

An Electron Diffraction Investigation of the Molecular Structure of *trans*-2-Methyl-1,3,5-hexatriene in the Vapour Phase

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The molecular structure of *trans*-2-methyl-1,3,5-hexatriene has been studied by the gas electron diffraction method. The molecule was found to have a planar carbon skeleton. The mean vibrational amplitudes for all interatomic distances have been calculated from an assumed force field and have been compared with those experimentally determined.

The following structural parameters have been obtained: C=C, 1.348 Å; C₂-C₃, 1.456 Å; C₂-C₇, 1.510 Å; C₁-H₁, 1.094 Å; C₇-H₇, 1.104 Å. The distances are given as *R*_a values. The distribution of bond angles is given in Table 2.

The molecular structures of *cis* and *trans* isomers of 1,3,5-hexatriene have been studied earlier.^{1,2} It will be of interest to see which changes in the structural parameters will be observed when a methyl group is introduced in 2-position. The structural study is also of interest as a contribution to the elucidation of molecular structures of conjugated aliphatic systems generally. The molecular structure of *cis*-2-methyl-1,3,5-hexatriene has been studied simultaneously and the results are published elsewhere.³

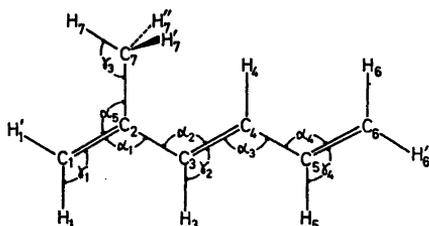


Fig. 1. *trans*-2-Methyl-1,3,5-hexatriene. Molecular model which shows the numbering of the atoms.

EXPERIMENTAL

The sample of *trans*-2-methyl-1,3,5-hexatriene used in the present study was kindly provided by the late professor R. B. Turner, Rice University, Houston, Texas.

The electron diffraction diagrams were recorded with the Oslo electron diffraction unit⁴ at camera lengths of approximately 48 and 20 cm. During the experiment the sample of *trans*-2-methyl-1,3,5-hexatriene was maintained at a temperature of 20 °C, while the temperature of the nozzle was about 30 °C. The electron wavelength was 0.06458 Å, corresponding to an accelerating potential of about 36 kV. The scattering data were treated in the usual way,⁵ and yielded an experimental modified molecular intensity function extending from $s = 1.375 \text{ \AA}^{-1}$ to $s = 42.75 \text{ \AA}^{-1}$. The Δs interval was 0.125 \AA^{-1} in the inner s region ($s < 9.5 \text{ \AA}^{-1}$) and 0.250 \AA^{-1} for the large-angle scattering data.

STRUCTURE ANALYSIS

Preliminary values for the structure parameters were obtained from the observed radial distribution (RD) curve, which is shown in Fig. 3 and from a study of experimental and theoretical autocorrelation power spectra.⁹ The bond distances and valence angles were refined by a least squares procedure applied to the observed molecular intensity function, a diagonal weight matrix being used.^{5,10} The scattering amplitudes and phases used in the theoretical equation were calculated by the methods described by Peacher and Wills,¹¹ using HF atomic potentials.

The peaks at about 1.1 and 1.4 Å on the experimental RD curve shown in Fig. 3 represent carbon hydrogen and carbon carbon bond

distances, respectively, while the peaks at about 2.15 and 2.5 Å contain contributions from the carbon hydrogen and carbon carbon nonbonded distances over one bond angle. The appearance of the fairly large peak at about 6.1 Å is a clear indication that *trans*-2-methyl-1,3,5-hexatriene must have an essentially planar carbon skeleton with *s-anti* conformation at the C₂-C₃ and C₄-C₅ single bonds.

In the electron diffraction studies of the *cis*¹ and *trans*² isomers of 1,3,5-hexatriene it was possible to show that the length of the central C=C double bond was somewhat larger than the terminal ones. It is more complicated to determine the bond distances in *trans*-2-methyl-1,3,5-hexatriene as introduction of a methyl group destroys the symmetry in the molecule and also adds two new types of bonds. In the present case it was not possible to distinguish between the central and terminal C=C double bonds, and the three C=C double bond distances were assumed to be equal.

