ACTA CHEMICA SCANDINAVICA 24 (1970) 2295–2313

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

VII. The Molecular Structures of three Isomeric 3,4-Dimethyl-2,4-hexadienes (*cis,cis*-, *cis,trans*-, and *trans,trans*-)

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The molecular structures of *cis,cis*-, *cis-trans*-, and *trans,trans*-3,4-dimethyl-2,4-hexadiene have been investigated using the gas electron diffraction sector method. The *cis,cis* isomer was found to have an essentially planar carbon skeleton, while the two other isomers were in approximately *gauche* conformations at the central CC single bond. The experimentally determined bond lengths and estimated error limits for the *cis,cis*, *trans,trans*, and *cis,trans* isomers of 3,4-dimethyl-2,4-hexadiene were the following:

$r(C_1-C_2)$:	1.521 ± 0.005 Å,	1.521 ± 0.006 Å,	1.528 ± 0.010 Å,
$r(C_2=C_3)$:	1.350 ± 0.005 Å,	1.349 ± 0.006 Å,	1.359 ± 0.010 Å,
$r(C_3-C_4)$:	1.473 ± 0.009 Å,	1.479 ± 0.010 Å,	1.460 ± 0.020 Å,
$r(C_1-H_9)$:	1.117 ± 0.007 Å,	1.119 ± 0.008 Å,	1.116 ± 0.010 Å.

The bond distances are given as $r_g(1)$ values.

The molecular structure of many acyclic molecules with conjugated double bonds are well known, for example butadiene,[1] 2,3-dimethyl-butadiene,[2] acrolein,[3,4] glyoxal,[3] *cis*- and *trans*-hexatriene.[5,6] The double bonds are nearly always found to be in a strictly planar *trans* conformation, but if a planar arrangement of conjugated double bonds is sterically hindered it will be of great interest to know which conformation is energetically the most favorable. In *trans,trans*-3,4-dimethyl-2,4-hexadiene repulsions between two pair of methyl groups will seriously unstabilize a heavy atom coplanar structure. The same kind of steric hindrance is encountered in *cis,trans*-3,4-dimethyl-2,4-hexadiene, and the third isomer, *cis,cis*-3,4-dimethyl-2,4-hexadiene also poses interesting structural problems.

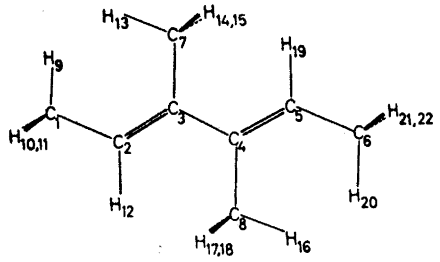

Fig. 1. cis,cis-3,4-Dimethyl-2,4-hexadiene. Molecular model which shows the numbering of the atoms.

EXPERIMENTAL PROCEDURE

The samples of the three isomeric 3,4-dimethyl-2,4-hexadienes used in the present investigation were kindly provided by Professor W. Doering, Yale University, New Haven, Conn., U.S.A. The three molecules were 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.[7]

Diffraction photographs were taken at nozzle temperatures varying from 35 to 38°C for the various exposures, with an accelerating potential of approximately 35 kV. Photographs were taken at two nozzle-to-plate distances, *i.e.* approximately 48 cm and 19 cm. For each molecule a minimum of four plates were used for each nozzle-to-plate distance. The plates were photometered and corrected in the usual way,[8] and for each molecule the average of the measured intensities for one nozzle-to-plate distance was applied in the structure analysis.

The corrected experimental intensities were modified by the function

$$\phi(s)=1/|f(s)_C|^2$$

where $f(s)_C$ are nonrelativistic partial waves atomic scattering factors for carbon, computed for 35 keV electrons.[9]

The experimental backgrounds had to be corrected several times before final experimental backgrounds were obtained. The corrections were based upon removal of any area on the radial distribution (RD) curves beyond the contributions from the shortest bond distances and, at later stages in the study, upon information deduced from theoretical molecular intensity functions.

By combining the data from the two nozzle-to-plate distances, experimental intensity ($sM(s)$) functions were obtained for the three isomeric molecules in the s region from 1.25 Å^{-1} to about 45.0 Å^{-1}. The quality of the scattering data for the *cis,cis* isomer was very good over the entire s region. For the other two isomers the experimental intensities based on the 48 cm exposures were of high quality, while the 19 cm experimental data were considerably less satisfactory. This is demonstrated in Figs. 3, 8, and 12, which show the experimental $sM(s)$ functions for the *cis,cis*, *trans,trans*, and *cis,trans* isomers of 3,4-dimethyl-2,4-hexadiene, respectively.

STRUCTURE ANALYSIS

cis,cis-*3,4-Dimethyl-2,4-hexadiene.* Preliminary values for the bond distances were obtained from auto- and crosscorrelation power spectra.[10] From the position of the peak at 2.53 Å on the experimental RD function it can be concluded that the average CC bond angle is somewhat larger than 120°. As the average CC bond angle around carbon atom No. 3 inevitably is equal to 120°, the $C_1C_2C_3$ bond angle must be larger than 120°.

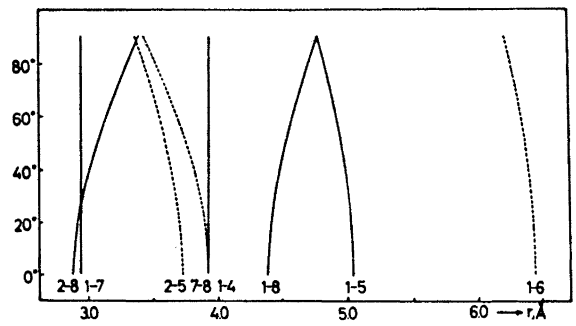

Fig. 2. cis,cis-3,4-Dimethyl-2,4-hexadiene. The CC nonbonded distances shown as functions of the torsion angle ($\angle\alpha_1$) around the C_3-C_4 bond. $\angle\alpha_1$ is here defined as zero when the two CC double bonds are in a planar *trans* conformation. The solid and dotted lines correspond to distances with multiplicities equal to two and one, respectively.

Although there is no particular steric hindrance for attaining a planar *trans* arrangement of the two conjugated CC double bonds in *cis,cis*-3,4-dimethyl-2,4-hexadiene, the possibility of a twist around the C_3-C_4 single bond was studied by means of a diagram showing the CC nonbonded distances as functions of a C_3-C_4 torsion angle. The diagram is shown in Fig. 2 and is constructed from the preliminary values for the bond distances and assumed values for the CC bond angles. The solid and dotted curves represent distances with multiplicities equal to two and one, respectively.

