alkylnaphthalenes higher than amylnaphthalene. The values of McClellan and Pimentel[2] for naphthalene are included for convenience. These authors estimate that their values are probably accurate to ±0.5 cal. per degree mole. The values for the substituted naphthalenes are subject to additional uncertainty. We estimate the uncertainty to range from 0.5 for the simpler derivatives at the lower temperatures to 1.0 for the larger molecules at the higher temperatures.

Acknowledgment.—We wish to acknowledge the aid of Mr. Donald E. Petersen in assisting with some of the calculations.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE PURDUE RESEARCH FOUNDATION, PURDUE UNIVERSITY]

An Electron Diffraction Investigation of the Molecular Structure of Trifluoroethanol[1]

BY R. L. LIVINGSTON AND G. VAUGHAN

RECEIVED JANUARY 9, 1956

The molecular structure of trifluoroethanol has been investigated by electron diffraction using the visual correlation procedure. The structural parameters as determined by this investigation are as follows: C–F = 1.34 ± 0.02 Å., C–C = 1.52 ± 0.05 Å., C–O = 1.41 ± 0.05 Å., ∠FCF = 108.5 ± 1.5°, and ∠CCO = 110 ± 4°.

Introduction

There has been considerable interest in the effect of halogen atoms on the carbon–carbon bond distances in simple organic halides. Early results[2] gave a C–C distance of about 1.45 Å. in C_2F_6 and CF_3CH_3 but more recent work indicates that these distances are considerably longer, probably between 1.50 and 1.54 A.[3,4] The determination of the structure of trifluoroethanol was undertaken to determine further the effect of fluorine atoms on the C–C distance and, in addition, to determine any effects on the C–O bond length and the CCO angle.

Experimental

The sample of trifluoroethanol used in this work was purchased from the Minnesota Mining and Manufacturing Company. A 60-ml. sample was rectified in a glass helices packed column which was equivalent to fifteen theoretical plates. Ten milliliters of the middle fraction, b.p. 77.7 ± 0.1° (uncorrected), was collected for use in preparing the diffraction photographs. The infrared spectrum of this fraction showed no spurious features when compared with the spectrum from a sample with a known purity greater than 99%.

The diffraction photographs were obtained in the usual manner[5] using a camera designed and constructed by Professor H. J. Yearian of the Purdue Physics Department. Twelve satisfactory photographs of varying density were obtained from the sample described above, using a camera distance of 108.2 mm., an electron wave length of 0.05923 Å. and Eastman Kodak 33 plates. Visual interpretation and measurements of the patterns were obtained out to a q-value of approximately 95 from three of the best plates.

Interpretation of the Diffraction Pattern.—The visual correlation method[5,6] and the radial distribution method[7,8] were used in the interpretation of the diffraction pattern. The measurements of the patterns are summarized in Table I. The q_0-values are based upon measurements of each feature by two independent observers. The qualitative

