The Molecular Structure of Gaseous 1,2-Hexadien-5-ylene (Propargylallene)

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The molecular structure and conformation of 1,2-hexadien-5-yne have been studied by gas electron diffraction. Semiempirical calculations (INDO, EH, MM) for various conformers of the compounds were also carried out.

The ED data were consistent with a syn/skew conformational mixture, corresponding to the two conformers being of approximately the same energy.

1,2-Hexadien-5-yne (in the following referred to as propargylallene) is an acyclic structural isomer of benzene. The molecule may in principle exist in different conformers because of internal rotation around the central C—C single bond. Earlier investigations of the properties of propargylallene include thermal and base catalyzed isomerization reactions, photoelectron and Raman spectroscopic studies.

In connection with the photoelectron spectroscopic studies by Gleiter et al. the energy of the propargylallene molecule was calculated as a function of the C3—C4 dihedral angle. The calculations were carried out within the extended Hückel approximation, and the only stable rotamer was found to be a skew conformer with a dihedral angle of ca. 110° (measured from s-cis or syn). The rotational barrier for the molecule was calculated to be 11.7 kJ/mol.

The IR spectra were obtained for the vapour, liquid and solid states, while the Raman spectra were obtained for the liquid and solid states. The spectra were interpreted in terms of a skew conformer with a dihedral angle of ca. 120° for all states, and no evidence was found for any additional conformers of propargylallene.

The present electron diffraction study was carried out as part of our investigation of unsaturated hydrocarbons and to supplement the structural information obtained for propargylallene from the EH calculations and from the spectroscopic study.

EXPERIMENTAL

The sample of propargylallene used in the present study was prepared by a method described earlier and was purified by preparative gas chromatography.

Electron diffraction diagrams were recorded with a Balzer's Eldigraph KD-G2 on 13 × 18 cm replica 23 Agfa-Gevaert photographic plates.

The experimental conditions were: nozzle to plate distances, 500.12 mm (3 plates) and 250.12 mm (3 plates); electron wavelength, determined by calibration to benzene, 0.05810 Å; nozzle temperature, 25°C. The ranges of data obtained with Δs = 0.125 and 0.250 (Å−1) were 1.000—15.625 and 2.000—30.750 (Å−1), respectively. The experimental data were processed in the usual way, and the intensities were modified by multiplication with the function s[∫fc]−2. The scattering amplitudes (r') were calculated by the partial-wave method, using Hartree-Fock atomic potentials. The experimental molecular intensity function of propargylallene is shown in Fig. 1, while the radial distribution (RD) curve obtained by Fourier transformation of the intensity values is shown in Fig. 2.

STRUCTURE ANALYSIS

Since propargylallene is composed of two supposedly linear CC fragments, shrinkage effects are
Fig. 1. Experimental (upper) and theoretical (lower) (calculated from the parameters in Table 3) molecular intensity functions and the difference curve for propargyllallene.

expected to be quite extensive. It is therefore important to calculate the nonbonded distances in the molecule from the geometrically consistent \( r_n \) parameters. Transformation between distances given as \( r_a \) or \( r_s \) (the electron diffraction distance) parameters may be achieved by using the approximation

\[
(r_{ij})_n = (r_{ij})_a + \frac{\mu_{ij}}{r_{ij}} - K_{ij},
\]

where \( \mu_{ij} \) is the mean square amplitude and \( K_{ij} \) is the perpendicular vibrational amplitude correction coefficient for the distance between the atoms \( i \) and \( j \).

Fig. 2. Experimental (upper) and theoretical (lower) RD and difference curves for propargyllallene. Artificial damping constant \( k = 0.002 \). The theoretical RD curve is calculated for the parameters in Table 3.

Table 1. Force constants applied in the normal coordinate analysis of propargyllallene.

