

Electron Diffraction Studies of *cis*- and *trans*-2-Butene

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The molecular structures of *cis*- and *trans*-2-butene have been determined by electron diffraction. The carbon-carbon bond distances are $r(\text{C}-\text{C}) = 1.508(0.002) \text{ \AA}$ and $r(\text{C}=\text{C}) = 1.347(0.003) \text{ \AA}$ in the *trans* isomer and $r(\text{C}-\text{C}) = 1.506(0.002) \text{ \AA}$ and $r(\text{C}=\text{C}) = 1.346(0.003) \text{ \AA}$ in the *cis* isomer. The $\text{C}-\text{C}=\text{C}$ valence angle in the *cis* isomer, $125.4^\circ (0.4^\circ)$ is larger than in the *trans* isomer, $123.8^\circ (0.4^\circ)$. In *cis*-2-butene the methyl groups are tilted $4.9^\circ (2.0^\circ)$ away from the double bond.

Even a casual glance at *cis*-2-butene (Fig. 1A) reveals that the molecule must be strained: If the bond distances and valence angles are normal, and if the methyl groups are staggered with respect to the vinylic hydrogen atoms, the distance between the two methyl hydrogen atoms in the carbon atom plane is less than 1.8 \AA . Indeed, the heat of hydrogenation of *cis*-2-butene is $28.6 \text{ kcal mole}^{-1}$,¹ while that of the *trans* isomer (Fig. 1B) is $27.6 \text{ kcal mole}^{-1}$.¹ The strain energy therefore amounts to $1.0 \text{ kcal mole}^{-1}$.

In an effort to determine how the strain energy in *cis*-2-butene is distributed over the internal coordinates of the molecule, we have undertaken simultaneous gas phase electron diffraction investigations of *cis*- and *trans*-2-butene.

EXPERIMENTAL AND CALCULATION PROCEDURE

cis- and *trans*-2-Butene (*purum*) was purchased from Fluka AG. The electron scattering patterns were recorded on the Oslo electron diffraction units^{2,3} with nozzle temperatures of $20 \pm 10^\circ\text{C}$. For the *trans* isomer exposures were made at nozzle-to-photographic-plate distances of about 48 cm, 20 cm, and 12 cm. Four plates from each set were photometered and used for this study. For the *cis* isomer, exposures were made at nozzle-to-photographic plate distances of about 130 cm, 48 cm, and 20 cm. Four plates from each set were used for this study. The data were corrected and processed in the usual way.⁴

The resulting modified molecular intensity points for *trans*-2-butene are shown in Fig. 2A. The data extend from $s = 3.00 \text{ \AA}^{-1}$ to 43.00 \AA^{-1} , [$s = (4\pi/\lambda)\sin(\theta/2)$ where λ is the electron wavelength and θ the diffraction angle]. The point density is four points per \AA^{-1} . The experimental modified molecular intensity points for *cis*-2-butene are shown in Fig. 3A. The data extend from 1.125 \AA^{-1} to 41.75 \AA^{-1} . Below $s = 5.00 \text{ \AA}^{-1}$ the point density is eight points per \AA^{-1} , above 5.00 \AA^{-1} four points per \AA^{-1} .

Theoretical intensity curves were calculated from

$$I_{CC}(s) = \sum_{i \neq j} \frac{|f_i(s)| \cdot |f_j(s)|}{|f_C(s)|^2} \cos[\eta_i(s) - \eta_j(s)] \frac{\sin(R_{ij}s)}{R_{ij}} \exp(-\frac{1}{2}u_{ij}^2s^2)$$

$$= \sum_{i \neq j} g_{ij/CC}(s) \frac{\sin(R_{ij}s)}{R_{ij}} \exp(-\frac{1}{2}u_{ij}^2s^2)$$

The sum extends over all atom pairs i, j in the molecule. R_{ij} is the internuclear distance, u_{ij} the root mean square amplitude of vibration. $f_j(s) = |f_j(s)| \exp[i\eta_j(s)]$ is the complex atomic scattering factor of atom j . It has been calculated for C and H by the partial wave approximation with a program written by Peacher.⁵ The scattering potential of carbon has been found by non-relativistic Hartree-Fock calculations.^{6,7}