By comparing the diagram in Fig. 2 and the experimental RD function it could be concluded that there is no serious twist around the C_3-C_4 bond. The conclusion is based upon three observations: 1) the quite sharp peak at 2.97 Å, 2) the small area around 3.5 Å and 3) the two well separated and quite sharp peaks at 4.43 Å and 4.96 Å on the RD function.

The steric problem in *cis,cis*-3,4-dimethyl-2,4-hexadiene is connected with the methyl groups in *cis* configuration at each of the CC double bonds. When

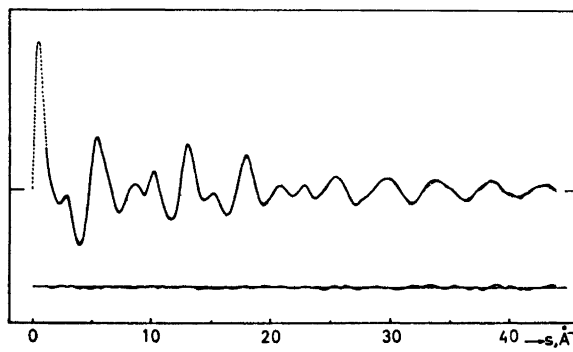

Fig. 3. cis,cis-3,4-Dimethyl-2,4-hexadiene. Experimental (———) and theoretical (- - -) $sM(s)$ functions and the deviations between the two.

only the torsional energy is considered the atoms H_9 and H_{13} would both prefer to be eclipsed with the $C_2=C_3$ bond. Even if the angles $C_1C_2C_3$ and $C_2C_3C_4$ are increased somewhat from 120°, the H_9H_{13} distance will be considerably smaller than the sum of the two van der Waals radii. The H_9H_{13} repulsion may be reduced in several ways: 1) by increasing the C=C–C angles, 2) by twisting the $C_2=C_3$ double bond, 3) by changed torsion angles at the C_1-C_2 and C_3-C_7 single bonds, and 4) by distortion of the methyl groups for example in such a way that their axes do not coincide with the methyl C–C bonds. The three first possibilities will obviously be more effective than the latter in reducing the H_9H_{13} repulsion.

After preliminary studies as described above and further study of the experimental RD function, the molecular structure was refined by the least squares method applied to the molecular intensity function.[11] In spite of the large number of atoms in *cis,cis*-3,4-dimethyl-2,4-hexadiene, only fourteen parameters are necessary to define the geometry (assuming identical structures for the C_1 and C_7 methyl groups), as the two halves of the molecule are identical. The independent bond lengths and bond angles were:

Bond lengths: C_1-C_2, $C_2=C_3$, C_3-C_4, C_1-H_9, C_2-H_{12}

Bond angles: $\angle C_1C_2C_3$, $\angle C_2C_3C_4$, $\angle C_2C_3C_7$, $\angle C-C-H$, $\angle C=C-H$

Three torsion parameters were necessary: $\angle\alpha_1$ which is the torsion angle around the C_3-C_4 bond,* $\angle\alpha_2$ which represents possible twists around the CC double bonds and $\angle\alpha_3$ which is the torsion angle of the C_1-C_2 bond ($\angle\alpha_3=0$ when H_9 is eclipsed with C_3). The fourteenth parameter allows the axes of the individual methyl groups to be tilted away from the direction of the adjoining CC single bond.

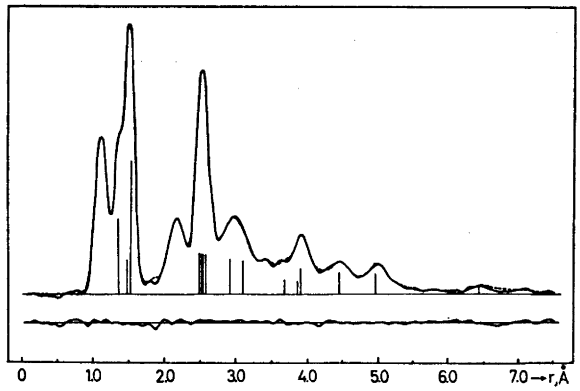

Fig. 4. cis,cis-3,4-Dimethyl-2,4-hexadiene. Experimental (———) and theoretical (- - -) radial distribution functions ($k=0.0009$) and the deviations between the two. The bars represent relative contributions from the CC interatomic distances.

* $\angle\alpha_1$ is here defined as zero when the two CC double bonds are in a planar *trans* conformation, even though this definition is not in agreement with the IUPAC nomenclature.[12]

At the end of the structural analysis of the *cis,cis* isomer it was possible to vary all geometrical parameters, except the C_2-H_{12} distance, simultaneously in the least squares refinement program. The difference in bond lengths between C_1-H_9 and C_2-H_{12} (ΔCH) was determined by a combined trial and error and least squares method. In several simultaneous least squares runs all the input data were identical except ΔCH which had a fixed, but slightly different value in each run. The standard deviations of the varied parameters and the weighted square error sums all had their minimum value when ΔCH was equal to 0.030 Å. It was not possible to detect any signs of tilts of the methyl groups. In order to reduce the size and complexity of the computer program the corresponding parameter was therefore omitted.

Table 1. *cis,cis*-3,4-Dimethyl-2,4-hexadiene. Experimentally determined molecular parameters and standard deviation values as results of least squares refinements of the molecular intensity data. The numbers in brackets are the multiplicities of the individual distances.

Distance	$r_g(1)$, Å	$\sigma(r_g(1))$, Å	u, Å	$\sigma(u)$, Å
$C_1-C_2(4)$	1.5205	0.0006	0.0490	0.0008
$C_2=C_3(2)$	1.3502	0.0007	0.0408	0.0014
$C_3-C_4(1)$	1.4732	0.0017	0.0458	0.0052
$C_1-H_9(12)$	1.1165	0.0009	0.0789	0.0010
$C_2-H_{12}(2)$	1.0865		0.0770[a]	

Angle	Degrees	σ
$\angle C_1C_2C_3$	126.61	0.27
$\angle C_2C_3C_4$	122.60	0.24
$\angle C_2C_3C_7$	122.27	0.25
$\angle C-C-H$	109.64	0.25
$\angle C=C-H$	119.05	0.77
$\angle\alpha_1$[b]	26.63	1.21
$\angle\alpha_2$[c]	16.37	1.31
$\angle\alpha_3$[d]	33.29	0.94

[a] Assumed value.
[b] $\angle\alpha_1$ is the torsion angle around the C_3-C_4 bond.
[c] $\angle\alpha_2$ is the deviation from planarity of the CC double bonds.
[d] $\angle\alpha_3$ is the torsion angle of the methyl groups.