<table>
<thead>
<tr>
<th>Stretch (mdyn Å⁻¹)</th>
<th>In-plane bend (mdyn Å rad⁻²)</th>
<th>Out-of-plane bend (mdyn Å rad⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C≡C</td>
<td>C≡C - C&lt;sub&gt;sp3&lt;/sub&gt;</td>
<td></td>
</tr>
<tr>
<td>C&lt;sub&gt;sp2&lt;/sub&gt; = C&lt;sub&gt;sp&lt;/sub&gt;</td>
<td>C&lt;sub&gt;sp2&lt;/sub&gt; - C&lt;sub&gt;sp&lt;/sub&gt; - H</td>
<td>0.52</td>
</tr>
<tr>
<td>C&lt;sub&gt;sp3&lt;/sub&gt; - C&lt;sub&gt;sp&lt;/sub&gt;</td>
<td>C&lt;sub&gt;sp3&lt;/sub&gt; - C&lt;sub&gt;sp&lt;/sub&gt; - H</td>
<td>0.52</td>
</tr>
<tr>
<td>C&lt;sub&gt;sp3&lt;/sub&gt; - C&lt;sub&gt;sp2&lt;/sub&gt;</td>
<td>C&lt;sub&gt;sp3&lt;/sub&gt; - C&lt;sub&gt;sp2&lt;/sub&gt; - C&lt;sub&gt;sp&lt;/sub&gt;</td>
<td>0.60</td>
</tr>
<tr>
<td>C&lt;sub&gt;sp3&lt;/sub&gt; - H</td>
<td>C&lt;sub&gt;sp3&lt;/sub&gt; - C&lt;sub&gt;sp2&lt;/sub&gt; - C&lt;sub&gt;sp&lt;/sub&gt;</td>
<td>0.70</td>
</tr>
<tr>
<td>C&lt;sub&gt;sp2&lt;/sub&gt; - H</td>
<td>H - C - H</td>
<td>0.40</td>
</tr>
<tr>
<td>C&lt;sub&gt;sp&lt;/sub&gt; - H</td>
<td>H - C - H</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Torsion (mdyn Å rad⁻²)</td>
<td>Linear bend (mdyn Å rad⁻²)</td>
<td></td>
</tr>
<tr>
<td>- C&lt;sub&gt;sp2&lt;/sub&gt; - C&lt;sub&gt;sp3&lt;/sub&gt;</td>
<td>C≡C - H</td>
<td>0.26</td>
</tr>
<tr>
<td>- C≡C = C&lt;sub&gt;sp&lt;/sub&gt;</td>
<td>C≡C - C≡C</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>C≡C = C≡C</td>
<td>0.30</td>
</tr>
<tr>
<td>Interaction force constants (mdyn Å⁻¹ or mdyn Å rad⁻²)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C≡C, C&lt;sub&gt;sp2&lt;/sub&gt; - C&lt;sub&gt;sp3&lt;/sub&gt;</td>
<td>0.150</td>
<td>C≡C, C - C - H</td>
</tr>
<tr>
<td>C≡C, C&lt;sub&gt;sp3&lt;/sub&gt; - C&lt;sub&gt;sp&lt;/sub&gt;</td>
<td>0.30</td>
<td>C≡C, C - C - H</td>
</tr>
<tr>
<td>C&lt;sub&gt;sp2&lt;/sub&gt; - C&lt;sub&gt;sp3&lt;/sub&gt;, C&lt;sub&gt;sp3&lt;/sub&gt; - C&lt;sub&gt;sp&lt;/sub&gt;</td>
<td>0.150</td>
<td>C≡C, C - C≡C</td>
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<tr>
<td>C≡C, C≡C</td>
<td>0.200</td>
<td>C≡C, C - C - C</td>
</tr>
<tr>
<td>C≡C, C&lt;sub&gt;sp2&lt;/sub&gt; - H</td>
<td>C≡C, C - H</td>
<td>0.100</td>
</tr>
<tr>
<td>C≡C, H - C - H</td>
<td>C≡C, C - C</td>
<td>-0.115</td>
</tr>
</tbody>
</table>

The vibrational amplitudes (uₗ) and Kᵢᵣ-values for all interatomic distances were calculated from an assumed force field.¹⁴ The calculations were carried out for syn and skew conformers of propargyllallene. The calculated uₗ and Kᵢᵣ-values were then applied in least squares refinements on the molecular intensities. This procedure was carried out for several different force fields, and the one that corresponds to the lowest R-factor (R=Σ|Wₗ(Iₗ(obs) - Iₗ(calc))/ΣWₗ|²) in the least squares analyses is given in Table 1. The calculated vibrational amplitudes and vibrational corrections (rₗ - rₗ) for the non-bonded CC distances in syn and skew propargyllallene are presented in Table 2.

The molecular structure and conformational composition of propargyllallene were studied by least squares refinements of the molecular intensity data in combination with information obtained from the experimental RD function.

