TABLE III

STRUCTURAL PARAMETERS DETERMINED FROM q_c/q_0 VALUES[a]

Parameter	Model										FINAL RESULTS WITH LIMITS OF ACCEPTABILITY
	Q_2	F_3	FK_3	K_3	KL_3	KQ_3	EF_4	K_4	EF_3	Q_3	Result
C–F	1.346	1.334	1.338	1.343	1.339	1.343	1.333	1.337	1.333	1.342	1.34 ± 0.02
C–C	1.558	1.505	1.509	1.515	1.531	1.535	1.483	1.508	1.483	1.554	1.52 ± .05
C–O	1.376	1.404	1.408	1.414	1.402	1.414	1.443	1.447	1.408	1.413	1.41 ± .05
∠FCF	108.5°	108.5°	108.5°	108.5°	108.5°	108.5°	108.5°	108.5°	108.5°	108.5°	108.5 ± 1.5°
∠CCO	107°	113°	111.5°	110°	110°	108.5°	111.5°	110°	113°	107°	110 ± 4°

[a] All values for interatomic distances are in Ångström units.

determined by this investigation are also included in this table.

Discussion of Results

An electron diffraction investigation[2] of CH_3CH_2OH gave C–C = 1.55 ± 0.02 Å., C–O = 1.43 ± 0.02 Å., and ∠CCO = 110 ± 3°; these results are in close agreement with the values of 1.54 and 1.43 Å. for the C–C and C–O distances, respectively, obtained in an electron diffraction study[2] of CH_2ClCH_2OH. Within the limits of accuracy of this investigation, the CCO angle is the same in CF_3CH_2OH and CH_3CH_2OH. Unfortunately, the uncertainties of the data do not permit an entirely valid comparison of the C–C and C–O distances in CF_3CH_2OH with these distances in ethanol and ethylene chlorohydrin, but the results of this investigation indicate that these distances are probably shorter in CF_3CH_2OH. Further, it appears that the C–C bond lengths in CF_3CH_2OH, CF_3CF_3 and CH_3CF_3 are very nearly the same (see Introduction).

The values for the C–F bond distance and the FCF angle (1.34 ± 0.02 Å. and 108.5 ± 1.5°, respectively) obtained in this investigation do not differ significantly from the values reported for other molecules containing the CF_3 group. A recent electron diffraction study of CHF_3 employing the rotating sector[12] gave C–F = 1.334 ± 0.005 Å. and ∠FCF = 108°30′ ± 30′; these values are in close agreement with the microwave results[13] of 1.332 Å. and 108°48′, respectively. The studies in this Laboratory of CF_3CF_3[3] and CH_3CF_3[4] yielded C–F = 1.330 ± 0.015 Å. and ∠FCF = 108.5 ± 1.5° for CF_3CF_3, C–F = 1.33 ± 0.02 Å. and ∠FCF = 108.5 ± 1.5° for CH_3CF_3. A determination of the structure of $CF_3C{\equiv}CH$[11] by a combination of the electron diffraction and microwave methods gave C–F = 1.335 ± 0.010 Å. and ∠FCF = 107.5 ± 1°. FCF angles less than tetrahedral have also been reported for $CF_3C{\equiv}CCF_3$[14] and CF_3CN.[15] It is to be noted that the C–F distance is nearly the same in all these cases.

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(12) L. O. Brockway, private communication.

(13) S. N. Ghosh, R. Trambarulo and W. Gordy, *J. Chem. Phys.*, **20**, 605 (1952).

(14) W. F. Sheehan and V. Schomaker, THIS JOURNAL, **74**, 4468 (1952).

(15) M. D. Danford and R. L. Livingston, *ibid.*, **77**, 2944 (1955).

[CONTRIBUTION NO. 2082, FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

The Molecular Structure of Cyclobutene, C_4H_6

BY ELIHU GOLDISH, KENNETH HEDBERG AND VERNER SCHOMAKER

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The molecular structure of cyclobutene has been studied by electron diffraction in the gas phase. The bond distance and bond angle results for a molecule of C_{2v} symmetry are $C{-}C_{ave}$ = 1.537 ± 0.010 Å., C=C = 1.325 ± 0.04 Å. and ∠C=C—C = 94.0 ± 0.8°; the lengths of the two types of single bonds probably do not differ by more than 0.06 Å. The bond lengths are discussed in connection with the possible effects of cross-ring repulsion, hyperconjugation, and angle stresses at the carbon atoms.

A considerable amount of structural evidence[1] indicates that carbon–carbon single bonds in three-membered rings are shorter, and in four-membered rings are longer than the standard distance, 1.54 Å. An explanation of the bond shortenings is suggested by Coulson and Moffitt's[2] treatment of bond angle strain, and Dunitz and Schomaker[1] have related the lengthenings to a plausible repulsion between non-bonded carbon atoms. Cyclobutene, with its four-membered ring, seemed to us to be a worthwhile subject for study in connection with these distance effects.

