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

II. The Molecular Structure of 1,3,5-*trans*-Hexatriene

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The molecular structure of 1,3,5-*trans*-hexatriene has been investigated using the gas electron diffraction sector method. The molecule is found to exist in an essentially planar conformation. The experimentally determined longer carbon carbon interatomic distances in the molecule are shorter than those calculated for a strictly planar molecule, but the shortenings can be reasonably ascribed as shrinkage effects caused by thermal vibrations in the molecule. Minor oscillations around the carbon-carbon bond distances can not be excluded. The experimentally determined molecular parameters and standard deviations as resulting from a least squares analysis of the molecular intensity data are the following:

$r_g(1)(C-H)$: 1.104 Å ± 0.003 Å, $u(C-H)$: 0.089 Å ± 0.003 Å,
$r_g(1)(C-C)$: 1.458 Å ± 0.002 Å, $u(C-C)$: 0.054 Å ± 0.002 Å,
$r_g(1)(C_1=C_2)$: 1.337 Å ± 0.002 Å, $u(C_1=C_2)$: 0.044 Å ± 0.001 Å,
$r_g(1)(C_3=C_4)$: 1.368 Å ± 0.004 Å, $u(C_3=C_4)$: 0.044 Å ± 0.003 Å,
$\angle C_1C_2C_3$: 121.7° ± 0.3°, $\angle C_2C_3C_4$: 124.4° ± 0.3°, $\angle C_2C_1H_1$: 120.5°,
$\angle C_4C_3H_3$: 115.0°, $\angle C_1C_2H_2$: 117.0°.

It is shown that the central and terminal carbon carbon double bonds in 1,3,5-*trans*-hexatriene are significantly different.

A precise determination of the molecular structure of 1,3,5-*trans*-hexatriene (in the following abbreviated to *trans*-hexatriene) has so far not been reported. The *trans*-hexatriene molecule poses several interesting structural problems and the molecule is a natural choice for inclusion in the present research series which is aimed at elucidating the factors determining the lengths of single and double bonds between sp^2-hybridized carbon atoms. Preliminary values for the structural parameters of *trans*-hexatriene have previously been published.[1]

Roos and Skancke [2] recently reported a scheme for evaluating semiempirical parameters in the Pariser-Parr-Pople approximation, which they applied to a series of unsaturated pure hydrocarbons, including the *trans*-hexatriene

molecule. Their calculated values for the terminal and central carbon carbon double bonds were 1.347 Å and 1.354 Å, while the carbon carbon single bond was calculated to be 1.461 Å. It is of special interest to note the difference between the lengths of the terminal and central carbon carbon double bonds. Even if this difference of 0.007 Å is so small that a similar difference obtained from an electron diffraction experiment probably would be smaller than the combined uncertainties of the two C=C double bonds, it is of interest to investigate whether the experimental data lend support to the results obtained bv Roos and Skancke or not.

EXPERIMENTAL PROCEDURE

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

Diffraction photographs were taken using nozzle-to-plate distances of about 48 cm and 19 cm. For both nozzle-to-plate distances the photometer curves of four single plates were studied. The photographic exposures were measured at intervals of $\Delta s = 0.25$ Å^{-1}, and the usual corrections were made for the effect of the photographic emulsion, for the use of plane photographic plates and for the accurate shape of the sector.[3] The intensities which extended from $s = 1.25$ Å^{-1} to $s = 45$ Å^{-1} were corrected for electron electron scattering and an experimental background function was subtracted in order to obtain the molecular intensity function ($sM(s)$ function).

The experimental backgrounds had to be corrected several times before the final experimental background was obtained. The corrections were based upon removal of any area, positive or negative, on the radial distribution (R.D.) curve beyond the contribution from the shortest bond distance, and also upon information deduced from theoretical molecular intensity functions corresponding to trial structures very close to the final experimentally determined structure. The experimental molecular intensity function is shown in Fig. 4.

DISTANCE AND BOND ANGLE PARAMETERS

The results for the molecular structure of *trans*-hexatriene reported in the present paper are based upon the same electron diffraction exposures as were the previously published preliminary structural parameters for this molecule.[1] The molecular structure presented below is, however, the result of a complete reexamination of the experimental material.