The following parameters were used to describe the molecular model of propargyllallene: seven bond lengths (C≡C, C<sub>sp</sub> - C<sub>sp3</sub>, C<sub>sp2</sub> - C<sub>sp3</sub>, C≡C, C<sub>sp3</sub> - H, C<sub>sp2</sub> - H, C<sub>sp</sub> - H), five bond angles (C≡C - C<sub>sp</sub>, C≡C - C<sub>sp</sub> - C<sub>sp3</sub> - H, C<sub>sp3</sub> - C<sub>sp2</sub> - H, C<sub>sp3</sub> = C<sub>sp</sub> - H) and one dihedral angle for each possible conformation. Within the rₗ model the C₁C₃ and C₄H₆ fragments were assumed to be linear. It was further necessary to assume that the bond lengths and bond angles were the same in the two conformers that were found to be present. This is expected to be a good approximation as far as the bond lengths are concerned, while the C≡C - C≡C and C≡C - C≡C valence angles in the two conformers may differ by 1 - 2°. The observed valence angles must therefore be considered as averages between the two conformers.

The largest CC distance in a syn conformer of propargyllallene is expected to be ca. 4.0 Å (see Table 2). The experimental RD curve has a quite large area outside this region. It is therefore obvious that other conformers must be present, and it was fairly easy to establish that a skew conformer must give a substantial contribution to the RD curve at r>4.0 Å.

In Fig. 3 theoretical RD curves for the all syn and all skew conformers of propargyllallene are compared with the experimental RD curve. Neither of the theoretical curves are in accordance with the experimental one, but the differences between syn and skew curves are not so striking as in many other
Table 2. Propargyllallene. Nonbonded carbon carbon distances for syn and skew conformations, calculated vibrational amplitudes, $u_{ij}$, and vibrational corrections $r_a - r_a = K - u^2/r_e$, in Å.

<table>
<thead>
<tr>
<th>Distance</th>
<th>syn $r_a$</th>
<th>$u$</th>
<th>$r_a - r_a$</th>
<th>skew $r_a$</th>
<th>$u$</th>
<th>$r_a - r_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3–5</td>
<td>2.477</td>
<td>0.0816</td>
<td>0.0037</td>
<td>2.477</td>
<td>0.0813</td>
<td>0.0064</td>
</tr>
<tr>
<td>2–4</td>
<td>2.480</td>
<td>0.0645</td>
<td>0.0054</td>
<td>2.480</td>
<td>0.0643</td>
<td>0.0051</td>
</tr>
<tr>
<td>1–3</td>
<td>2.596</td>
<td>0.0507</td>
<td>0.0135</td>
<td>2.596</td>
<td>0.0507</td>
<td>0.0242</td>
</tr>
<tr>
<td>4–6</td>
<td>2.644</td>
<td>0.0510</td>
<td>0.0121</td>
<td>2.644</td>
<td>0.0510</td>
<td>0.0211</td>
</tr>
<tr>
<td>3–6</td>
<td>3.529</td>
<td>0.1123</td>
<td>0.0002</td>
<td>3.529</td>
<td>0.1122</td>
<td>0.0123</td>
</tr>
<tr>
<td>1–4</td>
<td>3.661</td>
<td>0.0939</td>
<td>0.0020</td>
<td>3.661</td>
<td>0.0938</td>
<td>0.0118</td>
</tr>
<tr>
<td>2–5</td>
<td>2.835</td>
<td>0.1336</td>
<td>0.0031</td>
<td>3.531</td>
<td>0.1240</td>
<td>0.0014</td>
</tr>
<tr>
<td>2–6</td>
<td>3.567</td>
<td>0.2018</td>
<td>0.0088</td>
<td>4.560</td>
<td>0.1752</td>
<td>0.0017</td>
</tr>
<tr>
<td>1–5</td>
<td>3.647</td>
<td>0.1989</td>
<td>0.0073</td>
<td>4.709</td>
<td>0.1735</td>
<td>0.0021</td>
</tr>
<tr>
<td>1–6</td>
<td>4.045</td>
<td>0.3053</td>
<td>0.0196</td>
<td>5.700</td>
<td>0.2516</td>
<td>0.0103</td>
</tr>
</tbody>
</table>

Cases where two conformers might contribute. Mixtures of the two conformers do, however, give a very satisfactory fit between experimental and theoretical RD curves, as demonstrated in Fig. 2.

Throughout the study a substantial contribution from a syn conformer was always obtained. The percentage syn contribution was, however, somewhat dependent on the vibrational amplitudes and on the background scattering that was subtracted from the total scattered intensities. The results that are presented in Table 3 are based on data obtained with an automatically calculated background and should be more reliable than when hand drawn backgrounds were used in the first stages of the study. When all sources of errors are taken into consideration, the minimum contribution from the

Fig. 3. The experimental RD curve for propargyllallene (---) compared to theoretical RD curves for trial models of syn and skew conformers. The experimental curve is only shown for $r > 2.8$ Å.
Table 3. Propargyllallene. Structural results from least square refinements of the molecular intensity data. Bond distances in Å, (r), angles in degrees. The numbers in brackets are standard deviations as obtained from the least squares calculations.