The final geometrical parameters for *cis,cis*-3,4-dimethyl-2,4-hexadiene are presented in Table 1, column 2 with the corresponding standard deviation values listed in column 3. The observed mean vibrational amplitudes (u values) for the bond distances with their standard deviation values are given in the same table, columns 4 and 5.

In the present case it was possible to refine all u values for the CC non-bonded distances simultaneously. It was, however, necessary to assume that all CC distances over one bond angle have the same mean amplitude of vibra-

Table 2. cis,cis-3,4-Dimethyl-2,4-hexadiene. The CC nonbonded internuclear distances, mean amplitudes of vibrations and corresponding standard deviations as determined by least squares refinements of the molecular intensity data.

Distance	Multiplicity	$r_g(1)$, Å	u, Å	$\sigma(u)$, Å
C_2C_4	2	2.4772	0.0679[a]	0.0027
C_2C_7	2	2.5152	0.0679[a]	
C_1C_3	2	2.5655	0.0679[a]	
C_3C_8	2	2.5266	0.0679[a]	
C_3C_8	2	2.9138	0.0914	0.0044
C_1C_7	2	3.0898	0.0964	0.0050
C_2C_5	1	3.6707	0.0740	0.0069
C_7C_8	1	3.8494	0.1443	0.0211
C_1C_4	2	3.9040	0.0699	0.0035
C_1C_8	2	4.4268	0.1048	0.0064
C_1C_5	2	4.9643	0.1105	0.0077
C_1C_6	1	6.4294	0.1123	0.0205

[a] All u-values for the various CC distances over one bond angle were assumed to be equal.

Table 3. cis,cis-3,4-Dimethyl-2,4-hexadiene. The CH nonbonded internuclear distances as determined by least squares refinements of the molecular intensity data. (r and u values in Å).

Dist.	n	$r_g(1)$	u	Dist.	n	$r_g(1)$	u
C_1H_{12}	2	2.2030	0.1038[a]	C_3H_9	2	2.7691	0.1200
C_1H_{13}	2	2.8353	0.1300	C_3H_{10}	2	3.0729	0.1200
C_1H_{14}	2	3.3268	0.1300	C_3H_{11}	2	3.4073	0.1200
C_1H_{15}	2	4.1448	0.1300	C_3H_{12}	2	2.1042	0.1038[a]
C_1H_{16}	2	5.2970	0.1300	C_3H_{16}	2	3.4037	0.1200
C_1H_{17}	2	3.8242	0.1300	C_3H_{17}	2	2.5952	0.1200
C_1H_{18}	2	4.9780	0.1300	C_3H_{18}	2	3.0662	0.1200
C_1H_{19}	2	5.0061	0.1300	C_3H_{19}	2	2.7049	0.1200
C_1H_{20}	2	6.6408	0.1200	C_3H_{20}	2	4.1382	0.1200
C_1H_{21}	2	6.8216	0.1200	C_3H_{21}	2	4.4629	0.1200
C_1H_{22}	2	7.0945	0.1300	C_3H_{22}	2	4.5687	0.1200
C_2H_9	12	2.1676	0.1038[a]	C_7H_9	2	2.8693	0.1300
C_2H_{13}	2	2.6921	0.1200	C_7H_{10}	2	3.3317	0.1300
C_2H_{14}	2	3.0193	0.1200	C_7H_{11}	2	4.1404	0.1300
C_2H_{15}	2	3.3762	0.1200	C_7H_{12}	2	3.4828	0.1200
C_2H_{16}	2	3.8159	0.1200	C_7H_{16}	2	4.6778	0.1200
C_2H_{17}	2	2.4190	0.1200	C_7H_{17}	2	4.0837	0.1200
C_2H_{18}	2	3.5001	0.1200	C_7H_{18}	2	4.1940	0.1200
C_2H_{19}	2	3.9471	0.1300	C_7H_{19}	2	2.6597	0.1300
C_2H_{20}	2	5.1873	0.1300	C_7H_{20}	2	4.6737	0.1300
C_2H_{21}	2	5.4414	0.1300	C_7H_{21}	2	5.0796	0.1300
C_2H_{22}	2	5.8101	0.1200	C_7H_{22}	2	4.6521	0.1300

[a] Experimentally determined u value when all CH nonbonded distances over one bond angle were assumed to have the same u value. Standard deviation: 0.0030 Å. All the other mean vibrational amplitudes are assumed values.

tion. The results are listed in Table 2, column 4, with the standard deviation values in column 5. The determined u values appear to be reasonable. The CH nonbonded distances for *cis,cis*-3,4-dimethyl-2,4-hexadiene are listed in Table 3 along with the u values that were applied in the analysis.

Table 4. cis,cis-3,4-Dimethyl-2,4-hexadiene. Results from least squares refinements when one additional parameter is varied for each run. The numbers in brackets are the standard deviations multiplied by 10^3.

Parameter	Start value	I	II	III	IV	V
C_1-C_2	1.5222 Å	1.5211(.1010)	1.5212(.0991)	1.5213(.0995)	1.5216(.0960)	1.5210(.0772)
$C_2=C_3$	1.3520 Å	1.3509(.1400)	1.3503(.1406)	1.3503(.1398)	1.3502(.1359)	1.3508(.1142)
C_3-C_4	1.4700 Å	1.4714(.2880)	1.4711(.2890)	1.4709(.2845)	1.4703(.2892)	1.4721(.2453)
C_1-H_9	1.1170 Å	1.1165(.1981)	1.1162(.1971)	1.1162(.1971)	1.1166(.1916)	1.1162(.1543)
$\angle C_1C_2C_3$	126.0°	125.89(34.70)	126.03(34.87)	126.15(33.90)	126.25(34.12)	126.24(30.08)
$\angle C_2C_3C_4$	122.8°			*122.96*(36.15)	123.08(35.64)	123.13(31.34)
$\angle C_2C_3C_7$	122.8°				*121.73*(37.18)	122.36(30.92)
$\angle C-C-H$	110.0°	110.21(35.62)	110.29(36.15)	110.14(36.08)	110.03(35.10)	109.78(29.50)
$\angle C=C-H$	120.0°					
$\angle\alpha_1$[a]	20.0°	29.13(305)	29.87(301)	30.12(290)	28.42(283)	26.16(203)
$\angle\alpha_2$[a]	12.0°		*5.47*(437)	22.43(409)	17.49(360)	16.45(268)
$\angle\alpha_3$[a]	0.0°					*31.22*(232)
$\sum_i w_i \Delta_i^2 \times 10^{-4}$		1.13	1.12	1.11	1.05	0.687

[a] For explanation of the torsion angles, see footnote in Table 1.