The Structure Determination.—Samples of cyclobutene were kindly prepared for us by Drs. E. R. Buchman, J. C. Conly and W. Neville, by reduction of 1,2-dibromocyclobutane with zinc dust.[3] Electron diffraction photographs were made both in the old apparatus[4] and later in a newly con-

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(1) See J. D. Dunitz and V. Schomaker, *J. Chem. Phys.*, **20**, 1703 (1952).

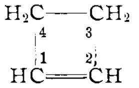
(2) C. A. Coulson and W. E. Moffitt, *ibid.*, **15**, 151 (1941); *Phil. Mag.*, **40**, 7th series, 1 (1949).

(3) J. C. Conly, Thesis, California Institute of Technology, 1950.

(4) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

structed apparatus, and were interpreted[5] by two of us independently. The work had been largely completed using the older data, but the much better newer plates enabled us to refine our results significantly.

Theoretical intensity curves were calculated over the shape parameter ranges $0.837 \leqslant \mathrm{C{=}C/C{-}C} \leqslant 0.889$, $0.673 \leqslant \mathrm{C{-}H_{ave}/C{-}C_{ave}} \leqslant 0.752$ and $-0.08 \leqslant \mathrm{C_1{-}C_4 - C_1{-}C_2} \leqslant +0.08$ Å. (see cut) for a



molecule of C_{2v} symmetry, assuming C_{2v} local symmetry for C_1 and C_2, $\angle \mathrm{C{=}C{-}H} = 125^1/_4 + {}^1/_2(125^1/_4 - \angle \mathrm{C_2{=}C{-}C})$ degrees, and, for most of the calculations, $\angle \mathrm{H{-}C{-}H} = 109^1/_2{}^\circ$.[6] In the vibration factors $\exp(-b_{ij}q^2)$, b_{ij} was taken as 0.00016 for C–H, 0.00030 for C . . . H, zero for C–C and C=C, and, usually, for best agreement beyond $q \sim 120$, between 0.00005 and 0.00010 for C . . . C. All terms except H . . . H were included and the effective value 1.25 was used for Z_H. As the work proceeded it became clear that a determination of the $\mathrm{C{-}H_{ave}}$ distance would have error limits of about ±0.06 Å. We, therefore, made the additional very reasonable assumption $\mathrm{C{-}H_{ave}} = 1.093 \pm 0.015$ Å. in order to simplify and make more precise the determination of the remaining parameters.

The effects of small variations of the several parameters are shown by the theoretical intensity curves in Fig. 1, all of which are in acceptable agreement with observation. The usual comparisons (Table I presents some of the quantitative comparisons) led to the following parameter values and limits of error: $\mathrm{C{=}C/C{-}C_{ave}} = 0.862 + 0.018 - 0.024$, $|\mathrm{C_2{-}C_3 - C_3{-}C_4}| \leqslant 0.08$ Å., $\mathrm{C{-}C_{ave}} = 1.537 \pm 0.010$ Å., $\mathrm{C{=}C} = 1.325 \pm 0.046$ Å. and $\angle \mathrm{C{=}C{-}C} = 94.0^\circ \pm 0.8^\circ$. For any difference $|\mathrm{C_2{-}C_3 - C_3{-}C_4}|$ less than 0.06 Å. the curves are about equally satisfactory.

TABLE I

DIFFRACTION DATA FOR CYCLOBUTENE, MODEL E

	Max.			Min.	
No.	q_{obsd}	q/q_{obsd}	No.	q_{obsd}	q/q_{obsd}
1	11.72	(1.126)	1	8.37	(1.039)
2	19.57	(1.022)	2	15.63	(0.985)
3	29.33	1.019	3	24.76	1.010
4	41.26	0.994	4	35.14	0.996
5	50.77	(1.024)	5	46.48	(1.033)
6	57.95	(0.982)	6	54.04	(1.007)
7	68.40	1.011	7	62.92	0.983
8	79.46	1.013	8	73.94	1.009
9	96.54	(0.993)	9	84.97	(1.030)
10	107.84	.996	10	101.91	1.005
11	121.34	(.989)	11	112.87	1.011
12	136.04	(.992)	12	128.20	0.975

av. 11 features 1.004
av. deviation 0.007

For best model: $\mathrm{C{-}C_{ave}} = 1.53 \times 1.0045 = 1.537$ Å.

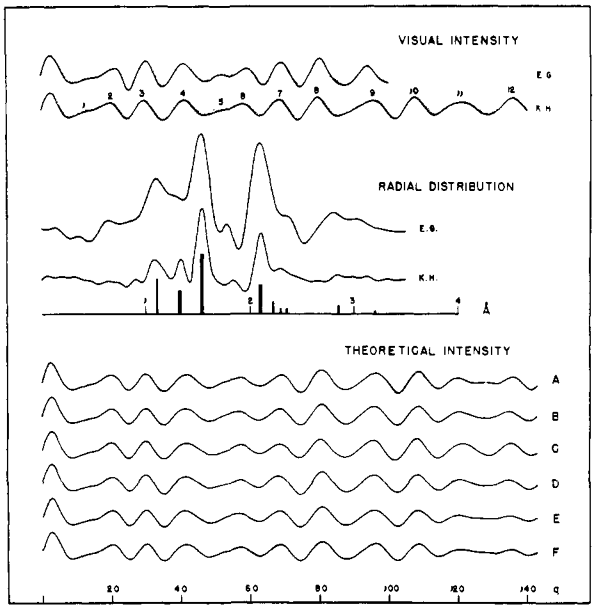


Fig. 1.—Electron diffraction curves for cyclobutene. The broad and narrow vertical bars represent, respectively, carbon–carbon and carbon–hydrogen interactions for the best model. The theoretical intensity curves are for the following parameter values.