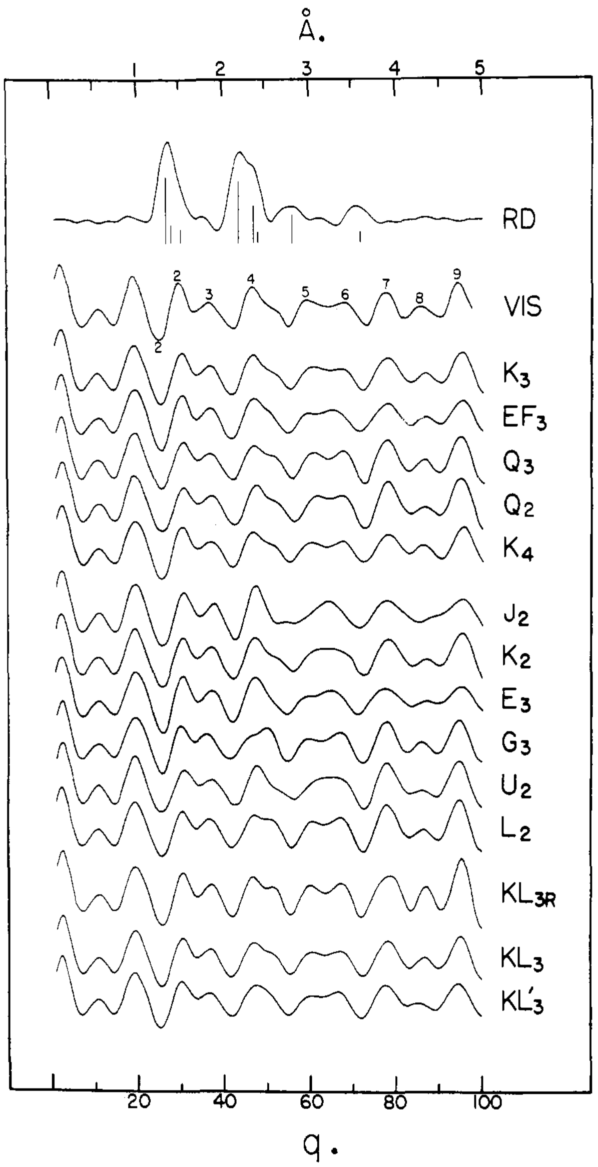

Fig. 1.—Radial distribution, visual intensity and theoretical intensity curves for trifluoroethanol.

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[1] Contains material from the Ph.D. thesis of G. Vaughan, Purdue Research Foundation Fellow in Chemistry, 1951–1953.

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TABLE I

q_c/q_0 VALUES FOR ACCEPTABLE MODELS OF TRIFLUOROETHANOL

Feature Max.	Feature Min.	q_0	Model Q_2	F_3	FK_3	K_3	KL_3	KQ_3	EF_4	K_4	EF_6	Q_3	Wt.
	1	14.78	0.966	0.961	0.962	0.964	0.963	0.964	0.963	0.960	0.964	0.962	0
1		18.50	1.038	1.045	1.044	1.042	1.041	1.038	1.045	1.038	1.049	1.031	0
	2	25.89	0.981	0.981	0.981	0.981	0.981	0.981	0.981	0.980	0.982	0.981	0
2		29.54	1.027	1.016	1.019	1.022	1.019	1.022	1.018	1.018	1.018	1.024	1
	3	32.88	1.027	1.011	1.014	1.021	1.014	1.022	1.022	1.021	1.016	1.023	1
3		36.45	1.003	0.993	0.996	1.000	0.996	1.000	1.003	0.999	0.998	0.996	1
	4	42.08	0.996	0.983	0.984	0.987	0.987	0.988	0.987	0.985	0.989	0.989	1
4		46.18	1.025	1.016	1.013	1.013	1.012	1.013	1.010	1.008	1.019	1.014	2
	5	54.66	1.028	1.003	1.010	1.015	1 014	1.017	0.998	1.004	1.001	1.018	4
5		58.92	1.038	1.015	1.020	1.029	1.022	1.032	1.005	1.015	1.017	1.024	2
	6	63.57	1.005	0.982	0.994	1.014	1.002	1.014	0.983	1.000	0.960	1.011	2
6		68.09	0.983	0.973	0.976	0.979	0.980	0.988	0.974	0.986	0.951	0.990	1
	7	72.86	0.997	0.989	0.992	0.994	0.994	0.996	0.984	0.992	0.984	0.996	4
7		76.65	1.013	1.016	1.015	1.014	1.015	1.014	1.016	1.016	1.015	1.011	4
	8	81.79	1.021	1.014	1.016	1.018	1.016	1.018	1.013	1.011	1.019	1.013	2
8		85.72	1.012	1.009	1.012	1.013	1 012	1.013	1.009	1.008	1.014	1.011	3
	9	90.43	0.997	1.000	1.001	1.004	1.000	1.001	1.005	1.004	1.001	0.999	2
9		94.52	1.001	1.004	1.005	1.007	1.003	1.005	1.010	1.008	1.007	1.001	2
Wt. mean			1.012	1.003	1.006	1.010	1.007	1.010	1.002	1.005	1.002	1.009	
Av. dev.			±0.012	±0.010	±0.010	±0.009	±0.009	±0.009	±0.010	±0.007	±0.014	±0.008	

appearance of the visual curve in Fig. 1 was drawn according to the interpretations of the patterns given by three independent observers, who were in close agreement on interpretations of all features. The shapes of the features in the interval $q = 0$ to $q = 22$ were copied from the most acceptable model, as is customary, in order to give a satisfactory radial distribution curve.

