

An Electron Diffraction Investigation of the Molecular Structure of Allene

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The electron diffraction sector method was used to determine the structure of allene vapour. The observed molecular parameters are the following: C—H: 1.081₆ Å ($u = 0.0795$ Å), C=C: 1.311₆ Å ($u = 0.0390$ Å), C₁C₂: 2.617₃ Å ($u = 0.0519$ Å) and $\angle\text{H—C=C}$: 120.8°. The C₁C₂ distance was found to be shorter than twice the C=C distance. This can be explained by out-of-linearity vibrations.

The molecular structure of allene was determined by the electron diffraction sector method, using a modified s^3 sector. The electron diffraction diagrams were taken at three different distances between the scattering point and the photographic plate (approximately 48, 19 and 12 cm). The photometer curves were read off and the usual corrections were carried out.

The subtraction of the background, *viz.* atomic and incoherent scattering, was carried out by fitting a theoretical background to the intensity curve by means of a least square treatment giving the intensity zero line and the intensity scale. An example of the correspondence between the background and the intensity curve is demonstrated in Fig. 1 for the average of the 48 cm plates. The correspondence is good except for the innermost part. As a general rule, the middle parts of the intensity curves fit well with the theoretical background. At the innermost and outermost parts corrections generally have to be made. The short distance curves (12 cm) were all treated separately. Because of the low intensity values the correspondence is less satisfactory. A small error in the readings gives rise to a relatively large error in the amplitudes. The background was fitted to each of the experimental curves and the difference curves were averaged. The curves from the various distances were normalized, and after the averaging of the overlapping regions the first total molecular intensity curve was obtained extending from $s = 1.25$ to $s = 65$ Å⁻¹.

By Fourier transformation of the damped molecular intensity curve (damping factor $e^{-0.0009 s^2}$) the corresponding radial distribution (R.D) curve was obtained. In this curve the Gaussian shaped peaks corresponding to the interatomic distances were completely resolved except for some unavoidable overlap of the C—H and C=C double bond peaks.

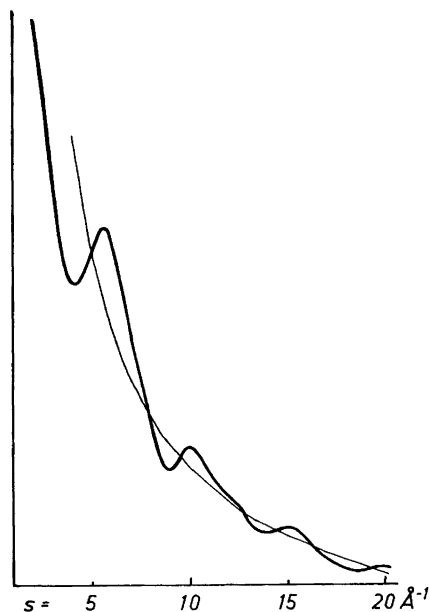


Fig. 1. Allene. Intensity curve from the 48 cm photographic plates with the theoretical background fitted in.

From this first R.D. curve, the most probable model of the molecule was determined and a theoretical intensity curve corresponding to this model computed. By means of the theoretical intensity curve it is possible to correct for the most serious errors in the background. In this case only small corrections were necessary for obtaining the final molecular intensity curve (Fig. 2) upon which the final conclusions were based.

A series of R.D. curves was calculated from the final intensity curve using different damping constants ($k = 0, 0.0009$ and 0.0015) and Δs values of $1/2$ and $1/4 \text{ \AA}^{-1}$. Three of these curves are presented in Fig. 3.

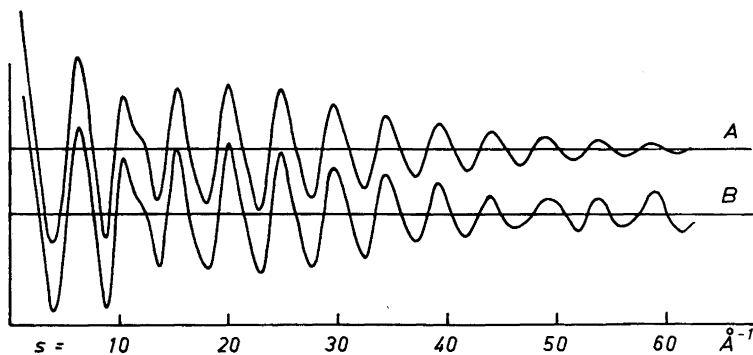


Fig. 2. Allene. Theoretical (A) and experimental (B) intensity curves.