<table>
<thead>
<tr>
<th></th>
<th>(r_{(\text{C} \equiv \text{C})})</th>
<th>(r_{(\text{C}<em>{sp} - \text{C}</em>{sp2})})</th>
<th>(r_{(\text{C}<em>{sp2} - \text{C}</em>{sp3})})</th>
<th>(r_{(\text{C}<em>{sp2} = \text{C}</em>{sp})})</th>
<th>(r_{(\text{C}_{sp} - \text{H})})</th>
<th>(r_{(\text{C}_{sp2} - \text{H})})</th>
<th>(r_{(\text{C}_{sp3} - \text{H})})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\mu_{\text{calc}})</td>
<td>1.208(1)</td>
<td>1.462(2)</td>
<td>1.514(3)</td>
<td>1.307(1)</td>
<td>1.08 (ass.)</td>
<td>1.102(5)</td>
<td>1.112(7)</td>
</tr>
</tbody>
</table>

\(\angle \text{C} - \text{C} - \text{C}\) 124.4(6)  
\(\angle \text{C} - \text{C} - \text{C}\) 113.8(7)  
\(\angle \text{H} - \text{C} - \text{H}\) 113.7(51)  
\(\angle \text{C}_{sp} = \text{C}_{sp} - \text{H}\) 119.9(23)  
\(\angle \text{C}_{sp} - \text{C}_{sp3} - \text{H}\) 124.3(15)

\(\alpha_{(\text{C}_{sp} - \text{C}_{sp} - \text{C}_{sp3})}\) 0  
\(\alpha_{(\text{C}_{sp} - \text{C}_{sp} - \text{C}_{sp3})}\) 123.8(39)  
\(\% \text{ syn}\) 39.0(7.1)  
\(\% \text{ skew}\) 61.0(7.1)

\(R = \sum w_{(I_{\text{obs}} - I_{\text{calc}})^2} / \sum w_{(I_{\text{obs}})^2} = 5.11 \times 10^{-3}\)

*The error limits are estimated to be 2 – 3 times the standard deviations.

The syn conformer is estimated to be 20% and the maximum contribution 50%. It was not possible to reliably refine the syn dihedral angle and the shortest C–H bond distance together with the other structural parameters. The \(r_{(\text{C}_{sp} - \text{H})}\) distance was set equal to 1.08 Å. Variation of the syn dihedral angle between 0 and 10° with increments 2° gave a continuous increase in the R-factor (expresses the quality of fit for the ED data, see Table 3 for definition) from 5.11 \times 10^{-3} to 5.13 \times 10^{-3}.

It is therefore probably safe to assume that the syn dihedral angle does not deviate significantly from 0°.

THEORETICAL CALCULATIONS

Since the observed conformational composition of propargyllallene is in disagreement with earlier theoretical and experimental results obtained for this molecule, it was decided to carry out some additional semiempirical calculations.

INDO calculations based on the ED geometry of propargyllallene and carried out for various structures of 1,2-Hexadien-5-yne

**Fig. 4.** Propargyllallene. Potential energy curves calculated as function of the \(\text{C}_{sp} - \text{C}_{sp2} - \text{C}_{sp3} - \text{C}_{sp}\) dihedral angle for various non-bonded potentials. Momany et al.\(^{24}\) (A), White and Bovill\(^{20}\) (B), Engler et al.\(^{21}\) (C), Chang et al.\(^{22}\) (D), Ermer and Lifson\(^{23}\) (E), Hendrickson\(^{19}\) (F).
of the molecule are also difficult to assess. The calculations were carried out using six different van der Waals potentials from the literature. The \( C=C-C \) and \( C-C=C \) valence angles were optimized during the calculations. The results from the MM calculations are presented in Fig. 4. All potential energy curves have minima corresponding to \( \text{syn} (\theta = 0^\circ) \) and \( \text{skew} (\theta \sim 120^\circ) \) conformers. Using Ermer and Lifson's van der Waals potentials the \( \text{syn} \) conformer was found to be of lowest energy, while the \( \text{skew} \) conformer was found to be the energetically most favourable when the other five van der Waals potentials were applied. Using Hendrickson's potentials the energy difference between the two conformers is, however, negligible (0.08 kJ/mol).