In the preliminary structure report, based upon the first treatment of the data, one could not distinguish between the central and terminal C=C double

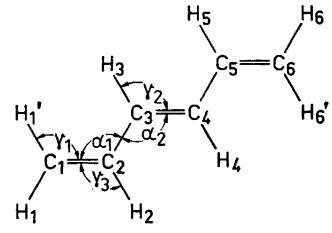

Fig. 1. 1,3,5-*trans*-Hexatriene. Molecular model which shows the numbering of the atoms.

bonds. The molecule was found to be essentially planar, but the out-of-plane motions led to shrinkage effects in the longer distances in the molecule. The observed internuclear distances were found to be best described by a molecular model where the terminal vinyl groups were rotated about 11.9° around the carbon-carbon single bonds, so that a projection of the molecule on a plane normal to the plane determined by the carbon atoms 2, 3, 4, and 5, assumes a boat comformation. The $C_1—C_6$ distance is the only distance in the molecule (except the longest carbon hydrogen distances, which give only minor contributions to the scattered intensities) that is dependent on whether the terminal vinyl groups rotate to the same side of the plane determined by the carbon atoms 2, 3, 4, and 5 or not. The $C_1—C_6$ distance was not resolved on the radial distribution curve in the previous handling of the experimental material. The conclusion concerning the conformation was therefore made as a result of a slightly smaller weighted square error sum for the "boat" form than for the "chair" form in the least squares refinement of the intensity data.

During the first treatment of the experimental scattering data it was a constant annoyance that the contribution to the radial distribution function from the $C_1—C_6$ distance was disguised by noise, as this longest carbon carbon distance is essential in determining the conformation of the molecule. It was therefore decided to reexamine the experimental scattering material, starting with the microphotometer traces of the photographic exposures. During this second handling of the data the utmost care was taken during all procedures in order to achieve the highest possible accuracy in the experimental molecular intensity function.

There is solid evidence that a higher accuracy in the experimental $sM(s)$ function really is obtained. The weighted square error sum obtained by least squares refinements of the first molecular intensity function is reduced to 40 % of its original value when the second $sM(s)$ function is used. The molecular model, the weighting function and the scattering region were of course the same in the two cases for the weighted square error sums to be comparable. It is also possible to identify the $C_1—C_6$ distance in the radial distribution function based on the new $sM(s)$ function.

The experimental radial distribution function is shown in Figs. 5 and 6. The carbon-carbon bond distances all contribute to the unresolved peak at about 1.47 Å. According to experience a number of theoretical R.D functions corresponding to different molecular models can be calculated, that will apparently fit the experimental C—C bond distance peak. The C—C bond distances can therefore not be precisely determined by studying the corresponding peak on the R.D. function, and this peak gives no clue as to whether the terminal and central C=C double bonds differ in lengths or not.

The experimental sharpened radial distribution (SRD) and autocorrelation power spectrum (APS) functions [4] are shown in Figs. 2 and 3. The peaks corresponding to the double and single bond distances are not very well resolved in these functions, especially not in the SRD function. The comparatively low resolution of the SRD and APS functions is a helpful observation. If the central and terminal double bonds were approximately the same, the difference between the single and double bond lengths would probably not be less than 0.12 Å, and two bond distances separated by this amount will usually

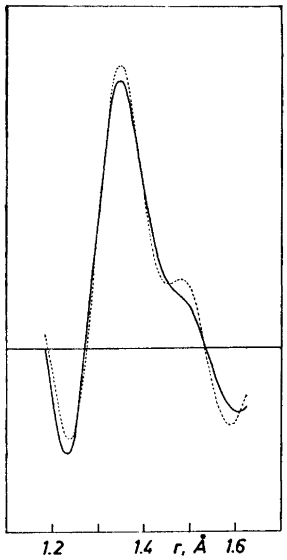

Fig. 2. 1,3,5-*trans*-Hexatriene. Experimental (———) and theoretical) (- - -) sharpened radial distribution function. Modification function:

$$\sqrt{2\lambda}\exp(-\lambda(s_{max}-s)),\ \lambda = 0.04.$$

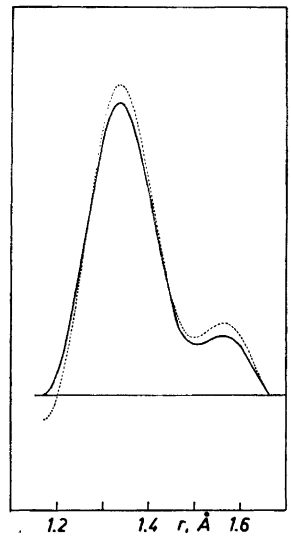

Fig. 3. 1,3,5-*trans*-Hexatriene. Experimental (———) and theoretical (- - -) autocorrelation power spectra. $\lambda = 0.04$.

be quite well resolved on the SRD and APS functions. At this stage it was therefore reasonable to assume that there is a difference in bond lengths between the terminal and central C=C double bonds.

The individual carbon-carbon bond distances and corresponding root-mean-square amplitudes of vibrations could not be precisely determined from the SRD and APS functions, but the C—C single bond length and the C=C terminal double bond length could be limited to the following intervals: 1.45 Å $<$ C—C $<$ 1.47 Å, 1.33 Å $<$ C_1=$C_2$$<$1.35 Å. A similar limitation of the interval for the central CC double bond could not be given with certainty, but trial models with values for this bond in the region 1.355—1.375 Å gave fairly good correspondence with the experimental SRD and APS functions. Based on studies of the SRD and APS functions the following bond distances were chosen for a zero'th order molecular model: C—H 1.100 Å, C_1=C_2 1.340 Å, C_3=C_4 1.365 Å, and C—C 1.460 Å.

In order to refine the bond distance parameters and also to determine the conformation of the carbon skeleton the theoretical molecular intensity function was adjusted to the experimental $sM(s)$ function by a least squares procedure. The least squares program makes use of a subprogram that 1) calculates the dependent distances in the molecule as functions of the independent ones and 2) calculates the matrix $C = (\partial r_{dependent}/\partial r_{independent})$. In order to perform the first task one has to make certain assumptions about the molecular model.

During the least squares refinements several molecular models were applied. The most important structural parameters for the various models are presented in Table 1, which also gives the corresponding weighted square error sums. The individual bond distances and the carbon-carbon bond angles are found to be approximately independent of the choice of model. The various models will be discussed under the section on conformational analysis below.

The distances corresponding to the three different C=C—H angles, γ_1, γ_2, and γ_3, could not be determined independently by the least squares refinement. It was first assumed that $\angle C_1C_2H_2 = \angle C_3C_2H_2$ and that $\angle C_2C_3H_3 = \angle C_4C_3H_3$. These two angles could be determined as the angles α_1 ($\angle C_1C_2C_3$) and α_2 ($\angle C_2C_3C_4$) were known quite accurately. The angle γ_1 ($\angle C_2C_1H_1$) was then varied in the least squares refinement. The weighted square error sum did diminish, but the resulting value for $\angle\gamma_1$ of 116.5° is probably too small according to similar angles in ethylene,[23] butadiene,[5] and other related molecules.

It soon became apparent that the assumptions about the CCH angles made in the foregoing section were not valid. Considerable efforts were made in order to determine the three γ angles. These efforts were based on combined studies of least squares refinements and comparison of the experimental R.D. function with theoretical R.D. functions for various molecular models.

It was established that the three different γ angles could not be treated independently. The arithmetic average of the γ angles was found to be equal to $\frac{1}{4}(2\gamma_1 + \gamma_2 + \gamma_3) = 118.25°$. If one of these angles is increased, one or both of the other two have to be reduced. The distribution of the angles that gave the smallest weighted square error sum, was the following: $\angle\gamma_1$ 120.5°, $\angle\gamma_2$ 115°, $\angle\gamma_3$ 117°.

