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

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The molecular structure of *cis*-2-methyl-1,3,5-hexatriene has been studied by the gas electron diffraction method. The $C_3=C_4$ and $C_5=C_6$ double bonds were found to be coplanar corresponding to *s-anti* conformation at the intervening CC single bond. The $C_1=C_2$ double bond was found to be out of the plane of the other CC double bonds. It was not possible definitely to distinguish between a *syn*-clinal and *anti*-clinal conformation at the C_2-C_3 single bond, but the results indicate that *syn*-clinal (*s-gauche*) is the correct one.

The following bond distances and mean vibrational amplitudes were observed:

$R(C=C)_{Av.}$: 1.345 Å, $u(C=C)_{Av.}$: 0.0391 Å, $R(C_{sp^2}-C_{sp^2})_{Av.}$: 1.462 Å, $u(C_{sp^2}-C_{sp^2})_{Av.}$: 0.0460 Å, $R(C_{sp^2}-C_{sp^3})$: 1.515 Å, $u(C_{sp^2}-C_{sp^3})$: 0.0461 Å, $R(C_{sp^2}-H)$: 1.094 Å, $R(C_{sp^3}-H)$: 1.104 Å, $u(C-H)_{Av.}$: 0.0775 Å. The distances are given as R_a values.

Nearly all experimentally determined noncyclic organic molecules with conjugated double bonds are found to have an essentially planar *anti* arrangement of two consecutive double bonds, *i.e.* an *s-anti* conformation at the intervening single carbon bond. The torsional potential energy connected with rotation about a $C_{sp^2}-C_{sp^2}$ single bond obviously has its lowest minimum at a dihedral angle equal to 180°. At this conformation the conjugation between the two neighbouring π-bonds is at its maximum while the repulsions between the bonds at the two carbon atoms constituting the single bond are minimal. However, very little is known about the general shape of the potential energy function in relation to the torsional angle around a single bond between two sp^2-hybridized carbon atoms. In order to elucidate this problem it is of interest to gather experimental information about molecular structures where other conformations than those corresponding to *s-anti* at the single bonds in conjugated systems might be observed. In *cis*-2-methyl-1,3,5-hexatriene there will be serious steric interaction between the methyl group and the methine group at C_5 if an all planar conformation of the carbon skeleton is assumed. It will be of special interest to find out how the steric inhibition is overcome in this case. A study of *trans*-2-methyl-1,3,5-hexatriene was carried out simultaneously.[13]

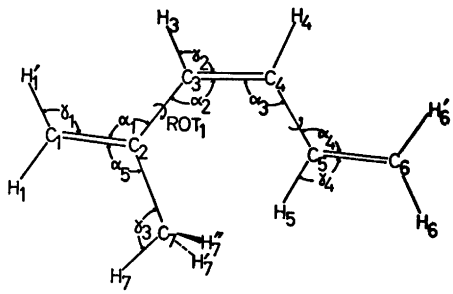

Fig. 1. cis-2-Methyl-1,3,5-hexatriene. Molecular model which shows the numbering of the atoms.

EXPERIMENTAL

The sample of *cis*-2-methyl-1,3,5-hexatriene used in the present study was kindly provided by the late professor R. Turner, Rice University, Houston, Texas. The electron diffraction pattern from the gas was recorded on the Oslo electron diffraction unit [1] at a temperature of about 30°C. Exposures were made at nozzle to photographic plate distances of about 48 cm and 20 cm. Four apparently faultless plates for each nozzle-to-plate distance were photometered and the data processed in the usual way.[2] The resulting molecular intensity function extended

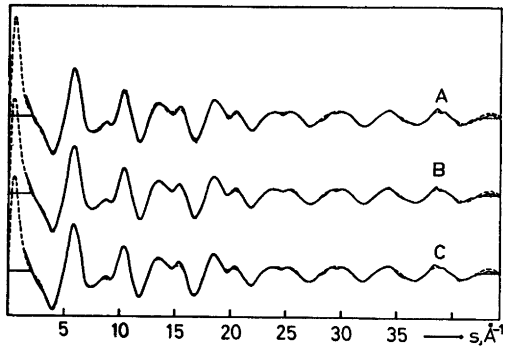

Fig. 2. cis-2-Methyl-1,3,5-hexatriene. Experimental (—) and theoretical (---) molecular intensity functions. The theoretical data correspond to A: Model I, B: Model II and C: Model III.

from $s = 1.375$ Å^{-1} to $s = 44.25$ Å^{-1}. $s = (4\pi/\lambda) \sin(\theta/2)$ where λ is the electron wavelength (determined by diffraction from gaseous CO_2) and θ is the diffraction angle. The modified experimental molecular $[sM(s)]$ function is shown in Fig. 2.

