THE MOLECULAR STRUCTURES OF SOME SIMPLE OLEFINS AND SMALL RING COMPOUNDS

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James Paul McHugh

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ABSTRACT

The structures of three simple olefins and three small ring compounds containing double bonds have been determined by electron diffraction, and the results discussed in terms of hyperconjugation, rehybridization, strain, and intramolecular repulsions.

In Part I, the structures of propene, isobutene, and *cis* butene-2 are described. The single bonds in these molecules have a length of about 1.50 A, exhibiting about half the shortening found in single bonds adjacent to triple bonds.

In Part II, an attempt is made to calculate the intramolecular repulsive energy of the methyl groups in *cis* butene-2, using intermolecular force constants.

Parts III, IV, and V describe the structure determinations of methylenecyclopropane, 1,3-dimethylenecyclobutane, and 1-methyl-3-methylenecyclobutene. In each case, the single bonds adjacent to double bonds are found to be short.

Part VI contains some further discussion of the factors which alter carbon-carbon single bond lengths.

TABLE OF CONTENTS

PART	TITLE	PAGE
I.	The Molecular Structures of Propene, Isobutene, and *Cis* Butene-2.	1
II.	The Intramolecular Repulsion of Methyl Groups.	21
III.	Methylenecyclopropane	25
IV.	1,3-Dimethylenecyclobutane	36
V.	1-Methyl-3-Methylenecyclobutene	46
VI.	Concluding Remarks	62
	References	68
	Propositions	71

THE MOLECULAR STRUCTURES OF PROPENE, ISOBUTENE, AND CIS BUTENE-2

Single bond lengths and bond angles in simple olefinic compounds are of fundamental interest to the organic and the structural chemist, yet little accurate experimental data on such structures are available in the literature. It has long been known that carbon-carbon single bonds adjacent to triple bonds are considerably shortened, even in non-conjugated systems, e.g., methyl acetylene, C-C = 1.46 A (1). It seems reasonable to expect a double bond to cause a similar shortening of adjacent single bonds, but this point has received little attention experimentally. The purpose of the present study is to provide some accurate structural data for three simple olefins having single bonds adjacent to double bonds in a non-conjugated situation.

Pauling and Brockway (2) studied a number of olefins including isobutene by electron diffraction, and came to the conclusion that single bonds adjacent to double bonds have the normal length of 1.54 A. An investigation of cis butene-2 gave a similar result (3). As will be shown later, the data in both cases were in reality insufficient to determine the molecular parameters with any accuracy. Propene, to our knowledge, has not been previously investigated.

Photographs were made with the new electron diffraction apparatus on Kodak 50 plates and interpreted in the usual manner (4). The samples were of Matheson C. P. propene, isobutene, and cis butene-2 (99%, used without further purification). The camera distance was about 10 cm., and the wave length, calibrated with zinc oxide (5), was about 0.06 A.

In the later stages of refinement, photographs were made using a rotating sector and Kodak Process plates. These were examined visually and were quite useful for checking many details of the original interpretation.

The original photographs were measured by two independent observers, and in addition, a set of measurements was made on a sectored plate for each compound. The three sets of measurements were averaged together to obtain the scale factor for each molecule. In computing the scale factor, features at $q < 30$ and shelves on major maxima were omitted. All other measurements were given equal weight.

For all three structures, theoretical intensity curves were calculated using the expression

$$sI(s) = \sum_{i \neq j} \frac{Z_i Z_j}{r_{ij}} e^{-a_{ij} s^2} \sin s r_{ij} \quad , \quad s = \frac{4\pi}{\lambda} \sin \frac{\theta}{2} = \frac{\pi}{10} q$$

for the shape parameter ranges $1.48/1.34 \leq C\text{-}C/C{=}C \leq 1.54/1.34$, and $120^\circ \leq \angle C{=}C\text{-}C \leq 127^\circ$. Methyl C-H and ethylenic C-H were assumed to be 1.09 and 1.07 A respectively, and $\angle$ H-C=C was assumed to be 120°. Difference curves were calculated to test the result of varying C-H, $\angle$ H-C=C, and the temperature factors. Any reasonable change in these quantities does not affect the results for carbon-carbon distances by more than a few thousandths of an A, even in the most unfavorable case.* All terms except H•••H were included in calculating the theoretical intensity curves. The values of a_{ij} in the temperature factor $e^{-a_{ij}s^2}$ are listed in Table 1.

Table 1

r_{ij}	a_{ij}
C-H	0.0023
C••H	0.0041
C-C	0.00025-0.00045
C••C	0.0010
C=C	0.0000

Propene

The radial distribution curve (RD), visual curve (V), and a few theoretical intensity curves for propene are shown in Fig. 1. Critical marks (6) point out the important deficiencies in the unacceptable calculated curves. The most sensitive region for the determination of C-C/C=C is $60 < q < 80$. Model B is the best model. In model A, maximum 7 is too low relative to maximum 8. In models C through E, maximum 7 becomes progressively too strong, while maximum 8 becomes too weak, finally disappearing in model E. It should be kept in mind that

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* The value methyl C-H = 1.10 A leads to slightly improved overall appearance of the curves for isobutene and cis butene-2 in the region $60 < q < 80$; the final carbon-carbon distances change by one or two thousandths of an Angstrom.

the appearance of this sensitive region as a whole is the criterion for acceptability, and this is sometimes difficult to discuss in terms of small differences in the appearance of individual features. Models F and G show approximately the limits of acceptability in the C-C=C angle determination. In model F, maximum 5 is too weak, maximum 10 is too convex inside, and maximum 11 is too narrow, as well as too strong relative to maxima 10 and 12. In model G, maximum 8 is too low, maximum 10 is a bit too concave, and maximum 11 has lost its asymmetry. Table 2 lists values of q/q_o for model B.

Isobutene

Fig. 2 shows the radial distribution curve, visual curve, and a few theoretical intensity curves for isobutene. Model C is the best model. Models A, B, D, and E do not show the correct relationship between the heights of maxima 7, 8, and 9, which is the critical point in the determination of the ratio C-C/C=C. The shape and width of the radial distribution peak corresponding to C...C suggests that the three C...C distances are very nearly equal. This leads to a C-C=C angle of 123 1/2^o. Model F is clearly unacceptable. Model G is also unacceptable, maximum 9 being a shade weak, and maxima 11 and 12 not having the correct asymmetries. Table 3 lists q/q_o values for model C.

Cis butene-2

The radial distribution curve, visual curve, and a few theoretical intensity curves for cis butene-2 are shown in Fig. 3. As would be expected, the photographs of cis butene-2 are very similar to those of isobutene. However, there are many clear and important dif-

Legend for Figure 1

Model	C-C/C=C	∠C-C=C
A	1.49/1.34	125°
B	1.50/1.34	125°
C	1.51/1.34	125°
D	1.52/1.34	125°
E	1.54/1.34	125°
F	1.50/1.34	122.5°
G	1.50/1.34	127°

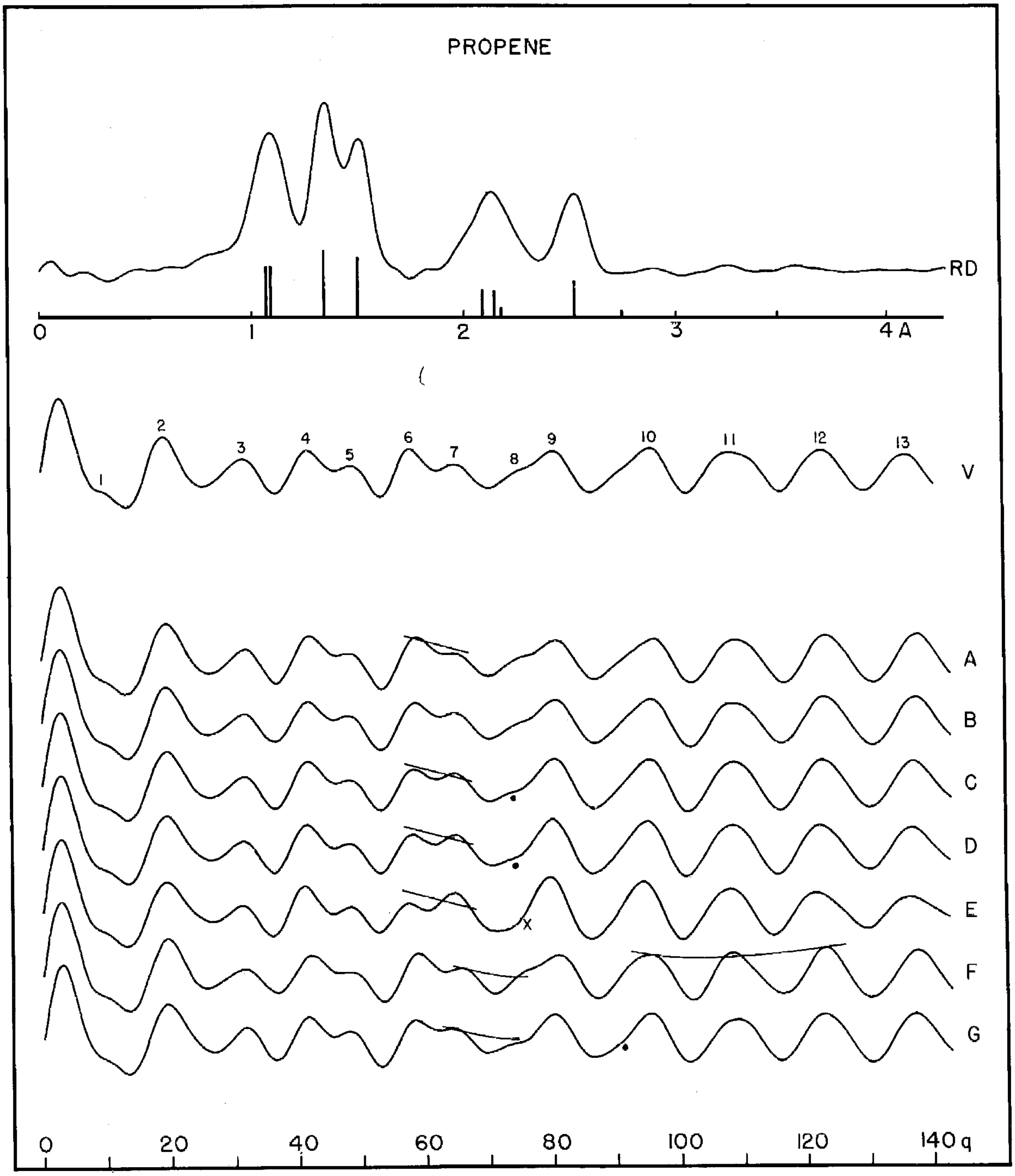
PROPENE
RD
0
1
2
3
4 A
1
2
3
4
5
6
7
8
9
10
11
12
13
V
A
B
C
D
E
F
G
x
0
20
40
60
80
100
120
140 q

Figure 1

Table 2

Diffraction Data for Propene, Model B

				q/q_o	
Min.	Max.	q_{calc}	(JPM non-sect.)	(VS non-sect.)	(JPM sect.)
1		8.6			
	1	10.5			
2		13.4	(1.000)	(1.017)	
	2	19.5	(1.045)	(1.016)	
3		26.1	(1.021)	(1.059)	
	3	31.65	0.983	0.997	
4		36.6	0.944	0.994	
	4	41.7	1.003	0.995	(1.014)
5		45.7	(1.008)	(1.002)	(1.000)
	5	48.0	(0.971)	(0.984)	(0.986)
6		53.2	0.992	1.005	0.998
	6	58.55	1.006	1.006	1.011
7		62.5	(1.006)	(1.010)	(1.005)
	7	65.0	(0.987)	(0.998)	(0.995)
8		70.25	1.002	1.011	1.000
	8	74.0	(0.993)	(1.005)	(0.993)
9		76.0	(0.976)	(0.992)	(0.992)
	9	80.6	0.987	1.004	0.997
10		86.55	0.990	1.006	1.003
	10	94.0	0.987	0.991	0.998
11		101.8	0.992	1.002	1.004
	11	108.8	0.991	0.992	1.000
12		116.25	0.998	1.000	1.001
	12	122.9	1.004	0.994	1.001
13		130.6	(0.990)	(0.999)	(1.009)
	13	137.5	(0.986)		(1.011)
	Average		0.9945	0.9998	1.0013
	Average dev.		0.0063	0.0051	0.0027

Total average 1/3(0.9945 + 0.9998 + 1.0013) = 0.9985

Results: C-C 0.9985 x 1.500 = 1.498 A

C=C 0.9985 x 1.340 = 1.338 A

∠C-C=C 125° ± 2°

Legend for Figure 2

Model	C-C/C=C	∠C-C=C
A	1.48/1.34	123.5°
B	1.50/1.34	123.5°
C	1.51/1.34	123.5°
D	1.52/1.34	123.5°
E	1.54/1.34	125°
F	1.51/1.34	120°
G	1.51/1.34	126°