The bond distance and bond angle parameters listed in Table 1 for the *cis,cis* isomer appear to be determined with fairly high precision and will be discussed more closely when the three isomeric 3,4-dimethyl-2,4-hexadienes

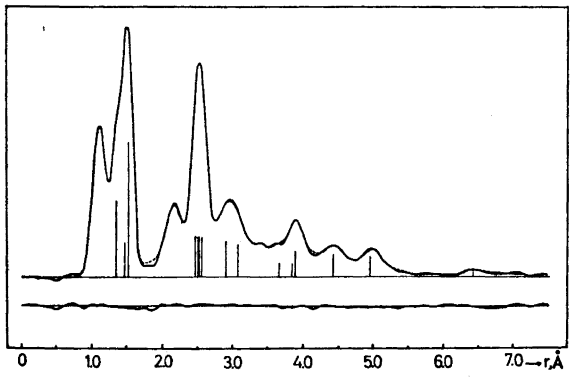

Fig. 5. cis,cis-3,4-Dimethyl-2,4-hexadiene. Experimental (———) and theoretical (- - -) radial distribution functions ($k=0.0015$) and the deviations between the two. The bars represent relative contributions from the CC interatomic distances.

are compared at the end of this paper. The three torsion angle parameters will be commented in the following.

The C_1C_7 distance increases rapidly with an increase in $\angle\alpha_2$ from 0°. The determined value for this parameter is so large that it is probably justified to claim that there is significant deviation from planarity of the CC double bonds.

$\angle\alpha_3$ is the torsion angle of the methyl groups. In order to support the least squares result for $\angle\alpha_3$ Table 4 is included. The table shows preliminary results from least squares refinements when one additional parameter is varied for each run. The initial value for $\angle\alpha_3$ is zero degrees and when $\angle\alpha_3$ is varied in run V it assumes a value close to the final result for this parameter. The important thing to notice is, however, the sharp decline in the weighted square error sum and in all the standard deviation values. The distortions of the methyl groups are coupled so that they increase the H_9H_{13} distance and the same is of course true about the small deviation from planarity of the $C_2=C_3$ double bond.

Table 5. cis,cis-3,4-Dimethyl-2,4-hexadiene. The CC distances that change with rotation around the C_3-C_4 bond length listed for a planar molecular model and with a C_3-C_4 torsion angle of 24.5°. (Internuclear distances in Å units.)

Distance	Planar model	24.5° rotation around C_3-C_4	Difference
C_2C_8	2.8551	2.9044	+0.0493
C_2C_5	3.7053	3.6733	−0.0320
C_7C_8	3.9023	3.8584	−0.0439
C_1C_8	4.3372	4.3720	+0.0348
C_1C_5	5.0300	5.0047	−0.0253
C_1C_6	6.4417	6.4205	−0.0212

The torsion angle around the C_3-C_4 bond is determined to 26.63°. This angle has probably no physical significance, as shrinkage effects[13] would influence the experimental data in much the same way as a torsion angle of the reported magnitude. The change in the CC internuclear distances with a small C_3-C_4 torsion angle is illustrated in Table 5.

trans,trans-*3,4-Dimethyl-2,4-hexadiene*. The experimental molecular intensity data for $s>35$ Å^{-1} are of poor quality for the *trans,trans* isomer. Instead of using correlation spectra for obtaining preliminary values for the bond distances, the bond parameters determined for *cis,cis*-3,4-dimethyl-2,4-hexadiene were adopted as initial values. The same method of analysis as for the *cis,cis* isomer was followed in this case too. Fig. 6 shows the distribution of the CC nonbonded distances as functions of the C_3-C_4 torsion angle. Comparison of the distance distribution diagram in Fig. 6 and the experimental RD functions in Figs. 9 and 10 reveals that there is a very large C_3-C_4 torsion angle in the molecule. The conclusion is primarily based upon the observation that there can be no CC interatomic distances larger than 4.5 Å contribut-

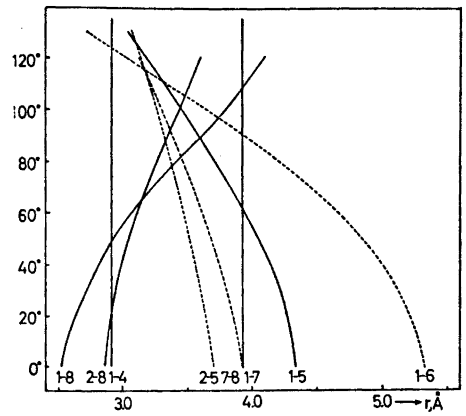

Fig. 6. *trans,trans*-3,4-Dimethyl-2,4-hexadiene. The CC nonbonded internuclear distances shown as functions of the torsion angle ($\angle\alpha_1$) around the C_3-C_4 bond. $\angle\alpha_1$ is here defined as zero when the two CC double bonds are in a planar *trans* conformation. The solid and dotted lines correspond to distances with multiplicities equal to two and one, respectively.

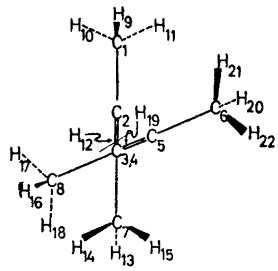

Fig. 7. The *trans,trans*-3,4-dimethyl-2,4-hexadiene molecule viewed along the C_3-C_4 bond.

ing to the experimental RD function. Fig. 7 shows a model of the *trans,trans*-3,4-dimethyl-2,4-hexadiene molecule viewed along the C_3-C_4 bond.