Theoretical intensity functions were calculated from eqn. (1)

$$sM(s) = \sum_{i \neq j} \frac{|f_i(s)||f_j(s)|}{|f_C(s)|^2} \cos\left[\eta_i(s) - \eta_j(s)\right] \times \frac{\sin(sR_{ij})}{R_{ij}} \exp(-\tfrac{1}{2}u_{ij}^2 s^2) \quad (1)$$

The sum extends over all atom pairs i, j in the molecule. R_{ij} represents an internuclear distance and u_{ij} the corresponding root-mean-square amplitude of vibration. $f_j(s) = |f_j(s)|\exp[i\eta_j(s)]$ is the complex atomic scattering factor of atom j.

Radial distribution (RD) functions were calculated by Fourier inversion of experimental and theoretical intensity functions after multiplication with the artificial damping function $\exp(-ks^2)$.

STRUCTURE ANALYSES

The interpretation of the peaks in the radial distribution curve for $R < 2.7$ Å is independent of the conformational arrangement. The peak at 1.1 Å represents the carbon hydrogen bond distances, while the peak at 1.4 Å contains contributions from the various carbon carbon bond distances. Non-bonded carbon hydrogen and carbon carbon distances over one valence angle is found at 2.14 Å and 2.5 Å, respectively.

Starting parameters for the bond distances were assigned by comparing experimental and theoretical autocorrelation power spectra.[3] In the electron diffraction studies of *cis* and *trans* isomers of 1,3,5-hexatriene [4,5] it was possible to show that the length of the central carbon carbon double bond was slightly different from the terminal ones. In the present case it is more complicated to determine the bond distances accurately as introduction of the methyl group destroys the symmetry in the molecule and adds two new types of bond distances. From the study of autocorrelation power spectra it was not possible to distinguish the central CC double bond from the terminal ones. In the following the lengths of the three CC double bonds were therefore assumed to be equal.

The outer part of the RD curve contains information about the overall conformation of the molecule. Calculation of a theoretical RD function corresponding to a planar carbon skeleton for *cis*-2-methyl-1,3,5-hexatriene was not in agreement with the experimental RD function, and this model was therefore rejected.

The conformation problem was attacked by making graphs of the nonbonded carbon carbon interatomic distances as functions of the C_2-C_3 and C_4-C_5 torsional angles. As the RD function showed no peak beyond the complex at about 4.5 Å that could clearly be attributed to a distance between carbon atoms, it was first assumed that torsional angles at both $C_{sp^2}-C_{sp^2}$ single bonds were different from 180° (*s-anti*). It was possible to find a model that fitted this description and that converged in the least squares refinement process. The implied torsional angles did refine in the least squares analysis and gave values of about 133° and 93° for the C_2-C_3 and C_4-C_5 torsional angles, respectively. The corresponding radial distribution curve is shown in Fig. 3, A. It is seen that the area of the peaks in the 3.0—4.0 Å region is considerably larger on the theoretical RD curve. The discrepancy might be somewhat diminished by altering the envelope [2] of the experimental RD curve, but is still significant. Besides it was not possible to get good correspondence between experimental and theoretical data in the region around 4.5 Å. Other models were therefore also tested.

If one of the torsional angles around C_2-C_3 or C_4-C_5 corresponds to *s-anti* conformation, the longest carbon carbon distance will appear

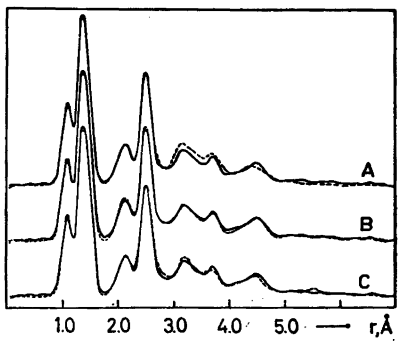

Fig. 3. cis-2-Methyl-1,3,5-hexatriene. Experimental (—) and theoretical (---) radial distribution functions. Artificial damping constant $k = 0.0015$ Å^2. The theoretical data correspond to A: Model I, B: Model II and C: Model III.

beyond the peak at 4.5 Å on the RD curve, probably around 5.6 Å. Even if no peak is clearly recognizable on the experimental RD curve, it is fully possible that a long carbon carbon non-bonded distance with large vibrational amplitude might give contribution in this region.