STRUCTURE ANALYSIS

trans-2-Butene. An experimental RD function for this compound is shown in Fig. 4. The peak at 1.1 Å corresponds to the C—H bond distances, the peak at 1.5 Å to the C1—C2 and C3—C4 bond distances and the unresolved shoulder at 1.35 Å to the C2=C3 double bond distance. The peak at 2.15 Å corresponds to all C···H nonbonded distances across one valence angle, and the peak at 2.6 Å to the C1···C3 and C2···C4 nonbonded distances. The peak corresponding to the C1···C4 distance is found at 3.9 Å.

It was assumed that *trans-2-butene* has the C_{2h} structure shown in Fig. 1B. It was further assumed that the methyl groups have C_{3v} symmetry. The

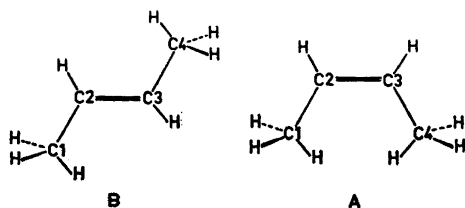


Fig. 1. Molecular models of *cis*- and *trans*-2-butene.

angle between the threefold axes and the C1—C2 and C3—C4 bonds (the methyl group “tilt”) was refined as an independent parameter. The tilt angle was defined as positive when the methyl hydrogen atoms are moved *away* from the double bond.

The molecular structure was refined by least-squares calculations on the intensity data with a diagonal weight matrix.⁴ In order to make the calculation converge, it was necessary to assume that all C—H bond distances have the same vibrational amplitude, and that all C···H nonbonded distances across one valence angle have the same amplitude. In the final least-squares cycle, however, the C—H(methyl) and C—H(vinyl) distances were assumed to have different amplitudes, and all C···H nonbonded distances were assumed to have different amplitudes unless molecular symmetry showed them to be equal. The H···H amplitude within a methyl group was fixed at 0.12 Å (the value found in methane⁸), all other H···H amplitudes at 0.20 Å; these amplitudes were not refined.

The most important final parameters and their estimated standard deviations are listed in Table 1, column A. The standard deviations obtained by

least-squares calculations have been multiplied by a factor of 2.0 for distances and angles, and a factor of 3.0 for amplitudes to account for correlation in the intensity data,⁹ and further expanded to take into account an uncertainty of 1.4 ppt in the electron wavelength.³

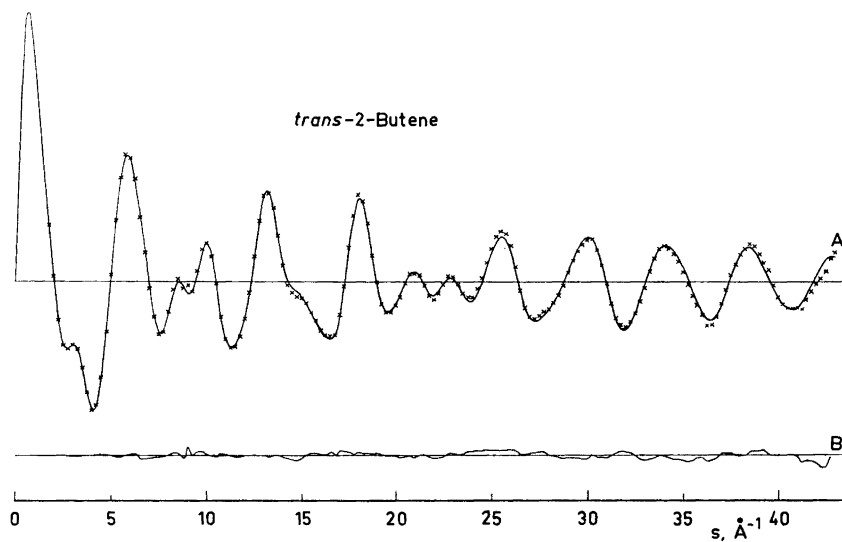


Fig. 2. A: theoretical modified molecular intensity curve of *trans*-2-butene with experimental values indicated by x. B: difference curve.