The visual appearance of the fourth maximum is very similar to features which appear on the diffraction pattern of carbon dioxide. Before the indicated shape was assigned to this maximum, a careful examination was made of carbon dioxide patterns which had been previously obtained in this Laboratory. The qualitative shape of the features for carbon dioxide is known with certainty as a result of independent spectroscopic investigations.[9,10]

A careful comparison of the doublet in the interval $q = 55$ to $q = 70$ with a similar doublet occurring in the diffraction pattern of 1,1,1-trifluoroethane led the observers to conclude that the sixth minimum was real. The patterns of this latter compound were particularly useful for the comparison since both sectored and unsectored photographs of this compound were available.[4]

The radial distribution function, Fig. 1, for trifluoroethanol was calculated using the equation[8]

$$rD(r) = \sum_{q=1}^{q_{\max}} I(q)_0 \exp(-bq^2) \sin \frac{\pi q}{10} r \qquad (1)$$

where $I(q)_0$ is the intensity read from the visual curve, Fig. 1. The value of b was determined by setting $\exp(-bq^2) = 0.1$ at $q = 95$. The curve shows four major peaks, each of which is generated by more than one interatomic distance. The peak at 1.37 A. corresponds to the C–F, C–C and C–O distances, that at 2.19–2.34 Å. to the F··F, C··O, C··F, C··H and O··H distances and those at 2.83 and 3.53 Å. to the O··F and H··F distances. Due to the complex nature of the peaks, no attempt was made to resolve the distances; it is to be noted, however, that the positions of the lines corresponding to the interatomic distances determined from the acceptable models agree favorably with the peaks observed in the radial distribution curve.

A complete determination of the structure of the trifluoroethanol molecule involves the evaluation of ten parameters if the usual assumptions of symmetry are made for the CF_3 group and only rigid models are considered. Preliminary investigation showed that varying the vibration factors from 0 to ∞ for all terms for interatomic distances involving H atoms had a negligible effect on the theoretical intensity curves; these factors were accordingly set equal to infinity for all of these distances.

C_{3v} symmetry was assumed for the CF_3 group, with the CCO plane bisecting an FCF angle. These assumptions, together with the omission of the H atoms, reduce the problem to one of five parameters provided only rigid models are considered. These are taken as ∠FCF, ∠CCO (hereafter referred to as α and β, respectively), the C–F distance, the C–C distance and the C–O distance.

The rigid models examined in this investigation covered three parameter fields in which β was set at 107, 110 and 113° and in which the C–C distance was varied from 1.46 to 1.54 Å. in steps of 0.04 Å. The C–O distances for the parameter fields were 1.36, 1.40 and 1.44 Å., respectively; in all cases, α was 108.5° and the C–F distance was 1.33 Å. Intensity curves were calculated on an I.B.M. tabulator using the equation[8]

$$I(q) = \sum_i \sum{}' \frac{Z_i Z_j}{r_{ij}} \exp(-b_{ij}q^2) \sin \frac{\pi q}{10} r_{ij} \qquad (2)$$

where the exponential term is omitted for rigid models.

Several of these rigid models gave rise to theoretical curves which were in fair agreement with the visual curve, but the resolution of the fifth and sixth maxima was too great and the shelf on the fourth maximum was too pronounced on all of these curves. Curve KL_{3R}, Fig. 1, is taken as a representative curve for the rigid models which were in best agreement with the visual curve.

The effect of vibration on the theoretical curves was then examined. A study of the vibration factors used in the determination of the structure of trifluoromethylacetylene[11] led to selection of the two sets of b_{ij} values shown in Table II. Several curves based on fairly acceptable rigid models were then calculated to determine if either set of b_{ij} values was

TABLE II

VALUES FOR b_{ij} USED FOR TRIFLUOROETHANOL MODELS[a]

Distance	Set A $b_{ij} \times 10^4$	Set B $b_{ij} \times 10^4$
C–F	0.16	0.16
C–O	.16	0.16
F··F	.68	1.04
C··F	.90	2.08
C··O	.90	2.08
O··F (gauche)	2.00	5.00
O··F (*trans*)	2.55	5.53

[a] b_{ij} values for all interatomic distances involving H atoms were taken to be ∞.