Because of the poor quality of the large angle scattering data, the outer s region had to be given very little weight. The following weight function was applied for the *trans,trans* isomer in the least squares refinements:

$$w(s)=\exp(-0.2(5.0-s)^2) \quad \text{for } s<5.0 \text{ Å}^{-1}$$
$$w(s)=1 \quad \text{for } 5.0 \text{ Å}^{-1} \leq s \leq 21.0 \text{ Å}^{-1}$$
$$w(s)=\exp(-0.011(s-21.0)^2) \quad \text{for } s>21.0 \text{ Å}^{-1}$$

It is easily seen that when identical structures for the C_1 and C_7 methyl groups are assumed, exactly the same parameters are necessary to define the geometry of *trans,trans*-3,4-dimethyl-2,4-hexadiene as those described for the *cis,cis* isomer. The difference in bond lengths between C_1-H_9 and C_2-H_{12} determined for the *cis,cis* isomer, was assumed to be the same in the present case. Signs of any deviation between the methyl group axes and the direction of the adjoining CC single bond could not be detected, and furthermore as there is no reason to expect tilted methyl groups in *trans,trans*-3,4-dimethyl-2,4-hexadiene, this parameter was omitted in the least squares refinements.

In the final stage of the structure analysis it was also in this case possible to vary all geometrical parameters simultaneously. The results are presented in Table 6. The standard deviation values are larger than those for the *cis,cis* isomer and reflect the somewhat lower quality of the scattering data compared to the excellent quality of those for the other molecule.

Table 6. trans,trans-3,4-Dimethyl-2,4-hexadiene. Experimentally determined molecular parameters and standard deviation values as results of least squares refinements of the molecular intensity data. The numbers in brackets are the multiplicities of the individual distances.

Distance	$r_g(1)$, Å	$\sigma(r_g(1))$, Å
$C_1-C_2(4)$	1.5210	0.0009
$C_2=C_3(2)$	1.3491	0.0012
$C_3-C_4(1)$	1.4793	0.0031
$C_1-H_9(12)$	1.1186	0.0014
$C_2-H_{11}(2)$	1.0886	
Angle	**Degrees**	σ
$\angle C_1C_2C_3$	123.45	0.35
$\angle C_2C_3C_4$	123.48	0.50
$\angle C_2C_3C_7$	121.42	0.73
$\angle C-C-H$	109.66	0.42
$\angle C=C-H$	122.0	
$\angle\alpha_1{}^a$	113.31	0.38
$\angle\alpha_2{}^a$	12.81	1.69
$\angle\alpha_3{}^a$	12.08	1.02

[a] For explanation of the torsion angles, see footnote in Table 1.

No standard deviation value is listed for $\angle C=C-H$. This parameter did refine in the least squares analysis but gave a very large angle of about 127° with a standard deviation value of several degrees. It was therefore decided to keep the $C=C-H$ angle fixed at a reasonable magnitude.

Table 7. trans,trans-3,4-Dimethyl-2,4-hexadiene. The CC nonbonded internuclear distances, as determined by least squares refinements of the molecular intensity data. The mean vibrational amplitudes are determined by trial and error from the RD-function.

Distance	Multiplicity	$r_g(1)$, Å	u, Å
C_2C_4	2	2.4920	0.0700
C_3C_7	2	2.5045	0.0700
C_1C_3	2	2.5290	0.0700
C_3C_8	2	2.5320	0.0700
C_1C_4	2	3.0167	0.0950
C_1C_6	1	3.3222	0.1100
C_7C_8	1	3.1567	0.0960
C_2C_5	1	3.2152	0.0960
C_1C_5	2	3.4251	0.0900
C_2C_8	2	3.5524	0.1150
C_1C_7	2	3.9231	0.0700
C_1C_8	2	3.9458	0.1100

It was not possible to refine the mean vibrational amplitudes for the bond distances simultaneously with refinements of the geometrical parameters. The u values determined for the *cis,cis* isomer were therefore adopted. Table 7 lists the CC nonbonded distances. The mean vibrational amplitudes for these distances could not be determined by least squares refinements. The u values listed in Table 7, column 4, are therefore derived by trial and error methods applied to the radial distribution functions.

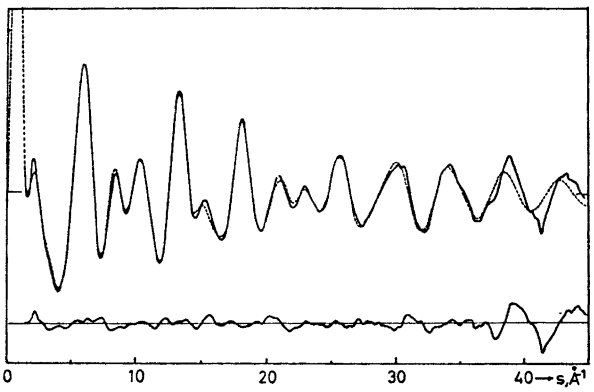

Fig. 8. trans,trans-3,4-Dimethyl-2,4-hexadiene. Experimental (———) and theoretical (- - -) $sM(s)$ functions and the deviations between the two.

The theoretical molecular intensity function for the final molecular model for *trans,trans*-3,4-dimethyl-2,4-hexadiene is shown in Fig. 8 together with the experimental $sM(s)$ function and the difference between the two. The

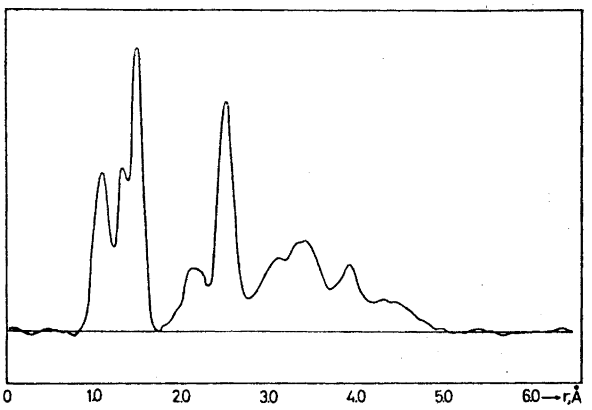

Fig. 9. trans,trans-3,4-Dimethyl-2,4-hexadiene. Experimental radial distribution function, $k=0.0009$.

overall correspondence is good except in the outer s region where the experimental data are of poor quality. In order to suppress termination effects in the experimental RD curve if the outer experimental $sM(s)$ data are omitted, or to reduce the influence on the RD curve from these data if they are included, it is necessary to apply a relatively large artificial damping constant k. Fig. 9 shows the experimental RD function based upon molecular intensity data out to $s = 45$ Å^{-1} with an artificial damping function equal to $\exp(-0.0009s^2)$. The peak at 2.1 Å is obviously deformed but other r regions may be affected as well. Fig. 10 shows the experimental and theoretical RD functions when $k = 0.0024$. The bars represent relative contributions from the CC interatomic distances.

