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# Short Communications

## The Molecular Structure of 1,2,4-Pentatriene (Vinylallene)

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The molecular structure of 1,2,4-pentatriene (in the following called vinylallene) has been studied by the gas electron diffraction method. The compound was synthesized according to known procedures,[1] and purified by distillation (b.p. 48 °C/760 Torr), followed by preparative gas chromatography on OPN at 40 °C.

A complete spectroscopic study of vinylallene has been carried out by Klæboe *et al.*[2] The infrared and Raman spectra were interpreted in terms of an *anti* conformation ($C_s$ molecular symmetry) with all atoms coplanar except the terminal allenic hydrogens. No evidence was found for any other conformers of vinylallene.

The conformation of vinylallene has also been studied by photoelectron spectroscopy[3] and by NMR spectroscopy.[4,5] The results obtained in these studies were also consistent with an *anti* conformation.

The electron diffraction intensity data were obtained with the Oslo diffraction camera.[6] Diffraction photographs were taken at two camera lengths (480.73 and 200.73 mm) at room temperature. The electron wavelength was as calibrated against diffraction patterns of gaseous benzene. The data were processed in the usual way[7] to yield the modified molecular intensity function shown in Fig. 1. The modification function used was $s|f'_C|^{-2}$. The scattering amplitudes and phases[7] were calculated using the partialwave method[8] based upon the analytical HF potentials[9] of the atoms. The inelastic scattering factors used were those of Tavard *et al.*[10]

The molecular structure of vinylallene was studied by least squares refinements on the molecular intensity data, combined with information obtained from radial distribution (RD) curves.

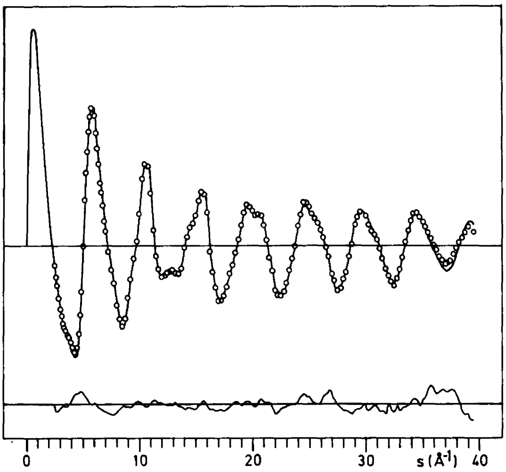

*Fig. 1.* Experimental (○) and theoretical (——) molecular intensity functions for vinylallene. The difference curve is shown in double scale.

The following assumptions about the molecular structure were made: All C–H bonds equal, $\angle C_2{=}C_1{-}H_1 = \angle C_2{=}C_1{-}H_1'$, $\angle C_4{=}C_5{-}H_5 = \angle C_4{=}C_5{-}H_5'$, $\angle C_3{-}C_4{-}H_4 = \angle C_4{-}C_3{-}H_3$ and $r(C_1{=}C_2) = r(C_2{=}C_3)$. A test was made for possible deviation from linearity of the allenic linkage, but as none could be detected, the $C_1{=}C_2{=}C_3$ valence angle was set equal to 180°. The $C_1C_3$ distance, together with $C_1C_4$ and $C_1C_5$ were however treated as independent parameters. The other nonbonded distances were calculated from the geometrically consistent $r_\alpha$-parameters, using the perpendicular amplitude correction coefficients and *u*-values from Ref. 11. The vibrational amplitudes (*u*-values) that could not be determined experimentally were also taken from Ref. 11.

The fairly large peak at about 4.9 Å in the RD-curve (see Fig. 2) is a clear indication that an *anti* conformer must dominate in the gas phase, as only the *anti* $C_1C_5$ distance may give substantial contribution in this region. Further studies gave no evidence of other conformers being present.

The final structural parameters determined for vinylallene are presented in Table 1. The bond

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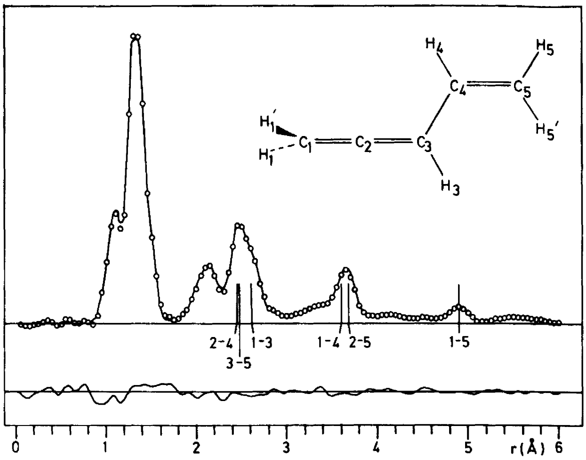

*Fig. 2.* Experimental (○) and theoretical (———) radial distribution functions for vinylallene. The difference curve is shown in double scale. Artificial damping constant equal to 0.0012 Å.[2]

*Table 1.* Structure parameters determined for vinylallene. The numbers in parentheses are standard deviations from the least squares analyses. Due to experimental uncertainties and data correlations the error limits are estimated to be 2 – 3 times larger than the standard deviations.

| Distance | $r_a$ (Å) | $u$ (Å) | $u_{calc.}$ (Å)[11] |
|---|---|---|---|
| $C_1=C_2$ | 1.310 (1) | 0.040 (1) | 0.040 |
| $C_4=C_5$ | 1.338 (2) |  | 0.042 |
| $C_3-C_4$ | 1.462 (2) | 0.053 (2) | 0.045 |
| C–H | 1.093 (2) | 0.081 (2) | 0.078 |
| $C_1C_3$ | 2.623 (3) | 0.051 (3) | 0.046 |
| $C_1C_4$ | 3.614 (9) | 0.097 (9) | 0.096 |
| $C_1C_5$ | 4.905 (9) | 0.100 (11) | 0.083 |
| $C_2C_4$ | 2.448 | 0.062 (3) | 0.068 |
| $C_2C_5$ | 3.672 | 0.067 (6) | 0.066 |
| $C_3C_5$ | 2.470 | 0.062 (3) | 0.066 |
| Angles ($\angle_\alpha$) | (degrees) |  |  |
| $C_2=C_3-C_4$ | 124.3 (.7) |  |  |
| $C_3-C_4=C_5$ | 124.1 (.6) |  |  |
| $C_2=C_1-H$ | 121.1 (1.3) |  |  |
| $C_4=C_5-H$ | 121.0 (1.5) |  |  |
| C–C–H | 119.1 (1.4) |  |  |

distances and valence angles are very similar to those of biallenyl.[12]

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