CONFORMATIONAL ANALYSIS

The molecular structure of 1,3-butadiene was recently studied by the electron diffraction method.[5] The molecule was found to exist in a planar *trans* conformation, but an oscillation around the *trans* position with a root-mean-square amplitude of about 10° could not be excluded. The *trans*-hexatriene molecule can be considered as an extension of the 1,3-butadiene molecule with a vinyl group, and it is of great interest to establish whether the atoms in the relatively big *trans*-hexatriene molecule remain in a planar conformation or not.

It was not difficult to reveal that the observed longer carbon-carbon internuclear distances in *trans*-hexatriene were shorter than those calculated for a planar molecular model and based on experimentally determined bond distance and bond angle parameters.

It is well known that thermal vibrations of molecules in many cases lead to shrinkage effects.[6,7] This effect has been especially studied in linear-skeleton molecules like allene [8] and butatriene,[9] and experimental data show that the longer interatomic distances along the molecular axes are shorter than the sums of the individual bond lengths composing them. Shrinkage effects have also been observed in non-linear molecules,[10,11] and the phenomena have been treated theoretically for some specially simple non-linear cases.[12–15]

It could not be easily decided whether the *trans*-hexatriene molecule has a planar structure with shrinkage-influenced longer carbon-carbon distances or if the molecule permanently assumes non-planar conformations. In order to clarify this point, several theoretical molecular models were studied.

The theoretical molecular intensity functions calculated for the different molecular models, were refined by the least-squares method.[16-18] The most important molecular parameters corresponding to minimum values of the weighted square error sums are listed in Table 1.

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

	Models								
Parameter	I	IIa	IIb	IIb [1]	III	IVa	IVb	IVc [a]	IVd [a]
C–H, Å	1.1038	1.1038	1.1038	1.1038	1.1040	1.1038	1.1038	1.1038	1.1037
C–C, Å	1.4568	1.4576	1.4576	1.4576	1.4574	1.4576	1.4576	1.4575	1.4576
$C_1=C_2$, Å	1.3370	1.3373	1.3373	1.3373	1.3375	1.3373	1.3373	1.3373	1.3372
$C_2=C_3$, Å	1.3683	1.3678	1.3679	1.3679	1.3675	1.3679	1.3679	1.3678	1.3680
$\angle\alpha_1$, °	121.96	121.76	121.77	121.77	121.61	121.80	121.80	121.81	121.79
$\angle\alpha_2$, °	124.12	124.38	124.39	124.39	124.38	124.55	124.54	124.57	124.56
$\angle\beta_1$, °		5.91	11.08	11.09		18.00	17.67	(18.87)	(19.29)
$\angle\beta_2$, °					26.60	28.44	27.76	(29.59)	(30.40)
$\sum_i w_i \Delta_i^2 \times 10^{-4}$	1.32	1.30	1.29	1.30	1.23	1.22	1.23	1.47	1.35

Model I: Planar molecule.

Model II: The terminal vinyl groups were allowed to rotate around the C–C single bonds. IIa: The C_1-C_6 distance determines the angle of torsion, $\angle\beta_1$. SIGN = −1, IIb and IIb:[1] The C_1-C_4 distance determines $\angle\beta_1$. IIb: SIGN = −1, IIb:[1] SIGN = + 1. The significance of the parameter "SIGN" is discussed in the text.

Model III: The two halves of the molecule were allowed to be distorted around the central C=C double bond. $\angle\beta_2$ is the angle of torsion.

Model IV: Distortions around the C–C single bonds ($\angle\beta_1$) and around the central C=C double bond ($\angle\beta_2$), IVa: SIGN 1 = −1, SIGN 2 = + 1, IVb: SIGN 1 = −1, SIGN 2 = −1, IVc: SIGN 1 = +1, SIGN 2 = −1, IVd: SIGN 1 = + 1, SIGN 2 = + 1. The significance of the parameters "SIGN 1" and "SIGN 2" is discussed in the text.

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

Model I has a planar conformation. In this model the C–C single bonds and C=C terminal double bonds are found to be slightly shorter than for the other models. These reductions of the bond distances are clearly a consequence of the fact that all the carbon carbon distances are forced to fit a strictly planar model. The carbon-carbon bond angles in this model are also somewhat different from those determined for the other models, but according to the same reasoning one should not pay too much attention to this finding.