	$\mathrm{C{-}C_{ave}}$, Å.	C=C, Å	$\mathrm{C_2{-}C_3}$ — $\mathrm{C_3{-}C_4}$, Å.	$\mathrm{C{-}H_{ave}}$, Å.	$a(q)_{\mathrm{C \ldots C}} \times 10^4$, Å^{-2}
A	1.53	1.30	0	1.09	0
B	1.53	1.30	0	1.09	0.5
C	1.53	1.33	0	1.09	0.5
D	1.53	1.30	0	1.06	0.5
E	1.53	1.30	0.04	1.09	0.5
F	1.52	1.30	0.04	1.09	0.5

Discussion.—Although the average carbon–carbon bond length in cyclobutane is very close to the standard length of 1.54 Å., it is substantially shorter than the abnormally long values found for other four-membered rings (all saturated), presumably because of the presence of the double bond. Just as for cyclobutane, a cross-ring repulsion[1] in excess of the bend-bond effect[2] probably exists, but it is here cancelled out by hyperconjugation shortening and the possibly shorter covalent radius of the trigonally bonded carbon atom[7] which amount to about 0.04 Å. for C–C adjacent to C=C in propene (1.49 Å.[8]), isobutene (1.50 Å.[8]) and *cis*-butene (1.51 Å.[9]). In addition, the angle stress at ∠C–C=C is most likely greater than at ∠C–C–C, so as to shorten the double

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(5) See K. Hedberg and A. J. Stosick, THIS JOURNAL, **74**, 954 (1952), for details of the method.

(6) No doubt ∠H–C–H is somewhat greater than tetrahedral (*cf.* ref. 1); however, we have found that variations as large as 10° produce only very small changes in the intensity curves. The assumption on ∠C=C—H is presumably better.

(7) C. A. Coulson, Victor Henri Commemorative Volume, "Contribution à l'étude de la structure Moléculaire," Desoer, Liege, 1948, p. 15.

(8) J. P. McHugh and V. Schomaker, Abstracts, American Crystallographic Association Meeting, Pasadena, California, June, 1955, p. 21.

(9) J. P. McHugh and V. Schomaker, private communication.

TABLE II

CARBON–CARBON BOND LENGTHS IN CYCLOBUTENE

	C_1–C_4	C_3–C_4	C_1=C_2
Standard length, Å.	1.540	1.540	1.330[a]
Estimated increments:			
Bent-bond effect	−0.012[b]	−0.012[b]	−0.006[c]
Cross-ring repulsion	+ .033[d]	+ .033[d]	+ .016[c]
Hyperconjugation[e]	− .040[a]	0	0
Differential angle stress[f]	0	+ .010	− .005
Resultant sums	1.521	1.571	1.335
Single bond average	1.538		
Obsd. lengths	1.537 ± 0.010		1.325 ± 0.046

[a] From propene, isobutene and *cis*-butene (ref. 8 and 9). [b] For an average angle strain of 27°, according to the Copley–Bernstein chord and arc interpretation (*cf.* ref. 1). [c] Half the corresponding single-bond values because of the difference in stretching force constant. [d] The observed lengthening in cyclobutene, corrected for an estimated bent-bond effect (ref. 1) of −0.005 Å. [e] Possible differences in higher-order hyperconjugation and hybridization (ref. 7) are here neglected. [f] For bending force constants (defined by $F = kl\Delta\nu$) of 0.33×10^5 dyne cm.$^{-1}$ rad.$^{-1}$ (propane: D. M. Gates, *J. Chem. Phys.*, **17**, 393 (1949)) and 0.51×10^5 dyne cm.$^{-1}$ rad.$^{-1}$ (propene: E. B. Wilson, Jr., *ibid.*, **9**, 319 (1941)), angle strains of 24° (C–C–C) and 31° (C=C—C) and stretching force constants of 4.7×10^5 dyne cm.$^{-1}$ (C—C) and 9.5×10^5 dyne cm.$^{-1}$ (C=C). The resulting Δl's are here multiplied by $^1/_6$ since, following the discussion of ref. 2, only roughly this fraction of the bending constant is *not* to be ascribed to direct interaction between the adjacent non-bonded atoms.

bond, leave the adjacent single bonds essentially unaffected, and lengthen the opposite single bond. As is shown in greater detail in Table II, these considerations lead to a reasonable accounting for the observed distances.

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