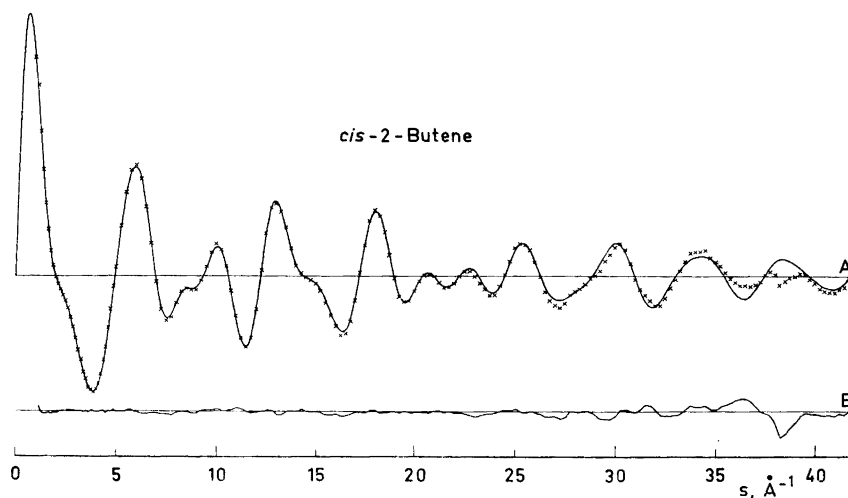


Fig. 3. A: theoretical modified molecular intensity curve of *cis*-2-butene with experimental values indicated by x. B: difference curve.

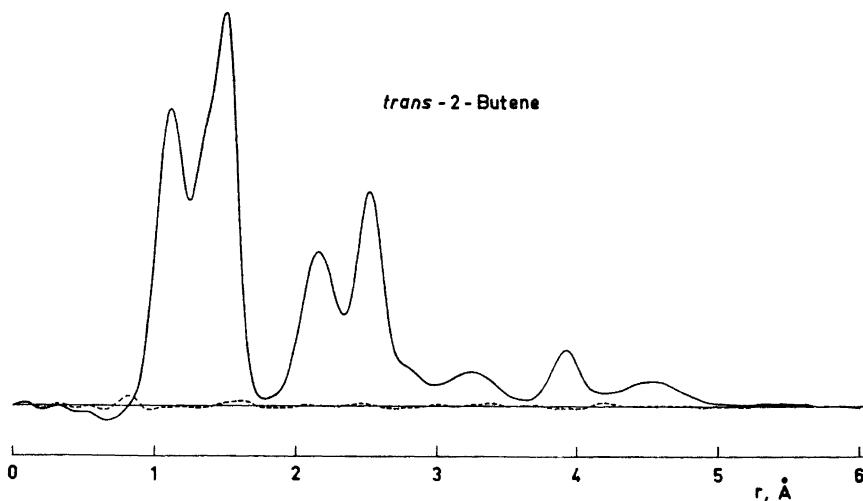


Fig. 4. Full line: experimental radial distribution curve of *trans*-2-butene. The artificial damping constant $k=0.002 \text{ \AA}^2$. Dashed line: difference between the experimental curve and a theoretical curve calculated for the best model.