In all the other models torsional displacements from planarity were allowed. In Model II the terminal vinyl groups were allowed to rotate around the carbon-carbon single bonds. A parameter "SIGN" in the least squares subprogram

determined whether the vinyl groups were displaced to the same (SIGN = + 1) or opposite (SIGN = −1) side of the plane defined by the carbon atoms 2, 3, 4, and 5. The angle of torsion around the carbon-carbon single bond ($\angle\beta_1$) may be determined from the C_1—C_6 distance or from the C_1—C_4 distance. Column 3 in Table 1 corresponds to a model where the C_1—C_6 distance is chosen as a variable parameter (SIGN = −1), and in columns 4 and 5 the C_1—C_4 distance determines the angle of torsion for SIGN = −1 and SIGN = + 1. It will be seen that the angle of torsion is about twice as big when it is determined as a function of the C_1—C_4 distance. This discrepancy is, however, not important, as the lengths of both the C_1—C_6 and C_1—C_4 distances are only slightly influenced by torsional displacements of the reported order of magnitude.

The C_1—C_6 distance is the only distance of significant contribution to the $sM(s)$ function, that is dependent on whether the terminal vinyl groups are displaced to the same or to the opposite side of the plane determined by the carbon atoms 2, 3, 4, and 5. From Table 1, columns 4 and 5, it is seen that the latter situation (SIGN = −1) leads to a slightly lower weighted square error sum, and the angle of torsion for this model is found to be 11° with standard deviation $^{+4.40}_{-8.59}$.

Model III corresponds to a molecule with a twisted central C=C double bond. The angle of torsion ($\angle\beta_2$) is determined as a function of the C_2—C_5 distance, and the minimum weighted square error sum for this model corresponds to a molecular model where the angle between the planes determined by the two halves of the molecule is 26.6° (standard deviation: $^{+3.85}_{-4.47}$). This model leads to a more effective shortening of the longer carbon-carbon internuclear distances in the molecule, a fact that is reflected in the considerable lowering of the weighted square error sum. From a physical point of view, however, the model is not easily acceptable.

The other four models that have been tested incorporate in them the intensions of both Model II and Model III. In all these models torsional displacements are allowed around the C—C single bonds and around the central C=C double bond. The angle of torsions around the C—C single bonds ($\angle\beta_1$) and central C=C double bond ($\angle\beta_2$) were determined as functions of the C_1—C_4 and C_2—C_5 distances, respectively. The directions of the torsional displacements are governed by two parameters, "SIGN 1" and "SIGN 2", in the least squares subprogram. "SIGN 1" has the same significance as the parameter "SIGN" discussed for Model II. The other parameter, "SIGN 2", may also assume the values + 1 or −1. The two parameters "SIGN 1" and "SIGN 2" may obviously be combined in four different ways. When SIGN 1 = −1 and SIGN 2 = + 1 the torsional displacement around the central C=C double bond reinforce the deviation from planarity caused by the torsional displacements around the C—C single bonds and the molecule as a whole is deformed into a slowly twisted helix. This situation corresponds to Model IVa, and the results of the least squares refinements of this model is shown in Table 1, column 7.