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reasonable for trifluoroethanol. Curves KL_3 and KL_3' are taken as representative curves showing the effects of these b_{ij} values on the theoretical curves; these curves were calculated from model KL_{3R} using set A and set B, Table II, respectively. Both curves represent the visual curve quite accurately in the intervals $q = 22$ to $q = 40$ and $q = 55$ to $q = 100$; however, the shelf on the fourth maximum had completely vanished in curve KL_3'. Since all observers agreed that the shape of the fourth maximum was well represented in the visual curve, set B was considered to be unacceptable and set A was chosen as a reasonable set of b_{ij} values.

Figure 2 shows the parameter fields for non-rigid models based on set A of the b_{ij} values. In these models, α and the C–F distance were constant at 108.5° and 1.33 Å., respectively. The groupings of the models in the following discussions were made according to the qualitative similarity of the theoretical intensity curves; the double letter designation refers to a model with parameters midway between those for models denoted by the individual letters.

Of models EF_4, F_3, K_3, KL_3 and KQ_3, curve K_3 is chosen as being representative; this curve, Fig. 1, is in excellent agreement with the visual curve in all respects.

Curves EF_3 and Q_3 were included in order to show the limits of acceptability for resolution and relative intensities of the fifth and sixth maxima and the acceptable range of shapes for the shelf on the fourth maximum. All curves with the resolution of the fifth and sixth maxima greater than that in curve Q_3 were rejected. This curve also shows the upper limit of acceptability for the prominence of the shelf on the fourth maximum, while curve EF_3 shows the lower limit of acceptability for the prominence of this shelf. Models giving rise to intensity curves with the relative intensity of the sixth maximum (as compared to the fifth maximum) greater than that in curve EF_3 were rejected. Both model EF_3 and model Q_3 are accepted as borderline fits.

Curves Q_2 and K_4 are included as acceptable curves for parameter fields C–O/C–F = 1.36/1.33 and 1.44/1.33, respectively. The heights of the sixth and seventh maxima and the depth of the seventh minimum have increased slightly, and the height of the eighth maximum has decreased slightly in curve Q_2. The height of the sixth maximum and the depth of the ninth minimum have increased in curve K_4, and the height of the seventh maximum has decreased in this curve. These discrepancies were not regarded as sufficient to justify rejection of these models, and both models are considered to be acceptable.

Of the group of models N_4, J_3, K_3, E_2, J_2 and N_2, curve J_2 is taken as representative. The complete disagreement with the visual curve beyond $q = 40$ permits rejection of this entire group.

Curve K_2 is the best curve from the group of models J_4, P_3, F_2, K_2 and P_2. The complete lack of resolution of the fifth and sixth maxima is the basis of rejection of the group although most models of this group show other discrepancies.

Of the group E_5, J_5, E_4, P_4, A_3 and E_3, curve E_3 is chosen as the best curve. The shelf on the fourth maximum has vanished, the intensity of the sixth maximum relative to the fifth and seventh maxima is too great, the eighth maximum is too weak and the ninth maximum is shown to be about as intense as the seventh maximum. All models in this group were rejected.

Curve G_3 is taken as a typical curve for the group of models F_5, F_4, G_4, L_4, B_3, G_3, G_2 and R_2. All models in this group may be rejected on several counts, but the obvious disagreement shown by the shape of the fourth maximum is sufficient to justify rejection of the entire group.

The group of models U_2, U_1 and V_1, of which U_2 is chosen as the best model, was rejected for a number of reasons. The shelf on the fourth maximum is too weak. The fifth and sixth maxima are completely unresolved, and the seventh minimum is too deep. The relative intensities of the seventh and eighth maxima are in disagreement with those in the visual curve, and the seventh and ninth maxima are of equal intensity.