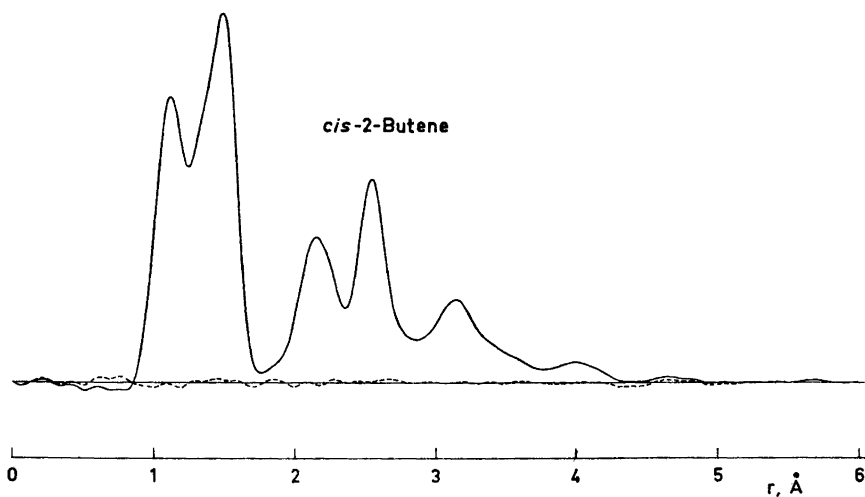


Fig. 5. Full line: experimental radial distribution curve of *cis*-2-butene. The artificial damping constant $k=0.002 \text{ \AA}^2$. Dashed line: difference between the experimental curve and a theoretical curve calculated for the best model.

A theoretical intensity curve calculated from the final parameters is shown in Fig. 2A. The difference between an experimental RD curve and a theoretical curve calculated from the final parameters is shown by the dashed curve in Fig. 4. The agreement is seen to be very good.

cis-2-Butene. An experimental RD curve for this compound is shown in Fig. 5. Below 2.9 Å the curve is very similar to that of the *trans* isomer. The peak corresponding to the C1...C4 distance, however, is now found at 3.15 Å.

It was assumed that *cis*-2-butene has the C_2 structure shown in Fig. 1A. The four carbon atoms are then no longer required by symmetry to lie in the same plane, and the angle between the planes through C1, C2, and C3 and the plane through C2, C3, and C4 (the "twist" of the double bond) was refined as an independent parameter. It was further assumed that the methyl groups have C_3 symmetry, and that the threefold axes and the vinylic hydrogen atoms lie in the plane through C1, C2, and C3 or in the plane through C2, C3, and C4. The tilt of the methyl groups, which was considered positive when the hydrogen atoms had been moved away from the double bond, was again refined as an independent parameter. Finally the two methyl groups were allowed to rotate about the adjacent C—C bonds (or more accurately about their threefold axes) in such a way as to increase the distance between the two crowded hydrogen atoms.

The molecule structure was refined by least-squares calculations in the same way as for the *trans* isomer. The most important final parameters and their estimated standard deviations are given in Table 1, column B. A theoretic-

Table 1. Structure parameters with estimated standard deviations of *trans*-2-butene (column A) and *cis*-2-butene, (columns B and C). The distances are given as r_a .¹⁰ The angles have not been corrected for shrinkage.

	A. <i>trans</i>	B. <i>cis</i>	C. <i>cis</i>
C1—C2	1.508(2) Å	1.506(2) Å	1.506(2) Å
C2—C3	1.347(3) Å	1.346(3) Å	1.346(3) Å
∠C1—C2—C3	123.8°(0.4°)	125.4°(0.4°)	125.4°(0.4°)
C1—H	1.10(4) Å	1.11(6) Å	1.11(4) Å
∠C2—C1—H	109.0°(5.0°)	110.5°(5.4°)	110.6°(3.6°)
tilt	0.6°(8.0°)	4.3°(8.6°)	4.9°(2.0°)
C2—H	1.15(14) Å	1.12(18) Å	1.13(0.14) Å
∠C3—C2—H	121.5°(4.0°)	114.1°(27.2°)	114.5°(18.6°)
C1—C2 twist	0.0 not refined	0.8°(10.6°)	9.0°(6.8°)
C2—C3 twist	0.0 ,,	20.6°(15.4°)	0.0 not refined
u (C—C)	0.044(3) Å	0.052(3) Å	0.053(3) Å
u (C—C)	0.037(3) Å	0.045(3) Å	0.045(3) Å
u (C1...C3)	0.063(3) Å	0.064(3) Å	0.063(5) Å
u (C1...C4)	0.078(14) Å	0.102(27) Å	0.110(39) Å

cal intensity curve calculated from the final parameters is shown in Fig. 3A. The difference between an experimental RD curve and a theoretical curve calculated from the final parameters is shown by the dashed line in Fig. 5.

