

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Electron Diffraction Investigation of the Molecular Structures of Ethyl Chloride, Ethyl Bromide, Isopropyl Chloride, Isopropyl Bromide, Methyl Chloroform and Isocrotyl Chloride¹

BY J. Y. BEACH AND D. P. STEVENSON²

In a previous paper³ we determined by the electron diffraction method the bond angles and bond distances in *t*-butyl chloride and *t*-butyl bromide. The bond distances in methyl chloride⁴ and methyl bromide⁵ also have been studied previously. In this paper we shall report an electron diffraction investigation of the molecular structures of ethyl chloride, ethyl bromide, isopropyl chloride and isopropyl bromide. This completes the investigation of the compounds derived from methyl chloride or methyl bromide by replacing zero, one, two or three hydrogen atoms by methyl groups. It is found in all cases that the distortion of the bond angles from the tetrahedral value is less than about 3°. However, we observe a trend in the bond angles which is probably real in going from the simpler molecules to the more complicated molecules. The interatomic distances are found to agree with those predicted by the table of covalent radii.

Methyl chloroform was studied for a comparison with *t*-butyl chloride. Methyl chloroform can be considered to be derived from *t*-butyl chloride by replacing the methyl groups by chlorine atoms and the chlorine atom by a methyl group.

In an electron diffraction investigation of phosgene and the chloroethylenes⁶ it was found that the interatomic distance for a carbon-chlorine bond adjacent to a double bond is less than the carbon-chlorine bond distance in saturated compounds. The present study of isocrotyl chloride constitutes an extension of that investigation.

The electron diffraction apparatus used in this investigation is similar to the one described by Brockway.⁷ The electron wave length, λ , was 0.0590 Å. The photographs were interpreted by the visual method⁸ and by the modified radial

distribution method. The theoretical scattering formula used in the visual method is $I = \sum_i \sum_j Z_i Z_j \sin sr_{ij}/sr_{ij}$. Z_i is the atomic number of the i^{th} atom, r_{ij} is the distance between the i^{th} and j^{th} atoms and $s = (4\pi \sin \theta/2)/\lambda$ where θ is the angle of scattering. Both sums are taken over all the atoms in the scattering molecule. The radial distribution method⁹ has recently been improved¹⁰ to give more detailed and reliable results. The coefficients in the radial distribution function were obtained from the visually estimated intensities by multiplying them by $s^2 e^{-as^2}$ where $se^{-as^2} = 0.1$ for the largest ring. We have used this modification of the radial distribution method throughout this paper.

Ethyl Chloride.—Kahlbaum ethyl chloride was used without further purification. The photographs showed eight measurable maxima. The

TABLE I

ETHYL CHLORIDE

Values in parentheses not included in the average.

Max.	Min.	I	s_0	s^a	s^a/s_0
1		9	3.22	3.29	(1.021)
	2		4.16	3.75	(0.901)
2		20	5.15	5.07	.984
	3		6.40	6.33	.989
3		18	7.50	7.62	1.016
	4		8.31	8.70	(0.955)
4		5	9.47	9.20	(1.029)
	5		10.62	10.56	0.994
5		12	11.91	12.05	1.012
	6		13.24	13.29	1.004
6		8	14.47	14.42	0.997
	7		15.63	15.67	1.003
7		1	16.56	16.79	1.013
	8		17.71	17.50	0.988
8		3	18.90	18.85	.997

Average 1.000

C-Cl = 1.76 Å.
long C-Cl = 2.74 Å.

^a Calculated for a model having a ratio of carbon-chlorine to carbon-carbon distance of 1.76/1.54 and a C-C-Cl angle of 112°.

(1) Most of these results were presented to the American Chemical Society at Baltimore, April, 1939.

(2) Now National Research Fellow in Chemistry at the California Institute of Technology.

(3) J. Y. Beach and D. P. Stevenson, *THIS JOURNAL*, **60**, 475 (1938).

(4) L. E. Sutton and L. O. Brockway, *ibid.*, **57**, 473 (1935).

(5) H. A. Lévy and L. O. Brockway, *ibid.*, **59**, 1662 (1937).

(6) L. O. Brockway, J. Y. Beach and L. Pauling, *ibid.*, **57**, 2693 (1935).

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

(8) L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 367 (1934).

(9) L. Pauling and L. O. Brockway, *THIS JOURNAL*, **57**, 2684 (1935).

(10) Ch. Degard, *Bull. Soc. Sci. Liège*, February, 1938; V. F. H. Schomaker, paper presented to the American Chemical Society at Baltimore, April, 1939. The modification of the radial distribution method used in this paper is not identical with the modification proposed by Schomaker.

observed values of $s(s_0)$ for the maxima and minima and the visually estimated intensities of the maxima are given in Table I. The fourth maximum is close to the third and is difficult to measure. The eight-term radial distribution function is shown in Fig. 1, curve A. The two principal peaks at 1.76 and 2.74 Å. represent the two carbon-chlorine distances in the molecule.

