

An Electron Diffraction Reinvestigation of the Molecular Structure of 1,3-Butadiene

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The electron diffraction sector method was used for a reinvestigation of the structure of 1,3-butadiene vapour. It was shown that the planar *trans* form is predominating, and no signs of other conformations were observed. The observed molecular parameters are the following: C—H: 1.082 Å, C—C: 1.483 Å, C=C: 1.337 Å, \angle C = C—C: 122.4°, and \angle C = C—H: 119.8°. The probable error of C = C is less than 0.005 Å. For the C—H and C—C distances the error is somewhat larger, about 0.01 Å.

The present work is a part of our endeavour to collect more precise informations of C-C bond lengths, particularly in conjugated systems. 1,3-butadiene was already studied in 1939 by Schomaker and Pauling¹, using the visual electron diffraction method. Their parameter determinations were in good agreement with the present knowledge of this type of distance.

The justification of the present work is the narrower error limits that can be obtained by the modern electron diffraction technique rather than any doubt of the values obtained earlier. The fact that the earlier work was not able to determine unambiguously the general shape of the molecule also made a reinvestigation desirable.

Electron diffraction diagrams were taken at various distances between the diffraction point and the photographic plate, using a somewhat modified s^3 -sector. Photometer records of the plates were read off at intervals of $\Delta s = 1/4 \text{ \AA}^{-1}$. The necessary corrections were made to transfer the photometer curves into intensity values. At this stage a theoretical background was fitted in. The overall correspondence between intensity curve and background was good except for the inner s range ($s < 5$). The background was fitted in by a least square procedure asking for the position of the intensity zero line and the intensity scale². After the sector correction had been carried out, minor refinements of the background were made and the corrected background subtracted from the intensity curve. The first radial distribution curves were calculated using a damping factor $\exp(-0.0009 s^2)$. The best molecular

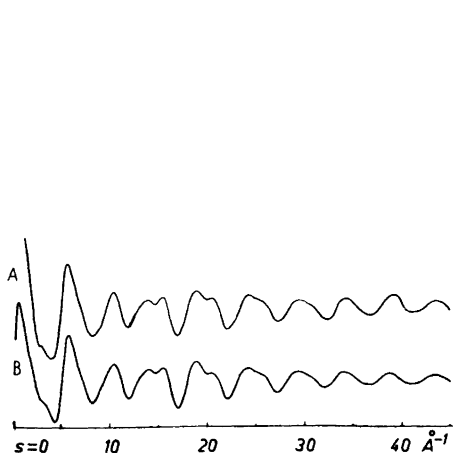


Fig. 1. Experimental (A) and theoretical (B) intensity curves for 1,3-butadiene.

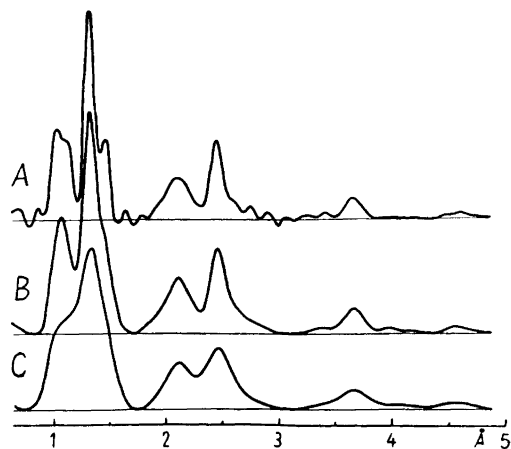


Fig. 2. Radial distribution curves of 1,3-butadiene. (A: $k = 0$, B: $k = 0.0009$, and C: $k = 0.0036$).

model obtained from these curves was used as a basis for theoretical intensity-curve calculations. The correspondence between experimental and theoretical intensity curves is very good (Fig. 1), except for some disagreement at the inner s -range indicating the necessity of a further background correction for $s < 5$. In fact a correction of this type has been necessary in a series of investigations, indicating a measurable deviation between calculated and observed backgrounds for small s values. After subtraction of the final background a series of radial distribution curves was calculated using three different k -values (0, 0.0009, and 0.0036) and Δs values of $1/4$ and $1/2$. As a matter of