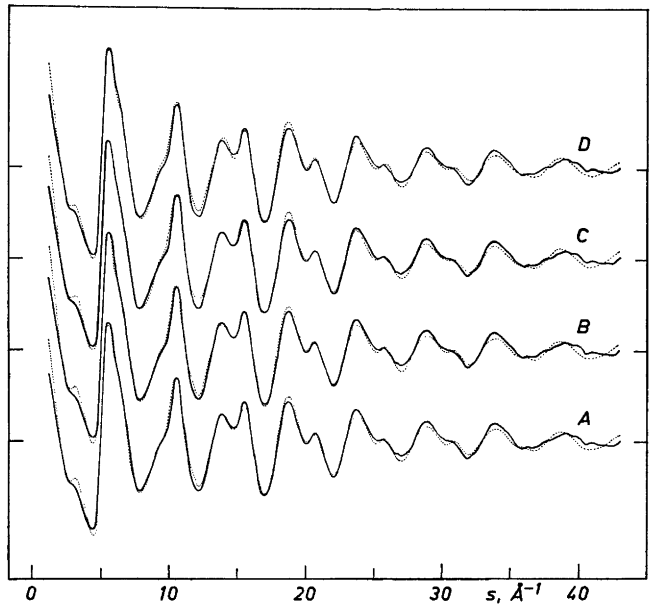

Fig. 4. 1,3,5-*trans*-Hexatriene. Comparison of the experimental (——) and four different theoretical (- - -) molecular intensity functions. A: Model I, B: Model IIb, SIGN = −1, C: Model III, D: Model IVa. The models are described in Table 1.

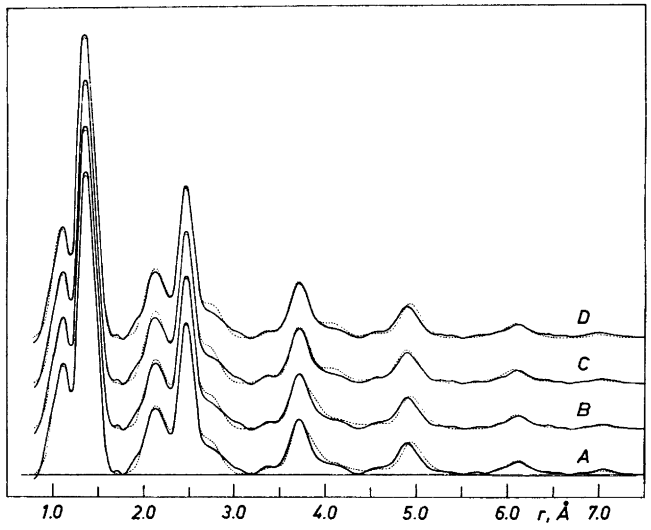

Fig. 5. 1,3,5-*trans*-Hexatriene. Comparison of the experimental (——) and four different theoretical (- - -) radial distribution functions (k = 0.0009). A: Model I, B: Model IIb, SIGN = −1, C: Model III, D: Model IVa. The models are described in Table 1.

When SIGN 1 = −1 and SIGN 2 = −1 the torsional distortion around the central C=C double bond counteracts to some extent the deviations from planarity caused by the displacements around the C—C single bonds. The results for this model are presented in Table 1, column 8. For the other two combinations of the parameters "SIGN 1" and "SIGN 2" the weighted square error sums did not converge toward well defined minima, but for completeness' sake these two models are also included in Table 1 (columns 9 and 10).

One can not uncritically conclude that the model that gives the lowest weighted square error sum in the least squares analysis gives the most true description of the actual molecule. The differences between the weighted square error sums for the various models are small, and one has to study in more detail the effects that are responsible for these differences.

The theoretical molecular intensity functions for Model I, Model IIb (SIGN = −1), Model III and Model IVa are shown in Fig. 4 along with the experimental $sM(s)$ function. Fig. 5 shows the theoretical radial distribution functions for the same models along with the experimental R.D.-function.

All the theoretical $sM(s)$ functions shown in Fig. 4 show minor deviations from the experimental $sM(s)$ function, and it is not feasible to decide which discrepancies are more serious than others. On the radial distribution functions the discrepancies can be connected with specific interatomic distances and they should therefore be more helpful in the conformation analysis.

From Fig. 5 it is seen that Model III is the only theoretical model that gives a good correspondence with the experimental peak around 4.9 Å. This peak represents the $C_1—C_5$ distance. This observation could therefore be taken as support for Model III, with an angle of torsion around the central C=C double bond of 26.6°. However, if this torsional displacement is responsible for the good fit between the theoretical and experimental $C_1—C_5$ distance peak, why does the $C_1—C_5$ distance peak for Model IVa fit the corresponding experimental peak so poorly, when $\angle\beta_2$ in this model (28.5°) is about the same as in Model III (26.6°)? The answer to this apparent inconsistency is found when the values for the carbon-carbon bond angles ($\angle\alpha_1$ and $\angle\alpha_2$) are considered. Both these angles are slightly larger in Model IVa than in Model III, and the increase in C—C bond angles results in an increase in the $C_1—C_5$ distance. The standard deviations for the carbon-carbon bond angles (see Table 2) are of the same order of magnitude as the differences between these angles in Model III and Model IVa. It is therefore not justified to conclude that Model III is better than the other models because it gives the best correspondence with the experimental $C_1—C_5$ distance.

