The Molecular Structure of Gaseous 1,2-Hexadien-5-yne (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 [1,2] and base catalyzed [3] isomerization reactions, photoelectron [4,5] as well as IR and Raman spectroscopic studies. [6]

In connection with the photoelectron spectroscopic studies by Gleiter *et al.*[4] the energy of the propargylallene molecule was calculated as a function of the C_3-C_4 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 [6] 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 [3] calculations and from the spectroscopic study. [6]

EXPERIMENTAL

The sample of propargylallene used in the present study was prepared by a method described earlier [7] and was purified by preparative gas chromatography.

Electron diffraction diagrams were recorded with a Balzer's Eldigraph KD-G2 [8,9] 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 $\Delta s = 0.125$ 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,[10] and the intensities were modified by multiplication with the function $s|f'_C|^{-2}$. The scattering amplitudes (f') were calculated by the partial-wave method,[11] using Hartree-Fock atomic potentials.[12] 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
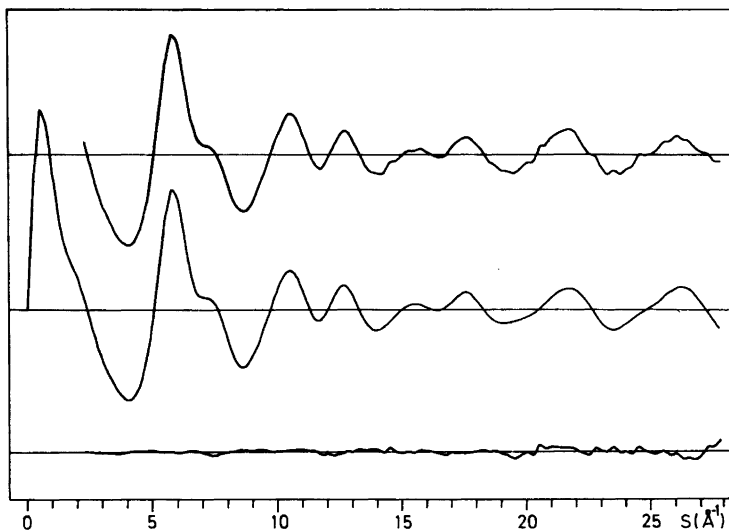
Fig. 1. Experimental (upper) and theoretical (lower) (calculated from the parameters in Table 3) molecular intensity functions and the difference curve for propargylallene.

expected to be quite extensive. It is therefore important to calculate the nonbonded distances in the molecule from the geometrically consistent r_α parameters. Transformation between distances given as r_α or r_a (the electron diffraction distance) parameters may be achieved by using the approximation $(r_{ij})_\alpha = (r_{ij})_a + u_{ij}^2/r_{ij} - K_{ij}$, where u_{ij}^2 is the mean square amplitude and K_{ij} is the perpendicular vibrational amplitude correction coefficient for the distance between the atoms i and j.
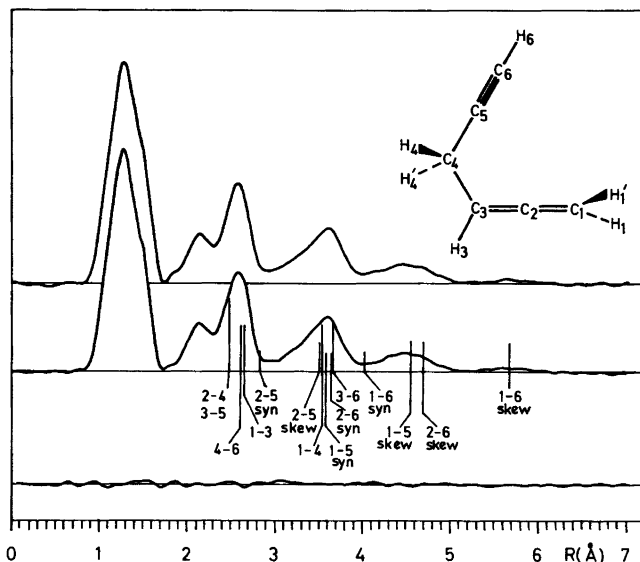

Fig. 2. Experimental (upper) and theoretical (lower) RD and difference curves for propargylallene. Artificial damping constant $k = 0.002$. The theoretical RD curve is calculated for the parameters in Table 3.