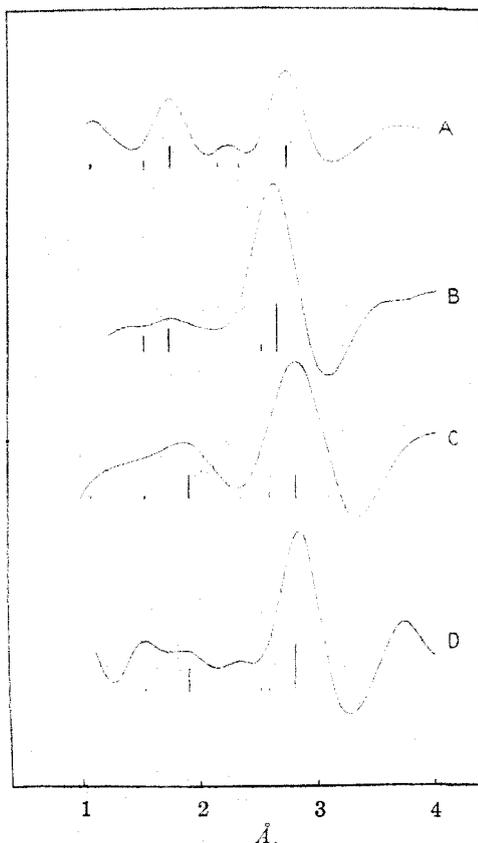


Fig. 1.—Modified radial distribution function for: A, ethyl chloride; B, isopropyl chloride; C, ethyl bromide; D, isopropyl bromide. The vertical lines indicate the final values for the interatomic distances and their importance.

The smaller peaks represent, less reliably, the less important distances in the molecule. In calculating the theoretical intensity curves the ratio of the carbon-chlorine distance to the carbon-carbon distance was taken to be 1.76/1.54. This was the only ratio tried as it gave a final value for the carbon-carbon distance of 1.54 Å., the value we assume to be correct. Other ratios lead to different carbon-carbon distances. No attempt was made to determine the motion of the methyl groups as their orientation has a negligible effect on the theoretical scattering curve.

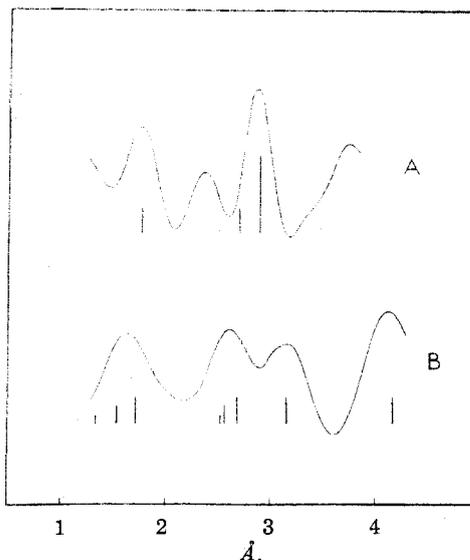


Fig. 2.—Modified radial distribution function for: A, methyl chloroform and B, isocrotyl chloride. The vertical lines indicate the final values for the interatomic distances and their importance.

For the purpose of calculating curves we assumed them to be oriented so that the hydrogen atoms avoided as much as possible the atoms on the other end of the molecule. Theoretical intensity curves were calculated for values of the C-C-Cl angle of $109^\circ 28'$ (tetrahedral), 112° and $114^\circ 30'$. These curves are shown in Fig. 3. The 112° curve agrees best with the photographs.

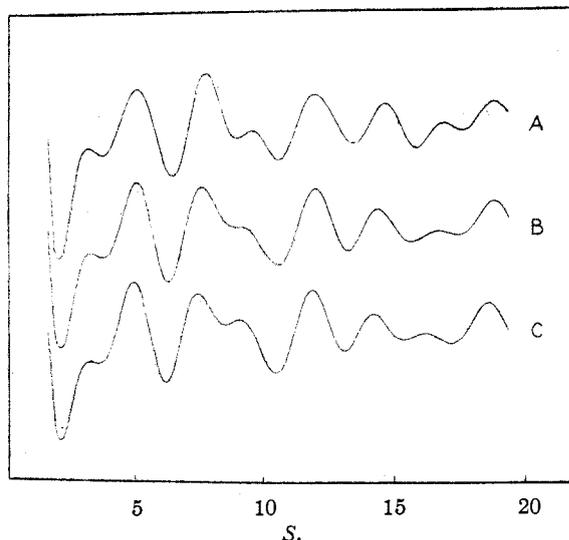


Fig. 3.—Theoretical intensity curves for ethyl chloride. The C-C-Cl angle is: curve A, $109^\circ 28'$; curve B, 112° ; curve C, $114^\circ 30'$. The ratio of carbon-chlorine distance to carbon-carbon distance is 1.76/1.54.

The seventh maximum on the $109^\circ 28'$ curve is higher than on the photographs. The $114^\circ 30'$ curve is unsatisfactory because the fourth maximum, or shelf, is too high. Quantitative comparison of the photographs with the 112° curve is made in Table I.

The final results are: carbon-chlorine bond distance, $1.76 \pm 0.02 \text{ \AA.}$; long carbon-chlorine distance, $2.74 \pm 0.02 \text{ \AA.}$; C-C-Cl angle, $111^\circ 30' \pm 2^\circ$. The carbon-carbon and carbon-hydrogen distances were assumed to be 1.54 and 1.09 \AA. , respectively.

Ethyl Bromide.—Eastman Kodak Co. ethyl bromide was purified by fractional distillation. The electron diffraction photographs showed six measurable maxima. The values of s_0 for the maxima and minima and the visually estimated intensities of the maxima are tabulated in Table II. The six-term radial distribution func-

shown in Fig. 4. When the C-C-Br angle is greater than the tetrahedral angle the fourth maximum on the calculated curves is much too low. A curve intermediate between curves A and B resembles the photographs most closely. Quantitative comparison of the photographs with both curves A and B is made in Table II. Theoretical intensity curves were also calculated for models in which the ratio of the carbon-bromine distance to the carbon-carbon distance were given values of 1.87/1.54 and 1.95/1.54. Decreasing the carbon-bromine distance has the same effect on the calculated curves as increasing the C-C-Br angle and therefore is impossible. Increasing the carbon-bromine distance is unsatisfactory because the fourth and fifth maxima merge into one.

TABLE II
ETHYL BROMIDE

Values in parentheses not included in the averages.

