The Single and Double Bonds between sp^2-Hybridized Carbon Atoms, as Studied by the Gas Electron Diffraction Method

III. The Molecular Structure of 1,3,5-*cis*-Hexatriene

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The molecular structure of 1,3,5-*cis*-hexatriene has been investigated using the gas electron diffraction sector method. The experimentally determined molecular parameters and standard deviations as resulting from least squares analysis of the molecular intensity data are the following:

$r_g(1)(\text{C}-\text{H})$: 1.090 Å ±0.002 Å, $u(\text{C}-\text{H})$: 0.085 Å ±0.004 Å,
$r_g(1)(\text{C}-\text{C})$: 1.462 Å ±0.002 Å, $u(\text{C}-\text{C})$: 0.053 Å ±0.002 Å,
$r_g(1)(\text{C}_1=\text{C}_2)$: 1.336 Å ±0.003 Å, $u(\text{C}_1=\text{C}_2)$: 0.043 Å ±0.002 Å,
$r_g(1)(\text{C}_3=\text{C}_4)$: 1.362 Å ±0.005 Å, $u(\text{C}_3=\text{C}_4)$: 0.044 Å ±0.003 Å,
$\angle\text{C}_1\text{C}_2\text{C}_3$: 122.1°$\pm0.2$°, $\angle\text{C}_2\text{C}_3\text{C}_4$: 125.9°$\pm0.2$°

It is shown that the central and terminal carbon carbon double bonds in 1,3,5-*cis*-hexatriene are significantly different. The physical significance of an observed torsional angle of 10° around the central carbon carbon double bond is discussed.

The molecular structure of 1,3,5-*cis*-hexatriene has never been studied experimentally, and as the molecule presents several interesting structural aspects, it is a natural choice for inclusion in the present research series which is aimed at elucidating the factors determining the carbon carbon bond lengths in conjugated systems.

Fig. 1 illustrates a molecular model of 1,3,5-*cis*-hexatriene (in the following abbreviated to *cis*-hexatriene) which shows the numbering of the atoms. The molecule has a carbon skeleton with three conjugated CC double bonds. Very few reliable experimental structural data are available for systems of this type. The molecular structure of 1,3,5-*trans*-hexatriene has previously been reported in the present research series.[1]

Since the terminating double bonds are located *cis* to each other the molecule will be more sterically crowded than 1,3,5-*trans*-hexatriene. It is of interest to study how the strain in the molecule will influence the other molecular parameters.
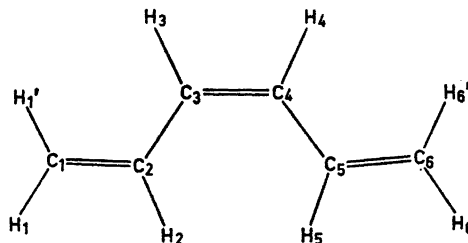
Fig. 1. 1,3,5-*cis*-Hexatriene. Molecular model which shows the numbering of the atoms.

EXPERIMENTAL PROCEDURE

The sample of *cis*-hexatriene used in the present investigation was kindly provided by professor W. Doering at Yale University, New Haven, Conn., U.S.A. The *cis*-hexatriene molecule was studied by the sector electron diffraction method, using a modified s^3 sector. The electron diffraction intensity data were obtained by the Oslo diffraction camera.[2]

Diffraction photographs were taken at a nozzle temperature of about 17°C, applying an accelerating potential of approximately 35 kV. Four sets of plates were used, taken with nozzle-to-photographic plate distances of approximately 48 cm and 19 cm, respectively. The corresponding s ranges are approximately $1.25-20.00$ Å^{-1} and $7.00-42.00$ Å^{-1}. The plates were photometered and corrected in the usual way.[3]

The corrected experimental intensities were modified by the function

$$\varphi(s) = 1/|f(s)_{\mathrm{C}}|^2$$

where $f(s)_{\mathrm{C}}$ is nonrelativistic partial waves atomic scattering factors for carbon, computed for 35 keV electrons.[4]