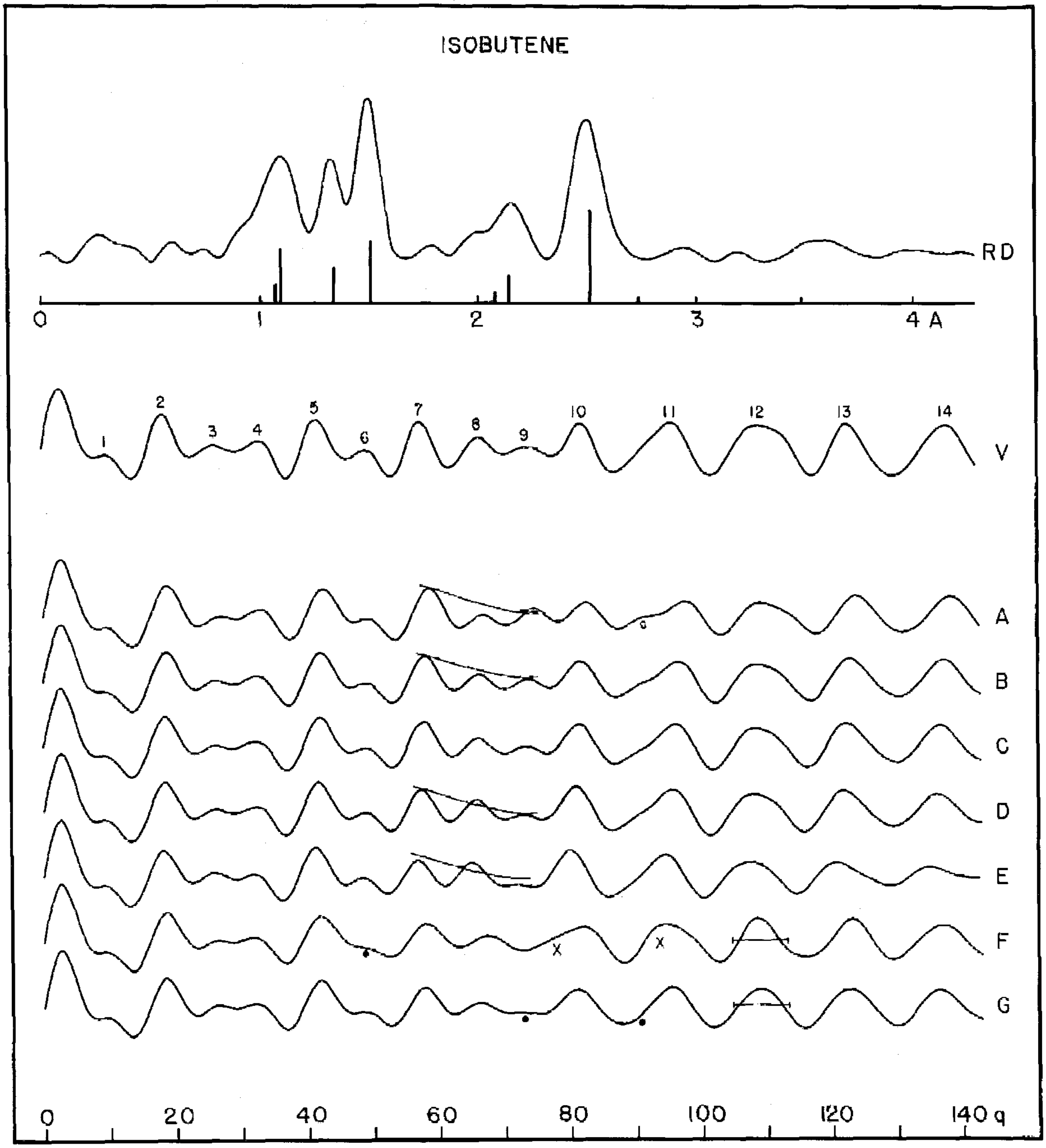
ISOBUTENE
RD
0
1
2
3
4 A
V
1
2
3
4
5
6
7
8
9
10
11
12
13
14
A
B
C
D
E
F
G
X
X
0
20
40
60
80
100
120
140 q

Figure 2

Table 3

Diffraction Data for Isobutene, Model C

			q/q_o		
Min.	Max.	$q_{calc.}$	(JPM non-sect.)	(VS non-sect.)	(JPM sect.)
1		7.5	(1.082)	(1.215)	
	1	9.5	(0.926)	(1.012)	
2		13.5	(0.975)	(0.981)	
	2	18.5	(1.005)	(1.029)	
3		22.7	(1.032)	(1.018)	
	3	25.9	(0.999)	(1.020)	
4		28.5	(0.965)	(1.010)	
	4	32.2	(0.965)	(0.992)	
5		37.1	0.994	1.004	
	5	42.0	1.008	0.998	0.999
6		46.5	(1.005)	(1.002)	(1.000)
	6	49.0	(0.987)	(0.987)	(0.989)
7		53.0	0.992	0.998	0.990
	7	57.8	1.001	0.992	0.997
8		62.3	0.998	0.996	0.998
	8	66.1	0.991	0.991	0.995
9		70.0	0.999	0.999	1.000
	9	73.45	0.994	0.995	0.999
10		76.75	0.987	0.990	0.996
	10	81.4	0.992	0.990	0.997
11		86.9	0.995	1.000	1.001
	11	96.2	1.006	1.004	1.005
12		102.0	0.999	1.003	1.002
	12	108.8	0.990	0.989	1.000
13		116.4	0.994	0.988	
	13	122.4	0.997	0.993	
14		130.0	(1.002)		
	14	136.9	(0.989)		
	Average		0.9961	0.9956	0.9984
	Average dev.		0.0044	0.0046	0.0027

Total average 1/3(0.9961 + 0.9956 + 0.9984) = 0.9967

Results:
C-C 0.9967 x 1.510 = 1.505 A
C=C 0.9967 x 1.340 = 1.336 A

$\angle$C-C=C 123 1/2° ± 2°

Legend for Figure 3

Model	C-C/C=C	∠ C-C=C
A	1.48/1.34	125°
B	1.50/1.34	125°
C	1.51/1.34	125°
D	1.52/1.34	125°
E	1.54/1.34	125°
F	1.50/1.34	122.5°
G	1.50/1.34	124°
H	1.50/1.34	126°
J	1.50/1.34	127°

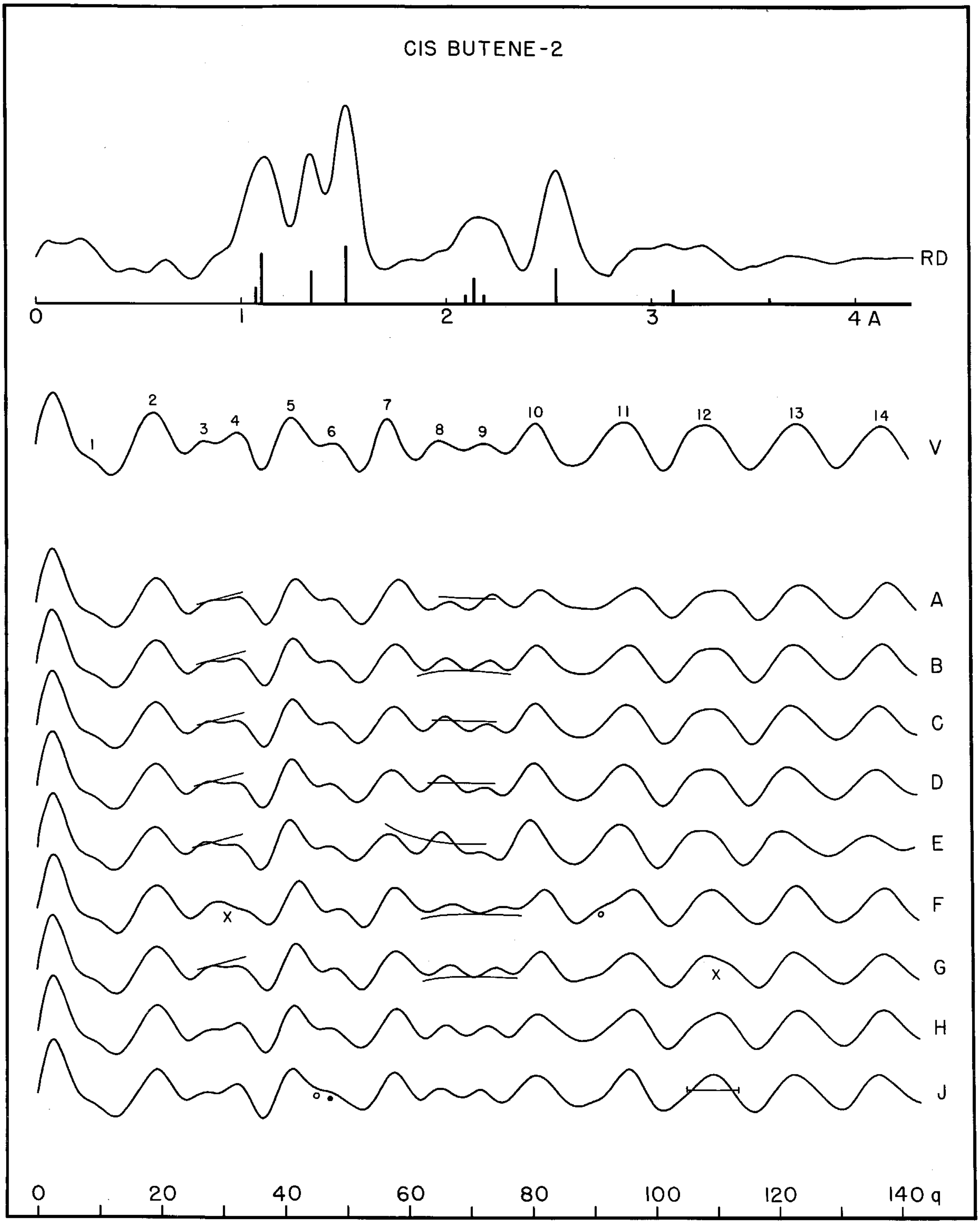
CIS BUTENE-2
RD
0
1
2
3
4 A
1
2
3
4
5
6
7
8
9
10
11
12
13
14
V
A
B
C
D
E
F
G
H
J
x
x
0
20
40
60
80
100
120
140 q

Figure 3

Table 4

Diffraction Data for Cis butene-2

Min.	Max.	$q_{calc.}$	q/q_o (JPM non-sect.)	q/q_o (VS non-sect.)	q/q_o (JPM sect.)
1		7.2	(1.051)		
	1	9.5	(1.051)		
2		12.6	(0.901)	(1.010)	
	2	19.3	(1.131)	(1.055)	
3		24.35	(1.035)	(1.047)	
	3	27.9	(1.047)	(1.039)	
4		29.5	(1.000)	(1.010)	
	4	32.45	(0.989)	(1.005)	
5		36.65	0.998	0.998	
	5	41.3	1.019	0.997	0.995
6		45.5	(1.004)	(1.011)	(0.989)
	6	47.3	(0.966)	(0.993)	(0.973)
7		52.15	0.988	1.000	0.989
	7	58.1	1.021	1.007	1.010
8		62.6	1.011	1.007	1.000
	8	66.0	1.009	0.995	1.000
9		69.3	1.000	1.006	1.003
	9	72.65	1.000	1.009	1.004
10		76.2	0.997	1.003	0.996
	10	80.3	0.991	0.993	0.987
11		88.1	1.020	1.020	1.006
	11	96.2	0.999	1.015	1.008
12		101.8	0.999	1.011	1.000
	12	109.2	1.009	1.003	1.001
13		116.3	1.003	1.005	1.003
	13	123.1	0.994	0.990	1.001
14		130.5	1.004		
	14	137.1	0.997		
	Average		1.0033	1.0038	1.0002
	Average dev.		0.0077	0.0063	0.0046

Total average 1/3(1.0033 + 1.0038 + 1.0002) = 1.0024

Results: C-C 1.0024 x 1.500 = 1.504 A

C=C 1.0024 x 1.340 = 1.343 A

∠ C-C=C $126^\circ \pm 1^\circ$

ferences. Maximum 3 is weaker and maximum 4 stronger, compared to isobutene. Maxima 8 and 9 appear as a pair of very nearly equal height, minimum 9 being shallower than 8 and 10. Minimum 11 and maximum 11 are shaped differently than for isobutene, while maximum 12 cuts off more sharply outside than inside, as opposed to isobutene where the opposite is true.

In models B, G, H, and J, maxima 8 and 9 have the correct relative heights, and give the C-C/C=C ratio. But there are other features which are quite sensitive to the C-C=C angle, thereby permitting a more accurate determination of this angle than was the case with either propene or isobutene. In models B and G, maximum 4 is too weak. Also minimum 9 is too deep relative to 8 and 10, giving maxima 8 and 9 less of a doublet appearance than does model H. Also, in model G, the wrong side of maximum 12 has the greater slope. In model J, maximum 6 is not sufficiently prominent, and maximum 12 is too narrow. Model H is therefore the best model. Table 4 lists q/q_0 values for model H.

The resulting parameters for the three molecules are listed in Table 5.

Table 5

	Propene	Isobutene	Cis butene-2
C-C	1.498 ± 0.014 A	1.505 ± 0.010 A	1.504 ± 0.010 A
C=C	1.338 ± 0.011 A	1.336 ± 0.012 A	1.343 ± 0.011 A
∠C-C=C	125° ± 2°	123 1/2° ± 2°	126° ± 1°

The old results for isobutene (2) and cis butene-2 (3) are listed in Table 6.

Table 6

	Isobutene	Cis butene-2
C-C	1.54 A	1.54 A
C=C	1.34 A	1.38 A
C-C=C	124 1/4°	125°

The failure of the previous investigators to observe any single bond shortening in these molecules may be attributed to the fact that their data did not extend into the critical region ($60 < q < 80$) for the determination of the C-C/C=C ratio, cutting off at about $q = 63$ for isobutene and at $q = 45$ for cis butene-2. The C-C/C=C ratio may be varied over wide limits without showing any disagreement with their data.