Max.	Min.	I	s_0	s^a	s^a/s_0	s^b	s^b/s_0
1		10	3.09	3.06	(0.990)	3.13	(1.013)
	2		3.91	3.75	(.958)	3.91	(0.999)
2		16	5.01	4.77	.951	4.87	.971
	3		5.98	5.96	.996	6.04	1.010
3		13	7.16	7.22	1.008	7.28	1.017
	4		8.13	8.52	1.047	8.70	1.070
4		5	9.31			10.10	(1.085)
	5		10.20			10.81	(1.060)
5		2	11.36	11.15	0.982	11.30	0.995
	6		12.36	12.46	1.008	12.53	1.014
6		4	13.84	13.73	0.992	13.84	1.000
			Average		0.998	1.010	
			C-Br = 1.91 \AA.		C-Br = 1.93 \AA.		
			long C-Br = 2.81 \AA.		long C-Br = 2.81 \AA.		

^a Calculated for a model having a ratio of carbon-bromine to carbon-carbon distance of 1.91/1.54 and a C-C-Br angle of $109^\circ 28'$. ^b Calculated for a model having a ratio of carbon-bromine to carbon-carbon distance of 1.91/1.54 and a C-C-Br angle of $107^\circ 30'$.

tion is shown in Fig. 1, curve C. The two peaks at 1.87 and 2.81 \AA. represent the two carbon-bromine distances in the molecule. In calculating the theoretical intensity curves the methyl group was assumed to possess a static configuration in which the hydrogen atoms avoid as much as possible the atoms on the other end of the molecule. The carbon-hydrogen distance was assumed to be 1.09 \AA. and all bond angles except the C-C-Br angle were assumed to be tetrahedral. Curves were calculated for models in which the ratio of the carbon-bromine distance to the carbon-carbon distance was 1.91/1.54, the C-C-Br angle ranging from $107^\circ 30'$ to $113^\circ 30'$. These curves are

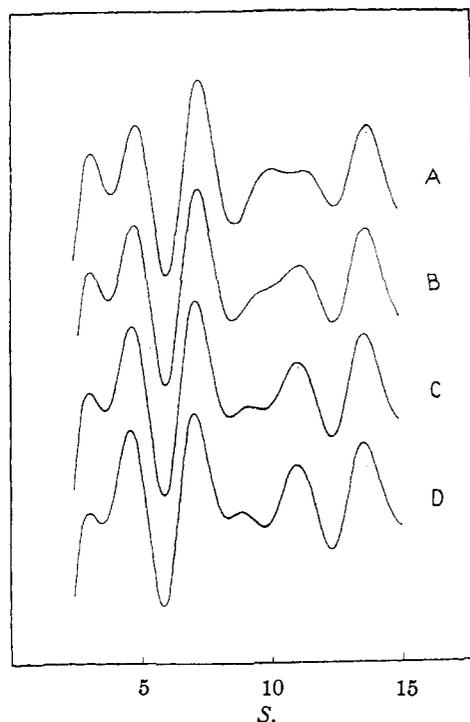


Fig. 4.—Theoretical intensity curves for ethyl bromide. The C-C-Br angle is: curve A, $107^\circ 30'$; curve B, $109^\circ 28'$; curve C, $111^\circ 30'$; curve D, $113^\circ 30'$. The ratio of the carbon-bromine distance to the carbon-carbon distance is 1.91/1.54.

Taking the results of the quantitative comparisons together with the radial distribution function we arrive at the final results: carbon-bromine bond distance, $1.91 \pm 0.02 \text{ \AA.}$; long carbon-bromine distance, $2.81 \pm 0.02 \text{ \AA.}$; C-C-Br angle, $109 \pm 2^\circ$.

Isopropyl Chloride.—Eastman Kodak Co. isopropyl chloride was purified by fractionation in a

thirty-inch (76-cm.) column. The photographs show six measurable maxima. The fifth is better defined than the fourth. The values of s_0 for the maxima and minima and the intensities of the maxima are listed in Table III. The radial dis-

TABLE III

ISOPROPYL CHLORIDE

Values in parentheses not included in the average.

Max.	Min.	l	s_0	s^a	s^a/s_0	s_b	s_b/s_0
1		10	3.22	2.95	(0.916)	3.02	(0.938)
	2		4.14	3.90	(.943)	3.96	(.957)
2		9	5.43	5.15	(.949)	5.23	(.963)
	3		6.44	6.37	.989	6.44	1.000
3		7	7.70	7.55	.980	7.65	0.993
	4		8.62	8.68	1.008	8.87	1.030
4		4	9.96	9.41	0.945	9.66	0.970
	5		10.91	10.78	.988	10.92	1.001
5		3	12.35	12.21	.989	12.34	0.999
	6		13.35	13.47	1.009	13.57	1.016
6		1	14.83	14.41	0.972	14.68	0.990
			Average		0.985	1.000	

$$\text{C-Cl} = 1.73 \quad \text{C-Cl} = 1.76$$

$$\text{long C-Cl} = 2.66 \quad \text{long C-Cl} = 2.66$$

^a Calculated for a model having a C-C-C angle of $109^\circ 28'$, a C-C-Cl angle of $109^\circ 28'$ and a ratio of carbon-chlorine to carbon-carbon distance of 1.76/1.54. ^b Calculated for a model having a C-C-C angle of $111^\circ 30'$, a C-C-Cl angle of $107^\circ 30'$ and a ratio of carbon-chlorine to carbon-carbon distance of 1.76/1.54.

