damping constant  $k$  equal to 0 (A) and 0.0009 (B).

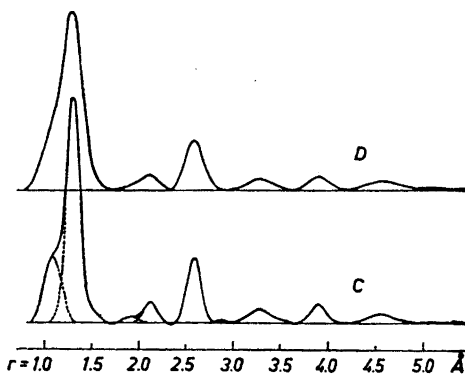


Fig. 3. Butatriene. Radial distribution curves with damping constant  $k$  equal to 0.0015 (C) and 0.0036 (D).

necessary and is carried out the following way: A preliminary background is subtracted and the molecular intensity curve thus obtained is submitted to a Fourier transformation, leading to a first radial distribution curve. From this curve a preliminary molecular model is obtained. Using this model a theoretical intensity curve is computed, and the background corrections are carried out by comparing the experimental and theoretical intensity curves. From the final experimental molecular intensity curve a series of radial distribution curves was calculated using four different  $k$ -values (0, 0.0009, 0.0015, and 0.0036). Figs. 2 and 3 show the corresponding four radial distribution curves.

From an analysis of these curves a set of internuclear distances was obtained. The correspondence between distances determined from curves with various damping factors was very good, and the mean values are listed in Table 1, second column. In the third column the observed root-mean-square deviation values for the various internuclear distances ( $u$ -values) are given.

The peak having a maximum at  $1.306_5$  Å is composed of contributions from the two  $sp^2$ - $sp$  C=C double bonds and from the  $sp$ - $sp$  double bond. The distance values of the two kinds of bonds are so close together that it is not possible to resolve the compound peak, even for the radial distribution curve of  $k = 0$ . The question now arises if the maximum position of the first CC peak corresponds to the arithmetical mean of the C=C double bond lengths. To check this two Gaussian curves were added, one with maximum at 1.28 Å and one with maximum at 1.31 Å, the latter one having a weight factor twice that of the first one. Both curves were based on the same  $u$ -value, namely 0.040 Å. The maximum position of the compound peak appeared to be off the value of the arithmetical mean by no more than  $3 \times 10^{-5}$  Å. This result shows that the following equation

$$1.306_5 = \frac{1}{3}[2 r_{C_1=C_1} + r_{C_1=C_2}] \quad (1)$$

is valid within the error of the method.

Table 1. Butatriene. Experimentally determined maxima of the radial distribution curves and the corresponding root-mean-square deviation values ( $u$ -values).

Type of distance	Observed internuclear distances	$u$ -values
C—H	1.082 <sub>0</sub>	0.079 <sub>9</sub>
C <sub>1</sub> =C <sub>2</sub> ; C <sub>2</sub> =C <sub>3</sub>	1.306 <sub>5</sub>	(0.047 <sub>0</sub> )
H <sub>1</sub> C <sub>2</sub>	2.114 <sub>4</sub>	0.061 <sub>8</sub>
C <sub>1</sub> C <sub>3</sub>	2.590 <sub>4</sub>	0.051 <sub>0</sub>
H <sub>1</sub> C <sub>3</sub>	3.277 <sub>4</sub>	0.102 <sub>3</sub>
C <sub>1</sub> C <sub>4</sub>	3.906 <sub>8</sub>	0.055 <sub>3</sub>
H <sub>1</sub> C <sub>4</sub>	4.571 <sub>0</sub>	0.111 <sub>8</sub>
H <sub>1</sub> H <sub>1</sub> '	1.89 <sub>2</sub>	
H <sub>1</sub> H <sub>4</sub> '	5.10 <sub>5</sub>	
H <sub>1</sub> H <sub>4</sub>	5.32 <sub>6</sub>	

If the butatriene molecule has a linear carbon skeleton, the C<sub>1</sub>C<sub>4</sub> distance length should be equal to three times the  $r$ -value of the first CC peak. This is not so. The observed value for the C<sub>1</sub>C<sub>4</sub> distance is 3.906<sub>8</sub> Å while three times the maximum position of the first CC peak is 3.919<sub>5</sub> Å. This corresponds to a shrinkage effect<sup>6</sup> equal to  $-\delta_{C_1C_4} = 0.0127$  Å.