There is also a quantitative disagreement between the old results and the present, which reflects the accuracy of measuring the photographs. In the case of isobutene, the old data give an average carbon-carbon distance for the molecule of 1.470 A, compared with 1.449 A on the basis of the new data, a disagreement of 1.4%, while for cis butene-2, the values are 1.485 A and 1.450 A, a disagreement of 2.4%. The inner part of the diffraction pattern is the most difficult to measure accurately because of the steep background which tends to deceive the eye as to the true position of the maxima and minima. In addition, the percentage error in the q/q_o values for the inner rings is relatively greater for a given absolute error in the measurement of a ring position. Since the old results are based on a few features lying chiefly in the region of the diffraction pattern which is very difficult to measure accurately, they cannot be considered reliable.

Another factor which probably contributes to this quantitative disagreement is the degree of accuracy to which the wave length of the electrons is known. The voltage regulation on the new apparatus in these laboratories is much better than it was on the apparatus on which the old work was done. Voltage fluctuations during a given experiment are of the order of a few hundredths of a percent. Reproducibility, as determined from zinc oxide calibration photographs taken at different times, is better than 0.1%. This is to be contrasted with the old apparatus, where voltage drifts of the order of 1% were not uncommon. The modern experiment can therefore be considered more reliable.

The disagreement with respect to bond angles is rather small, being within the limits of error of the two determinations, but none the less deserves comment. Pauling and Brockway were unable to determine the C-C=C angle in isobutene, but assumed that it was the same as they found for tetramethylethylene, i.e., 124 1/4°. However, in view of the probable methyl group repulsions, one expects the C-C=C angle to be slightly smaller in isobutene than in tetramethylethylene, the angle in the latter lying somewhere between that found for isobutene and that found for <u>cis</u> butene-2. Brockway and Cross simply assumed a C-C=C angle of 125° for <u>cis</u> butene-2 and evidently made no survey of parameter space to test this assumption.

A part of the observed single bond shortening is probably due to a decrease in the bonding radius of the carbon atom. The covalent radius of a carbon atom for a particular bond will surely depend on the way in which all the valencies of the atom are engaged, and may be decreased if some of the valencies are involved in multiple bonding. In other words, the length of a given bond should depend on how the orbitals of the carbon atom as a whole are hybridized, and variations in hybridization will produce variations in bond length.* Some idea of the magnitude of this effect can be obtained by considering the lengths of carbon-hydrogen bonds in three situations. Herzberg and Stoicheff (10) give the following C-H bond lengths:

$-\overset{|}{\underset{|}{C}}-H$ 1.095 A $\qquad =\overset{|}{C}-H$ 1.071 A $\qquad \equiv C-H$ 1.065 A

The bonding radius of a carbon atom therefore seems to decrease by about 0.024 A if the atom is engaged in double bond formation, and by about 0.030 A if it is engaged in triple bond formation.

The remainder of the single bond shortening, about 0.020 A for propene and 0.013 A for isobutene and cis butene-2, is presumably due to hyperconjugation. A detailed discussion of this phenomenon is given by Mulliken, Rieke, and Brown (11). Using thermodynamic data, they arrive

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* This idea has been discussed by a number of investigators, for example Pauling, Springall, and Palmer (1c), Coulson (7), Duchesne (8), and Walsh (9).

at empirical hyperconjugation energies per methyl group of 1.2, 0.7*, and 0.06 kcal. for propene, isobutene, and cis butene-2 respectively. These figures are certainly compatible with the bond shortenings attributed to hyperconjugation above. They are, however, only approximate, and are subject to corrections which could easily amount to several tenths of a kcal. The reader is referred to reference 11 for more details.

The infrared spectrum of ethylene was studied by Gallaway and Barker (12), and they arrived at a value of 1.353 A for the C=C bond length. Using Gallaway and Barker's value for the rotational constant A_o and a more recent value of B_o determined from the Raman spectrum (13), Stoicheff (14) calculated a value of 1.344 A for the double bond length in ethylene. This latter value is in better agreement with the double bond lengths found for the simple olefins studied in the present investigation. The H-C-H angle in ethylene, 119°55' (12), is very nearly the 120° which would be expected, according to Coulson (15), if the orbitals of the carbon atoms were pure sp^2 orbitals. However, as soon as one or more of the hydrogen atoms in ethylene are replaced by methyl groups, the bonding situation seems to change somewhat, so that the bonding is no longer sp^2. The resulting bonding is characterized by a considerable change in bond angle, and possibly by a slight decrease in the length of the double bond, although the uncertainties in the structure determinations are sufficient to leave the latter open to question.

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* Their Table VIII gives 1.45 for this value, but this is evidently a computational error.

The difference in bond angle between propene and isobutene may be due in part to a difference in hybridization occurring when two methyl groups are bonded to the same carbon atom instead of only one. Distortion resulting from steric and electrostatic repulsion of the methyl groups could account for the remainder of the difference.

The C-C=C angle observed for cis butene-2 differs from that found in propene by 1°. This difference can be explained in terms of the mutual repulsion of the two methyl groups. Although the methyl carbon atoms are much farther apart in cis butene-2 than in isobutene, the orientation of the methyl groups is such that they show more mutual interference in cis butene-2. This can easily be verified by making a drawing of the molecules to scale using any arbitrary radius for the hydrogen atoms greater than 1 A. The matter of methyl-methyl repulsions will be discussed in more detail later.

The dipole moments of propene (16) and isobutene (17) are 0.34 and 0.49 D. A value for cis butene-2 is not available. If the value for propene is taken as a standard, and if the dipole moment is considered as a sum of vector components, one for each methyl group along the direction C...C rather than along C-C (see Fig. 4), a simple trigonometric calculation gives $\mu = 0.54$ for isobutene, in good agreement with the experimental value.* Similarly, a value of 0.33 D is calculated

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* This is, of course, a maximum value for the calculated dipole moment of isobutene. It could be brought into exact agreement with experiment by directing μ_1 and μ_2 from C_1 to a point a short distance along the double bond toward C_2. However, the data are probably not precise enough to merit further consideration. Nevertheless, it is interesting that this crude analysis produces some clue regarding the charge distribution in the molecule independent of any theoretical valence considerations.

for the dipole moment of <u>cis</u> butene-2.

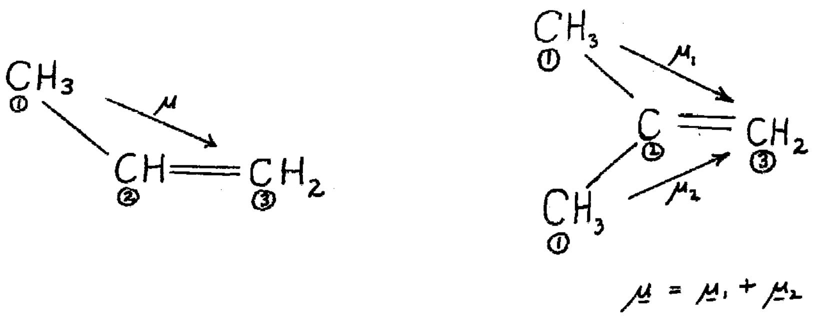
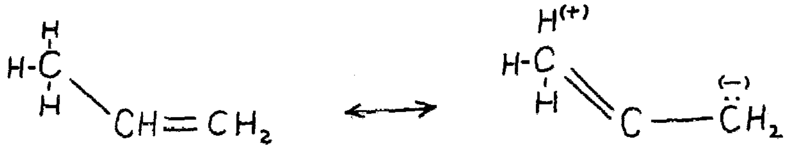


Figure 4

Structures such as



are sometimes written for propene to explain bond shortening. It is interesting that the observed dipole moment limits the contribution of such ionic structures to the extent that they can account for a bond shortening of only about 0.01 A.

THE INTRAMOLECULAR REPULSION OF METHYL GROUPS

It was suggested on page 19 that the difference in the C-C C bond angle between cis butene-2 and propene is the result of the mutual repulsion of the methyl groups in cis butene-2. This point will now be considered in more detail.

The heats of hydrogenation of cis and trans butene-2 differ by 1 kcal./mole (18). Since the two molecules hydrogenate to the same molecule, this difference must reflect a difference in energy between the two olefin molecules. This energy difference can be satisfactorily explained as arising principally from the repulsion of the two methyl groups in cis butene-2. The interaction of the methyl groups in trans butene-2 is assumed to be small.

Consider the interaction of the two methyl groups to be very similar to the interaction of two methane gas molecules undergoing collision. Assume that a Lennard-Jones potential function of the form

$$V = 4\epsilon\left[(\sigma/r)^{12} - (\sigma/r)^{6}\right]$$

is applicable, where ϵ is the depth of the potential minimum, r is the distance between the two methyl carbon atoms, and σ is the effective "collision" diameter. The appropriate value of σ is obtained by the relation $r_e = 2^{1/6}\sigma$, where r_e, the equilibrium internuclear distance, is assigned the value 3.6 A. This is roughly the minimum intermolecular contact distance for methyl groups in crystals (19). The empirical value of ϵ for methane is used (20). The potential energy curve is shown in Fig. 5.

The methyl-methyl distance in cis butene-2, 3.10 A, falls on the potential energy curve at a point about 0.60 kcal. above the potential minimum. Since trans butene-2 is not really at the potential minimum, the energy difference between cis and trans butene-2 is somewhat less than this, say 0.50 kcal. The slope of the curve at this point corresponds to a repulsive force of 2.72×10^{-5} dynes per molecule. This force is to be compared with the force necessary to bend the two C-C=C bond angles one degree. The two forces should, of course, be equal. For this calculation, we use the relation

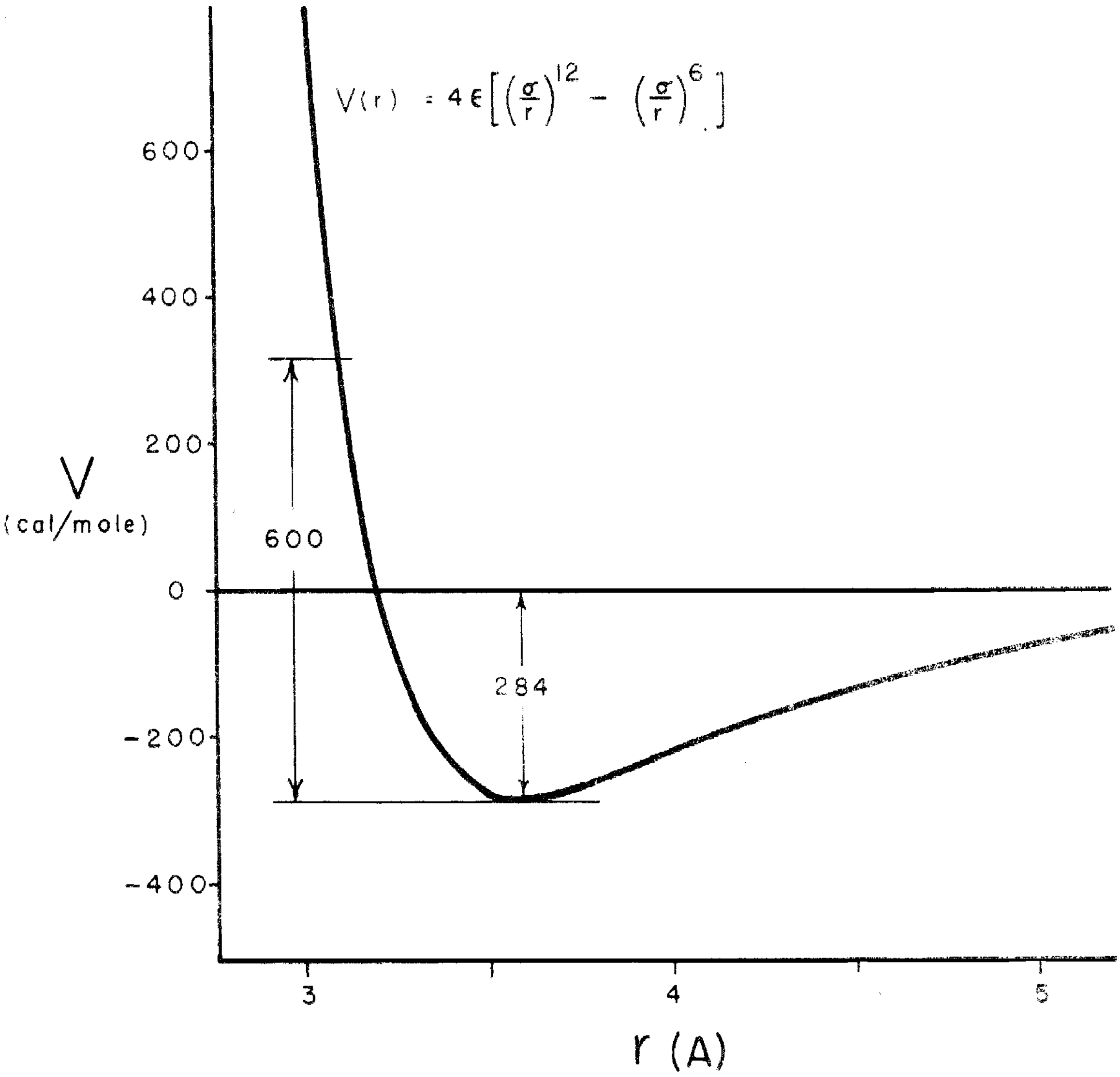
$$V = \frac{1}{2} K \ell^2 \delta^2$$

where k has the value (21) 0.5×10^5 dyne cm./radian^2, ℓ is the single bond length, and δ is the angle of distortion in radians. Putting in the appropriate numbers leads to the result V = 27 cal./mole for each distorted C-C=C angle. The force required to bend the two bond angles one degree is

$$F = 2 \frac{\partial V}{\partial(\ell\delta)} = 3.24 \times 10^{-5} \text{ dynes}$$

Considering the approximations involved, the agreement between the two forces is quite pleasing.