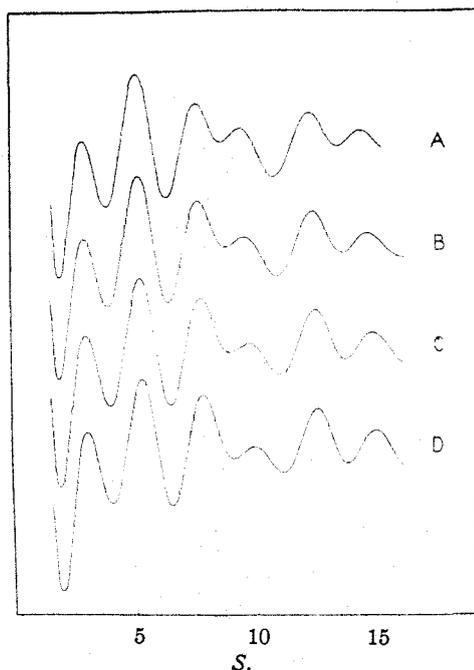


Fig. 5.—Theoretical intensity curves for isopropyl chloride. The C-C-C angle and the C-C-Cl angle, respectively, are: curve A, $107^\circ 30'$ and $111^\circ 30'$; curve B, $109^\circ 28'$ and $109^\circ 28'$; curve C, $111^\circ 30'$ and $107^\circ 30'$; curve D, $113^\circ 30'$ and 106° . The ratio of the carbon-chlorine distance to the carbon-carbon distance is 1.76/1.54 for all four curves.

tribution function is shown in Fig. 1, curve B. The principal peak at 2.64 Å. is an unresolved combination of the long carbon-carbon distance and the two equal long carbon-chlorine distances. If the carbon-carbon distance is 2.52 Å., the value which would obtain if the carbon-carbon bond distance were 1.54 Å. and the C-C-C angle were $109^\circ 28'$, then the long carbon-chlorine distance would be 2.66 Å. To make this calculation it is assumed that the observed position of the radial distribution peak is a weighted mean of the two contributing distances, the weighting factors being the importance of the interatomic distance in the scattering function. If all the bond angles in the molecule are tetrahedral and the carbon-chlorine and carbon-carbon distances are 1.76 and 1.54 Å., respectively, then the long carbon-chlorine distance would be 2.70 Å. The value 2.66 Å. obtained from the radial distribution function indicates that the C-C-Cl angle is somewhat less than the tetrahedral value or that the bond distances just assumed are too great. We shall assume that the carbon-carbon distance has the value 1.54 Å., and show that the carbon-chlorine distance is not appreciably less than 1.76 Å., but that the C-C-Cl angle is slightly less than the tetrahedral value.

A theoretical intensity curve was first calculated for the model having all tetrahedral angles and a ratio of carbon-chlorine distance to carbon-carbon distance of 1.76/1.54. This curve is in satisfactory qualitative agreement with the photographs and is shown in Fig. 5, curve B. Quantitative comparison of the photographs with this curve is made in Table III. This comparison leads to a carbon-carbon distance of 1.52 Å., 0.02 Å. less than the value we assume to be correct. Quantitative comparison with curves for models having a larger C-C-Cl angle lead to still smaller values for the carbon-carbon distance so these models are discarded. Curve C, Fig. 5, calculated for a model having a C-C-Cl angle of $107^\circ 30'$, is in satisfactory qualitative agreement with the photographs. Quantitative comparison is made in Table III. Curve D, Fig. 5, calculated for a model in which the C-C-Cl angle is 106° , is unsatisfactory because the fourth maximum is too low. Models having a ratio of carbon-chlorine distance to carbon-carbon distance much different from 1.76/1.54 are not in satisfactory qualitative agreement with the photographs or lead to values for the carbon-carbon distance different from 1.54.

The results in Table III and the radial distribution function lead to the final results: carbon-chlorine distance, $1.75 \pm 0.02 \text{ \AA.}$; long carbon-chlorine distance, $2.66 \pm 0.03 \text{ \AA.}$; C-C-Cl angle $109 \pm 3^\circ$; C-C-C angle $110 \pm 3^\circ$.

Isopropyl Bromide.—Eastman Kodak Co. isopropyl bromide was purified by fractional distillation. The photographs possess eight measurable maxima, the seventh being the most difficult to measure. The values of s_0 for the maxima and minima and the intensities of the maxima are given in Table IV. The radial distribution func-

TABLE IV

ISOPROPYL BROMIDE

Values in parentheses not included in the average.

Max.	Min.	I	s^a	s^b	s^a/s_0	s^b	s^b/s_0
1	2	18	3.00	2.85	(0.950)	2.86	(0.953)
			3.94	3.78	(.960)	3.85	(.977)
2	3	20	5.10	4.88	(.957)	4.95	(.971)
			6.03	6.02	.999	6.06	1.005
3	4	17	7.21	7.16	.993	7.25	1.005
			8.24	8.31	1.009	8.42	1.022
4	5	11	9.64	9.41	0.977	9.55	0.991
			10.50	10.47	.997	10.67	1.016
5	6	4	11.56	11.47	.992	11.68	1.010
			12.57	12.54	.996	12.68	1.007
6	7	7	13.79	13.72	.995	13.83	1.003
7	8	1	15.77	16.50	(1.047)	16.60	(1.052)
			18.04	18.11	1.004	18.21	1.010
			Average		0.996	1.008	
			C-Br = 1.90 \AA.		C-Br = 1.93 \AA.		
			long C-Br = 2.81 \AA.		long C-Br = 2.81 \AA.		