Some assumptions were also made concerning the positions of the hydrogen atoms. All C=C-H angles (γ_1) involving the terminal methylene groups were assumed to be equal. The C₃=C₄-H₄ (γ_2) angle was assumed to be the same as \angle C₄=C₃-H₃. The three-fold axis of the methyl group was assumed to coincide with the C₂-C₇ single bond and one of the methyl hydrogens assumed to be eclipsed with the C₁=C₂ double bond.

When the assumptions described above were applied a rigid molecular model of *trans*-2-methyl-1,3,5-hexatriene could be described by three CC and two CH bond lengths, five CCC and four CCH bond angles and the C₂-C₃ and C₄-C₅ dihedral angles. It was not possible to vary all these geometrical parameters simultaneously in the least squares refinements. Some of the bond angle parameters were therefore determined applying an indirect approach. One angle was studied at a time by running several parallel least squares programs. In all runs the conditions were identical except for the angle being studied, which was slightly different from one run to another. By studying the squared error sums and standard deviations of the refining parameters the best value for the angle in question was chosen. This process was continued until self-consistency.

The model used to describe the *trans*-2-

Table 1. *trans*-2-Methyl-1,3,5-hexatriene. Calculated and observed mean vibrational amplitudes for the carbon carbon distances. The numbers in parentheses are standard deviation values, as resulting from least squares intensity refinements.

Distance	$u^{obs.}, \text{Å}$	$u^{calc.}, \text{Å}$
C=C	0.0391 (8)	0.0409
C ₂ -C ₃	0.0460 (12)	0.0487
C ₂ -C ₇	0.0462 (16)	0.0492
C ₁ -H ₁	0.0775	0.0790
C ₇ -H ₇		0.0791
C ₁ ...C ₇		0.0771
C ₁ ...C ₃	0.0550	0.0795
C ₄ ...C ₆		0.0776
C ₃ ...C ₅		0.0771
C ₂ ...C ₄		0.0768
C ₃ ...C ₇	0.1128 (25)	0.0836
C ₄ ...C ₇		0.1562
C ₁ ...C ₄		0.0767
C ₃ ...C ₆	0.0759 (26)	0.0772
C ₂ ...C ₅		0.0794
C ₅ ...C ₇	0.1550 (25)	0.1627
C ₁ ...C ₅	0.0739 (83)	0.1046
C ₂ ...C ₆		0.1015
C ₆ ...C ₇	0.1350 (172)	0.2253
C ₁ ...C ₆	0.0875 (25)	0.0976

methyl-1,3,5-hexatriene molecule contains all together sixtyeight different carbon-carbon and carbon-hydrogen distances. It is not possible to determine vibrational parameters for all of these internuclear distances from the electron diffraction data. In order to assign plausible mean vibrational amplitudes (u values) to the distances whose u values could not be directly determined, theoretical values for all mean vibrational amplitudes were calculated from an assumed force field. The calculations were made according to Gwinn's method,¹³ which is based on an expansion of interatomic distances in terms of cartesian displacement coordinates. The computer program has been adjusted for practical use in an electron diffraction study by Stølevik *et al.*¹⁴ The assumed force field was taken from data published by Allinger *et al.*¹⁵

The calculated u values for the carbon carbon distances in the molecule are listed in Table 1, which also presents the observed mean vibrational amplitudes for these distances. It will be seen that some of the observed u values are assumed to be the same for groups of non-bonded distances. These assumptions were

reasonable as judged by the similarities of the calculated u values within one group. On an average the calculated mean vibrational amplitudes were found to be larger than those observed experimentally. Apart from this general deviation the correspondence between calculated and observed u values is satisfactory.

If the longest non-bonded carbon carbon distances are treated as independent parameters in the least squares analyses, they are found to be a trifle smaller than when calculated for a planar

molecular model. This observation must be described to shrinkage effects,^{16,17} as the mean vibrational amplitude for the $C_1 \cdots C_6$ distance is found to be quite small. When the longer non-bonded CC distances were treated as dependent distances and the C_2-C_3 and C_4-C_5 dihedral angles were varied systematically, best correspondence between experimental and theoretical data was obtained when the two dihedral angles were about 170° instead of 180° for an all planar conformation.