Models III, IVa, and VIb give clearly lower weighted square error sums than the other models. In all these models the angle of torsion ($\angle\beta_2$) around the central C=C double bond is found to be approximately the same. $\angle\beta_2$ is determined as a function of the $C_2—C_5$ distance, and the standard deviation for the determination of this distance is found to be ± 0.0122 Å. The real error, including uncertainties in the bond distances, might be as large as 2.5 times the standard deviation (0.0305 Å). This means that while the $C_2—C_5$ distance in Model III is found to be 3.8158 Å it might be as large as 3.8463 Å (corresponding to $\angle\beta_2 = 15.8°$). A planar molecular model with the same bond distance and bond angle parameters as in Model III has a $C_2—C_5$ distance

equal to 3.8558 Å. The difference between this value and the maximum experimental value (0.0095 Å) is of the order of magnitude one might expect to observe because of shrinkage effects.

As a result of the conformational analysis it can be concluded that the *trans*-hexatriene molecule assumes an essentially planar conformation in the vapor phase. Minor oscillations around the carbon-carbon bond distances can not be excluded on the basis of the experimental material studied in the present investigation. The shortening of the longer carbon-carbon interatomic distances in the molecule compared to those calculated for a strictly planar model and based on the experimentally determined bond distance and bond angle parameters, can reasonably be explained as shrinkage effects.

FINAL RESULTS

The final molecular parameters for 1,3,5-*trans*-hexatriene are presented in Table 2. It can be concluded that the central C=C double bond is significantly longer than the terminal C=C double bonds. The longer carbon-

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

Distance	$r_g(1)$, Å	$\Delta r_g(1)$, Å	δ, Å	u, Å	Δu, Å
C—H	1.103_8	0.003_2		0.089_3	0.002_8
C—C	1.457_6	0.002_0		0.053_7	0.001_5
$C_1=C_2$	1.337_3	0.001_9		0.043_8	0.001_2
$C_3=C_4$	1.367_8	0.003_5		0.044_3	0.002_5
$C_1—C_3$	2.441	0.003_6		0.058_2	0.002_9
$C_2—C_4$	2.499	0.003_6		0.058_0	0.002_9
$C_1—C_4$	3.696	0.006_1	0.010	0.084_0	0.015_0
$C_2—C_5$	3.816	0.012_2	0.040	0.066_0	0.005_2
$C_1—C_5$	4.896		0.044	0.095_2	
$C_1—C_6$	6.080		0.045	0.092_5	
$\angle C_1C_2C_3$ ($\angle\alpha_1$):	121.7° ± 0.3°				
$\angle C_2C_3C_4$ ($\angle\alpha_2$):	124.4° ± 0.3°				
$\angle C_2C_1H_1$ ($\angle\gamma_1$):	120.5° [a]				
$\angle C_4C_3H_3$ ($\angle\gamma_2$):	115.0° [a]				
$\angle C_1C_2H_2$ ($\angle\gamma_3$):	117.0° [a]				

[a] No standard deviation values can be given for the CCH angles as they are not independently determined (see the text).

carbon interatomic distances in the molecule are found to be somewhat shorter than those calculated for a strictly planar molecule and based on the experimentally determined bond distance and bond angles parameters. These shortenings of the longer C—C distances can be reasonably ascribed to shrinkage effects caused by thermal vibrations in the molecule. Minor oscillations around the carbon-carbon bond distances can, however, not be excluded.