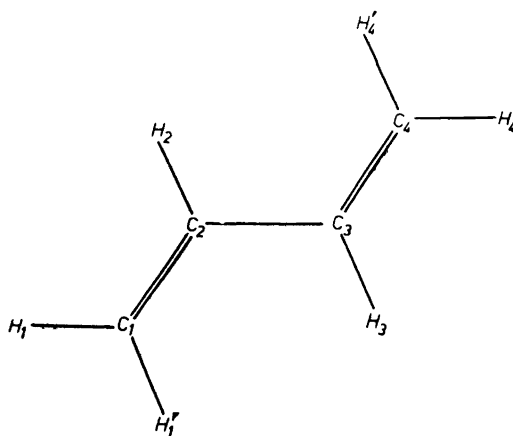


Fig. 3. Numbering of the atoms in the 1,3-butadiene molecule.

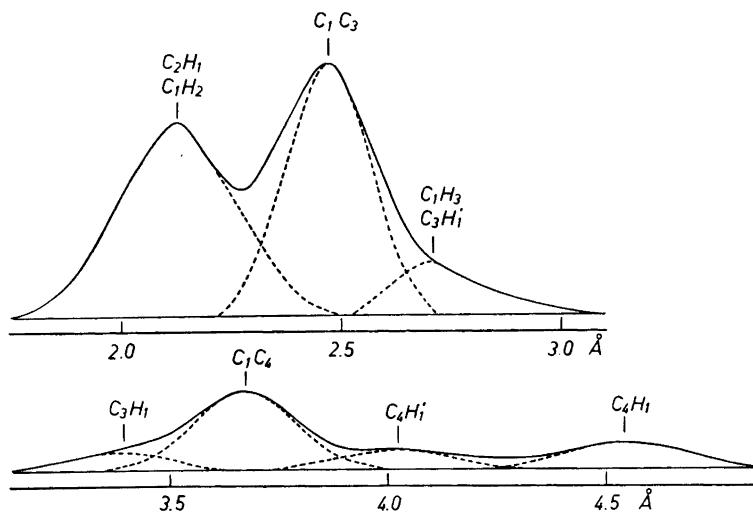


Fig. 4. An example of the resolution of parts of a radial distribution curve in Gaussian-like peaks ($k = 0.0036$).

fact two complete sets of diagrams were taken and each set treated independently by two persons. As a whole the correspondence between the results of the two investigations was very good, and the preliminary results as to structure data were almost identical. Therefore, in the final refinements it was preferred to use curves obtained as an average of the two sets.

In Fig. 2 three radial distribution curves are given with damping constants $k = 0$, 0.0009, and 0.0036, respectively.

From an analysis of the radial distribution curves a set of internuclear distances was obtained. These distances are listed in Table 1, second column. The numbering of the atoms in the first column of Table 1 is demonstrated in Fig. 3. For the shorter distances (bond distances) the values obtained from the radial distribution curve of $k = 0$ gave the best consistency. For the longer distances the radial distribution curves of higher k values were preferred. As a matter of fact the longest C—H distances are hardly recognizable on a radial distribution curve from an undamped intensity curve. On the other hand the radial distribution curves of $k = 0.0036$ have easily separable peaks corresponding to the larger C—H distances. The internuclear distances mentioned were obtained by resolving the radial distribution curves into Gaussian peaks including the use of the least square method. In Fig. 4, as an example, there is shown the outer parts of a radial distribution curve ($k = 0.0036$) resolved in Gaussian shaped peaks corresponding to the various distances.

The observed distance values settle beyond doubt the overall structure of the molecule. The molecular structure is a planar *trans* form without observable contribution from other conformations.

Table 1. Internuclear distances in the 1,3-butadiene molecule.