The four sets of intensities for each nozzle-to-plate distance were averaged before experimental backgrounds were subtracted. When the 48 cm and 19 cm molecular intensity curves were scaled, the overlap region revealed that there was a systematic discrepancy between the s-scale of the two intensity curves. This is demonstrated in Fig. 2, A. By careful examination of the experimental data it could be established that the
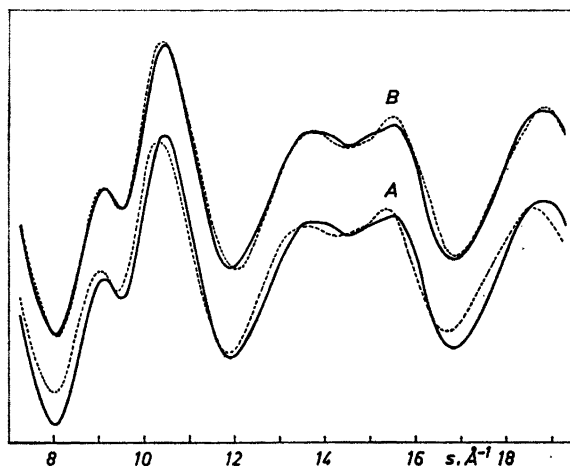

Fig. 2. 1,3,5-*cis*-Hexatriene. A: Original overlap region between 48 cm and 19 cm intensity data. B: Overlap region for corrected 19 cm nozzle-to-photographic plate distance.

error had to be in the s-scale of the 19 cm intensity curve. It would obviously be desirable to repeat the recording of the 19 cm scattering data, but there was no more left of the compound and a new sample of 1,3,5-cis-hexatriene could not be easily obtained.

As the correspondence between the four individual 19 cm intensity curves was very good, the error responsible for the shift in the s-scale was most likely to be in the electron wavelength or in the nozzle-to-plate distance. The 48 cm and 19 cm data were recorded on the same day under stable voltage conditions, and an error in the wavelength was therefore considered to be highly unprobable. An error in the electron wavelength, λ, would produce a linear scale factor in s ($s=4\pi\sin\theta/\lambda$), while the relationship between s and the nozzle-to-plate distance is more complicated.

By studying the positions of the extreme points in the overlap region it was found that a nozzle-to-plate distance of 19.175 cm instead of the recorded value of 19.386 cm would give maximum correspondence between 48 cm and 19 cm data in the overlap region. A new s-scale was calculated using the corrected nozzle-to-plate distance and the four photometer curves were read off and handled as before, yielding a corrected 19 cm molecular intensity function. The resulting overlap region is shown in Fig. 2, B. Because of the implied uncertainties in the 19 cm data, the overlap region was not averaged, but the 48 cm and 19 cm intensity data were matched at $s=17.75$ Å^{-1}.

STRUCTURE DETERMINATION

Since the intensity data for $s>17.75$ Å^{-1} in the present case are less reliable than those for smaller s-values, the bond distances can not be determined by using short-interval auto- and crosscorrelation functions.[5] It is, however, reasonable to assume that the bond distances in cis-hexatriene are similar to those in 1,3,5-trans-hexatriene, for which experimentally determined values are available.[1]

The experimental radial distribution function is shown in Fig. 5. The peak around 1.1 Å corresponds to the carbon hydrogen bond distances, while the neighbouring peak with maximum at 1.4 Å represents the carbon carbon bond distances in the molecule. Theoretical peaks based on the bond distance parameters for 1,3,5-trans-hexatriene show fairly good correspondence with the experimental cis-hexatriene radial distribution peaks, indicating that the assumption made above about the similarity of the bond distances in the cis- and trans-1,3,5-hexatriene molecules is justified. The 1,3,5-trans-hexatriene bond distance parameters were therefore used as zero'th order parameters in least squares refinements of the molecular intensity function.