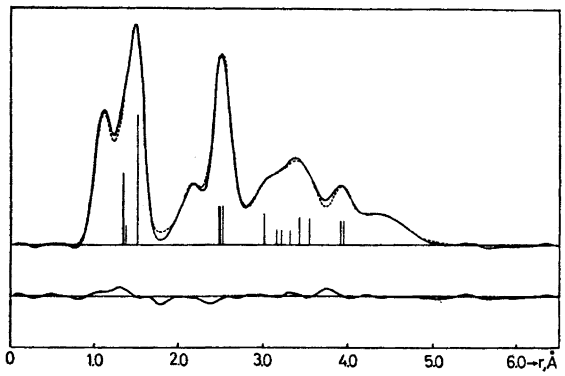

Fig. 10. trans,trans-3,4-Dimethyl-2,4-hexadiene. Experimental (———) and theoretical (- - -) radial distribution functions (k=0.0024) and the deviations between the two. The bars represent relative contributions from the CC interatomic distances.

The bond distance and bond angle parameters determined for *trans,trans*-3,4-dimethyl-2,4-hexadiene will be discussed at the end of the paper. The C_3-C_4 torsion angle is determined to be 113.3° which corresponds closely to *gauche* conformation. It is quite reasonable that *trans,trans*-3,4-dimethyl-2,4-hexadiene does not have an essentially planar carbon skeleton like the *cis,cis* isomer. In the latter molecule the main steric problem is caused by repulsions between the two *cis* methyl groups at each of the C=C double bonds. In the *trans,trans* isomer, however, there are no important steric repulsions within one isolated half of the molecule. If the two C=C double bonds were in a planar *trans* conformation, the pairwise repulsions between the methyl groups at C_2 and C_4 and at C_3 and C_5 would be more serious than the repulsions in the *cis,cis* isomer. In the *trans,trans* compound the repulsions may be overcome by rotation around the C_3-C_4 single bond. It is interesting to note that the observed torsion angle ($\angle\alpha_1$) corresponds to a *gauche* conformation of the two C=C double bonds. Even if a torsion angle of 180° corresponding to *cis* arrangement of the double bonds is not sterically possible in the present case, the results obtained here may indicate that conjugated double bonds generally

have energy minima for *trans* (*anti*) and *gauche* conformations and not *trans* and *cis* as is widely believed.[14]

The observed value of 12.8° for $\angle\alpha_2$ which represents the deviation from planarity of the CC double bonds, is hardly physically significant. Even if this parameters was of the same order of magnitude for the *cis,cis* isomer (16.4°) and was there claimed probably to be of physical significance, there are important differences between the two molecules. The most important distance that changes with $\angle\alpha_2$ is the C_1C_7 distance. The length of this distance decreases with an increase in $\angle\alpha_2$ for the *trans,trans* isomer and is therefore effected in the same way as by shrinkage.[13]

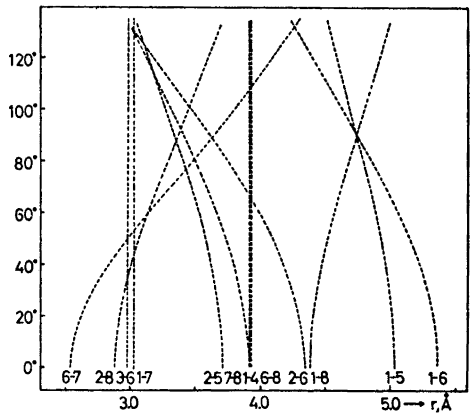

Fig. 11. *cis,trans*-3,4-Dimethyl-2,4-hexadiene. The CC nonbonded internuclear distances shown as functions of the torsion angle ($\angle\alpha_1$) around the C_3-C_4 bond. $\angle\alpha_1$ is here defined as zero when the two CC double bonds are in a planar *trans* conformation.

It is also questionable if the observed torsion angle for the methyl groups (12°) is of physical significance.

cis,trans-*3,4-Dimethyl-2,4-hexadiene.* The third isomer was studied in about the same way as described above when the two other molecules were discussed. The structural problem is, however, considerably more complex for the *cis,trans* isomer, as the two halves of the molecule are no longer identical. By studying the CC distance distribution diagram in Fig. 11 and the experimental RD function shown in Fig. 13 it could be concluded that the C=C double bonds in *cis,trans*-3,4-dimethyl-2,4-hexadiene are in an approximately *gauche* conformation at the C_3-C_4 single bond.

Because of the complexity of the *cis,trans*-3,4-dimethyl-2,4-hexadiene molecule it was necessary to make certain assumptions about the molecular structure. The difference between the C_1-H_9 and C_2-H_{12} bond lengths was assumed to be the same as determined for the *cis,cis* isomer, the two C=C double bonds were assumed to have the same bond length, $\angle\alpha_3$ for the *trans* part of the molecule was assumed to be equal to zero and all C–C–H angles were assumed to be equal. The same assumption was made about the C=C–H angles. It was also necessary to reduce the number of CC bond angles. The final structural results are based on the assumptions that $\angle C_1C_2C_3 = \angle C_2C_3C_7$ and that $\angle C_3C_4C_5 = \angle C_4C_5C_6$. The latter assumption is based on the results for these angles in the *trans,trans* isomer (123.45° and 123.48°) as the environ-

ments in the *trans* parts of the two molecules are very similar. The other assumption might be less convincing. The observed $C_1C_2C_3$ and $C_2C_3C_7$ angles in the *cis,cis* isomer differ by several degrees (126.61° and 122.27°), and even if the *gauche* conformation around the C_3-C_4 bond in *cis,trans*-3,4-dimethyl--2,4-hexadiene compared to the *anti* conformation in the *cis,cis* isomer will tend to decrease the difference in magnitude between the $C_1C_2C_3$ and $C_2C_3C_7$ angles, the assumption made about their equality is probably somewhat dubious. This assumption will, however, influence the determination of the other parameters to only minor extents.