Distances and angles	Observed values	2nd order approximation values
C—H	1.083 Å	1.082 Å
C=C	1.341 Å	1.337 Å*
C—C	1.484 Å	1.483 Å
\angle C=C—C		122.40°
\angle C=C—H		119.78°
$\left. \begin{array}{l} C_2H_1 \\ C_1H_2 \end{array} \right\}$	2.125 Å	2.124 Å
$\left. \begin{array}{l} C_1C_3 \\ C_1H_3 \end{array} \right\}$	2.477 Å	2.472 Å
$\left. \begin{array}{l} C_3H_1' \\ C_3H_1 \end{array} \right\}$	2.721 Å	2.699 Å
$\left. \begin{array}{l} C_3H_1 \\ C_1C_4 \end{array} \right\}$	3.402 Å	3.453 Å
$\left. \begin{array}{l} C_4H_1' \\ C_4H_1 \end{array} \right\}$	3.680 Å	3.688 Å
	4.031 Å	4.019 Å
	4.568 Å	4.567 Å

As is seen from Table 1 there are altogether 10 observed internuclear distances. If a planar *trans* molecule is assumed, the carbon structure is described by three parameters. If the hydrogen atoms are included, two additional parameters have to be considered, even with the assumption of the same C—H bond distances and the same C=C—H angles throughout the molecule. There should then be 10 equations for the determination of 5 parameters. The parameters were now determined by a least square procedure, using proper weight factors on the various observed distances. Except for minor changes in the fourth decimal place, the parameters and the deduced internuclear distances of the 1st approximation were preserved in the 2nd approximation. The results are given in third column of Table 1.

Because of the unavoidable overlap of the C=C and C—C bond peaks, the accuracy of these bond distances is somewhat lower than in the cases of well-resolved peaks. The C=C double bond distance is determined with an error less than 0.005 Å, but for the C—C single bond distance the situation is less favourable. The rather large C—C distance of 1.483 Å is obtained even if the zero order approximation value in the least square procedure is as low as 1.473 Å. Though the analysis of the inner part of the radial distribution curve of $k = 0$ strongly indicates this large distance, it has to be admitted that a least square analysis of the carbon-carbon bond complex in a radial distribution curve with $k = 0.0009$ leads to a value of 1.473 Å for the single bond. If the observed value of 1.484 Å is substituted by 1.473 Å in the list of second column of Table 1, the final C—C bond distance from the least square calculations is as large as 1.478 Å, while the other parameters are practically uninfluenced. This demonstrates that the longer internuclear distances are

* *Added in proof:* After this article was submitted for publication a study of the infrared spectra of ethylene has been published (Allen, H. C. and Plyler, E. K., *J. Am. Chem. Soc.* **80** (1958) 2763). The C=C distance is found to be 1.337 Å in good agreement with the result of this work and with the electron diffraction study of ethylene (Bartell, L. S. and Bonham, R. A., *J. Chem. Phys.* **27** (1957) 1414).

Table 2. Theoretical and experimental values for areas under the peaks in the radial distribution curves.

Distances	Theoretical	Experimental
C—H	41.7	38
C=C	53.5	55
C—C	24.7	22
C ₁ H ₂ ; C ₂ H ₁ ; C ₃ H ₂	28.2	23
C ₁ C ₃	29.0	24
C ₁ H ₃ ; C ₃ H' ₁	10.8	9
C ₃ H ₁	4.3	3
C ₁ C ₄	9.8	12
C ₄ H' ₁	3.7	4
C ₄ H ₁	3.3	4

in better accordance with the large C—C bond distance. It is very difficult to give a definite statement concerning the error limits of the single bond, but it is unlikely that the error is more than 0.01 Å. However, the analysis indicates an unsymmetrical error distribution, making an error of + 0.01 Å less probable than an error of — 0.01 Å.

In order to look for a possible contribution of a *cis* form, the areas under the resolved peaks of the radial distribution curves have been studied. Again the less damped curves were used for the inner peaks and the more damped curves for the outer peaks. These areas were compared with the theoretical calculated values obtained by the formula $n \cdot Z_i Z_j / r_{ij}$, where n is the number of times the distance in question occurs in the molecule and r_{ij} is the distance itself. Z is 6 for carbon and 1.25 for hydrogen. The theoretical and measured areas are listed in Table 2, normalized on the same arbitrary scale. The correspondence is satisfactory and gives no indication of any misinterpretation of the peaks. In fact the experimental area for the C₁C₄ peak is somewhat larger than anticipated from theory. If any other conformations than the *trans* form were present, this peak should have a smaller area than that calculated for a rigid *trans* molecule. The deviation in the area of the C₁C₄ distance is probably merely due to errors caused by difficulties in determining the exact form of the envelope.³

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