Models with *s-anti* conformation at the C_4-C_5 bond were clearly superior to those with *s-anti* conformation at the C_2-C_3 bond. This observation is in agreement with what would be expected, as more strain will be relieved by rotation around the C_2-C_3 bond than by a similar effect at the C_4-C_5 bond.

Inspection of a chart showing the distribution of CC nonbonded distances as functions of the C_2-C_3 dihedral angle indicated that a dihedral angle corresponding to *s-gauche* conformation at the C_2-C_3 bond should give fairly good correspondence with peaks on the experimental RD curve. A molecular model corresponding to this conformation (Model B) converged in the least squares analyses, and it was possible to refine the C_2-C_3 as well as the C_4-C_5 dihedral angles. However, it is not surprising that it was also possible to get good correspondence between theoretical and experimental data for a model that differed from the one described above in that the C_2-C_3 dihedral angle is about 120°, corresponding to *anti*-clinal conformation (Model C). The main difference in electron-diffraction data from molecules corresponding to Model B and Model C is in the relative scattering power of a methyl and a methylene group as these are interchanged in the two models. The prospect of distinguishing these two models was therefore not very promising.

The two molecular models discussed above were treated independently. During the structure refinements the following assumptions were made in addition to those discussed above for the CC bond distances: all $C=C-H$ angles involving the terminal methylene groups were set equal, $\angle C_3=C_4-H_4$ was supposed to be equal to $\angle C_4=C_3-H_3$, the three-fold axes of the methyl group was supposed to coincide with the C_7-C_2 bond and one of the hydrogens in the methyl group was supposed to be eclipsed with the $C_1=C_2$ double bond.

When these assumptions were made the geometry of the molecular structure is given by the following 16 parameters:

Five bond distances:
$C=C$, C_2-C_3, C_2-C_7, C_1-H_1 and C_7-H_7

Five CCC bond angles:
$\angle C_1=C_2-C_3(\alpha_1)$, $\angle C_2-C_3=C_4(\alpha_2)$,
$\angle C_3=C_4-C_5(\alpha_3)$, $\angle C_4-C_5=C_6(\alpha_4)$,
$\angle C_1=C_2-C_7(\alpha_5)$

Four CCH bond angles:
$\angle C_2=C_1-H_1(\gamma_1)$, $\angle C_3=C_4-H_4(\gamma_2)$,
$\angle C_2-C_7-H_7(\gamma_3)$, $\angle C_6=C_5-H_5(\gamma_4)$

Two dihedral angles:
$\angle C_1=C_2-C_3=C_4(\mathrm{ROT}_1)$ and
$\angle C_3=C_4-C_5=C_6(\mathrm{ROT}_2)$

It was not possible to vary all the bond angles simultaneously in the least squares refinements. This problem was solved by picking out some of the bond angles and keeping these constant within a least squares run. These bond angles were studied by running several least squares programs simultaneously. In each run all starting parameters were identical except for the bond angle that was being studied and that was systematically varied within the expected range. The squared error sums and the standard deviations of the parameters that were refined in the least square process were studied in order to find the best value for each of the bond angles in question. This process was repeated until selfconsistency. The results were practically independent of which of the bond angles that were picked out and treated as described above.

Table 1. cis-2-Methyl-1,3,5-hexatriene. Results obtained by least squares refinements of the molecular intensity data. The two models correspond to *syn*-clinal (II) and *anti*-clinal (III) conformations at the C_2-C_3 bond. The numbers in brackets are standard deviation values.