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

Stretch (mdyn Å^{-1})		In-plane bend (mdyn Å rad^{-2})	
$C\equiv C$	14.70	$C_{sp3}-C_{sp2}-H$	0.52
$C_{sp2}=C_{sp}$	8.00	$C_{sp2}-C_{sp3}-H$	0.52
$C_{sp3}-C_{sp}$	5.40	$C_{sp2}-C_{sp3}-C_{sp}$	0.60
$C_{sp3}-C_{sp2}$	4.80	$C_{sp3}-C_{sp2}-C_{sp}$	0.70
$C_{sp3}-H$	4.52	$H-C-H$	0.40
$C_{sp2}-H$	4.90		
$C_{sp}-H$	5.93	Out-of-plane bend (mdyn Å rad^{-2})	

$$=\overset{\overset{\displaystyle H}{\displaystyle |}}{C}-C \qquad 0.15$$

Torsion (mdyn Å rad^{-2})		Linear bend (mdyn Å rad^{-2})	
$-C_{sp2}-C_{sp3}-$	0.07	$C\equiv C-H$	0.26
$-C==C-$	0.16	$C-C\equiv C$	0.30
		$C=C=C$	0.30

Interaction force constants (mdyn Å^{-1} or mdyn Å rad^{-2})			
$C=C, C_{sp2}-C_{sp3}$	0.150	$C=C, C-C-H$	-0.115
$C\equiv C, C_{sp3}-C_{sp}$	0.30	$C-C, C-C-H$	0.300
$C_{sp2}-C_{sp3}, C_{sp3}-C_{sp}$	0.150	$C-C, C-C=C$	0.500
$C=C, C=C$	0.200	$C-C, C-C-C$	0.400
$C=C, C_{sp2}-H$	0.115	$C\equiv C-H, C-C\equiv C$	0.100
$C=C, H-C-H$	-0.115		

The vibrational amplitudes (u_{ij}) and K_{ij}-values for all interatomic distances were calculated from an assumed force field.[14] The calculations were carried out for *syn* and *skew* conformers of propargylallene. The calculated u_{ij} and K_{ij}-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 ($R=\Sigma w_i(I_{obs}-I_{calc})^2/\Sigma w_i I_{obs}^2$) in the least squares analyses is given in Table 1. The calculated vibrational amplitudes and vibrational corrections (r_a-r_α) for the non-bonded CC distances in *syn* and *skew* propargylallene are presented in Table 2.

The molecular structure and conformational composition of propargylallene 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 propargylallene: seven bond lengths ($C\equiv C$, $C_{sp}-C_{sp3}$, $C_{sp2}-C_{sp3}$, $C=C$, $C_{sp3}-H$, $C_{sp2}-H$, $C_{sp}-H$), five bond angles ($C-C=C$, $C-C-C$, $H-C_{sp3}-H$, $C_{sp3}-C_{sp2}-H$, $C_2=C_1-H$) and one dihedral angle for each possible con-

former. Within the r_α model the C_1C_3 and C_4H_6 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 $C-C-C$ and $C=C-C$ 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 propargylallene 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 propargylallene 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. Propargylallene. Nonbonded carbon carbon distances for *syn* and *skew* conformations, calculated vibrational amplitudes, u_{ij}, and vibrational corrections $r_a - r_\alpha = K - u^2/r_\alpha$, in Å.