^a Calculated for a model in which the C-C-C angle and the C-C-Br angle are both equal to $109^\circ 28'$ and the ratio of the carbon-bromine distance to the carbon-carbon distance is 1.91/1.54. ^b Calculated for a model in which the C-C-C angle and the C-C-Br angle are equal to $111^\circ 30'$ and $107^\circ 30'$, respectively, and the ratio of the carbon-bromine distance to the carbon-carbon distance is 1.91/1.54.

tion is shown in Fig. 1, curve D. The large peak at 2.84 \AA. represents the long carbon-bromine distance. This peak is not shifted appreciably by the long carbon-carbon distance because the long carbon-bromine distance is of much greater importance in the scattering function. The value calculated for this distance from a tetrahedral bond angle and 1.91 and 1.54 \AA. for the carbon-bromine and carbon-carbon bond distances, respectively, is 2.82 \AA. The two small peaks at 1.53 and 1.86 \AA. represent less reliably the carbon-carbon and carbon-bromine bond distances.

Theoretical intensity curves were calculated for models in which the C-C-C angle ranged from $107^\circ 30'$ to $113^\circ 30'$, the C-C-Br angle ranged from 106° to $111^\circ 30'$ and the ratio of the carbon-bromine distance to the carbon-carbon distance

varied from 1.87/1.54 to 1.95/1.54. Curve A, Fig. 6, is calculated for a model having tetrahedral angles and a ratio of carbon-bromine distance to carbon-carbon distance of 1.91/1.54. This curve is in good qualitative agreement with the photographs and quantitative comparison is made in Table IV. When the C-C-Br angle is decreased below $107^\circ 30'$, the seventh maximum becomes too prominent (see curve C, Fig. 6). When this angle is made larger than $111^\circ 30'$ the seventh maximum is too low. When the photographs are compared quantitatively with curves for models in which the ratio of the carbon-bromine distance to the carbon-carbon distance is different from 1.91/1.54, a carbon-carbon distance is obtained which differs from the value 1.54. These models are therefore eliminated.

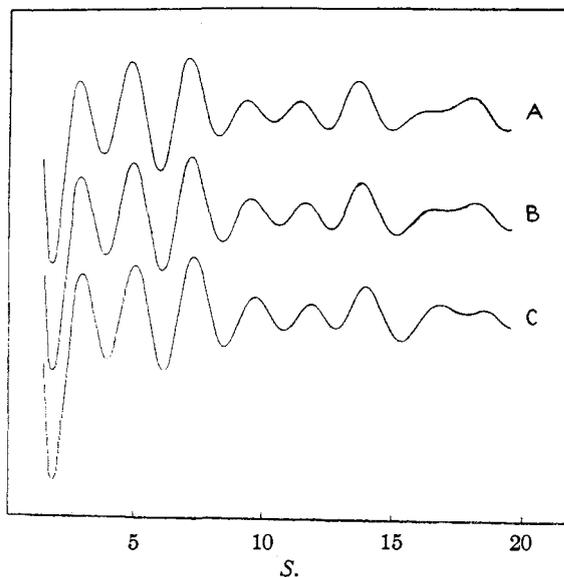


Fig. 6.—Theoretical intensity curves for isopropyl bromide. The C-C-C angle and the C-C-Br angle, respectively, are: curve A, $109^\circ 28'$ and $109^\circ 28'$; curve B, $111^\circ 30'$ and $107^\circ 30'$; curve C, $113^\circ 30'$ and 106° . The ratio of the carbon-bromine distance to the carbon-carbon distance is 1.91/1.54 for all three curves.

The quantitative comparisons in Table IV and the radial distribution function lead to the final results: carbon-bromine bond distance, $1.91 \pm 0.03 \text{ \AA.}$; long carbon-bromine distance $2.81 \pm 0.03 \text{ \AA.}$, C-C-C angle, $109^\circ 28' \pm 3^\circ$; C-C-Br angle $109^\circ 28' \pm 3^\circ$.

Methyl Chloroform.—Eastman Kodak Co. methyl chloroform was purified by fractional distillation. The photographs show eight measurable maxima. The values of s_0 for the maxima and minima and the intensities of the maxima

TABLE V
METHYL CHLOROFORM

Values in parentheses not included in the average.

Max.	Min.	<i>I</i>	<i>s</i> ₀	<i>s</i> ^a	<i>s</i> ^a / <i>s</i> ₀
1		16	2.95	2.75	(0.937)
	2		4.05	3.75	(.926)
2		20	5.15	4.91	(.953)
	3		6.27	6.12	.976
3		16	7.34	7.31	1.010
	4		8.38	8.36	0.998
4		12	9.33	9.31	.998
	5		10.57	10.41	.985
5		14	11.50	11.61	1.010
	6		12.83	12.77	0.996
6		7	13.78	13.87	1.006
	7		14.78	14.74	0.997
7		5	15.73	15.76	1.002
	8		16.88	16.95	1.004
8		3	17.91	18.19	1.016
Average					1.000

C-Cl = 1.76 Å.
Cl-Cl = 2.88 Å.

^a Calculated for a model having tetrahedral bond angles and a ratio of carbon-chlorine distance to carbon-carbon distance of 1.76/1.54.

are given in Table V. The radial distribution function, shown in Fig. 2, curve A, possesses two large peaks at 1.75 and 2.87 Å. The first peak represents the carbon-chlorine bond distance. The second is due principally to the chlorine-chlorine distance. It is shifted slightly by the long carbon-chlorine distance. If this distance is taken to be 2.70 Å, calculated from a tetrahedral bond angle, a carbon-chlorine distance of

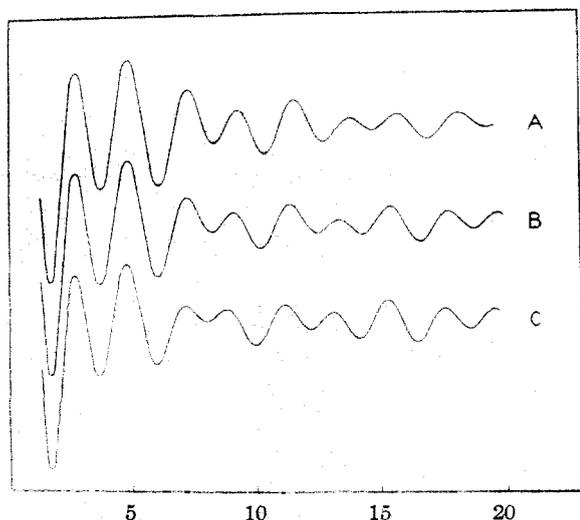


Fig. 7.—Theoretical intensity curves for methyl chloroform. The C-C-Cl angle is: curve A, 109° 28'; curve B, 112°; curve C, 114° 30'. The ratio of the carbon-chlorine distance to the carbon-carbon distance is 1.76/1.54.