The least squares program minimizes the weighted square error sum, $\sum_i w_i\Delta_1^2$, by varying the molecular parameters. Because of the uncertainty in the s-scale for the 19 cm intensity data the experimental data for large s values are less reliable than those for smaller s values. The large-angle scattering data therefore have to be given lower weight in the least squares refinements. The following weighting scheme was applied:

$$w(s) = \exp(-0.20(5.00-s)^2) \qquad \text{for } s\leq5.0$$
$$w(s) = 1.00 \qquad \text{for } 5.0<s\leq17.75$$
$$w(s) = \exp(-0.05(s-17.75)^2) \qquad \text{for } s>17.75$$

Theoretical intensities corresponding to several different molecular models were fitted to the experimental intensities. The most important structural parameters for the various models are presented in Table 1, which also gives the corresponding weighted square error sums.

Table 1. 1,3,5-*cis*-Hexatriene. Molecular parameters corresponding to least squares minima for various molecular models.

Parameter	I	IIa	IIb	Models III	IVa	IVb	IVc [a]	IVd [a]
C−H,Å	1.0904	1.0897	1.0892	1.0902	1.0901	1.0901	1.0901	1.0901
C−C,Å	1.4623	1.4602	1.4594	1.4618	1.4620	1.4620	1.4620	1.4620
$C_1=C_2$,Å	1.3375	1.3344	1.3329	1.3365	1.3362	1.3362	1.3362	1.3362
$C_2=C_3$,Å	1.3597	1.3656	1.3682	1.3616	1.3621	1.3621	1.3621	1.3621
$\angle \alpha_1^\circ$	121.94	122.51	122.73	122.14	122.13	122.14	122.13	122.14
$\angle \alpha_2^\circ$	126.16	125.88	125.70	125.98	125.94	125.93	125.94	125.93
$\angle \beta_1^\circ$	—	8.71	9.06	—	0	0	0	0
$\angle \beta_2^\circ$	—	—	—	9.88	10.13	9.86	10.18°	9.84
$\sum_i w_i \Delta_i^2 \times 10^{-4}$	.331	.328	.334	.319	.315	.317	.327	.327

Model I: Planar molecule.
Model II: The terminal vinyl groups were allowed to rotate around the CC single bonds. $\angle \beta_1$ is the angle of torsion. IIa: SIGN1 = +1(C_S-symmetry), IIb: SIGN1 = −1(C_2-symmetry).
Model III: The two halves of the molecule were allowed to be distorted around the central CC double bond. $\angle \beta_2$ is the angle of torsion.
Model IV: Distorsions around the CC single bonds ($\angle \beta_1$) and around the central CC double bond ($\angle \beta_2$). IVa: SIGN1 = +1, SIGN2 = +1, IVb: SIGN1 = +1, SIGN2 = −1, IVc: SIGN1 = −1, SIGN2 = +1, IVd: SIGN1 = −1, SIGN2 = −1. The significance of the parameters "SIGN1" and "SIGN2" is discussed in the text.

[a] These models did not lead to well-defined minima in the least squares refinement.

Model I has a planar conformation. In the other models distortions around the CC single bonds and/or the central CC double bond were allowed. In Model II the terminal vinyl groups were allowed to rotate around the carbon carbon single bonds. A parameter "SIGN1" in the least squares subprogram determines the directions of the distorsions. When "SIGN1" is equal to +1 or −1 the molecular symmetry is C_S and C_2, respectively.

Model III corresponds to a molecule with a twisted central CC double bond and with C_2 symmetry. The angle of torsion ($\angle \beta_2$) is determined as a function of the C_2C_5 distance.