Curve L_2 is chosen to represent models K_5, Q_4, L_3, L_2, V_2, Q_1 and R_1. The shelf on the fourth maximum is too prominent and the sixth maximum is too high relative to the fifth maximum. Since the remainder of the models in this group showed at least one of these discrepancies to a greater degree than that in L_2, all models in this group were rejected.

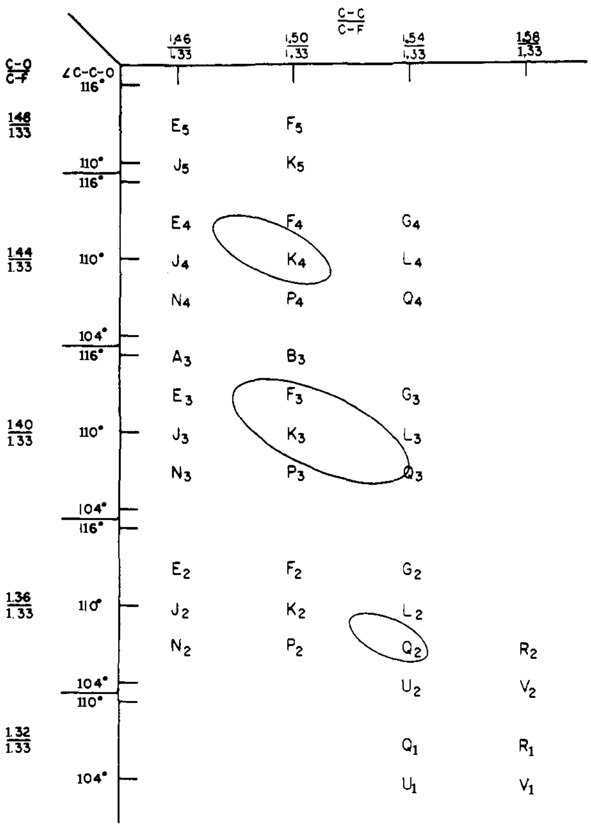

Fig. 2.—Parameter chart for CF_3CH_2OH. The FCF angle was 108.5° in the majority of models (see text).

Theoretical curves for nine models with $\alpha = 110.5°$ and eleven models with $\alpha = 106.5°$ (C–F = 1.33 Å. in all cases) were calculated. These models were ones with interatomic distances in at least fair agreement with the radial distribution curve. For all models with $\alpha = 106.5°$, the resolution of the fifth and sixth maxima is considerably greater than that observed in curve Q_3, and in addition, the shape of the fourth maximum is in complete disagreement with that in the visual curve. Models with $\alpha = 110.5°$ gave rise to curves in which the fifth maximum appears as a very weak shelf on the inside of the sixth maximum or does not appear at all. In most cases the fourth maximum shows complete disagreement with the visual curve, and the eighth maximum has vanished. It seemed quite likely that these curves could not be brought in agreement with the visual curve by any reasonable values for vibration factors.

The effect of restricted rotation on the theoretical intensity curves for trifluoroethanol was not considered in this investigation since the contributions from rotational terms would be relatively small compared to contributions from the general vibrational terms; in this case, compensation for the effect of restricted rotation can be taken into account by a slight increase of b_{ij} values for the interatomic distances involved.

From the above considerations, models Q_2, F_3, FK_3, K_3, KL_3, KQ_3, EF_4 and K_4 are regarded as acceptable fits, while models EF_3 and Q_3 are accepted as borderline fits. The q_c/q_0 values for these models are summarized in Table I.

The weightings for each feature are indicative of the reliability of that feature for comparison with theoretical curves. Low weightings were assigned to the inner features as these generally have been found to give less satisfactory agreement than do those at somewhat larger q values. Features for which reproducible measurements could not be obtained or which were part of an unresolved peak or involved a very asymmetric peak were also given low weights. The outer-most features were assigned relatively low weights as is customary for features at large scattering angles.

Table III summarizes the molecular parameters calculated from the mean values of the q_c/q_0 ratios. The accepted values of these parameters and the limits of error as

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.

Acknowledgments.—The authors wish to thank Professor Yearian for the use of his electron diffraction apparatus. They are also grateful to the Purdue Research Foundation for financial support of this work.

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[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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