A simple model thus accounts for 0.50 + 0.05 = 0.55 kcal. of the 1 kcal. energy difference between cis and trans butene-2. The potential energy curve rises very rapidly with decreasing r in the region



$V(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$
600
400
200
V
(cal/mole)
0
-200
-400
600
284
3
4
5
r (A)

Figure 5

of interest, so a slightly larger value of σ would give a considerably larger energy of repulsion. Since the slope of the curve does not change very rapidly in this region, a few tenths of a kcal. more energy could be obtained without greatly unbalancing the two opposing forces. However, the original numbers are very satisfying and indicate that the assumed model is reasonable.

The fact that the model works is attributed to the physical reality of the similarity of the interactions involved in the collision of two slow methane molecules and in the repulsion of methyl groups in the same molecule. Methane molecules consist of hydrogen atoms bonded to carbon atoms, and their interaction on collision results from fields generated by the system hydrogen-bonded-to-carbon. Two such systems in the same molecule would be expected to repel one another in almost exactly the same way, since the influence of other parts of the molecule on the parts under discussion is in general relatively small. The chief difficulty in applying the method lies in choosing a proper value for σ . This value will depend on how the groups are oriented relative to one another, as well as their distance apart. A reasonable estimate may be made by considering a projection drawn to scale, using some arbitrary standard radius for the hydrogen atoms, and noting the amount the hydrogen atoms overlap.*

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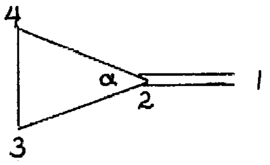
* A value of about 1.2 A for the radius of the hydrogen atom is convenient. Calculations show that about 80% of the electron is contained within a sphere of this radius (22).

METHYLENECYCLOPROPANE

The sample of methylenecyclopropane was prepared by M. Vogel. It boiled at 8.0° uncorrected. Impurities were believed to be of such a nature as not to interfere with the electron diffraction experiment.

Both ordinary and sectored photographs were obtained for this compound under the usual experimental conditions. The unsectored photographs were used only to determine the inner part of the diffraction pattern ($q < 40$). The rest of the pattern was obtained by visual examination of the sectored photographs. A microphotometer trace of one of the sectored plates was secured, and parts of it were found useful in reinforcing the visual interpretation of certain important features of the diffraction pattern. The method of working up such microphotometer data is discussed later under the structure of 1-methyl,3-methylene-cyclobutene.

The carbon atoms are numbered as indicated below, so that α is the angle C_3-C_2-C_4. Hydrogen atoms bear the same numbers as the carbon atoms to which they are bonded.



Theoretical intensity curves were calculated for the shape parameter ranges $1.49/1.33 \leq C_2-C_3/C=C \leq 1.52/1.33$ and $61^\circ \leq \alpha \leq 64^\circ$. C_3-H_3 and C_1-H_1 were assumed to be 1.09 and 1.07 A, and $\angle C_2=C_1-H_1$ to be 120°. Some question arose as to the proper value to use for the angle $H_3-C_3-H_3$. Most of the theoretical curves were calculated with this angle equal to 118°. Decreasing it to 114° has no significant effect on the curves, so this angle could not be usefully determined.* The projection of C_3-H_3 onto the plane of the molecule was assumed to bisect the angle $C_2-C_3-C_4$. Difference curves showed that reasonable variations in the temperature factors and in the various assumed quantities would not change the final bond lengths to be determined by more than a few thousandths of an A. The values of a_{ij} used in the temperature factors are listed in Table 7.

Table 7

r_{ij}	$a_{ij}(s)$
C-H	0.0023
C..H	0.0041
C-C	0.00025
C..C	0.00045
C=C	0.000

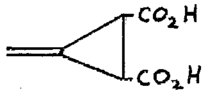
---

* A number of three-membered ring compounds having one of the methylene groups replaced by nitrogen (23), oxygen (24), or sulfur (25) have been studied by microwaves, and were all found to have H-C-H angles between 116° and 117°. The actual value in methylenecyclopropane is probably very nearly the same. Calculations by Coulson and Moffitt (26) predict an angle of 116° for cyclopropane.

The visual curve (V), radial distribution curve (RD), and a few theoretical intensity curves are shown in Fig. 6. The diffraction pattern is most sensitive to variation of α and C_2-C_3/C=C in the range $50 < q < 100$. Maxima 5 and 6 are essentially a single feature, minimum 6 being virtually non-existent. Maximum 6 contrasts with maximum 8 in that it is well above the zero line, whereas maximum 8 is below. Minima 7 and 8 are of very nearly equal depth. Maxima 11, 12, and 13 are quite broad, but their detailed shape could not be observed.

None of the calculated curves quite agrees with the experimental curve in all the essential details. The curves were improved by increasing the C-H distances put into the calculations. Values of 1.10 and 1.085 for C_3-H_3 and C_1-C_1 respectively were found satisfactory. Multiplication by the scale factor leads to final C-H bond lengths of 1.085 and 1.070 A. The best model was found by interpolating between several curves as indicated on the plot of parameter space in Fig. 7. Table 8 lists q/q_0 values for a few models.

The final parameters for methylenecyclopropane are given in Table 9, along with the equivalent parameters for Feist's acid,



, as determined in a recent crystal structure investigation (27).

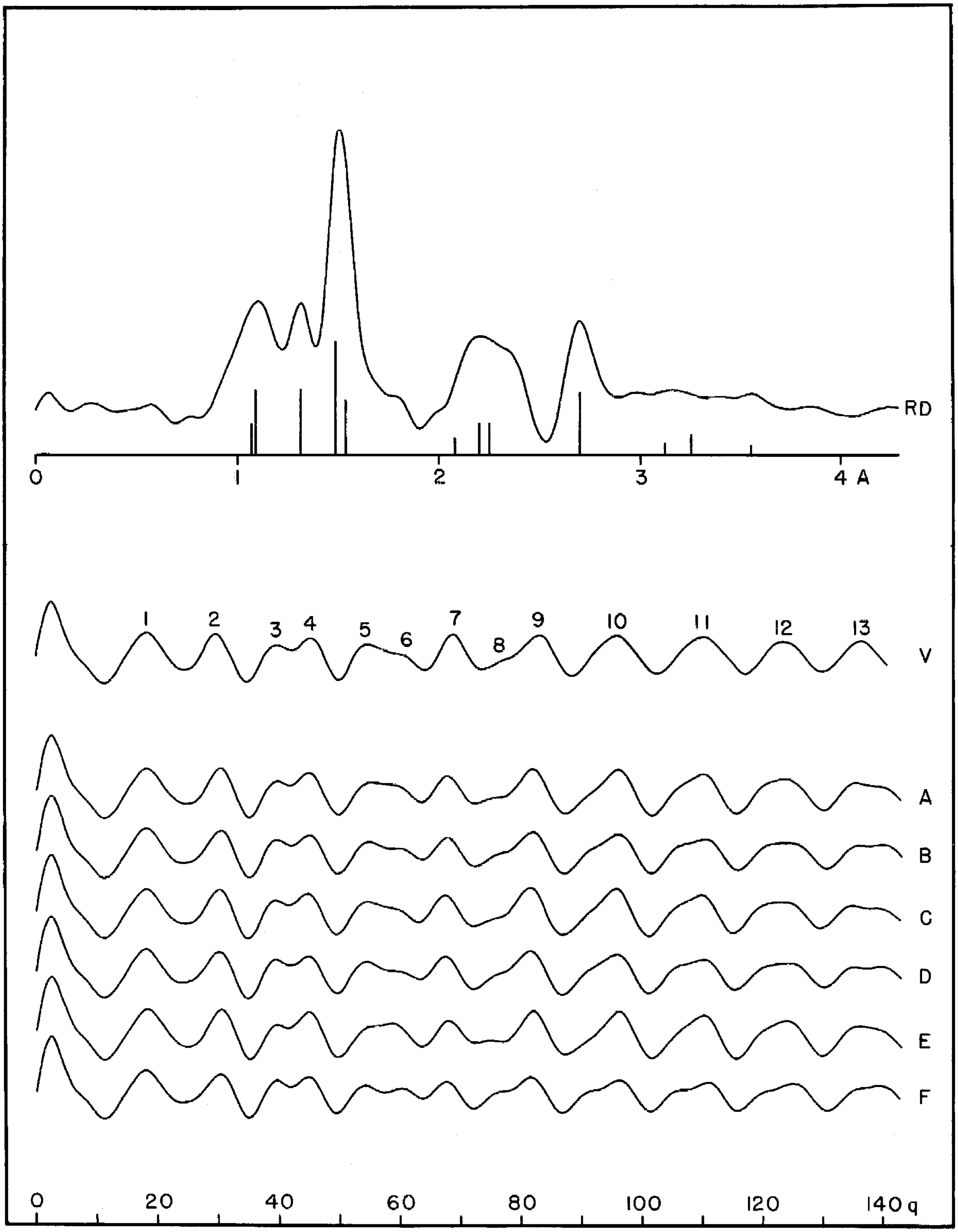

RD
0
1
2
3
4 A
1
2
3
4
5
6
7
8
9
10
11
12
13
V
A
B
C
D
E
F
0
20
40
60
80
100
120
140 q

Figure 6

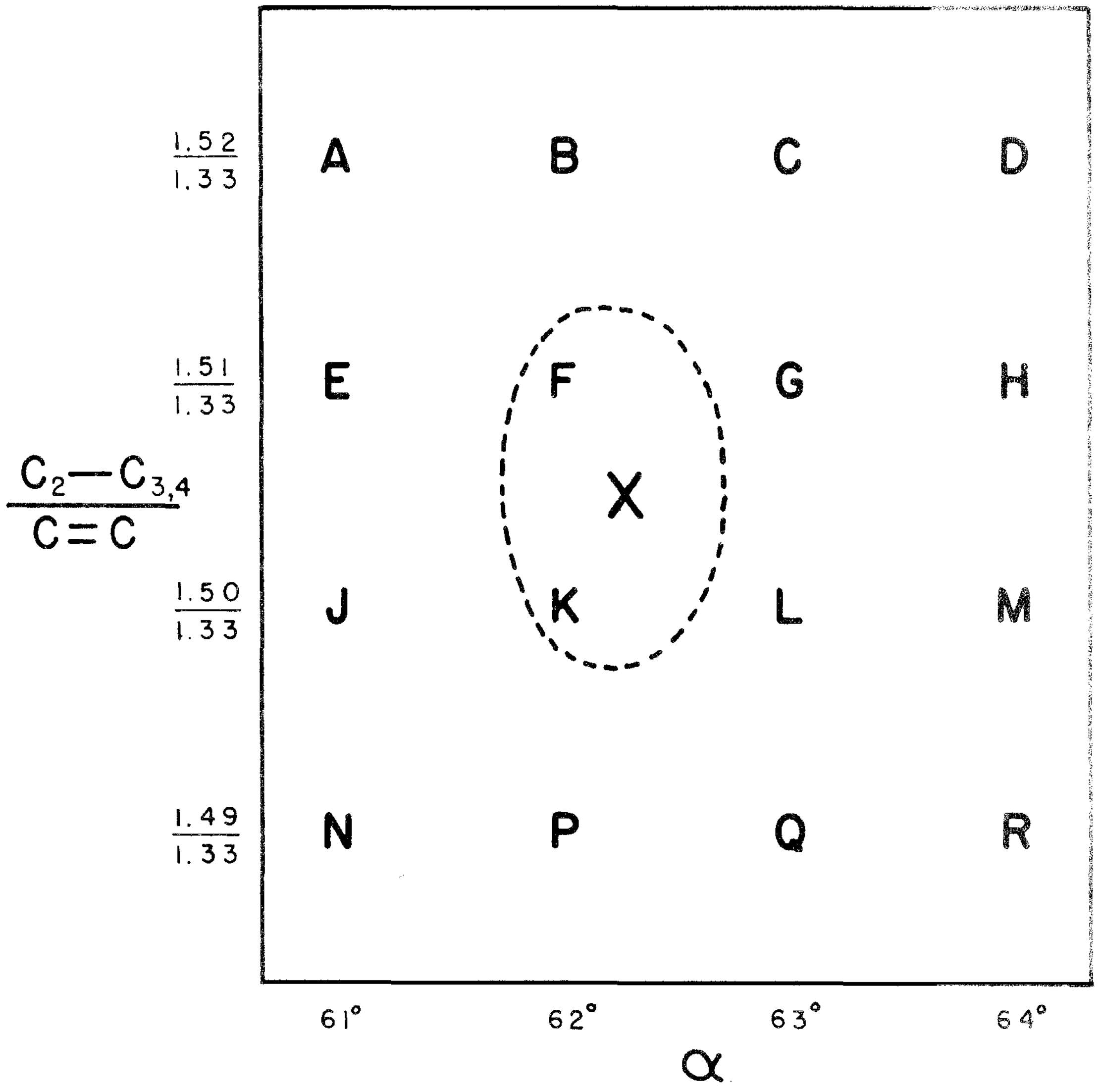

A
B
C
D
E
F
G
H
X
J
K
L
M
N
P
Q
R
1.52 / 1.33
1.51 / 1.33
1.50 / 1.33
1.49 / 1.33
$\frac{C_2—C_{3,4}}{C=C}$
61°
62°
63°
64°
α