1.76 Å. and a carbon-carbon distance of 1.54, the chlorine-chlorine distance must be about 2.92 Å. This value indicates that the Cl-C-Cl angle is slightly greater than the tetrahedral value. Theoretical intensity curves were calculated for models having a Cl-C-Cl angle of from 109° 28' to 114° 30'. The ratio of carbon-chlorine distance to carbon-carbon distance was taken to be 1.76/1.54. No attempt was made to determine the movement of the methyl group. The calculated curves are shown in Fig. 7. The 109° 28' curve is in satisfactory qualitative agreement with the photographs. Quantitative comparison is made in Table V. Curve B is unsatisfactory because the sixth maximum is too low. Curve C is unsatisfactory because it leads to a carbon-carbon distance less than 1.54 Å. The final results for methylchloroform are: carbon-chlorine distance, 1.76 ± 0.02 Å.; chlorine-chlorine distance, 2.89 ± 0.03 Å.; Cl-C-Cl angle, 110 ± 2°.

Isocrotyl Chloride.—The isocrotyl chloride, (CH₃)₂CCHCl, used in this investigation was an Eastman Kodak Co. product which was carefully fractionated in a thirty-inch (76-cm.) distilling column. The photographs show seven maxima, the third being close to the second and difficult to read. An eighth maximum is visible but no reliable measurements could be made on it. The radial distribution function is shown in Fig. 2, curve B. The peak at 1.63 Å. is composed of the carbon-carbon single bond distance and the carbon-chlorine bond distance. If the carbon-carbon single bond distance is assumed to be 1.54 Å. and the observed position of the peak is a weighted mean, then the carbon-chlorine distance is 1.70 Å. The peak at 2.61 Å. consists of the next longer carbon-chlorine distance and the distance between methyl carbon atoms. If the carbon-carbon distance is 2.52 Å. (calculated from a tetrahedral bond angle and a bond distance of 1.54 Å.) the carbon-chlorine distance is 2.64 Å. The peaks at 3.15 and 4.12 Å. represent the two longest carbon-chlorine distances.

In calculating theoretical intensity curves only models were considered which were planar (except for hydrogen atoms) and which had a carbon-carbon single bond distance of 1.54 Å. The methyl groups were assumed to be stationary. Curves were calculated for ten models. The C-C-Cl angle was varied from 109° 28' to 112°, the C-C-Cl angle was varied from 125° 16' to 122° and the ratio of the carbon-chlorine dis-

tance to the carbon-carbon double bond distance was varied from 1.76/1.34 to 1.72/1.34. Some of the calculated curves are shown in Fig. 6. The difficultly measurable third maximum appears, at most, as a shelf, so while it can be included in the radial distribution function it cannot be used in the quantitative comparisons between curves and photographs. Curves A and B are both for models in which the C-C-C angle and the C-C-Cl angle are tetrahedral and the C-C-Cl angle is $125^{\circ} 16'$. The ratio of the carbon-chlorine distance to the carbon-carbon double bond distance is 1.76/1.54 for curve A and 1.72/1.54 for curve B. Both curves are unsatisfactory because the fifth maximum is not sufficiently prominent. Curve C differs from curve B in that the C-C-Cl angle has been decreased to 122° . This curve is in satisfactory qualitative agreement with the photographs. Quantitative comparison is made in Table VI. If the C-C-C angle is increased much above the tetrahedral value, the fifth maximum again becomes too small.

The final results, obtained from Table VI and from the radial distribution function, are: carbon-chlorine bond distance, $1.72 \pm 0.02 \text{ \AA.}$; C-C-Cl angle, $123 \pm 2^{\circ}$; C-C-C angle $111 \pm 3^{\circ}$.

TABLE VI

ISOCROTYL CHLORIDE

Values in parentheses not included in the average.

Max.	Min.	I	s_0	s^a	s^a/s_0
1		7	3.23	3.10	(0.960)
	2		4.11	3.86	(.939)
2		12	4.92	5.05	1.026
3		5	6.35
	4		7.28	6.97	0.957
4		7	8.12	8.06	.993
	5		9.08	9.25	1.019
5		3	10.08	10.47	1.039
	6		11.53	11.40	0.989
6		4	12.55	12.50	.996
	7		13.53	13.62	1.007
7		1	14.45	15.20	1.052
Average					1.008

C-Cl 1.73 Å.

^a Calculated for a model having a C-C-C angle of $109^{\circ} 28'$, a C-C-Cl angle of 122° and a ratio of carbon-chlorine distance to carbon-carbon double bond distance of 1.72/1.34.