The other four models that have been tested incorporate the intensions of both Model II and Model III, and torsional displacements were allowed around the CC single bonds and around the central CC double bond. The directions of the torsional displacements are governed by the parameters "SIGN1" and "SIGN2" in the least squares subprogram, where "SIGN1" has the same directional significance as discussed for Model II. The other parameter, "SIGN2", determines the direction of the angle of distortion around the central CC double bond relative to the distortions around the CC single bonds and may also assume the values +1 or −1. The two parameters may

obviously be combined in four different ways. For Model II best results were obtained when the terminal vinyl groups were displaced to the same side of the plane defined by carbon atoms 2, 3, 4, and 5 (SIGN1=+1). When SIGN1=+1 and SIGN2=+1 the torsional displacement around the central CC double bond reinforces the deviation from planarity caused by the torsional displacements around the CC single bonds. This situation corresponds to Model IVa, and the results of the least squares refinements for this model are presented in Table 1, column 6. When SIGN1=+1 and SIGN2=−1 the torsional displacement around the central CC double bond counteracts to some extent the deviations from planarity caused by the displacements around the CC single bonds. The results for this model are listed in Table 1, column 7. For the other two combinations of the parameters "SIGN1" and "SIGN2" the weighted square error sum did not converge towards well defined minima.

From Table 1 it can be seen that the bond distances and the carbon carbon bond angles in cis-hexatriene as determined by the least squares refinements are approximately independent of the choice of model. The lowest weighted square error sums were obtained when torsional displacement around the central CC double bond was allowed. Also for the 1,3,5-trans-hexatriene molecule a model with twisted central CC double bond gave best correspondence between experimental and theoretical data. But for that molecule shrinkage effects would influence the longer internuclear distances in approximately the same way as a twisted central CC double bond. It was therefore concluded

Table 2. 1,3,5-cis-Hexatriene. Experimentally determined interatomic distances, root-mean-square amplitudes of vibrations, bond angles and standard deviations as results of least squares refinements of the molecular intensity data.

Distance	$r_g(1)$, Å	$\Delta r_g(1)$, Å	u, Å	Δu, Å
$C-H$	1.090_1	0.002_0	0.085_4	0.003_6
$C-C$	1.462_0	0.002_0	0.052_5	0.002_1
$C_1=C_2$	1.336_2	0.003_1	0.043_0	0.002_0
$C_3=C_4$	1.362_1	0.004_6	0.044_2	0.002_9
C_1C_3	2.450		0.057_3	0.003_6
C_2C_4	2.516		0.059_3	0.003_6
C_1C_4	3.721		0.087_7	0.015_6
C_2C_5	3.085		0.066_6	0.006_0
C_1C_5	4.417		0.090_2	
C_1C_6	5.748		0.095	

$\angle C_1C_2C_3(\angle \alpha_1)$: $122.13° \pm 0.21°$
$\angle C_2C_3C_4(\angle \alpha_2)$: $125.94° \pm 0.23°$
$\angle C_2C_1H_1(\angle \gamma_1)$: $124.0°$ [a]
$\angle C_4C_3H_3(\angle \gamma_2)$: $118.0°$ [a]
$\angle C_1C_2H_2(\angle \gamma_3)$: $116.9°$ [a]
Angle of distortion around central CC double bond $\angle \beta_2 = 10.13° {}^{+0.87°}_{-1.08°}$

[a] No standard deviation values can be given for the CCH angles as they are strongly inter-related.

that the 1,3,5-*trans*-hexatriene molecule has a planar arrangement of bonds around the central CC double bond and that the shortening of the longer internuclear distances may be accounted for by shrinkage effects.

For the *cis*-hexatriene molecule, however, the situation is different, as a twisted central CC double bond will increase the lengths of the longer non-bonded internuclear distances. The significance of the observed angle of torsion around the central CC double bond will be discussed below.

The final molecular parameters for *cis*-hexatriene are presented in Table 2. The three different C=C—H angles, $\angle \gamma_1$, $\angle \gamma_2$, and $\angle \gamma_3$, could not be determined independently by the least squares refinements. It was only possible to determine an average C=C—H angle of 120.7°, and by "trial and error" the best fit between theoretical and experimental radial distribution functions was found for the CCH angle combination given in Table 2.