Figure 7

Table 8

Max.	Min.	q_o	q/q_o(K)	q/q_o(L)	q/q_o(F)	q/q_o(G)
	1	(12.80)	(0.883)	(0.875)	(0.883)	(0.883)
1		(18.62)	(0.977)	(0.977)	(0.972)	(0.972)
	2	(24.83)	(1.000)	(0.983)	(0.991)	(0.983)
2		(29.61)	(1.027)	(1.027)	(1.020)	(1.022)
	3	(34.81)	(1.011)	(1.008)	(1.005)	(1.003)
3		39.96	0.991	0.991	0.986	0.988
	4	42.73	0.981	0.983	0.974	0.981
4		45.54	0.988	0.988	0.984	0.984
	5	49.95	0.997	0.997	0.992	0.993
5		(54.32)	(1.011)	(1.005)	(1.007)	(1.003)
	6	(57.67)	(0.997)	(0.997)	(0.988)	(0.997)
6		(60.35)	(0.986)	(0.994)	(0.978)	(0.996)
	7	64.40	0.989	0.989	0.981	0.984
7		68.81	0.986	0.985	0.980	0.981
	8	73.95	0.978	0.979	0.977	0.977
8		(77.11)	(0.979)	(0.982)	(0.973)	(0.982)
	9	(79.21)	(0.972)	(0.985)	(0.972)	(0.978)
9		83.01	0.987	0.985	0.983	0.982
	10	88.37	0.987	0.987	0.984	0.982
10		(95.46)	(0.998)	(0.999)	(0.994)	(0.995)
	11	102.48	0.989	0.990	0.992	0.988
11		110.33	0.987	0.987	0.983	0.984
	12	117.13	0.987	0.989	0.985	0.986
12		123.64	0.996	0.997	0.991	0.995
	13	(129.93)	(1.003)	(1.007)	(0.997)	(1.003)
13		(136.28)	(1.007)	(1.011)	(1.010)	(1.010)
Average, 13 features			0.9879	0.9882	0.9840	0.9850
Average deviation			0.0035	0.0036	0.0040	0.0038

Scale factor $\frac{3(K + F) + (L + G)}{8} = 0.9861$

Results:

C=C 1.330 x 0.9861 = 1.312 A

C_2-$C_{3,4}$ 1.505 x 0.9861 = 1.484 A

α 62.25°

Table 9

	Methylenecyclopropane	Feist's acid
C=C	1.312 ± 0.010 A	1.317 A
C_2-$C_{3,4}$	1.484 ± 0.010	1.494 (average)
C_3-C_4	1.535 ± 0.015	1.545
α	$62^{\circ}15' \pm 30'$	$62^{\circ}45'$

The bond lengths in Feist's acid have an average standard deviation* of about 0.01 A. The equivalent parameters for the two molecules are thus in fairly good agreement.

It is of interest to compare methylenecyclopropane with cyclopropane. Günthard, Lord, and McCubbin (28), from the interpretation of infrared spectra, report a value of 1.524 ± 0.014 A for the C-C bond length in cyclopropane. They were unable to determine absolute values for the C-H bond length and the H-C-H bond angle, but they could determine C-H as a function of ∠ H-C-H. The most reasonable values of C-H and ∠ H-C-H deduced from this relationship were 1.07 A and 120°. This value for C-H seems rather short, while the H-C-H angle seems a bit large. A calculation using their moment of inertia and assuming

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* Limits quoted for molecular parameters in recent electron diffraction work in these laboratories are equivalent to about 2σ, where σ is the standard deviation commonly quoted in X-ray crystal structure determinations. The parameters are therefore determined more accurately for methylenecyclopropane than for Feist's acid.

C-H = 1.086 and ∠ H-C-H = 116°, which seems reasonable, leads to a value of 1.511 A for the C-C bond length. H. Pfeiffer (29) found a C-C bond length of 1.518 A in an electron diffraction investigation. This value is squeezed down to about 1.507 A if the model is forced to fit the spectroscopic moment of inertia. Dunitz and Schomaker (30) calculate a value of 1.504 A for the C-C bond length in cyclopropane from the relationship $d = 1.542 \sin \theta / \theta$, where θ is the half angle strain. Preliminary results of an electron diffraction investigation by Almenningen and Bastiansen indicate a C-C bond length of 1.504 A (31). The bulk of the data thus seems to favor a value of 1.51 A or less for the C-C bond length in cyclopropane. For convenience in the following discussion, we will assume that the C-C bond length in cyclopropane is 1.51 A.

The C-C bonds in the three-membered ring would presumably be even shorter were it not for the partial relief in strain provided by the expanded H-C-H angles. The central carbon atom in spiropentane does not have this strain relieving factor, so it is not surprising that the average C-C bond length in this molecule, 1.49 A (32), is shorter than in cyclopropane. The only relief from strain for the central carbon atom in spiropentane results from a small amount of differential angle strain which arises from the peripheral carbon atoms, with their expanded H-C-H angles, being less strained than the central carbon atom. The experimental bond lengths are central C-C = 1.48 A and peripheral C-C = 1.51 A (32).

One might expect the single bonds in methylenecyclopropane to be even shorter than those in spiropentane, if the former is considered the limiting case of angle strain in the series 1,1-dimethylcyclopropane*, spiropentane, methylenecyclopropane. However, the average C-C bond length in methylenecyclopropane, 1.501 A, although shorter than in cyclopropane, is longer than in spiropentane. This apparent anomaly can perhaps be explained in terms of effective angle strain as measured by strain energy, instead of nominal angle strain. If we consider strain energy per methylene group, the results are not very satisfying. For example, from the heats of combustion per methylene group of cyclohexane (33) (unstrained), cyclopropane (34), and ethylene (33), we obtain strain energies per methylene group of 9.2 kcal. for cyclopropane and 11.1 kcal. for ethylene. If, however, we consider the strain energy per methylene group in a double bond as the C-C bond energy less half the C=C bond energy**, we get a strain energy of 8.6 kcal., to be compared with the value of 9.8 kcal. derived from bond energies and the heat of formation of cyclopropane. Neither of these calculations is completely satisfactory, and perhaps all we can infer is that the strain energy per methylene group is roughly the same for a double bond and a cyclopropyl ring. However, another point of view is to consider the total strain, which is about 50% greater in a cyclopropyl ring than in a double bond.

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* Unfortunately, no structural parameters are available for this compound. The bonds in the ring, however, should differ negligibly from those in cyclopropane.

** Bond energies are taken from reference 35.

The double bond in methylenecyclopropane contributes less strain to the molecule as a whole than does the second cyclopropyl ring in spiropentane. If we accept this assessment of the effective angle strain along with the rather general observation that bonds under angle strain tend to be short and that this shortening is greater the greater the strain, then the fact that the ring bonds are longer in methylenecyclopropane than in spiropentane becomes reasonable.

It is realized that the arguments in the preceding paragraph are weak. Reliable heats of combustion for methylenecyclopropane and spiropentane* would be of considerable help. Perhaps a redetermination of the structure of spiropentane is also in order.

Differential angle strain in methylenecyclopropane, which stretches the C_3-C_4 bond about 0.025 A, would tend to shorten the C_2-$C_{3,4}$ bonds by about half that amount, or about 0.013 A. The remaining shortening observed in the C_2-$C_{3,4}$ bonds may be accounted for by hyperconjugation and possibly rehybridization**.

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* Humphrey and Spitzer (36) found a value of 785.3 kcal./mole for the heat of combustion of spiropentane. This leads to a strain energy in spiropentane which is less than twice the strain energy in cyclopropane, which does not seem reasonable. However, they had considerable trouble in getting a complete combustion, so their answer could well be a little low. A value one or two percent higher would yield a strain energy in better agreement with what elementary strain considerations would predict.

** The value of 0.025 A suggested on page 17 for shortening due to the decreased bonding radius of a trigonal carbon atom would not be expected to apply in this case. The shortening of the C-C bonds in cyclopropane is probably due at least in part to rehybridization (23), and it is not clear how much more shortening from this source, if any, the presence of the double bond would induce.

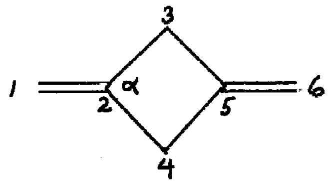
The double bond in methylenecyclopropane, 1.312 A, is rather short. It is suggested that this shortening is caused by strain, i.e., the short double bond helps minimize the strain in the molecule. Allene, with its two adjacent double bonds of length 1.309 A (14), presents a similar situation; the double bonds are strained and also short. Another example of a molecule with a short double bond is cyclopropene, $C=C = 1.28_6 \pm 0.04$ A (37), and this molecule is also highly strained.

1,3-DIMETHYLENECYCLOBUTANE

The sample of 1,3-dimethylenecyclobutane (DMC) was prepared by Dr. F. F. Caserio. It is a colorless liquid, boiling at 68°C. Its configuration was confirmed by nuclear magnetic resonance and infrared spectra.

Both sectored and unsectored diffraction photographs of DMC were made, using Kodak Process plates for the former and Kodak 50 plates for the latter. The camera distance was about 10 cm. and the accelerating potential about 40 kv. The unsectored photographs were used only to obtain data for the region $q < 30$. The sectored photographs were interpreted visually and provided the bulk of the data.

The carbon atoms are numbered as indicated below; α is the angle C_3-C_2-C_4. Hydrogen atoms bear the same number as the carbon atoms to which they are bonded. The molecule was assumed to have C_{2v} symmetry.



For purposes of simplicity and clarity in the actual determination of this structure, we distinguish between major and minor shape parameters. The major shape parameters are the ratio C-C/C=C, the angle α , and the dihedral angle. The remaining shape parameters are designated minor parameters and have the properties that (1) reasonable variations in them produce only small changes in the calculated curves and (2) more accurate values for them can in general be guessed a priori than can actually be determined. Each minor parameter is assigned some reasonable value which is held constant in all the theoretical curves calculated in the process of determining the major parameters. Difference curves are calculated to test the effect of changing individual minor parameters. In the final analysis, after the major parameters have been determined as well as possible, the minor parameters are altered as necessary to produce the best possible fit with the experimental intensity curve. With the difference curves available, it is possible to keep clearly in mind the effects on the curves of varying the minor parameters when accepting or rejecting the theoretical curves calculated in the process of surveying major parameter space.

Theoretical intensity curves were calculated for planar models in the shape parameter ranges $1.51/1.34 \leq C-C/C=C \leq 1.56/1.34$ and $91^\circ \leq \alpha \leq 95^\circ$. In addition, a number of curves were calculated for models bent up to 20°. In calculating the curves, methylenic and ethylenic C-H were assigned the values 1.09 and 1.07 A respectively; $\angle H_3-C_3-H_3$ was taken as 118°, and $\angle H_1-C_1-H_1$ as 120°. Values of a_{ij} in the temperature factor $e^{-a_{ij}s^2}$ are listed in Table 10.

As theoretical intensity curves were calculated, it became apparent that the region most difficult to interpret precisely on the photographs, $50 < q < 70$, was also the region most sensitive to variations in the major parameters. Maximum 6 appears to have a slight bump at its base where it merges into minimum 7. The exact shape of minimum 7

Table 10

r_{ij}	a_{ij}
C-H	0.0023
C..H	0.0041*
C-C	0.00025-0.00045**
C..C	0.00045
C=C	0.0000

is difficult to judge, except that it is rather flat and shallow and seems to slope upward slightly into the base of maximum 6. Due to this uncertainty, some latitude was allowed in the shape of this feature when accepting or rejecting theoretical models. Maxima 7 and 8 appear as a doublet, with maximum 8 slightly broader and stronger than 7. There are only a few other features which can be used for criteria of acceptability. Maximum 2 has a slight bump outside. Maximum 6 is considerably higher than the average of 5 and 8. The difference in intensity between minimum 7 and maximum 8 is less than the difference between minimum 5 and maximum 5.