Even if the INDO, EH and MM calculations are not in quantitative agreement as to the energy difference between the conformers of propargyllene, they do, however, all give energy minima corresponding to \( \text{syn} \) and \( \text{skew} \) conformers — and do therefore support the results obtained from the experimental ED data.

**DISCUSSION**

The final structural parameters obtained for propargyllene are presented in Table 3.

The CC triple bond is found to be slightly smaller than what is normally observed in other alkynes \((\text{HC} \equiv \text{CH})_{25} \ 1.212 \, \text{Å}; \text{CH} \equiv \text{C} = \text{C} \equiv \text{CH})_{26} \ 1.214 \, \text{Å}\), but corresponds closely to recent MW results for methylaetylene \((r_{\text{C} \equiv \text{C}})_{1.207 \, \text{Å}}\). The \( \text{C}_{sp} \equiv \text{C}_{sp} \) bond is also slightly, but not significantly smaller than what is observed in similar structural fragments \((\text{CH} \equiv \text{C} \equiv \text{CH})_{27} \ 1.470 \, \text{Å} \) and \( \text{CH} \equiv \text{C} = \text{C} \equiv \text{CH})_{26} \ 1.468 \, \text{Å}\).

The cumulated CC double bonds are within the error of the method found to be equal to those in biallenyl \((1.312 \, \text{Å})\) and in vinylallene \((1.310 \, \text{Å})\).

The two CCC valence angles at the central \( \text{C}_{3} \text{C}_{4} \) bond may be compared to those recently observed in 1-butene in a combined ED, MW and MOCED study by Hemelrijk et al.\(^{30}\) They were able to determine the valence angles for both conformers observed (17 \% \text{syn}, 83 \% \text{skew}). The \( \text{C} = \text{C} - \text{C} \) angle in 1-butene was for both conformers found to be larger (\text{syn}: 127.2\(^\circ\), \text{skew}: 125.6\(^\circ\)) than the observed average \( \text{C} = \text{C} - \text{C} \) angle in propargyllene. On the other hand the \( \text{C} - \text{C} - \text{C} \) valence angles in 1-butene (\text{syn}: 114.9\(^\circ\), \text{skew}: 111.7\(^\circ\)) were found to be slightly smaller than corresponding to the average \( \text{C} = \text{C} - \text{C} \) angle in propargyllene (40 \% \text{syn} + 60 \% \text{skew}, based on the 1-butene angles give an average of 113.0\(^\circ\), as compared to 113.8\(^\circ\) observed for propargyllene). This difference is, however, hardly significant. It is not unreasonable that the \( \text{syn} \) \( \text{C} = \text{C} - \text{C} \) angle is somewhat larger in 1-butene than in propargyllene because of the larger size of the methyl group, compared to the \( \text{C}_{3} \) atom of the acetylenic group. It is, however, unreasonable that the \( \text{skew} \) \( \text{C} = \text{C} - \text{C} \) angle should be substantially larger in 1-butene. The difference between the observed average \( \text{C} = \text{C} - \text{C} \) angles in the two molecules is, however, so large that it must be supposed to be real. One reason could be that the \( \text{syn} \) conformer in propargyllene is stabilized by homoconjugation and that a reduced \( \text{C} = \text{C} - \text{C} \) angle enhances this effect. If the \( \text{skew} \) \( \text{C} = \text{C} - \text{C} \) angle in propargyllene is assumed to be equal to that observed for 1-butene (125.6\(^\circ\)), the \( \text{syn} \) \( \text{C} = \text{C} - \text{C} \) angle must be ca. 122.6\(^\circ\) for the average angle to correspond to the observed value of 124.4\(^\circ\).

The observed conformational composition of propargyllene is not in agreement with the earlier calculation and spectroscopic studies, where only the \( \text{skew} \) conformer is found to be present. From the present study there can, however, be no doubt that the \( \text{syn} \) conformer is also appreciably populated in the gas phase. The various semiempirical calculations carried out in the present study, do support the results obtained from the electron diffraction data. The observed conformational composition corresponds to the \( \text{syn} \) conformer being slightly more stable (0.71 kJ/mol) than \( \text{skew} \), when the entropy difference is set equal to Rln2. The error in the conformational composition is, however, too large to justify a statement to that account. It may, however, be concluded that the energy of the \( \text{syn} \) and \( \text{skew} \) conformers are comparable. The population of the \( \text{syn} \) conformer is found to be larger in propargyllene than in 1-butene.\(^{21}\) This could be a result of a stabilizing homoconjugative effect. Further experimental studies of molecules where homoconjugation could be of importance for the conformations preferred must, however, be carried out before this can be established with certainty.

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REFERENCES


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