The angles of torsion, $\angle \beta_1$ and $\angle \beta_2$, were determined by the lengths of the C_1C_4 and C_2C_5 distances, respectively. The contributions from these distances give rise to the peak at 2.5 Å in the radial distribution function (see Fig. 5). When only torsional displacements around the CC single bonds were allowed, $\angle \beta_1$ was found to be about 9°. At first sight it might seem surprising that this angle is reduced to zero when the restriction of coplanar bonds around the central CC double bond is relaxed. This is, however, easily explained when the error limits of the torsional angles are considered. For Model IIb (see Table 1, column 4) the standard deviation for $\angle \beta_1$ is $^{+4.76}_{-8.83}$, which implies that $\angle \beta_1$ is not significantly different from zero.

From Table 2 it will be seen that the standard deviation for $\angle \beta_2$ $^{(+0.87)}_{-1.08}$ is an order of magnitude smaller than the standard deviation for $\angle \beta_1$. As a small change in $\angle \beta_2$ gives rise to a fairly large change in the C_2C_5 distance while the C_1C_4 distance is only slightly influenced by changes in $\angle \beta_1$, the differences in standard deviations for the two torsional angles are hardly surprising.

The 1,3,5-*cis*-hexatriene molecule is sterically strained because of over-crowdedness. If a planar conformation with normal valence angles is considered the nonbonded C_2C_5 and H_2H_5 distances will be considerably smaller than the sums of the van der Waals' radii. The repulsions between these pairs of atoms can be released by stretching the C_3C_4 double bond, by increasing the $C_2C_3C_4$ and $H_2C_2C_3$ bond angles or by a rotation around the C_3C_4 double bond.

It is true that the C_3C_4 double bond is found to be larger in *cis*-hexatriene than the CC double bond in ethylene.[6] The lengthening of the central CC double bond in *cis*-hexatriene is, however, certainly not a result of the non-bonded repulsions in the molecule, as the same bond length distribution is found in 1,3,5-*trans*-hexatriene where the discussed steric problem does not exist. It is also well known that it is energetically considerably less favourable to stretch or compress a bond than to bend it.

The $C_2C_3C_4$ angle ($\angle \alpha_2$) is found to be equal to about 126°. The increase in CC bond angle from 120° costs about 0.8 kcal/mole, but as the increase in angle strain is proportional to the square of the bending a further increase of $\angle \alpha_2$ leads to a relatively much larger energy increase. The observed $C_2C_3C_4$

Table 3. The interatomic distances that are most influenced by a twisted central CC double bond calculated for an angle of torsion equal to 0° and 10°.

Distance	Planar conformation	Distorted conformation	Δ	Van der Waals' distance
C_2C_5	3.0807	3.0874	0.0067	3.40
H_2H_5	2.2250	2.2566	0.0316	2.40
C_2H_5	2.8358	2.8493	0.0135	2.90
H_3H_4	2.3855	2.3913	0.0058	2.40

angle deformation lowers the van der Waals' compression energy but still the van der Waals' radii of the C_2C_5 and H_2H_5 atom pairs interpenetrate.

Another way of lowering the nonbonded repulsion energy is by distortion around the C_3C_4 double bond. Table 3 shows how the observed torsional angle of about 10° around the C_3C_4 double bond influences the lengths of the strained atom pairs.

The van der Waals' energy for the planar and distorted conformations of *cis*-hexatriene has been calculated.[7] Two parameters are necessary for each of the carbon and hydrogen atoms: one is the van der Waals' radius (r^*) and the second is an energy parameter (ε) which measures the depth of the van der Waals' minimum energy:

$$E_V/\varepsilon = -2.25\alpha^{-6} + 8.28 \times 10^{-5} \exp(-\alpha/0.0736)$$

where $\alpha = r/(r_1^* + r_2^*)$.

The calculations show that the van der Waals' energy is lowered by a distorsion around the C_3C_4 double bond. The quantitative results depend, however, on the choice of parameters, and as there is considerable uncertainty as to the magnitude of these,[8] no reliable values can be given.