The visual curve (V), radial distribution curve (RD), and a few theoretical intensity curves are shown in Fig. 8 . Among the planar

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* Except $a_{C_2..H_1} = 0.0030$

** A value of about 0.00035 seems best.

Legend for Figure 8

Model	C-C/C=C	α	Dihedral angle
A	1.52/1.34	92°	0°
B	1.53/1.34	93	0
C	1.54/1.34	92	0
D	1.54/1.34	93	0
E	1.55/1.34	92	0
F	1.55/1.34	93	0
G	1.56/1.34	92	0
H	1.54/1.34	91	0
J	1.54/1.34	94	0
K	1.54/1.34	92	10

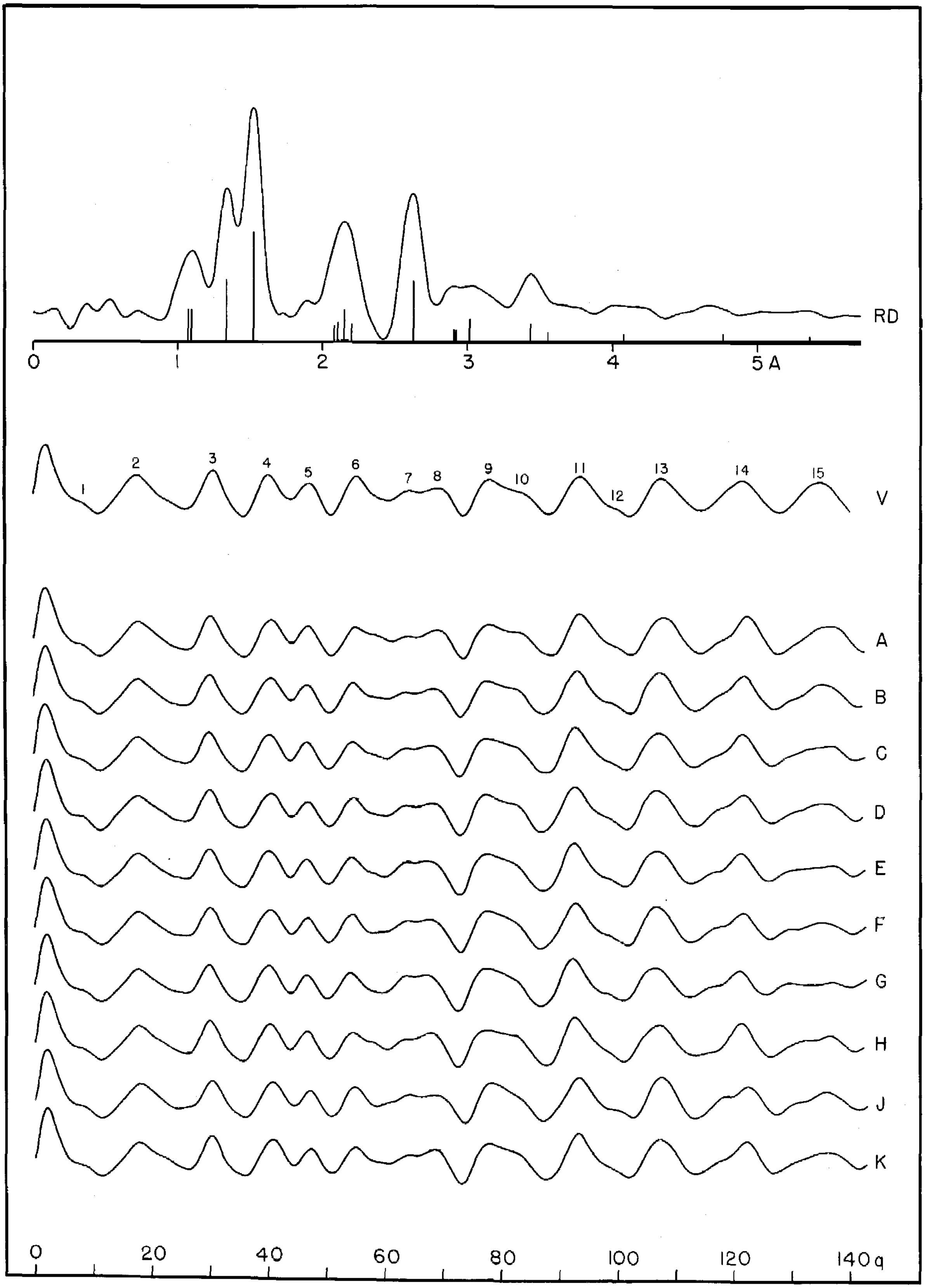
RD
0
1
2
3
4
5 A
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
V
A
B
C
D
E
F
G
H
J
K
0
20
40
60
80
100
120
140 q

Figure 8

models, A has the wrong appearance in the region $40 < q < 75$. Models B, C, D, E, and F reproduce the overall appearance of the photographs pretty well, although E and F are slightly less satisfactory than the others in the region of minimum 7 and maxima 7 and 8. The difference in intensity between minimum 7 and maximum 7 in model G is great enough to reject this model. Also maxima 7 and 8 are too nearly equal. In model H, minimum 7 does not have the correct shape, maximum 6 is too weak, and maximum 8 is much too strong. In model J, the bottom of minimum 2 has the wrong shape, as does minimum 7, and maxima 7 and 8 are too nearly equal. Model K, which is the same as model C except for a dihedral angle of 10°, shows the bump on the outside of maximum 2 which does not appear on any of the planar models except model D. Minimum 7 is acceptable, but maximum 8 is a little too strong. Increasing the angle α by only 1° over its value in model C makes models with a dihedral angle of 10° unacceptable in the region $55 < q < 70$; dihedral angles over 10° also cause trouble in this region.

The best model is an average of models C and D, with the addition of a small dihedral angle*, yielding the following parameters:

C-C	1.526 ± 0.012 A
C=C	1.328 ± 0.012 A
α	$92.5^\circ \pm 1^\circ$
dihedral ∠	$5^\circ \pm 5^\circ$

Values of q/q_o for models C and D are listed in Table 11.

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[*] The dihedral angle presumably refers to an average configuration, with the molecule vibrating back and forth through the planar equilibrium configuration.

Table 11

Max.	Min.	q_o	q/q_o(C)	q/q_o(D)
	1	6.92	(0.983)	(0.983)
1		8.31	(1.011)	(1.011)
	2	11.19	(1.028)	(1.028)
2		17.90	(1.006)	(1.000)
	3	26.66	(0.990)	(0.975)
3		31.08	(0.972)	(0.974)
	4	36.28	0.990	0.990
4		40.61	1.001	1.005
	5	44.61	0.993	0.998
5		47.62	0.989	0.993
	6	51.46	0.989	0.991
6		55.86	0.983	0.985
	7	60.54	(1.006)	(1.004)
7		64.27	0.998	0.996
	8	67.13	0.983	0.988
8		70.35	0.975	0.981
	9	74.14	0.988	0.991
9		78.21	0.997	0.995
10		84.30	0.985	0.983
	11	88.95	0.990	0.983
11		94.30	0.988	0.988
	12	98.79	0.992	0.992
12		100.22	0.993	0.998
	13	102.76	0.993	0.994
13		108.35	0.993	0.990
	14	115.31	0.985	0.988
14		122.16	0.999	0.992
	15	128.90	(0.987)	(0.987)
15		135.63	(1.006)	(0.999)

	q/q_o(C)	q/q_o(D)
Average, 20 features	0.9902	0.9911
Average deviation	0.0047	0.0044

Scale factor 1/2 (C + D) = 0.9907

Results:

C-C 1.526 A

C=C 1.328 A

α 92.5°

Putting the methylenic and ethylenic C-H distances into the calculations at 1.10 and 1.08 A respectively improves the curves somewhat. These parameters then become 1.090 and 1.070 A after multiplication by the scale factor. Reducing $\angle H_3-C_3-H_3$ to 114° or less causes the shape of minimum 2 and the height of maximum 6 to be slightly less attractive on the planar models, but these effects are canceled by bending the molecule a few degrees out of planarity. The distances in the best model are in excellent agreement with the radial distribution curve.

The carbon-carbon single bonds in DMC are 0.042 A shorter than those in cyclobutane, where C-C = 1.568 A (30).* The single bonds in isobutene were found to be 0.037 A shorter than the standard value of 1.542 A, and this shortening was attributed to the decreased bonding radius of a trigonally bonded carbon atom plus hyperconjugation. These two effects should cause roughly the same amount of shortening in DMC as they do in isobutene, but not exactly the same amount, since the bonding in the two molecules is not identical. For example, the trigonal carbon atom in the four-membered ring is probably not hybridized exactly the same as the trigonal carbon atom bonded to the methyl groups in isobutene, so there may be a difference in the bonding radii of the trigonal carbon atoms in the two molecules. In addition, some extra shortening should appear in DMC because of angle strain, which is greater in DMC than in cyclobutane, and not present at all in isobutene.

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* A preliminary report on a new electron diffraction study of cyclobutane (31) gives a C-C bond length of 1.546 A, considerably shorter than the old value. The final results of this investigation are awaited with great interest.

It is interesting to compare DMC with methylenecyclobutane, which has an average carbon-carbon single bond length of 1.55 A (38). If the bonds opposite the double bond are assumed to have the length 1.568 $+ \epsilon$, longer by ϵ than in cyclobutane because of differential angle strain, then the bonds adjacent to the double bond would have a length of 1.532 $- \epsilon$, in essentially perfect agreement with the bond lengths observed in DMC if, as seems reasonable from other estimates of differential angle strain (39), ϵ amounts in this case to a few thousandths of an Angstrom. In addition, the angle strains in DMC are greater than in methylenecyclobutane, and this could account for some of the difference between 1.532 and 1.526 A, to say nothing of error in the two structure determinations.

The double bonds in DMC are also short. The ratio of the double bond shortening in DMC to that in methylenecyclopropane is very nearly the ratio of the half angle strains on the ring trigonal carbon atoms in the two molecules. This lends some support to the suggestion on page 35 that the double bond shortening is connected with strain.

The apparent dihedral angle of 5° in DMC may be compared with the value of 20° found in cyclobutane (30). The torsional strain which tends to favor the non-planar configuration in cyclobutane should be quite small in DMC. Also, the greater angle strain in DMC would tend to favor the planar configuration. The smaller apparent dihedral angle in DMC is therefore not surprising.

The value found for α seems quite reasonable. It would be expected to be greater than 90° because of the greater strain involved in distorting the bond angles of a trigonally bonded carbon atom compared with those of a tetrahedrally bonded carbon atom.

The rather short $C_2 \cdot\cdot C_5$ distance in this molecule, 2.10 A, suggests the possibility of a bonding interaction across the ring. The observed value of α might be determined in part by such an interaction. However, if such an effect does exist, the absence of any severe abnormality in the observed molecular parameters suggests that it is not a large one.

1-METHYL-3-METHYLENECYCLOBUTENE

A sample* of a compound believed to be 1,3-dimethylenecyclobutane was submitted for a structure determination by electron diffraction. The infrared spectrum and the preliminary electron diffraction work cast considerable doubt on the compound's actually being what it was supposed to be. Later, the nuclear magnetic resonance spectrum was obtained and interpreted in terms of 1-methyl-3-methylenecyclobutene (MMC), and finally authentic 1,3-dimethylenecyclobutane was produced. But since the electron diffraction data had already been obtained, and since providing a confirmation and details of the structure of MMC was also of interest to the writer, the electron diffraction work was continued.

The sample was a pale, straw-colored liquid boiling at 68.5°C. It polymerized easily at room temperature, but could be safely stored at dry ice temperature.

Diffraction photographs were taken on Kodak Process plates, using a rotating sector. The camera distance was about 10 cm. and the wave length about 0.06 A. Photographs made with both the large and small sector beam stops provided data extending from about $q = 13$ to $q = 140$. Microphotometer traces** of a few of the best plates were prepared, the

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* Prepared by Dr. D. H. Parker

** The writer wishes to thank Professor J. L. Greenstein for permitting the use of the Astrophysics Department microphotometer for this work.

plates being spun about the center to average out blemishes. The final experimental intensity curve was derived from the microphotometer traces by a series of operations which will be described in some detail.

The complete equation for the scattering of electrons by randomly oriented gas molecules is

$$I(s) = \text{const.}\ \frac{1}{s^4}\left[\sum_i (Z_i - f_i)^2 + \sum_i Z_i S_i + \sum_{i \neq j} (Z_i - f_i)(Z_j - f_j)\, e^{-a_{ij}s^2} \frac{\sin s r_{ij}}{s r_{ij}}\right]$$

The first two summations represent the atomic and inelastic scattering which give rise to the smooth background observed on the photographs. The third summation is the structure sensitive part of the scattering expression, and is all we shall be concerned with for the present. This expression may be rewritten as

$$s I(s) = \text{const.}\ \frac{1}{s^4} \sum_{i \neq j} \frac{(Z_i - f_i)(Z_j - f_j)}{r_{ij}}\ e^{-a_{ij}s^2}\ \sin s r_{ij}$$

which in the present case is approximated by (40)

$$s I(s) = \text{const.}'\ (Z_c - f_c)^2\ \frac{1}{s^4} \sum_{i \neq j} \frac{Z_i Z_j}{r_{ij}}\ e^{-a_{ij}s^2}\ \sin s r_{ij} \qquad (1)$$

The problem is to put the microphotometer data in such a form that they may be easily compared with calculated theoretical intensity curves.

For each plate, a full scale (0-100% transmittance) microphotometer trace was made. But since the actual transmittance of a given plate varied over only a few percent, these traces were used only to fix the transmittance scale on other traces made at much higher amplification. A q scale was placed on the traces and the deflections at integral q values were read with a centimeter scale and converted to transmittances and to optical densities. Optical density of the plates is here designated by I_p.

The corrections necessary to put the data in the desired form are indicated on the left of equation 2.

$$\left[\frac{r^3}{\alpha}\frac{q^3}{r^3}\frac{1}{\cos^3\theta}\, q\, I_p - B\right]q = (z_c - f_c)^2 \sum \frac{z_i z_j}{r_{ij}}\, e^{-a_{ij}s^2} \sin s r_{ij} = sI(s) \quad (2)$$

The term α measures the angular opening of the sector. It was convenient to introduce it as the factor r^3/α, where r is the distance from the center of the sector. The factor $1/\cos^3\theta$ corrects for the diminishing of intensity with increasing scattering angle arising from the use of a flat photographic plate. B is the background arising from atomic and inelastic scattering, as well as stray scattering from the apparatus, and is subtracted graphically.

Three overlapping traces were required to cover the entire diffraction pattern from q = 13 to q = 140, and up to this point, these were treated separately. The three traces had different intensity scales, i.e., were traced at different amplification. After subtracting the background, they were plotted on the same paper, and the overlapping regions were used to obtain factors for putting all three sections on the same intensity scale. Now if, after completing the operations indicated on the left of equation 2, the curve is divided by $(Z_c - f_c)^2$, the result is a curve of the form

$$sI(s) = e^{-a_{c=c} s^2} \sum_{i \neq j} \frac{Z_i Z_j}{r_{ij}} e^{-\delta a_{ij} s^2} \sin s r_{ij} \qquad (3)$$

where $a_{c=c} + \delta a_{ij} = a_{ij}$. Equation 3 is of the form used for calculating theoretical intensity curves in ordinary visual work, with the exception of the factor $e^{-a_{c=c} s^2}$. For ease in calculation, this factor was omitted when calculating curves until a reasonably good fit with the experimental curve was obtained. It was then included in the best models for final comparison with the experimental curve.