Finally the refinement was repeated with the twist of the double bond fixed at 0°, *i. e.* with a model with a planar carbon skeleton. This model

gave nearly as good a fit to the experimental data as the twisted one; the final weighted-square-error sum was only 3 % higher. The parameters obtained and their estimated standard deviations are listed in Table 1, column C.

DISCUSSION

The carbon-carbon bond distances in the two isomers (given in Table 1 as r_a^{10}) are equal to well within their error limits. It does not appear, therefore, that the strain in the *cis*-isomer has any effect on the bond distances.

The sp^2 - sp^3 single bond distances agree well with the length similar bonds in 2,3-dimethylbutadiene,¹¹ $r_a=1.511$ (0.003) Å, and isobutylene,¹² $r_g=1.505$ (0.001) Å, as determined by electron diffraction. The sp^2 - sp^2 double bond distances agree well with the length of the similar bonds in 2,3-dimethylbutadiene,¹¹ $r_a=1.349$ (0.003) Å, and butadiene,¹⁴ $r_a=1.344$ (0.001) Å (also by ED), but not with the double bond distance in isobutylene,¹² $r_g=1.331$ (0.0015) Å. We can suggest no explanation for this difference.

The C=C-C valence angle in *trans*-2-butene agrees well with the corresponding angle isobutylene,¹⁶ 124°, and butadiene,¹⁴ 122.9°(0.5°), but less well with the corresponding angle in the more crowded molecule 2,3-dimethylbutadiene,¹¹ 120.2°(0.7°). The value obtained for the angle in the *cis*-isomer is significantly larger than in all these molecules. The value is moreover in excellent agreement with the value obtained by internal rotation analysis of the microwave spectrum,¹⁵ 125.0°. There is no doubt that the intramolecular strain in *cis*-2-butene is partly relieved through an opening of the C=C-C valence angle.

Our attempt to determine whether there also in a twist of the double bond has not been successful; the twist angle obtained is unreasonable, and the estimated standard deviation is so large as to make the result meaningless. The reason for this failure is probably that the angle of twist is strongly coupled to the methyl group tilt, the correlation coefficient is -0.9. Sarachman¹⁵ argues that the value of $I_a+I_b-I_c=6.1898$ amu Å² rules out a nonplanar arrangement of the carbon atoms. The molecular structure was therefore refined anew with the twist angle fixed at 0°. The resulting parameters are listed in Table 1, column C. For this model the distance between the two congested hydrogen atoms is 2.06(0.11) Å. The strain appears to be partially relieved through rotation, 9.0°(6.8°), and tilt, 4.9°(2.0°) of the methyl groups. This is again in agreement with the microwave study:¹⁵ the observed moments of inertia can best be reconciled with reasonable values of the bond distances and valence angles if the methyl groups are tilted away from the double bond.

The barrier to internal rotation of the methyl groups in *trans*-2-butene has been determined from thermodynamic data, $V_0=1.95$ kcal mole⁻¹.¹⁶ This is very similar to the barrier in propylene as determined from the microwave spectrum, 1.98 kcal mole⁻¹.¹⁷ The barrier to internal rotation in *cis*-2-butene as determined from the microwave spectrum is 0.73 kcal mole⁻¹.¹⁵ Dauber and Pitzer¹⁸ have suggested that substitution *cis* to a double bond generally raises the energy of the minimum of the potential energy without similarly increasing the maximum, thus decreasing the depth of the potential well.

Using the molecular parameters obtained for *trans*-2-butene we calculate that the shortest distance between hydrogen atoms in different methyl groups in a *cis*-2-butene molecule where *one* methyl group is rotated into an eclipsed position relative to the vinylic hydrogen is 2.3 Å. It would therefore appear that the molecule with a methyl group in a position of maximum potential energy is otherwise unstrained. This view is supported by the fact that the sum of the strain energy and potential barrier in the *cis*-isomer is roughly equal to the potential barrier in the *trans* isomer.

Acknowledgements. We are grateful to the Norwegian Research Council for Science and the Humanities for financial support.

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Received May 9, 1969.