The π bond of the distorted C_3C_4 double bond may be considered to be the result of lateral overlap between two *p*-orbitals whose axes are non-parallel. As an approximation the overlap integral and thereby also the π bond bonding energy may be assumed to be proportional to the square cosine of the angle between the *p* orbitals ($\angle \beta_2$). If the bond energy for a normal CC π bond is assumed to be 63.2 kcal/mole the bond energy is only reduced by 1.9 kcal/mole when $\angle \beta_2$ is equal to 10°. This is a fairly small amount of energy and it is therefore not unreasonable that the observed twisted central CC double bond may be a physical reality.

FINAL RESULTS

The final molecular parameters for 1,3,5-*cis*-hexatriene are presented in Table 2. It can be concluded that the central carbon carbon double bond is significantly longer than the terminal CC double bonds.
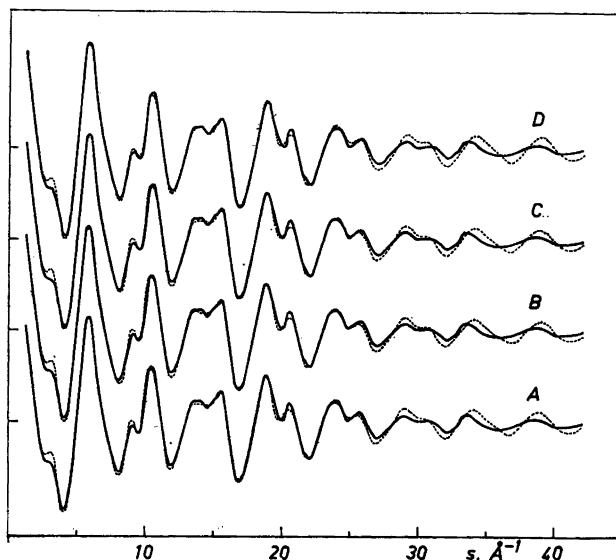
Fig. 3. 1,3,5-*cis*-Hexatriene. Comparison of the experimental (—) and four different theoretical (---) molecular intensity functions. A: Model I, B: Model IIa, C: Model III, D: Model IVa. The models are described in Table 1.

Since the terminal vinyl groups are located *cis* relative to the central CC double bond there is considerable steric strain in the molecule. In order to reduce the non-bonded interatomic van der Waals' repulsion energy the $C_2C_3C_4$ valence angle is opened up to 126°. It is also found that the van der Waals' repulsion energy is lowered as a result of a 10° torsional angle around the central CC double bond.

The theoretical molecular intensity functions for four different molecular models are shown in Fig. 3 along with the experimental intensity function. Fig. 4 shows the experimental and theoretical radial distribution functions (damping constant $k=0.0009$) for the same molecular models. The theoretical radial distribution function shown in Fig. 5 is based on the final molecular parameters for 1,3,5-*cis*-hexatriene as listed in Table 2, columns 2 and 4.