It should be mentioned that the point at which the background is subtracted is largely a matter of convenience. Subtracting a very steep background or one with a very large curvature introduces large errors. On some of the traces, better results were obtained by subtracting the background from $(r^3/\alpha)(q^3/r^3)I_p q^{1/2}$, then multiplying by $q^{3/2}$. The inner part of the pattern had a sharply curving background.

In order to reduce this curvature, the corrected I_p was multiplied by a modification function, which was then divided out after subtracting the background.

Since microphotometer data for $q < 13$ was lacking, this portion of the experimental curve was copied from a theoretical intensity curve. When the complete experimental intensity curve was plotted, it was obvious that there was considerable error in the position of the zero line in the region $q < 50$. It was later found that if the peaks appearing below 0.9 A on the radial distribution curve were transformed and subtracted from the original experimental curve, this error in the zero line was greatly diminished. The final experimental intensity curve includes this correction.

The MMC molecule has too many parameters for a complete structure determination. The method of attacking the problem was to postulate a few models based on the interpretation of the radial distribution curve combined with structural knowledge derived from other molecules, then to vary bond angles and temperature factors in an effort to obtain a good fit by the correlation procedure. It was thereby possible to obtain reasonably good values for a number of parameters without making a complete survey of parameter space.

Considerable structural information was obtained from the analysis of the radial distribution curve (shown in Fig. 9). The partial resolution of the complex peak at about 1.4 A suggests that one of the single bonds is rather short. This peak also indicates an average carbon-carbon single bond distance of about 1.505 A. The peak at about 2.1 A contains a number of distances, including the cross-ring terms, so the average cross-ring distance could not be determined directly with any accuracy. The complex peak at 3.3 to 3.6 A contains principally the $C_3 \cdot\cdot C_5$ and $C_1 \cdot\cdot C_6$ distances[*], making it possible to set rather narrow limits on values for these two distances. The $C_1 \cdot\cdot C_6$ distance at 4.86 A is clearly resolved. The peak at 2.65 A contains the distances $C_2 \cdot\cdot C_5$, $C_4 \cdot\cdot C_5$, $C_2 \cdot\cdot C_6$, and $C_4 \cdot\cdot C_6$, in addition to one small C-H term. Therefore the average value and the limiting values for these distances are immediately deduced. The shape of this peak also suggests that one of these distances is quite a bit longer than the average of the other three.

In constructing models, the following very reasonable assumptions, based on structural knowledge derived from other molecules and on minimizing strain in this molecule, were utilized:

C_1-C_4	shortest single bond because of first order conjugation.
C_1-C_2	longest single bond because of differential angle strain.
C_2-$C_3 \leq C_1$-C_2	
C_3-C_6	assumed to be 1.50 A, from isobutene value.
C_1=C_5	assumed to be 1.33 A, from DMC value.
C_3=C_4	assumed to be 1.35 A, greater than normal because of cross-ring repulsions.

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[*] See Fig. 10 for the numbering of the carbon atoms. Hydrogen atoms bear the same numbers as the carbon atoms to which they are bonded.

$\angle C_4-C_1-C_2 > \angle C_1-C_2-C_3$ from strain considerations.

$\angle C_1-C_4-C_3 \geq C_2-C_3-C_4$ from strain considerations.

These assumptions, combined with the information derived from the radial distribution curve, enable the carbon skeleton to be constructed with only small possibilities for variation, except for the exocyclic bond angles, which can vary over a range of about 20°, though not independently, and still give distances which fit the radial distribution curve. (Although the $C_1 \cdot\cdot C_6$ and $C_3 \cdot\cdot C_5$ distances are known fairly accurately from the radial distribution curve, they are rather insensitive to considerable changes in the exocyclic bond angles.)

The information thus far derived was used to construct models by means of accurate scale drawings, proceeding by trial and error until a good fit with the available data was obtained.

In calculating theoretical curves, the following assumptions were made: methyl and methylenic C-H = 1.10 A, ethylenic C-H = 1.07 A, $\angle H_2-C_2-H_2 = 116^\circ$ (with the plane of $H_2-C_2-C_2$ bisecting the angle $C_1-C_2-C_3$), $\angle H_5-C_5-H_5 = 120^\circ$, and $\angle C_3-C_4-H_4 = 131^\circ$.

The calculated curves were found to be quite sensitive to changes in the exocyclic bond angles, enabling them to be determined with some accuracy.

Only slight variations in the four-membered ring are possible, if good agreement with the radial distribution curve and the assumptions listed on page 51 is to be preserved, and these involve altering the relative single bond lengths. Some of the best calculated curves are shown in Fig. 9. These all have the exocyclic bond angles and temperature factors adjusted to give the best fit with the experimental curve. Model A fits the experimental curve pretty well in all the essential features, except that minimum 7 is much too shallow. This deficiency is corrected in model C. Model B, which is the same as C except C_1-C_2 is lengthened 0.01 A to 1.53 A, shows some slight disagreement with the experimental curve in the depth of minimum 7, but otherwise is quite good. Model D, with all the ring single bond distances equal, is clearly unacceptable, the shapes of maxima 5, 6, 8, 9, and 11 being quite incorrect. The best model is taken to be an average of models B and C.

Values of q/q_o for the two best models are listed in Table 12. Table 13 lists values of the temperature factors found best. The final bond lengths and bond angles, along with limits of error estimated from the radial distribution curve, theoretical curves or both, may be found in Table 14. For convenient reference, a projection of the molecule showing bond lengths and bond angles is shown in Fig. 10.

The C_5..C_6 distance on the best model is about 0.02 A longer than the peak on the radial distribution curve indicates. Similarly, if the C_1..C_6 distance were about 0.01 A shorter, it would fit the radial distribution curve better. These small discrepancies might be due to experimental error, but a more satisfying explanation may be that the out-of-plane bending vibrations cause the average position of the C_3-C_6 bond, and possibly to a lesser extent the C_1-C_5 bond, to be a few degrees out of the plane of the molecule. Such a situation would shorten the aforementioned distances without significantly affecting the other distances in the molecule.

Figure 9

Single bond distances in the four-membered ring for the theoretical models shown

Bond	Model A	Model B	Model C	Model D
C_1-C_2	1.54	1.53	1.52	1.51
C_2-C_3	1.53	1.52	1.52	1.51
C_1-C_4	1.46	1.46	1.46	1.51

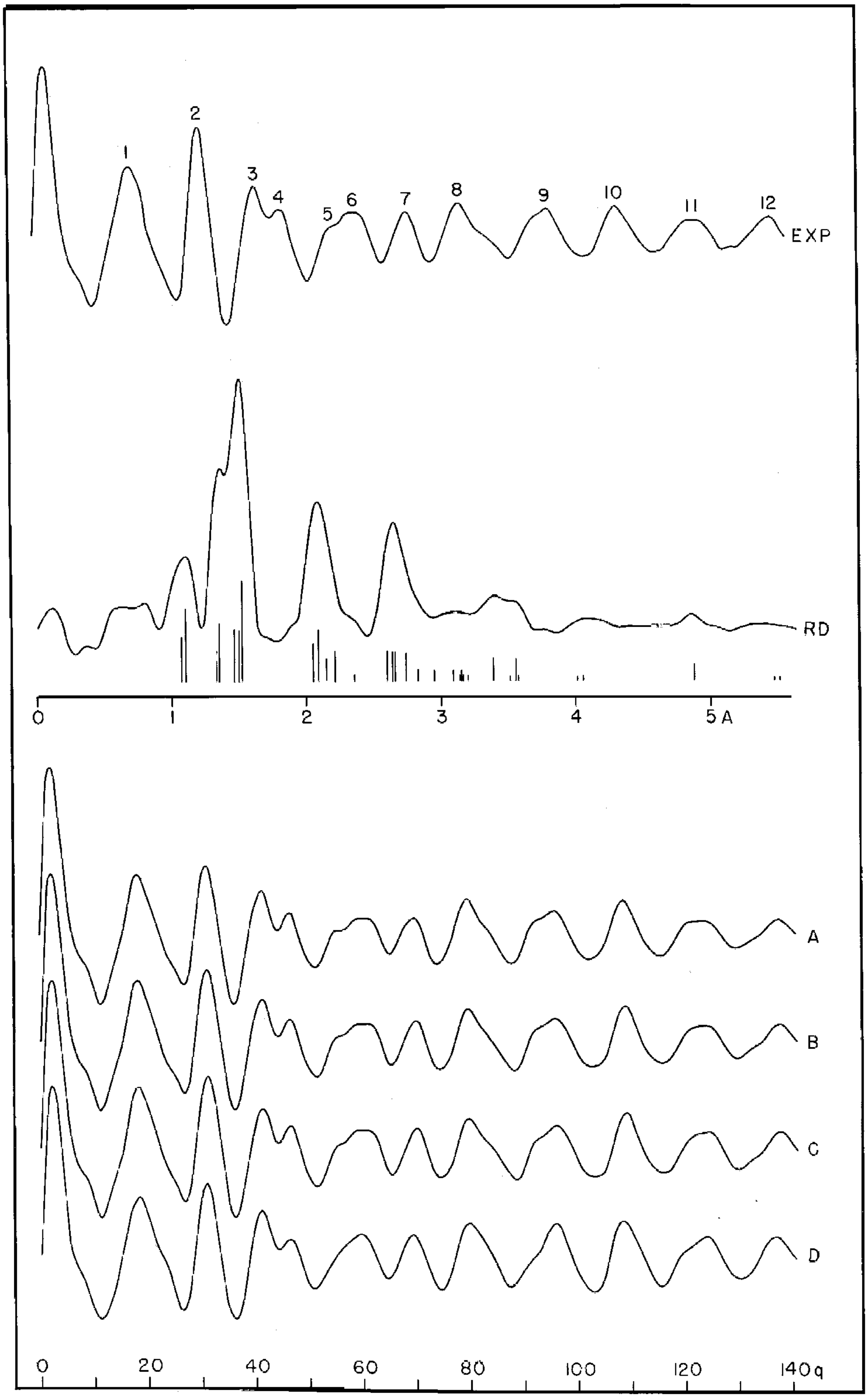
1
2
3
4
5
6
7
8
9
10
11
12
EXP
RD
0
1
2
3
4
5 A
A
B
C
D
0
20
40
60
80
100
120
140 q

Figure 9

Table 12

Max.	Min.	q_o	$q/q_o(B)$	$q/q_o(C)$
	1	11.2	1.000	1.000
1		18.0	1.011	1.011
	2	26.8	1.000	1.000
2		30.8	1.006	1.006
	3	36.2	1.000	1.000
3		41.3	1.000	1.000
	4	44.2	1.002	1.002
4		46.1	1.007	1.007
	5	51.3	1.002	1.002
5		55.8	0.995	0.995
6		59.8	1.005	1.003
	7	65.2	1.002	1.002
7		69.6	1.003	1.004
	8	74.0	1.005	1.005
8		79.3	1.004	1.004
	9	88.5	0.997	0.998
9		95.5	1.002	1.004
	10	102.5	1.001	1.005
10		108.4	1.003	1.004
	11	115.6	1.001	1.002
11		122.6	1.003	1.003
	12	129.6	1.001	1.002
12		137.1	1.003	1.003

Average, all features	1.0023	1.0027
Average deviation	0.0022	0.0023

Best model 1/2 (B + C), yielding scale factor of 1.0025

Table 13

Temperature Factors

r_{ij}	$a_{ij}(s)$
C=C	0.00050
C_1-C_4	0.00061
C_1-C_2	0.00075
C_2-C_3	0.00075
C_6-C_3	0.00075
C_1..C_3	0.00095
C_2..C_4	0.00095
C_5..C_2	0.00095
C_5..C_4	0.00095
C_5..C_3	0.00095
C_6..C_1	0.00095
C_6..C_2	0.00151
C_6..C_4	0.00151
C_5..C_6	0.00151
C-H	0.00280
C..H	0.00460

Table 14

Bond lengths and bond angles in MMC

$C_3=C_4$	1.353 ± 0.015 A
$C_1=C_5$	1.333 ± 0.015 A
C_1-C_4	1.464 ± 0.020 A
C_1-C_2	1.529 ± 0.015 A
C_2-C_3	1.524 ± 0.015 A
C_6-C_3	1.504 ± 0.015 A
$\angle C_1-C_2-C_3$	$84.5 \pm 1.5^\circ$
$\angle C_2-C_3-C_4$	$93.2 \pm 1.5^\circ$
$\angle C_3-C_4-C_1$	$93.5 \pm 1.5^\circ$
$\angle C_4-C_1-C_2$	$88.8 \pm 1.5^\circ$
$\angle C_5-C_1-C_2$	$134.2 \pm 2.0^\circ$
$\angle C_5-C_1-C_4$	$137.0 \pm 2.0^\circ$
$\angle C_6-C_3-C_2$	$129.5 \pm 2.5^\circ$
$\angle C_6-C_3-C_4$	$137.3 \pm 2.5^\circ$