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

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
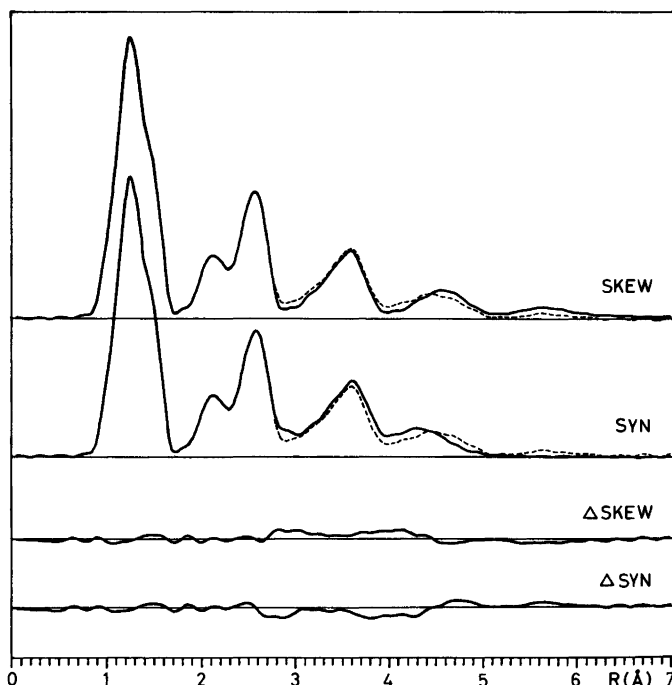

Fig. 3. The experimental RD curve for propargylallene (---) compared to theoretical RD curves for trial models of *syn* and *skew* conformers. The experimental curve is only shown for $r > 2.8$ Å.

Table 3. Propargylallene. Structural results from least square refinements of the molecular intensity data. Bond distances in Å, (r_a) angles in degrees. The numbers in brackets are standard deviations[a] as obtained from the least squares calculations.

		u_{calc}
$r(C\equiv C)$	1.208(1)	0.0367
$r(C_{sp}-C_{sp3})$	1.462(2)	0.0470
$r(C_{sp2}-C_{sp3})$	1.514(3)	0.0504
$r(C_{sp2}=C_{sp})$	1.307(1)	0.0424
$r(C_{sp}-H)$	1.08 (ass.)	0.0741
$r(C_{sp2}-H)$	1.102(5)	0.0778
$r(C_{sp3}-H)$	1.112(7)	0.0794
$\angle C-C=C$	124.4(6)	
$\angle C-C-C$	113.8(7)	
$\angle H-C-H$	113.7(51)	
$\angle C_2=C_3-H$	119.9(23)	
$\angle C_2=C_1-H$	124.3(15)	
$\omega(-C_3-C_4-)_{syn}$	0	
$\omega(-C_3-C_4-)_{skew}$	123.8(39)	
% syn	39.0(7.1)	
% skew	61.0(7.1)	

$R=\Sigma w_i(I_{obs}-I_{calc})^2/\Sigma w_i(I_{obs}^2)=5.11\times10^{-3}$

[a]The error limits are estimated to be $2-3$ times the standard deviations.

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 C_{sp}–H distance (r_a) 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 5.11×10^{-3} to 5.13×10^{-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 propargylallene is in disagreement with earlier theoretical[4] and experimental[6] results obtained for this molecule, it was decided to carry out some additional semiempirical calculations.

INDO calculations[15] based on the ED geometry of propargylallene and carried out for various

C_3-C_4 dihedral angles (θ), gave energy minima at θ equal 0 and 120°, the *syn* conformer being about 6.7 kJ/mol more stable, with a fairly high barrier (*ca.* 32 kJ/mol) at $\theta=60°$ and a low barrier in the *anti* position.

Extended Hückel (EH) calculations[16] were also carried out for the propargylallene conformers described above. The EH energies gave again minima at *syn* and *skew*, the *syn* conformer being energetically more favourable, but by a smaller amount (ΔE *ca.* 2.5 kJ/mol) than indicated by the INDO results. The EH energy curve was found to vary somewhat irregularly with θ. No useful information about the torsional barriers could therefore be extracted from these results.