Discussion

In studying the structure of molecules as complicated as the molecules discussed in this paper it is not possible to determine all of the structure parameters from the electron diffraction data alone. In the case of these molecules we have not

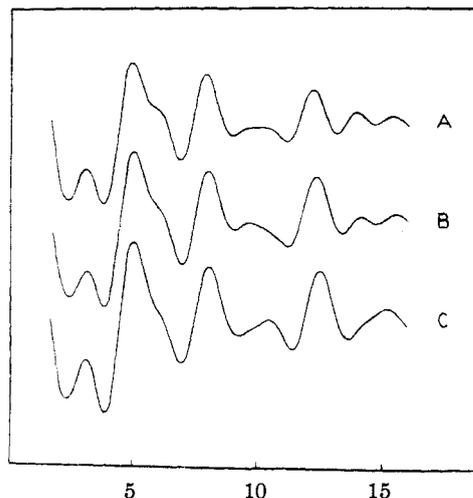


Fig. 8.—Theoretical intensity curves for isocrotyl chloride. The C-C-C angle is $109^{\circ} 28'$ in all three curves. The C-C-Cl angle is $125^{\circ} 16'$ in curves A and B, and 122° in curve C. The ratio of the carbon-chlorine distance to the carbon-carbon double bond distance is 1.76/1.34 in curve A, and 1.72/1.34 in curves B and C.

attempted to rule out, on the basis of the electron diffraction data, all of the structures bearing no geometrical relation to the conventional chemical structural formula. The number of conceivable (not chemically conceivable) arrangements of, say, ten atoms is tremendous and we have made no attempt to ascertain which non-chemical arrangements, if any, are compatible with the data. In all cases we have assumed that the structure of the molecule was essentially determined by the chemical structural formula, and then proceeded to determine the bond distances and bond angles. We have not attempted to determine the carbon-hydrogen bond distance for in all cases the hydrogen atoms contribute so little to the total electron scattering of the molecule that their positions can be assumed without fear of affecting the other results even though the assumptions are not accurate. We assumed throughout that the carbon-hydrogen bond distance is 1.09 Å., the value found for methane.¹¹ No attempt was made to determine the orientation of the methyl groups about the carbon-carbon bonds, and in calculating the theoretical intensity curves it was assumed that the hydrogen atoms avoid other atoms and each other as much as possible. Also, we have assumed the value 1.54 Å. for the carbon-carbon single bond distance. This distance is known with certainty from the X-ray study of

(11) Ginsburg and Barker, *J. Chem. Phys.*, **3**, 668 (1935).

diamond¹² and the electron diffraction studies of a large number of saturated hydrocarbons.¹³

The C-C-Cl bond angles in ethyl chloride, isopropyl chloride and *t*-butyl chloride³ are $111^{\circ} 30' \pm 2^{\circ}$, $109 \pm 3^{\circ}$ and $107 \pm 2^{\circ}$, respectively. These three values are equal to the tetrahedral angle within the experimental error. However, we believe the trend in angles to be real.

The fact that the C-C-Cl angle in *t*-butyl chloride is less than the tetrahedral value shows that the exchange repulsions and electrostatic repulsions between the methyl groups together with the electrostatic attraction of the chlorine atom for the hydrogen atoms is greater than the steric repulsion between the chlorine atom and the methyl groups. The C-C-Cl angle in methyl chloroform is $109 \pm 2^{\circ}$. This molecule is similar to *t*-butyl chloride, the groups attached to the central carbon atom merely being interchanged. Here again the bond angle between unlike groups is less than the tetrahedral value. In both compounds the electrostatic repulsion of like groups and attraction of unlike groups determines the direction of the distortion of the bond angles from the tetrahedral values. The steric repulsions between attached groups in these two molecules must be roughly equal.

The C-C-Br angles in ethyl bromide, isopropyl bromide and *t*-butyl bromide are $109 \pm 2^{\circ}$, $109^{\circ} 28' \pm 3^{\circ}$ and $107^{\circ} 30' \pm 2^{\circ}$. The trend, observed in the case of the chlorides, while present is not pronounced.

The carbon chlorine single bond distance given by the table of covalent radii^{13,14} is 1.76 Å. The carbon-chlorine distance observed in methyl chloride⁴ is 1.77 ± 0.02 Å. The carbon-chlorine distances observed in ethyl chloride, isopropyl chloride and *t*-butyl chloride³ are 1.76 ± 0.02 Å., 1.75 ± 0.03 Å. and 1.78 ± 0.03 Å., respectively. In methylchloroform the carbon-chlorine distance is 1.76 ± 0.03 Å. The carbon-chlorine distance in methyl chloride in which zero, one, two or three hydrogen atoms are replaced by methyl groups is found to be in agreement with the value given by the table of covalent radii.

The carbon-bromine distances in methyl bromide,⁵ ethyl bromide, isopropyl bromide and *t*-butyl bromide are 1.91 ± 0.06 Å., 1.91 ± 0.02 Å., 1.91 ± 0.03 Å. and 1.92 ± 0.03 Å. The value

given by the table of covalent radii for this distance is 1.91 Å. Here, as in the case of the chlorides, complete agreement is found.

In isocrotyl chloride, $(\text{CH}_3)_2\text{CCHCl}$, we have assumed the carbon-carbon single bond distance to be 1.54 Å., the value given by the table of covalent radii,^{13,14} and found to obtain in isobutene.¹³ The carbon-carbon double bond distance was assumed to be 1.34 Å., the value given by the table of covalent radii and found in ethylene¹³ and allene.¹³ The carbon-hydrogen bond distance was assumed to be 1.09 Å., the methane¹¹ value. The carbon-chlorine distance was found to be 1.72 ± 0.02 Å. The difference of 0.04 Å. between this value and the value found for the compounds discussed above is very probably real and is in fact not surprising. The effect of an adjacent double bond on a carbon-chlorine bond distance already has been observed. It was found in the case of the chloroethylenes⁶ that the carbon-chlorine bond distance is less than the normal value; the shortening is greatest in the case of vinyl chloride and decreases as the number of chlorine atoms is increased. The shortening in isocrotyl chloride, 0.04 Å., is not so great as in vinyl chloride, 0.08 Å. As both compounds have one atom adjacent to the double bond this is at first surprising. The shortening in isocrotyl chloride is about the same as the shortening in trichloroethylene. The presence of two methyl groups decreases the shortening approximately as much as two chlorine atoms. This shows that there is some conjugation of the carbon-carbon single bonds with the double bond, decreasing the shortening in isocrotyl chloride to about the same extent that the additional chlorine atoms decrease the shortening in trichloroethylene. This conjugation will have some effect on the carbon-carbon single bond distance which we assumed to be 1.54 Å. The shortening of a single bond adjacent to a triple bond has been observed in methylacetylene^{15,16} to be 0.08 Å. The shortening of a carbon-carbon single bond adjacent to a benzene ring is negligible. The carbon-carbon single bond distance in hexamethylbenzene is 1.53 Å.¹⁷ We would, therefore, estimate the carbon-carbon single bond distance in isocrotyl chloride to be between 1.51 and 1.53 Å.