If the molecular geometry is based on a R_α structure¹⁴ the shrinkage effects should be included, as R_α gives the distance between average positions of two atoms. The distances displayed in a RD function are R_a distances. The relationship between a R_a and a R_α interatomic distance is approximately:

$$R_a = R_\alpha + K - u^2/R_c$$

K is the perpendicular amplitude correction coefficient.¹⁴ If the K values for all interatomic distances are known, it is possible to determine an R_α structure from electron diffraction data. The K values were calculated by the same program that was used for calculation of the mean vibrational amplitudes. In the present case the quality of the parameters determined from a R_α structure was somewhat inferior to those determined from a R_a structure, when the squared error sum and standard deviation values were used as criteria. This might be due to inaccurate perpendicular amplitude correction coefficients. The determined parameters based on an R_α and an R_a structure were, however, practically identical. The final parameters for *trans*-2-methyl-1,3,5-hexatriene, based on refinements on a R_a structure are presented in Table 2.

Table 2. *trans*-2-Methyl-1,3,5-hexatriene. Structure parameters obtained by least squares refinements on the intensity data. Distances (R_a values⁶) and mean amplitudes of vibrations (u) in Å, angles in degrees. The standard deviations given in parentheses have been corrected to take into account data correlation⁷ and have also been increased to include the uncertainty arising from error in the electron wavelength.⁸

Distances	R_a	u
C=C	1.3477 (20)	0.0391 (20)
C ₂ -C ₃	1.4562 (30)	0.0460 (30)
C ₂ -C ₇	1.5104 (40)	0.0462 (40)
C ₁ -H ₁	1.0940 (25)	
C ₇ -H ₇	1.1040 (25)	
C ₁ ⋯C ₇	2.4889	0.0550 ^a
C ₁ ⋯C ₃	2.4181	
C ₄ ⋯C ₆	2.4819	
C ₃ ⋯C ₅	2.4716	
C ₃ ⋯C ₄	2.4919	
C ₃ ⋯C ₇	2.5677	
C ₄ ⋯C ₇	3.0069	0.1128 (60)
C ₁ ⋯C ₄	3.6764	0.0759 (64)
C ₃ ⋯C ₆	3.7071	
C ₃ ⋯C ₅	3.8406	
C ₅ ⋯C ₇	4.4598	0.1550 (60)
C ₁ ⋯C ₅	4.8829	0.0739 (200)
C ₃ ⋯C ₆	4.9713	
C ₆ ⋯C ₇	5.3119	
C ₁ ⋯C ₆	6.1163	0.1350 (300)
C ₁ ⋯C ₅		0.0875 (60)
Angles		
∠C ₁ =C ₂ -C ₃ (α_1)	119.1	
∠C ₂ -C ₃ =C ₄ (α_2)	125.4	
∠C ₃ =C ₄ -C ₅ (α_3)	124.5 ^a	
∠C ₄ -C ₅ =C ₆ (α_4)	124.5 ^a	
∠C ₁ =C ₂ -C ₇ (α_5)	121 ^a	
∠C ₂ =C ₁ -H ₁ (γ_1)	122 ^a	
∠C ₃ =C ₄ -H ₄ (γ_2)	118.5 ^a	
∠C ₃ -C ₇ -H ₇ (γ_3)	110.5 ^a	
∠C ₆ =C ₅ -H ₅ (γ_4)	116 ^a	

^a Determined by combined trial and error/least squares procedure (see text).

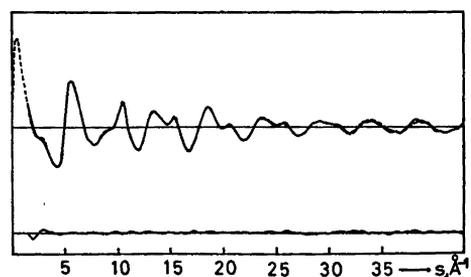


Fig. 2. *trans*-2-Methyl-1,3,5-hexatriene. Experimental (—) and theoretical (---) molecular intensity functions with difference curve.