When the restrictions described above were imposed, fifteen parameters were necessary to define the rigid *cis,trans*-3,4-dimethyl-2,4-hexadiene molecule. Fourteen of these were varied simultaneously in the least squares refinements. The fifteenth parameter, $\angle C_5C_4C_8$, was determined by the combined trial and error and least squares method described above, not because the parameter did not refine, but because the memory of the computer was not large enough to store enough information for variation of all fifteen parameters simultaneously. The final results from the least squares refinements are

Table 8. *cis,trans*-3,4-Dimethyl-2,4-hexadiene. Experimentally determined molecular parameters and standard deviation values as results of least squares refinements of the molecular intensity data. The numbers in brackets are the multiplicities of the individual distances.

Distance	$r_g(1)$, Å	$\sigma(r_g(1))$, Å
$C_1-C_2(4)$	1.5284	0.0009
$C_2=C_3(2)$	1.3589	0.0013
$C_3-C_4(1)$	1.4603	0.0025
$C_1-H_9(12)$	1.1158	0.0017
$C_2-H_{13}(2)$	1.0858	
Angle	**Degrees**	σ
$\angle C_1C_2C_3$[a]	123.01	0.43
$\angle C_2C_3C_4$	120.56	0.56
$\angle C_3C_4C_5$[b]	123.29	0.38
$\angle C_5C_4C_8$	122.25[c]	
$\angle C-C-H$	108.98	0.47
$\angle C=C-H$	122.08	5.63
$\angle \alpha_1$[d]	114.27	1.26
$\angle \alpha_2$,[d] *cis*	18.14	2.40
$\angle \alpha_2$,[d] *trans*	8.91	3.02
$\angle \alpha_3$,[d] *cis*	0.0	

[a] $\angle C_2C_3C_7$ is assumed equal to $\angle C_1C_2C_3$.
[b] $\angle C_4C_5C_6$ is assumed equal to $\angle C_3C_4C_5$.
[c] this parameter is determined by combined trial and error and least squares methods (see text).
[d] For explanation of the torsion angles, see footnote in Table 1.

Table 9. cis,trans-3,4-Dimethyl-2,4-hexadiene. The CC nonbonded internuclear distances as determined by least squares refinement of the molecular intensity data.

Distance	Multiplicity	$r_g(1)$, Å	u, Å
C_2C_4	1	2.4489	0.0700
C_3C_5	1	2.4814	0.0700
C_2C_7	1	2.5388	0.0700
C_5C_8	1	2.5297	0.0700
C_4C_6	1	2.5422	0.0700
C_1C_3	1	2.5388	0.0700
C_3C_8	1	2.5134	0.0700
C_4C_7	1	2.5408	0.0700
C_3C_6	1	3.0062	0.0950
C_1C_7	1	3.0511	0.0950
C_2C_8	1	3.5205	0.1100
C_5C_7	1	3.5740	0.1100
C_2C_5	1	3.1560	0.0980
C_6C_7	1	3.9899	0.1100
C_7C_8	1	3.1521	0.0980
C_2C_6	1	3.3316	0.0900
C_1C_4	1	3.8595	0.0750
C_6C_8	1	3.9557	0.0750
C_1C_8	1	4.9275	0.1100
C_1C_5	1	4.4875	0.1100
C_1C_6	1	4.2861	0.1100

presented in Table 8 while Table 9 lists the CC nonbonded distances determined for the molecule. The *gauche* conformation around the $C_3 - C_4$ bond is confirmed. It is surprising that $\angle\alpha_3$ for the *cis* part of the molecule is found to be equal to zero, as an about 30° angle for this parameter was so essential in describing the molecular structure of the *cis,cis* isomer. It is possible that this parameter

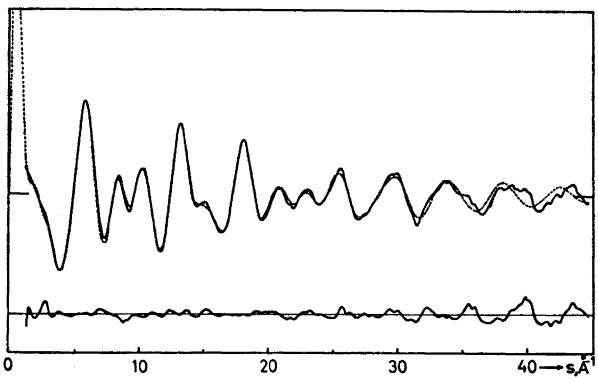

Fig. 12. cis,trans-3,4-Dimethyl-2,4-hexadiene. Experimental (———) and theoretical (- - -) $sM(s)$ functions and the deviations between the two.

is especially sensitive to the assumptions made about the structure. The orientation of the methyl groups are generally not too well defined in the *cis,trans* isomer. This is visualized in Fig. 13 where the correspondence between the experimental and theoretical radial distribution functions in the outer r region ($r>4.2$ Å) is unsatisfactory. In this region the CH nonbonded distances are predominating.

The experimental and theoretical $sM(s)$ functions for *cis,trans*-3,4-dimethyl-2,4-hexadiene are shown in Fig. 12. The relative contributions from CC distances are indicated on the theoretical RD function in Fig. 13.

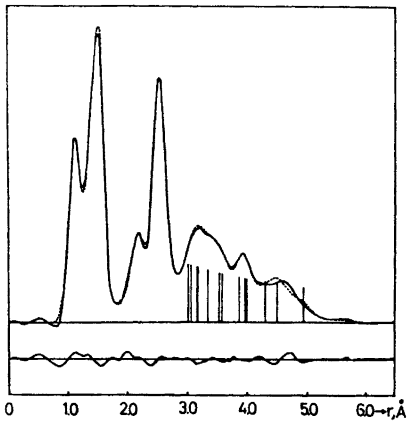

Fig. 13. *cis,trans*-3,4-Dimethyl-2,4-hexadiene. Experimental (———) and theoretical (- - -) radial distribution functions ($k=0.0024$) and the deviations between the two. The bars represent relative contributions from CC interatomic distances for $r>2.7$ Å.

FINAL RESULTS

cis,cis-*3,4-Dimethyl-2,4-hexadiene* is found to have an essential planar carbon skeleton, while the two other isomers, *trans,trans* and *cis,trans*, are shown to have approximately *gauche* conformations at the central CC single bond. The determined molecular parameters and standard deviations for the *cis,cis*, *trans,trans*, and *cis,trans* isomers of 3,4-dimethyl-2,4-hexadiene are presented in Tables 1, 6, and 8, respectively. The most important bond length, bond angle and torsion angle parameters for the three molecules are summarized in Table 10.