(15) L. Pauling, H. D. Springall and K. J. Palmer, *THIS JOURNAL*, **61**, 927 (1939).

(16) G. Herzberg, F. Patat and H. Verleger, *J. Phys. Chem.*, **41**, 123 (1937).

(17) L. O. Brockway, paper presented to the American Chemical Society at Baltimore, Md., April, 1939.

(12) "Strukturbericht."

(13) L. Pauling and L. O. Brockway, *THIS JOURNAL*, **59**, 1223 (1937).

(14) L. Pauling and M. L. Huggins, *Z. Krist.*, **87A**, 205 (1934).

This will not affect materially the carbon-chlorine distance of 1.72 Å. we obtained assuming 1.54 Å.

Of the compounds discussed in this paper only ethyl chloride and ethyl bromide have been studied previously by the electron diffraction method.¹⁸ The results were: 1.81 ± 0.1 Å. for the carbon-chlorine distance in ethyl chloride and 2.07 ± 0.07 Å. for the carbon-bromine distance in ethyl bromide. Both of these values are somewhat higher than the values reported by us. We believe our values to be more reliable because of the advances which have been made in electron diffraction technique since the other work was done.

Summary

Electron diffraction has been used to determine

(18) L. Bru, *Anal. soc. españ. fis. quim.*, **31**, 115 (1933).

the molecular structures of ethyl chloride, ethyl bromide, isopropyl chloride, isopropyl bromide, methyl chloroform and isocrotyl chloride. The results are given in Table VII.

TABLE VII

Compound	C-Cl distance, Å.	C-C-Cl angle
	Ethyl chloride	1.76 ± 0.02
Isopropyl chloride	1.75 ± 0.03	$109 \pm 3^\circ$
	C-Br	C-C-Br
Ethyl bromide	1.91 ± 0.02	$109 \pm 2^\circ$
Isopropyl bromide	1.91 ± 0.03	$109^\circ 28' \pm 3^\circ$
	C-Cl	C-C-Cl
Methylchloroform	1.76 ± 0.02	$109 \pm 2^\circ$
Isocrotyl chloride	1.72 ± 0.02	$123 \pm 2^\circ$

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF NORTH CAROLINA]

The Constitution of Natural Tannins. VI.¹ Coloring Matters Derived from 2,5-Dihydroxyacetophenone

BY ALFRED RUSSELL AND SAMUEL FRIEND CLARK²

The material already reported includes a description of polyhydroxychalcones derived from various 2-hydroxy ketones (notably resacetophenone, phloracetophenone, and gallacetophenone) and hydroxyaldehydes (notably protocatechualdehyde, vanillin, *m*-hydroxybenzaldehyde, and *p*-hydroxybenzaldehyde). By reduction of these 2'-hydroxychalcones with zinc dust and dilute alcoholic acids are obtained light colored amorphous products; when these amorphous products are water-soluble (those derived from protocatechualdehyde only), they are qualitatively indistinguishable from natural phlobatanins. On various grounds it is probable that the amorphous products are flavopinacols hydroxylated on the patterns of the parent chalcones; for the sake of simplicity they are formulated as of the *bis* type, although their structure may be more complicated.

To continue the series so far described, polyhydroxychalcones derived from the various hydroxyaldehydes with three other hydroxy ketones should

(1) The present paper forms a continuation of a series of five articles published in the Journal of the Chemical Society; Russell and co-workers, *J. Chem. Soc.*, 218, 1066, 1506, 1940 (1934); 421 (1937); cf. also Russell, *Chem. Rev.*, **17**, 155 (1935).

(2) From a dissertation submitted to the Faculty of the University of North Carolina in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1939.

be examined; these ketones are the dihydroxyacetophenones, 2,3-, 2,6- and 2,5-. The reason for selecting 2,3-dihydroxyacetophenone is the frequent occurrence of catechol as a fission product of natural materials, it not being at all certain that this always comes from a benzopyran compound hydroxylated in the 3',4'-positions (I)—an hydroxyl group may in some cases be located in the 8-position (II) (the second one ortho to the first appearing after fission). 2,6-Dihydroxyacetophenone must be included because of the frequent occurrence of resorcinol, not necessarily resulting from a compound hydroxylated in the 7-position (III) but possibly from a compound hydroxylated in the 5-position (IV). 2,5-Dihydroxyacetophenone is selected because of the occasional occurrence of quinol as a decomposition product of natural materials, suggesting a benzopyran compound hydroxylated in the 6-position (V). In particular, the monomethyl ether of quinacetophenone has been isolated as a decomposition product of a yellow coloring matter from a European variety of stemless primrose.³ Moreover, Nierenstein⁴ has reported finding quinol amongst the decomposition products of quebracho tannin.

(3) Goris and Canal, *Compt. rend.*, **200**, 1990 (1935).

(4) Nierenstein, *Collegium*, **65** (1905).