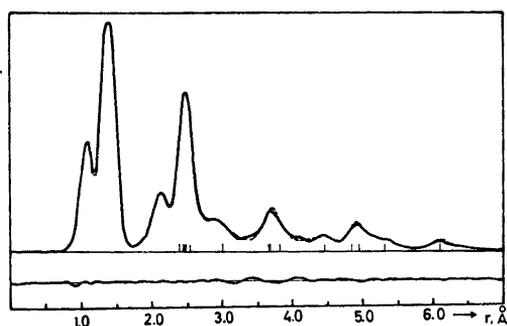


Fig. 3. *trans*-2-Methyl-1,3,5-hexatriene. Experiment (—) and theoretical (---) radial distribution functions and difference curve. Artificial damping constant $k = 0.0015 \text{ \AA}^2$.

The theoretical molecular intensity function calculated on the basis of the parameters listed in Table 2, is shown in Fig. 2 along with the experimental $sM(s)$ function, while Fig. 3 shows the corresponding theoretical and experimental radial distribution functions.

DISCUSSION

In Table 3 the structural parameters for *trans*-2-methyl-1,3,5-hexatriene are compared with similar data obtained for its *cis* isomer and for *trans* and *cis* isomers of 1,3,5-hexatriene. It will be seen that the various types of bond distances are found to be approximately the same in all four molecules. When the bond angles for the two 2-methyl-1,3,5-hexatrienes are compared, the increased values for $\angle\alpha_2$ and $\angle\alpha_3$ for the *cis* isomer should be noticed. Such enlarged CCC valence angles are to be expected because of the larger steric strain in this molecule. The same difference in $\angle\alpha_2$ ($\angle\alpha_3$) for the *cis* and *trans* isomers of 1,3,5-hexatriene is also observed, although the discussed angles are generally found to be somewhat smaller in these molecules. There appears to be a large unexplainable discrepancy between $\angle\alpha_5$ in *trans*- and *cis*-2-methyl-1,3,5-hexatriene. For both molecules there is, however, a high degree of coupling between $\angle\alpha_1$ and $\angle\alpha_5$. The average of these two angles is approximately the same for the two molecules and the apparent deviations should therefore not be taken too seriously.

Table 3. Comparison of structural parameters determined for *trans* (I) and *cis*² (II) isomers of 2-methyl-1,3,5-hexatriene and *trans*² (III) and *cis*¹ (IV) isomers of 1,3,5-hexatriene. Distances (R_a) in Å and angles in degrees.

	I	II	III	IV
C=C	1.348	1.345	1.347 ^a	1.345 ^a
C ₂ -C ₃	1.456	1.462	1.458	1.462
C ₂ -C ₇	1.510	1.515		
C ₁ -H ₁	1.094	1.091	1.104	1.090
C ₇ -H ₇	1.104	1.101		
$\angle\alpha_1$	119.1	122.6	121.7	122.1
$\angle\alpha_2$	125.4	128.7	124.4	126
$\angle\alpha_3$	124.5	127.5	124.4	126
$\angle\alpha_4$	124.5	124.5	121.7	122.1
$\angle\alpha_5$	121	117.5		
$\angle\gamma_1$	122	119.1	120.5	124
$\angle\gamma_2$	118.5	114	115	118
$\angle\gamma_3$	110.5	110.5		
$\angle\gamma_4$	116	116	117	116.9

^a Average value.

$\angle\gamma_2$ should be studied in connection with the average of $\angle\alpha_2$ and $\angle\alpha_3$ for both the 2-methyl-1,3,5-hexatriene molecules. In the *cis* isomer, where a considerable increase in $\angle\alpha_2$ and $\angle\alpha_3$ is observed, the decrease in $\angle\gamma_2$ compared to the structure of the *trans* isomer is to be expected.

$\angle\alpha_4$ are for both isomeric 2-methyl-1,3,5-hexatriene molecules found to be slightly, but not significantly, larger than in the 1,3,5-hexatriene molecules. Comparable angles in 1,3-butadiene,¹⁸ *trans*-2-butene,¹⁹ and propene²⁰ are found to be 122.8, 123.8, and 124.8°, respectively.

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