Distance	II R_a, Å	II u, Å	III R_a, Å	III u, Å
C=C	1.3445(5)	0.0391(9)	1.3445(6)	0.039
C_2-C_3	1.4616(10)	0.0462(33)	1.4653(23)	
C_2-C_7	1.5148(20)	0.0459(44)	1.5080(41)	
$C_{sp}-H$	1.0914(13)	0.0775	1.0915(18)	
$C_1\cdots C_7$	2.4461			
$C_1\cdots C_3$	2.4619			
$C_4\cdots C_6$	2.4840			
$C_3\cdots C_5$	2.5172	0.0600		
$C_2\cdots C_4$	2.5305			
$C_3\cdots C_7$	2.5766			
$C_2\cdots C_5$	3.1490	0.1300[a]		
$C_1\cdots C_4$	3.2071	0.1000[a]		
$C_1\cdots C_5$	3.4040	0.1800[a]		
$C_4\cdots C_7$	3.6932	0.0800[a]		
$C_3\cdots C_6$	3.7304	0.0800[a]		
$C_5\cdots C_7$	4.3136	0.1300[a]		
$C_2\cdots C_6$	4.4750	0.0850[a]		
$C_1\cdots C_6$	4.6104	0.0900[a]		
$C_6\cdots C_7$	5.6558	0.2000[a]		
	II		III	
$\angle\alpha_1$	122.6 (0.3)°		128.3 (1.2)°	
$\angle\alpha_2$	128.7 (0.3)°		128.4 (0.5)°	
$\angle\alpha_3$	127.5°		126.5°	
$\angle\alpha_4$	124.5°		123°	
$\angle\alpha_5$	117.5°		118.5°	
$\angle\gamma_1$	119.1 (0.7)°		116°	
$\angle\gamma_2$	114°		115°	
$\angle\gamma_3$	110.5°		110.5°	
$\angle\gamma_4$	116°		115°	
$\angle ROT_1$	58.0 (0.8)°		115.6 (1.8)°	
$\angle ROT_2$	193.1 (4.6)°		197.4 (6.7)°	

[a] Assumed value.

Table 1 shows results obtained for the two models under consideration. Theoretical RD curves corresponding to the parameters listed in Table 1 for Models B and C are presented in Fig. 3. The correspondence between experimental and theoretical RD curves is clearly best for Model B. Only in the region around 4.0 – 4.2 Å do the theoretical data for Model C give a better fit.

There is no doubt that it will be possible to improve the fit between the theoretical RD curve for Model C and the experimental RD curve by adjusting some of the u values for non-bonded CC distances. Most of the u values used so far were estimated by analogy from similar molecules, and it is of course possible that the estimates have been better for Model B than for Model C. In order to increase the objectivity when comparing the three models it was decided to calculate the mean vibrational amplitudes for the three models that have been discussed for *cis*-2-methyl-1,3,5-hexatriene, using Gwinn's method.[7,8] The calculations were based on force field parameters published by Allinger *et al.*[9] Even if the resulting u values for the long distances might be inaccurate, the distribution between small and large vibrational amplitudes within one model should be correct. The quality of the calculated u values for the three models should also be the same. If the three models were compared using least squares refinements and the calculated mean vibrational amplitudes, they should therefore be judged on an objective scale.

Table 2. cis-2-Methyl-1,3,5-hexatriene. Calculated mean vibrational amplitudes for the carbon carbon interatomic distances that vary with torsion around the C_2-C_3 and C_4-C_5 bonds. The calculations are carried out for three different conformations.

Distance	A R_a, Å	u, Å	B R_a, Å	u, Å	C R_a, Å	u, Å
$C_2\cdots C_5$	3.08	0.1534	3.13	0.1535	3.15	0.1535
$C_1\cdots C_4$	3.11	0.1292	3.20	0.1218	3.63	0.0882
$C_1\cdots C_5$	3.20	0.2218	3.40	0.2091	4.20	0.1629
$C_4\cdots C_7$	3.71	0.0882	3.67	0.0933	3.15	0.1290
$C_3\cdots C_6$	3.41	0.1079	3.75	0.0769	3.75	0.0769
$C_5\cdots C_7$	4.36	0.1578	4.26	0.1636	3.33	0.2148
$C_2\cdots C_6$	3.73	0.1865	4.47	0.1520	4.50	0.1520
$C_1\cdots C_6$	3.86	0.2370	4.68	0.2304	5.52	0.1666
$C_6\cdots C_7$	4.71	0.2167	5.56	0.1677	4.59	0.2396

A: ROT_1, 50°; ROT_2, 90°.
B: ROT_1, 60°; ROT_2, 180°.
C: ROT_1, 120°; ROT_2, 180°.

Table 3. cis-2-Methyl-1,3,5-hexatriene. Parameters determined from least squares intensity refinements for three different conformations, when theoretically calculated mean vibrational amplitudes were applied.

Parameter	I	II	III
C=C	1.3450(9) Å	1.3446(7)	1.3439(7)
C_2-C_3	1.4631(15) Å	1.4631(15)	1.4615(15)
C_2-C_7	1.5327(36) Å	1.5158(32)	1.5149(31)
C_1-H_1	1.0903(22) Å	1.0893(18)	1.0889(18)
$\angle C_2-C_3=C_4$	124.5(0.6)°	126.7(0.5)°	128.2(0.6)°
$\angle C_1=C_2-C_3$	124.3(0.6)°	123.4(0.5)°	128.9(0.7)°
$\angle C_2=C_1-H_1$	118.1(1.7)°	119.6(1.3)°	119.9(1.3)°
$\sum_i w_i \Delta_i^2$	0.471×10^5	0.320×10^5	0.321×10^5
ROT_1	50°	60°	120°
ROT_2	90°	180°	180°

The number in brackets are standard deviations as resulting from the least squares refinements.