DISCUSSION OF THE RESULTS

Table 4 gives the bond distances and the carbon carbon bond angles as determined by electron diffraction studies of the *cis* and *trans* [1] isomers of 1,3,5-hexatriene. When uncertainties in the measurements are accounted for the bond lengths are found to be the same in the two molecules. The present study therefore confirms the results obtained for 1,3,5-*trans*-hexatriene that the central and terminal CC double bond lengths are significantly different. The terminal CC double bond in the 1,3,5-hexatrienes is the same as that in
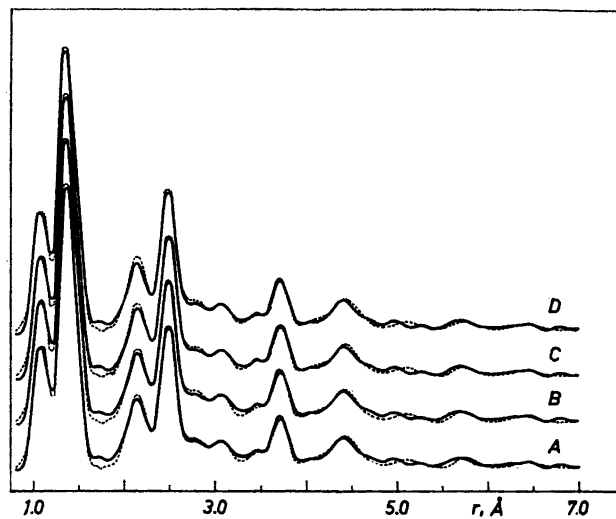
Fig. 4. 1,3,5-*cis*-Hexatriene. Comparison of the experimental (—) and four different theoretical (---) radial distribution functions (artificial damping constant $k=0.0009$). A: Model I, B: Model IIa, C: Model III, D: Model IVa. The models are described in Table 1.
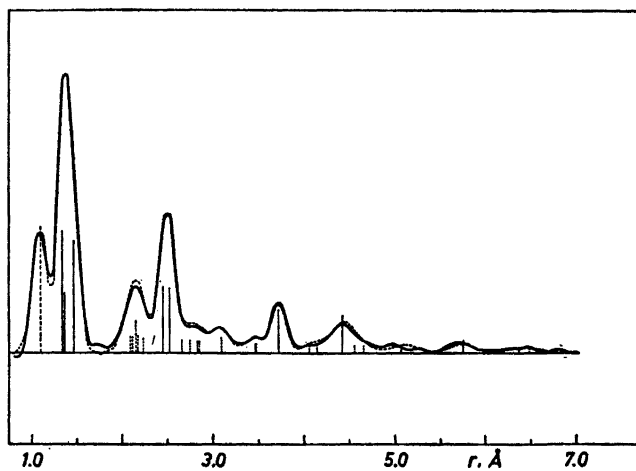

Fig. 5. 1,3,5-*cis*-Hexatriene. Experimental (—) and theoretical (---) radial distribution functions ($k=0.0009$). The solid and dotted bars represent relative contributions from CC and CH distances, respectively.

Table 4. Comparison of bond distance and bond angle parameters for *cis* and *trans* 1,3,5-hexatriene.

Parameter	*cis*	*trans*	Difference
C–H,Å	1.090	1.104	−0.014
C–C,Å	1.462	1.458	+0.004
$C_1=C_2$,Å	1.336	1.337	−0.001
$C_3=C_4$,Å	1.362	1.368	−0.006
$\angle C_1C_2C_3$,	122.1	121.7	+0.4
$\angle C_2C_3C_4$,	125.9	124.4	+1.5

ethylene,[6] while the CC single bond is a trifle smaller and the central CC double bond is slightly larger than the CC single and double bonds in 1,3-butadiene.[9]

Roos and Skancke[10] have reported a scheme for evaluating semi-empirical parameters in the Pariser-Parr-Pople approximation. The scheme was applied to a series of unsaturated hydrocarbons, including the *cis* and *trans* 1,3,5-hexatrienes. Their calculated values for the terminal and central CC double bonds were 1.347 Å and 1.354 Å, while the CC single bond distance was calculated to be 1.461 Å. The theoretical calculation therefore also gave different bond lengths for the two kinds of double bonds, although the calculated difference of 0.007 Å is smaller than the observed differences of 0.031 Å and 0.026 Å for the *trans* and *cis* isomers, respectively.

The $C_2C_3C_4$ angle is significantly larger in *cis*-hexatriene than in the 1,3,5-*trans*-hexatriene molecule. The increase in the valence angle is easily explained by the additional steric strain in the *cis* isomer.

The most uncertain point in the present study is the observation of the angle of torsion around the central carbon carbon double bond. Since the experimentally determined torsional angle is ten times as large as the standard deviation of the determination it is probably justified to claim that the observation has physical significance. The bond energy resulting from p orbital overlap will only be reduced by about 1.9 kcal/mole by a distortion of the reported order of magnitude, while the steric strain in the molecule will be reduced by a similar amount of energy.

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