Finally molecular mechanics (MM) calculations were performed for θ values between 0 and 180° with $\Delta\theta$ equal to 30°.[17,18] It is not easy to find a reliable torsional potential function for torsion in $C_{sp}-C_{sp3}-C_{sp2}=C_{sp}$ fragment. A three-fold barrier with a barrier height of 8.33 kJ/mol and maximum at $\theta=60°$ was chosen. The van der Waals interactions between the two unsaturated halves
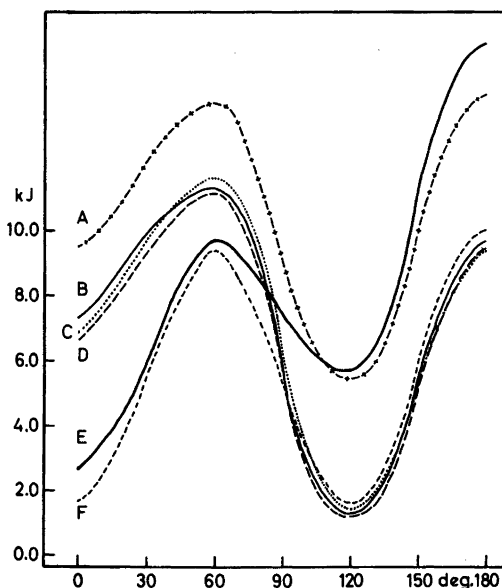

Fig. 4. Propargylallene. Potential energy curves calculated as function of the C_3-C_4 dihedral angle for various non-bonded potentials. Momany *et al.*[24] (A), White and Bovill[20] (B), Engler *et al.*[21] (C), Chang *et al.*[22] (D), Ermer and Lifson[23] (E), Hendrickson[19] (F).

of the molecule are also difficult to assess. The calculations were carried out using six different van der Waals potentials[19-24] 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 *syn* ($\theta = 0°$) and *skew* ($\theta \sim 120°$) conformers. Using Ermer and Lifson's[23] van der Waals potentials the *syn* conformer was found to be of lowest energy, while the *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 propargylallene, they do, however, all give energy minima corresponding to *syn* and *skew* conformers − and do therefore support the results obtained from the experimental ED data.

DISCUSSION

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

The CC triple bond is found to be slightly smaller than what is normally observed in other alkynes ($HC\equiv CH$,[25] 1.212 Å; $CH_3-C\equiv C-CH_3$,[26] 1.214 Å), but corresponds closely to recent MW results for methylacetylene[27] ($r_s(C\equiv C)$:1.207 Å). The $C_{sp}-C_{sp3}$ bond is also slightly, but not significantly smaller than what is observed in similar structural fragments ($CH_3-C\equiv CH$,[27] 1.470 Å and $CH_3-C\equiv C-CH_3$,[26] 1.468 Å).

The cumulated CC double bonds are within the error of the method found to be equal to those in biallenyl[28] (1.312 Å) and in vinylallene[29] (1.310 Å).

The two CCC valence angles at the central C_3C_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 % *syn*, 83 % *skew*). The $C=C-C$ angle in 1-butene was for both conformers found to be larger (*syn*: 127.2°, *skew*: 125.6°) than the observed average $C=C-C$ angle in propargylallene. On the other hand the $C-C-C$ valence angles in 1-butene (*syn*: 114.9°, *skew*: 111.7°) were found to be slightly

smaller than corresponding to the average $C-C-C$ angle in propargylallene (40 % *syn* + 60 % *skew*, based on the 1-butene angles give an average of 113.0°, as compared to 113.8° observed for propargylallene). This difference is, however, hardly significant. It is not unreasonable that the *syn* $C=C-C$ angle is somewhat larger in 1-butene than in propargylallene because of the larger size of the methyl group, compared to the C_5 atom of the acetylenic group. It is, however, unreasonable that the *skew* $C=C-C$ angle should be substantially larger in 1-butene. The difference between the observed average $C=C-C$ angles in the two molecules is, however, so large that it must be supposed to be real. One reason could be that the *syn* conformer in propargylallene is stabilized by homoconjugation and that a reduced $C=C-C$ angle enhances this effect. If the *skew* $C=C-C$ angle in propargylallene is assumed to be equal to that observed for 1-butene (125.6°), the *syn* $C=C-C$ angle must be ca. 122.6° for the average angle to correspond to the observed value of 124.4°.

The observed conformational composition of propargylallene is not in agreement with the earlier calculation[4] and spectroscopic[6] studies, where only the *skew* conformer is found to be present. From the present study there can, however, be no doubt that the *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 *syn* conformer being slightly more stable (0.71 kJ/mol) than *skew*, when the entropy difference is set equal to $R\ln 2$. 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 *syn* and *skew* conformers are comparable. The population of the *syn* conformer is found to be larger in propargylallene 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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