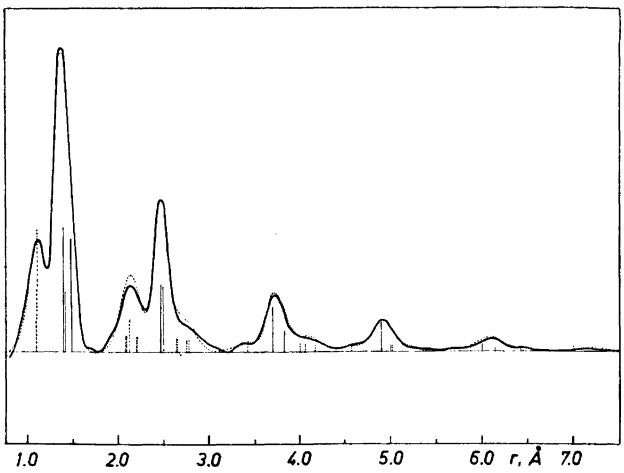

Fig. 6. 1,3,5-*trans*-Hexatriene. Experimental (——) and theoretical (- - -) radial distribution functions (k = 0.0009). The solid and dotted bars represent relative contributions from C—C and C—H distances, respectively.

The observed shrinkages are listed in Table 2, column 4. The theoretical molecular intensity functions for four different molecular models are shown in Fig. 4 along with the corresponding experimental function. Fig. 6 shows the experimental and theoretical radial distribution function (damping constant k = 0.0009). The theoretical R.D. function shown in Fig. 6 is based on the final molecular parameters for 1,3,5-*trans*-hexatriene as listed in Table 2, columns 2 and 5.

The standard deviations for the internuclear distance parameters, the root-mean-square amplitudes of vibrations and the carbon-carbon bond angles are also listed in Table 2. The standard deviation values do of course not include uncertainties because of possible wavelengths error and other factors that will influence the scale of the molecule. For the control of the absolute distance values of our electron diffraction studies a series of analysis has been made on the study of gaseous CO_2. This control analysis indicates that the data from the last few years may be approximately 0.2 % too large.

DISCUSSION OF THE RESULTS

Table 3 lists single and double bond distances between sp^2 hybridized carbon atoms for various molecules. Most of the data are taken from recent electron diffraction structure studies.

It is seen that the terminal C=C double bond in 1,3,5-*trans*-hexatriene is the same as that in ethylene. The values for the C—C single bond is smaller and for the central C=C double bond is larger than the values for the C—C single and double bonds in 1,3-butadiene. These observations correspond to an increased π bond order for the C—C single bond and to a decreased π

Table 3. Reported single and double bonds between sp^2 hybridized carbon atoms. The electron diffraction data are all given as $r_g(1)$ values.

Molecule	C=C, Å		C—C, Å	Method	Reference
1,3,5-*trans*-Hexatriene	1.337	(terminal)	1.457	E.D.	Present study
	1.368	(central)			
	1.347	(terminal)	1.461	T.C.	2
	1.354	(central)			
1,3,5-*cis*-Hexatriene	1.336	(terminal)	1.462	E.D.	20
	1.362	(central)			
1,3-Butadiene	1.344		1.467	E.D.	5
1,3,5,7-Cyclooctatetraene	1.340		1.476	E.D.	5
1,3,5-Cycloheptatriene	1.356		1.446	E.D.	21
Acrolein	1.345		1.470	M.W.	22
Ethylene [a]	1.338			E.D.	23

E.D.: electron diffraction
T.C.: theoretical calculations
M.W.: microwave

[a] corrected to $r_g(1)$ value.

bond order for the central C=C double bond. A simple inspection of the possible charged resonance structures for 1,3,5-*trans*-hexatriene reveals that the $C_3—C_4$ bond should actually have a lower π bond order than the $C_1—C_2$ bond in this molecule and also than the C=C double bond in 1,3-butadiene.

The present investigation shows that the central C=C double bond in *trans*-hexatriene is significantly longer than the C=C double bond in ethylene and 1,3-butadiene. It is more dubious whether the observed difference between the C—C single bonds in 1,3-butadiene and 1,3,5-*trans*-hexatriene can be claimed to be significant. This difference of 0.010 Å corresponds approximately to the combined error limits for the two bond distance determinations. The observed shortening of the C—C single bond in the *trans*-hexatriene molecule is, however, worth noticing, and the simultaneously observed increase in the central C=C double bond length lends support to the idea that the shortening might be a real effect.

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