Table 4. Comparison of bond distances in structurally similar molecules. The distances are given in Å as R_a values.

	C=C	$C_{sp^2}-C_{sp^2}$	$C_{sp^2}-C_{sp^3}$	$C_{sp^2}-H$	$C_{sp^3}-H$
cis-2-Methyl-1,3,5-hexatriene[b]	1.345	1.462	1.515	1.091	1.101
trans-2-Methyl-1,3,5-hexatriene [13]	1.348	1.456	1.510	1.094	1.104
cis-1,3,5-Hexatriene [5]	1.345[a]	1.462		1.090	
trans-1,3,5-Hexatriene [4]	1.347[a]	1.458		1.104	
1,3-Butadiene [12]	1.344	1.467			
trans-trans-3,4-Dimethyl-2,4-hexadiene [6]	1.349	1.479	1.521		1.119
cis-cis-3,4-Dimethyl-2,4-hexadiene [6]	1.350	1.473	1.521		1.117

[a] Average value.
[b] Present study.

The calculated mean vibrational amplitudes for the carbon carbon non-bonded distances of the three models are listed in Table 2. As might be expected the u values calculated for Model A are on average somewhat larger than those for the other models.

The results of the least squares refinements of the three models, when calculated mean vibrational amplitudes were applied, are presented in Table 3. In accordance with earlier obtained results Model A is clearly inferior to the other models. The squared error sums and standard deviations for the varied parameters were essentially the same for Model B and Model C. The results will be discussed below.

The outer, conformation-dependent part of the RD curves with calculated mean vibrational amplitudes and based on the parameters listed in Table 3, are shown in Fig. 4.

DISCUSSION

The bond distances obtained for *cis*-2-methyl-1,3,5-hexatriene are compared with structurally similar molecules in Table 4. The bond distances for this molecule are in especially good agreement with results obtained for bond distances in *cis* and *trans* isomers of 1,3,5-hexatriene,[4,5] both of which are found to have planar conformation. This lend support to the view that conjugation effects are of minor importance for the length of a single bond between two sp^2-hybridized carbon atoms.[10]

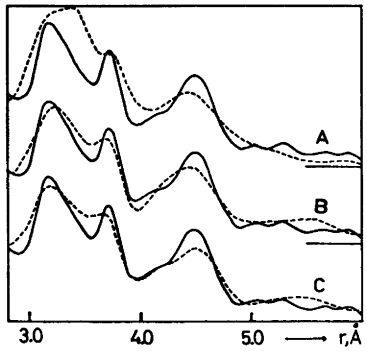

Fig. 4. cis-2-Methyl-1,3,5-hexatriene. The outer, conformation dependent part of the radial distribution functions for Model A, Model B, and Model C. The theoretical RD functions are based on the parameters listed in Table 3 and on calculated mean vibrational amplitudes.

The distribution of C=C–C bond angles may be seen from Table 1 (Model B). The fairly large values for $\angle C_2-C_3=C_4$ and $\angle C_3=C_4-C_5$ should be noted. These angles appear to be somewhat larger than corresponding angles in *cis*-2-butene and *cis*-1,3,5-hexatriene. In both the latter cases the relevant angles were about 126°. The differences can, however, not be claimed to be significant.

When the results obtained for Models B and C (Tables 1 and 3) are compared, one should notice the large difference in the $C_1=C_2-C_3$ bond angle which is found for both approaches. For Model B this bond angle is found to be about 123° while for Model C the angle is about 128°. C=C–C bond angles in comparable structural environments are usually observed to be in the 122° – 124° range. The result obtained for this bond angle in Model C is therefore unreasonable. If, however, one should try to fit a false molecular model with a C_2-C_3 dihedral angle of about 120° to data corresponding to a molecule where the dihedral angle actually is about 60°, one would expect to observe an increased $C_1=C_2-C_3$ angle to account for the difference in magnitude between the $C_1=C_2$ and C_2-C_7 bonds. Even if the observations made above cannot be considered as decisive evidence, they indicate that Model B is slightly preferred over Model C.

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