Table 1. Allene. Internuclear distances and mean amplitudes of vibrations.

Distances	Observed r values	Observed u values	u values calculated from spectroscopic data
C—H	1.0816	0.0795	0.0772
C=C	1.3116	0.0390	0.0401
C ₂ H ₁	2.0840	0.1046	0.1015
C ₁ C ₃	2.6173	0.0519	0.0451
C ₃ H ₁	3.2963	0.1272	0.1144
<H—C=C: 120.8°			

These R.D. curves were also resolved into Gaussian peaks. The internuclear distances and mean amplitudes of vibration ($u = \sqrt{(r - r_0)^2}$) are presented in Table 1. If a linear carbon skeleton is assumed the structure is determined from three parameters. (The question of the relative position of the HCH planes has been ignored).^{*} The R.D. curves give altogether five distances, and the best set of parameters was calculated using the method of least squares. The parameters thus obtained are: C—H: 1.083 Å, C=C: 1.308 Å and H—C=C angle 120.6°.

It is worth noting that the C=C value obtained by this procedure is 0.003 Å smaller than that computed directly from the C=C peak of the R.D. curves. This of course corresponds to the fact that the C₁C₃ distance as found from the R.C. curves is about 0.006 Å smaller than twice the C=C distance obtained in the same way. Even if this effect is very small we are inclined to believe that it is real. The effect can easily be explained by an out-of-linearity vibration. If this argument holds the best C=C distance should be 1.312 Å instead of 1.308 Å.

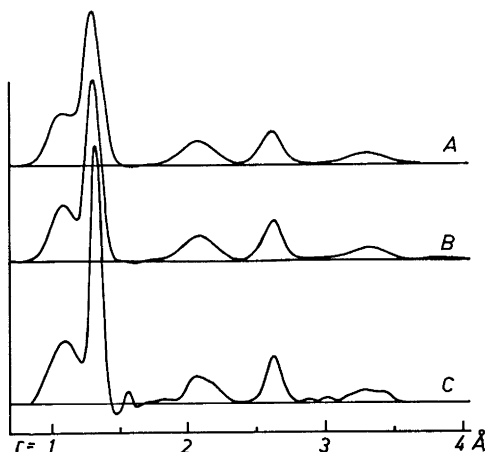


Fig. 3. Allene. Radial distribution curves with different damping constants (A: $k = 0.0015$, B: $k = 0.0009$, and C: $k = 0$).

^{*} *Added in proof:* A closer examination of the R. D. curves reveals the presence of HH distance peaks beyond the largest CH peaks, corresponding to an angle of 90° between the two HCH planes.

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

Distances	Theoretical areas	Experimental areas
C—H } C=C }	54.80	54.5
C ₂ H ₁	9.54	9.6
C ₁ C ₃	9.12	9.1
C ₃ H ₁	6.03	4.7

A similar effect which can also be interpreted by the assumption of out-of-linearity vibrations was observed for dimethyldiacetylene¹.

The structure parameters obtained for allene are in accordance with the values obtained by Stoicheff from high resolution Raman spectroscopy². Using both allene and allene-d₄ the C=C distance of 1.309 Å is obtained. Assuming a C—H distance of 1.07 ± 0.01 Å as found in an earlier work on ethylene³, he obtains an HCH angle of 117° (H—C=C angle equal to 121.5°). We feel that Stoicheff's assumed C—H distance is a trifle too small.

It is of interest to compare our parameters with the recently obtained values for ethylene⁴⁻⁶. The data obtained from three independent methods are: C—H: 1.086 ± 0.003 Å, C=C: 1.337 ± 0.003 Å and $\angle \text{H—C=C}$: $121.5^\circ \pm 1^\circ$. This shows that the CH₂ group in ethylene, within rather narrow error limits, has the same structure as in allene. However, the C=C distance is, as pointed out by Overend and Thompson⁷ and by Stoicheff³, no doubt larger in ethylene than in allene.

In the last column of Table 1 the *u* values calculated from spectroscopic data by Cyvin⁸ have been presented. The correspondence is satisfactory except for the C₁C₃ distance where a significant discrepancy seems to be present. This discrepancy can be satisfactorily explained by the mentioned out-of-linearity vibration. The spectroscopic calculations were based upon the assumption of a linear model. The out-of-linearity vibrations should not only lead to a decrease in the C₁C₃ distance but should also lead to an increase in the mean amplitude of vibration for this distance.

As a control of the reliability of the R.D. curves the measured areas have been compared with the theoretical ones on a relative scale. The values are given in Table 2.

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

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Received June 20, 1959.