Examining the shape of the C<sub>1</sub>C<sub>3</sub> and C<sub>1</sub>C<sub>4</sub> peaks of the radial distribution curves, it is seen that the right side slope of each of the peaks is steeper than that of the left side. This is in contrast to the effect usually observed and ascribed to anharmonicity in the molecular vibrations.

The shrinkage effect has earlier been explained by out-of-linearity vibrations, assuming a linear equilibrium conformation<sup>7,8</sup>. These vibrations can also explain the described asymmetry of the C<sub>1</sub>C<sub>3</sub> and C<sub>1</sub>C<sub>4</sub> peaks.

In the electron diffraction investigation of allene a shrinkage effect of the same order of magnitude as for butatriene was observed. In the allene case the effects caused by out-of-linearity vibrations can easily be treated theoretically<sup>8</sup>. It is considerably more complicated to carry out the same sort of calculations for butatriene, as this molecule exhibits more complicated out-of-linearity vibrations.

The main problem and the most difficult problem in the investigation of the molecular structure of butatriene is to determine the lengths of the two different types of double bonds. If a linear and rigid molecule is assumed, the end C=C double bond could be obtained by subtracting the observed C<sub>1</sub>C<sub>3</sub> distance from the corresponding C<sub>1</sub>C<sub>4</sub> distance. The length of the central C=C double bond could then be calculated from eqn. (1). In the actual case, a subtraction of the observed C<sub>1</sub>C<sub>3</sub> from the observed C<sub>1</sub>C<sub>4</sub> distance leads to an end C=C double bond length of 1.316<sub>4</sub> Å. This value must be too low as the observed C<sub>1</sub>C<sub>4</sub> distance probably is more influenced by out-of-linearity vibrations than is the C<sub>1</sub>C<sub>3</sub> distance. By inserting 1.316<sub>4</sub> Å for the  $sp^2-sp$  double bond length in eqn. (1), the value 1.286<sub>7</sub> Å is obtained for the  $sp-sp$  double bond length, a value which according to the same line of argument must be too high.

Table 2. Results of refinement calculations for linear molecular models using: a) the observed CC distances only, b) the CC as well as the CH distances.

Parameters	CC distances	CC and CH distances
$C_1=C_2$	1.3173 Å	1.3270 Å
$C_2=C_3$	1.2730 Å	1.2572 Å
C-H		1.0834 Å
$\angle H-C=C$		122.5°

By a least-squares calculation based on observed interatomic distances, the molecule has to be described by a static model. Doing so it might be of interest to study the possibility of describing the molecule by a non-linear model. If butatriene is treated as a non-linear molecule and a *trans* configuration is assumed, three parameters are necessary for describing the carbon skeleton, namely the  $C_1=C_2$  and  $C_2=C_3$  double bond distances and the  $C_1C_2C_3$  angle. There are all together three observable CC peaks in the radial distribution curves, and the corresponding maximum values may be combined in a set of three equations with the three unknown parameters. By solving these equations, the following values are obtained:  $C_1=C_2$  1.320 Å,  $C_2=C_3$  1.280 Å and  $\angle C_1C_2C_3$  170°, *i.e.*, a 10-degree deviation from linearity.

Least-squares calculations were carried out by adjusting both a linear and a non-linear molecular model to the observed interatomic distances. Both models were studied using (a) only the observed CC distances, and (b) CC distances as well as CH distances. For these calculations the following zeroth order set of parameters was chosen based upon a preliminary examination of the radial distribution curves:  $C_1=C_2$  1.316<sub>0</sub> Å,  $C_2=C_3$  1.289<sub>0</sub> Å, C-H 1.082<sub>0</sub> Å and  $\angle H-C=C$  122°. In Table 2 the results of the refinements are given when a linear model is assumed. The error square sums before and after adjustment were  $398.0 \times 10^{-4}$  and  $22.8 \times 10^{-4}$  when only the CC distances were considered. In the other case treated, the same values were  $1096.8 \times 10^{-4}$  and  $340.7 \times 10^{-4}$ , respectively.