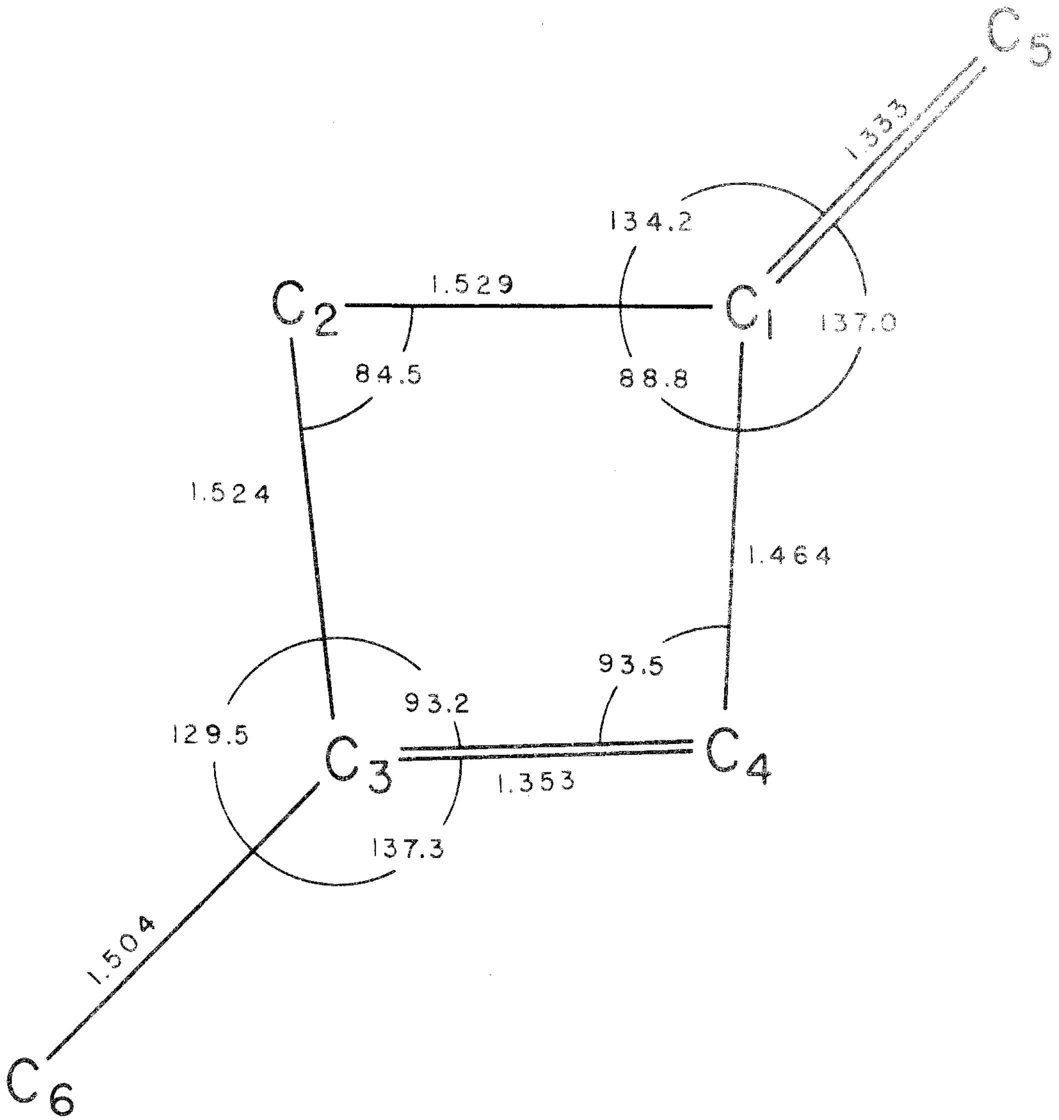
C5
1.333
134.2
C2
1.529
C1
137.0
84.5
88.8
1.524
1.464
93.5
93.2
129.5
C3
C4
1.353
137.3
1.504
C6

Figure 10

The lengths of the ring C-C bonds seem reasonable. The C_1-C_4 bond is expected to be rather short since it is part of a conjugated system. It has about the same length as the equivalent bond in 1,3-butadiene (41), although we might expect cross-ring repulsion to lengthen this bond in MMC relative to butadiene. It may be that the severe strain in this bond causes enough shortening to nullify the effect of the cross-ring repulsions. The C_1-C_2 and C_2-C_3 bonds average to about the DMC value, so that the two opposing influences of differential angle strain, which would tend to lengthen these bonds relative to DMC, and the greater total angle strain, which would tend to shorten them, seem to cancel one another. The greater differential angle strain to which the C_1-C_2 bond is exposed would tend to make it a little longer than the C_2-C_3 bond. The average single bond length in cyclobutene is 1.537 A (42), 0.01 A longer than the average of C_1-C_2 and C_2-C_3 in MMC. We expect the C_2-C_3 bond in MMC to be very nearly the same length as the equivalent bonds in cyclobutene. However, we expect the C_1-C_2 bond in MMC to be considerably shorter than the equivalent bond in cyclobutene because of the additional strain, hyperconjugation, etc. introduced by the exocyclic double bond. Unfortunately, experimental values for the individual C-C bond lengths in cyclobutene are not available, but if we assume that the C_2-C_3 bond in MMC and the equivalent bonds in cyclobutene have about the same length, then it follows that the C_1-C_2 bond in MMC is about 0.034 A shorter than the equivalent bond in cyclobutene.

An interesting point in this structure is the C_6-C_3-C_4 bond angle. In forming the four-membered ring, $\angle C_2$-C_3-C_4 is strained about 30° from the isobutene value. Strain on the C_3 carbon atom is evidently minimized when the methyl group swings around toward C_2 through an angle, 14°, which is about half the strain angle arising from the C_2-C_3 bond being part of the four-membered ring.

Best agreement with the data requires $\angle C_5$-C_1-C_4 to be a little larger than $\angle C_5$-C_1-C_2. This may be attributed to the significant double bond character of the short C_1-C_4 bond tending to force the exocyclic double bond towards a linear arrangement of atoms C_5, C_1, and C_4.

CONCLUDING REMARKS

Table 15 lists a number of molecules containing single bonds adjacent to double bonds whose bond lengths the writer believes have been determined with sufficient accuracy to be useful for making comparisons. The bond lengths given refer to single bonds adjacent to double bonds. In the case of small rings, the reader should keep in mind that the proper standards for comparison are cyclobutane, C-C = 1.568 A, and cyclopropane, C-C = 1.510 A.

Table 15

Compound	C-C	Reference
propene	1.498	This thesis
isobutene	1.505	This thesis
cis butene-2	1.504	This thesis
toluene	1.51	43
cyclobutene	1.537[a]	42
methylcyclobutene	1.54[b]	38
methylenecyclobutane	1.55[c]	38
1,3-dimethylenecyclobutane	1.526	This thesis
1-methyl-3-methylenecyclobutene	1.505[d] 1.527[e]	This thesis
methylenecyclopropane	1.484	This thesis
cyclopropene	1.525[f]	37

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[a] Average, two short, one long.

[b] Average, ring + exocyclic.

[c] Average, two short, two long (see page 44).

[d] Average, including conjugated bond in ring and exocyclic bond.

[e] Average of the two non-conjugated ring C-C bonds.

[f] These single bonds are subjected to a strong lengthening effect from differential angle strain.

We see that in all cases*, the single bonds adjacent to double bonds are short. Moreover, this shortening is about half the shortening observed in single bonds adjacent to triple bonds. Variations occur in the actual bond shortenings observed in individual molecules, but this is not surprising, since we would expect the exact bonding situation to be somewhat different in different molecules.

There seems to be a remarkable additivity among the single bond shortenings found in unsaturated, non-aromatic molecules. In addition to the double bond - triple bond relationship already mentioned, we notice that the two double bonds in butadiene cause a shortening of the single bond to 1.46 A (41). This is just equal to the shortening caused by a triple bond, and twice that caused by a double bond. The single bond length in diacetylene is 1.375 A (1d), so two triple bonds cause twice the shortening of one triple bond and four times the shortening of a double bond. The single bond adjacent to both a double bond and a triple bond in pirylene has a length of 1.42 A (44), half way between the values for butadiene and diacetylene. In short, each carbon-carbon π bond adjacent to a single bond causes a shortening of about 0.04 A, whether the molecule is propene, with one π bond adjacent to the single bond, or diacetylene, with four.

Bond shortenings in these situations are often referred to conjugation and hyperconjugation, and the usual feeling seems to be, in agreement with the distinction implied by the names, that the two effects

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* Except in cyclopropene. However, see footnote f, Table 15.

are of greatly different importance. The elementary theoretical treatments of conjugation in themselves have been conducive to such a feeling; so often the hyperconjugation situation has arbitrarily been ignored or assigned low importance, and, more fundamentally, the secular equations, involving the whole electronic system, automatically bring attention to the interaction - even cooperation - of different parts of the system, in analogy to the most characteristic conjugated systems, such as benzene or a carotenoid. To be sure, the equation for hyperconjugation is often solved by perturbation methods so as to get an additive effect[*], but this seems not to have been considered as justifiable for conjugation.

Nothing in the bond length data seems to discriminate between conjugation and rehybridization as explanations for these bond shortenings, but if we assume that conjugation is the important effect, then we are led to the conclusion that, contrary to the picture presented in last paragraph, hyperconjugation and conjugation, in simple systems and measured by bond shortenings, are, by virtue of the above-mentioned additivity, substantially equivalent, conjugation between two double bonds amounting to just twice the hyperconjugation of the single bond with one double bond. If, on the other hand, the single bond shortenings are referred to rehybridization effects, these must also be called additive.

In discussing the structures described in this thesis, we have considered a number of factors which we might expect to cause variations in carbon-carbon single bond lengths. These include hyperconjugation,

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[*] For example, see reference 11.

rehybridization, total angle strain, differential angle strain, and cross-ring repulsions. In complex molecules, we can, in general, say what factors may be operating and give their sign (bond shortening or bond lengthening). By extrapolating from simple molecules, where few bond altering factors are present, we can make a quantitative estimate of the total effect of many such factors, if we assume that each acts independently. Such procedure has proved quite successful in most cases. However, a notable exception is indicated in Table 16.

Table 16

A	B	C	D	E
	1.542		1.505	0.037
	1.568		1.526	0.042
	1.510		1.484	0.026 (0.013)

In Table 16, column B gives the C-C bond lengths for the base structures shown in column A. Column D gives the lengths of the single bonds adjacent to the double bonds in the structures listed in column C. Column E gives the total single bond shortening induced by the double bonds. We would expect the numbers in column E to increase down the table, with the total shortening equal to 0.037 $+ \epsilon$, where ϵ measures the additional shortening over that in isobutene caused by the increasing strain introduced by the double bond. However, this is not the case, the shortening induced by the double bond in methylenecyclopropane being <u>less</u> than the shortening induced by the double bond in isobutene. If we make a correction for differential angle strain, (value in parentheses), the situation becomes even worse. This apparent anomaly may be due to a failure of additivity, or to our lack of knowledge of what is to be added, or both. Although neglect of the interaction of the various bond altering factors has been found to be a good approximation in most cases, this may no longer be true for the highly strained methylenecyclopropane molecule. Also, the comparisons under consideration are not strictly valid, e.g., the net change in hybridization is probably not the same when a double bond is added to propane to form isobutene as when a double bond is added to cyclopropane to form methylenecyclopropane, so that the resultant bond shortenings from this source may not be the same. The difficulty appears to lie not so much in our methods, but rather in extrapolating too far into a region where we have insufficient experimental data.

Perhaps a word should be said about experimental error. We have generally discussed our experimental results as if they were exact. This is perhaps too much to hope for, but we are certainly confident that our answers are sufficiently close to the correct ones to make our discussions and arguments valid. It is sometimes not easy to assess the reliability of the results of other investigators, but the general compatibility of the various results compared in our discussions would seem to indicate that none of them is seriously in error.

To summarize briefly, we have been able to give a reasonable and detailed explanation of most, if not all, of our results. The simplicity and general success of our methods certainly cannot be denied, although we have sometimes been embarrassed by having to deal with too many reasonable explanations and too little experimental data. Considerable work in this field, both theoretical and experimental, will be needed before a true understanding can be reached.

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PROPOSITIONS

1. Bond angle distortions are often attributed to intramolecular repulsions. It is proposed that such arguments may be put on a more or less quantitative basis by considering intramolecular repulsive interactions as analogous to intermolecular collisions of molecules in a gas.

2. No less than six "determinations" of the structure of acetone have been made (1). It is proposed that none of these is conclusive. The fundamental importance of this molecule makes it worthy of a careful structure determination.

3. A mechanism is proposed to explain the relative ease of substitution of bromine on triethylsilane when allyl bromide is used as a brominating agent (2), compared with some other brominating agents (2,3).

4. The bond lengths and bond angles found in trimethylene oxide and 3-methylenetrimethylene oxide (4) not only discourage the idea of cross ring bonding in the latter compound, but further suggest that there is a significant repulsive interaction between the oxygen atom and the opposite carbon atom.

5. It is proposed that the potential barriers to internal rotation derived by Pitzer (5) for cis and trans butene-2 and isobutene are incorrect. Minimum values for these barriers, based on the molecular configurations of these molecules, are suggested.

6. A mechanism for the anomalous rearrangement in the acylation of cyclopropane (6) is proposed.

7. An empirical relation involving electronegativities is proposed for predicting variations in carbon-halogen bond lengths in halomethanes. The average deviation between the calculated and the experimentally determined C-X bond lengths is less than 0.007 A for twenty-two cases.

8. The use of difference intensity curves to follow the effects of varying minor parameters is a very useful technique in the electron diffraction correlation procedure, and should be more widely used.

9. An accurate and detailed electron diffraction investigation of 1,3-butadiene, with particular attention to the C-C=C bond angles, would provide structural information of theoretical significance.

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