The structural parameters for *cis,cis*-3,4-dimethyl-2,4-hexadiene are generally very well determined. The results for the *trans,trans* isomer are of good, but somewhat lower accuracy due to poorer quality of the experimental large angle scattering data. The experimental intensity data for *cis,trans*-3,4-dimethyl-2,4-hexadiene are of about the same quality as those for the *trans,trans* isomer. Because of the complexity of the molecular structure, several restrictions of the geometrical parameters had to be imposed in the structure analysis of this molecule. The determined parameters for *cis,trans*-3,4-dimethyl-2,4-hexadiene therefore have to be assigned higher error limits than those for the other molecules. In Table 10 estimated error limits are assigned to those parameters where it is felt that it can be done with confidence.

Table 10. Comparison of the experimentally determined structural parameters for the three isomeric 3,4-dimethyl-2,4-hexadienes.

Parameter	*cis,cis*	*trans,trans*	*cis,trans*
C_1-C_2	1.521±0.005 Å	1.521±0.006 Å	1.528±0.010 Å
$C_2=C_3$	1.350±0.005 Å	1.349±0.006 Å	1.359±0.010 Å
C_3-C_4	1.473±0.009 Å	1.479±0.010 Å	1.460±0.020 Å
C_1-H_9	1.117±0.007 Å	1.119±0.008 Å	1.116±0.010 Å
$\angle C_1C_2C_3$	126.6±0.8°	123.5±1.0°	123.0°
$\angle C_2C_3C_4$	122.6±0.8°	123.5±1.0°	120.6°
$\angle C_2C_3C_7$	122.3±0.8°	121.4±1.0°	123.0°
$\angle C_7C_3C_4$	115.1°	115.1°	116.4°
$\angle C_3C_4C_5$	122.6±0.8°	123.5±1.0°	123.3°
$\angle C_4C_5C_6$	126.6±0.8°	123.5±1.0°	123.3°
$\angle C_5C_4C_8$	122.3±0.8°	121.4±1.0°	122.3°
$\angle C_8C_4C_6$	115.1°	115.1°	114.4°
∠C−C−H	109.6±0.8°	109.7±1.0°	109.0±1.0°
∠C=C−H	119.1±2.0°	122.0°	122.1°
$\angle\alpha_1$[a]	26.6°	113.3±2.0°	114.3±3.0°
$\angle\alpha_2$[a]	16.4°	12.8°	18.1° (*cis*) 8.9° (*trans*)
$\angle\alpha_3$[a]	33.3±5.0°	12.1±13.0°	0°

[a] For explanation of the torsion angles, see footnote in Table 1.

The estimated error limits are based upon least squares standard deviation values, consideration of the correlation among the parameters and on estimates of systematic effects such as errors in electron wavelength, camera distance, *etc.*

In *cis,cis*-3,4-dimethyl-2,4-hexadiene the methyl groups in *cis* position at each of the CC double bonds interfere sterically with each other. The analysis shows that the interatomic repulsions are reduced by the combined effects of increased C−C=C bond angles, slightly twisted CC double bonds, and torsion angles of about 33° at the $CH_3-C=$ single bonds.

The same kind of steric interference is found in the *cis* part of *cis,trans*-3,4-dimethyl-2,4-hexadiene. Increased C−C=C bond angles and a slightly twisted CC double bond (18.1°) are observed for this molecule also, while the methyl hydrogens could not be detected to deviate from a conformation in which they were eclipsed with the CC double bond. It is, however, the author's opinion that the *cis* methyl groups are distorted in *cis,trans*-3,4-dimethyl-2,4-hexadiene also, but that the torsion angle could not be observed because of the restrictions imposed in the structure analysis for this molecule.

DISCUSSION OF THE RESULTS

The consistency between the bond distances determined for the three molecules is satisfactory. The bond lengths determined for the *cis,cis* and *trans,trans* isomers are nearly identical. Even though the difference in C_3-C_4

bond lengths for these molecules is too small to be significant, it is interesting to point out that the largest C_3-C_4 distance is observed for the *trans,trans* isomer where the possibilities for electron delocalization is reduced because of the *gauche* conformation of the double bonds. The C_1-C_2 and $C_2=C_3$ bond lengths are found to be somewhat larger and the C_3-C_4 bond length is found to be somewhat shorter for *cis,trans*-3,4-dimethyl-2,4-hexadiene than for the other isomers. The differences are, however, not significant.

The CC double bond is observed to be slightly larger in the three molecules studied here than what is usually encountered in other conjugated hydrocarbons. Exactly the same bond length (1.349 Å) is, however, recently observed for the CC double bond in 2,3-dimethylbutadiene in an electron diffraction study by Aten *et al.*[2] In the same paper the two kinds of CC single bonds are reported to be 1.491 Å and 1.511 Å with an average CC single bond of 1.504 Å. These values should be compared to the same kind of bond lengths in *cis,cis*-3,4-dimethyl-2,4-hexadiene (1.473 Å and 1.521 Å). The agreement is not quite satisfactory, but it is worth noting that if the two kinds of CC single bonds in 2,3-dimethylbutadiene were assigned the bond lengths determined for *cis,cis*-3,4-dimethyl-2,4-hexadiene, the average CC single bond would be almost identical to that observed by Aten *et al.* (1.5047 Å *vs.* 1.504 Å).

It is difficult to discuss the distribution of bond angles in the three molecules simultaneously, as the differences in conformation and *cis trans* isomerism influence the bond angles in a much larger and more unpredictable way than they do the bond lengths. The only CC bond angles that can be directly compared are $\angle C_3C_4C_5$, $\angle C_4C_5C_6$, and $\angle C_5C_4C_7$ in the *trans,trans* and *cis,trans* isomers and the correspondence between these angle parameters is seen to be very good. The CC bond angles in the *cis* parts of the *cis,cis* and *cis,trans* isomers are not directly comparable as the repulsions between the methyl group at C_3 and the bonds at $C_4=C_5$ in the *cis,cis* isomer are reduced for the other molecule due to the large C_3-C_4 torsion angle.

Acknowledgement. The author is greatly indebted to Professor W. Doering, Yale University, who provided the samples of the isomeric 3,4-dimethyl-2,4-hexadienes. She also wants to acknowledge interesting and stimulating discussions with Professor Otto Bastiansen, Oslo University, and to express her gratitude to cand. real. Arne Almenningen for making all the electron diffraction diagrams. Financial support from *Norges almenvitenskapelige forskningsråd* is gratefully acknowledged.

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Received December 18, 1969.