Zeroth order parameters used for the study of non-linear models were the same as for a linear molecular model, but in addition a zeroth order parameter for  $\angle C_1C_2C_3$  of 170° was assumed. In Table 3 the results of the refinements are given when a non linear model is assumed. The error square sums before

Table 3. Results of refinement calculations for non-linear molecular models using: a) the observed CC distances only, b) the CC as well as the CH distances.

Parameters	CC distances	CC and CH distances
$C_1=C_2$	1.320 Å	1.3278 Å
$C_2=C_3$	1.280 Å	1.2693 Å
C-H		1.0827 Å
$\angle H-C=C$		121.76°
$\angle C_1C_2C_3$	170°	169.02°

and after adjustment were  $25.3 \times 10^{-4}$  to  $5.2 \times 10^{-4}$  and  $307.0 \times 10^{-4}$  to  $97.6 \times 10^{-4}$ , respectively, in the two cases.

The calculations show that the butatriene molecule neither can be described by a linear nor a non-linear static model, and the correspondence between parameters determined from the four different approaches is not satisfactory.

In order to determine the two types of C=C double bond distances the work was, at this stage of the investigation, concentrated on the peak at  $1.306_s$  Å on the radial distribution curves. Theoretical radial distribution curves composed of Gaussian curves with contribution from the C=C double bond distances were calculated. The four parameters, the two equilibrium C=C double bond distances and their corresponding  $u$ -values, were varied in small intervals over a large  $r$ -range. The following set of values gave a very satisfactory agreement between the theoretical and observed peak: C<sub>1</sub>=C<sub>2</sub> 1.318 Å, C<sub>2</sub>=C<sub>3</sub> 1.283 Å,  $u_{C,C_1}$  0.040 Å,  $u_{C,C_2}$  0.039 Å. In obtaining these results the  $u$ -values and bond distances were restricted to certain limitations. For instance the  $u$ -values should be in reasonable agreement with earlier obtained values for double bonds, and the bond lengths should be kept within the limits given above.

#### CONCLUSION

As a result of this electron diffraction investigation the following structure parameters for butatriene can be given:

C—H	1.083 Å	$u_{C-H}$	0.080 Å
C <sub>1</sub> =C <sub>2</sub>	1.318 Å	$u_{C_1=C_2}$	0.040 Å
C <sub>2</sub> =C <sub>3</sub>	1.283 Å	$u_{C_2=C_3}$	0.039 Å

It is very difficult to give definite statements concerning the error limits for the structure parameters. It is felt that an error limit of  $\pm 0.005$  Å can be given both for the distance parameters and for the  $u$ -values.

*Acknowledgement.* This investigation has been sponsored by the *United States Air Force Development Command* under contract AF 61(052)-72.

The authors wish to thank Dr. Else Kloster-Jensen, University of Oslo, who kindly prepared the butatriene used in the present investigation. The authors also wish to acknowledge the valuable advice given by Dr. A. T. Morse, Merck and Co., Montreal, in connection with the synthesis of the compound.

#### REFERENCES

1. Stoicheff, B. P. *Can. J. Phys.* **35** (1957) 837.
2. Stoicheff, B. P. *Can. J. Phys.* **33** (1955) 811.
3. Morse, A. T. *Private communication* (1959).
4. Schubert, W. M., Liddicoet, T. H. and Lanka, W. A. *J. Am. Chem. Soc.* **76** (1954) 1929.
5. Almenningen, A., Bastiansen, O. and Fernholt, L. *Kgl. Norske Videnskab. Selskabs. Skrifter* **1958** No. 3.
6. Almenningen, A., Bastiansen, O. and Trættestad, M. *Acta Chem. Scand.* **13** (1959) 1699.
7. Munthe-Kaas, T. *Thesis, University of Oslo* (1955).
8. Trættestad, M. *Thesis, Technical University of Norway, Trondheim* (1960).

Received April 7, 1961.