heated at 200–220° for twelve hours to yield amyl mercaptan (30%), b. p. 116–118°, and camphor anil.

Anil Scission by Hydrogen Sulfide.—Dry hydrogen sulfide gas is bubbled through dry benzophenone anil at 220° for two hours. Aniline, unchanged anil, and thiobenzophenone are recovered from the reaction products. The thiobenzophenone fraction, green oil of boiling range 170–175° (14 mm.), proved to be a mixture of the thioketone and the oxyketone into which the former is changed by exposure to moist air.

Summary

Ketone anils have been prepared by the sulfur dehydrogenation of mixed alkyl-aryl secondary amines of the type, Ph-NH-CHR_2.

Acetone anil has been prepared by the sulfur dealkanation of tertiary isopropyl anilines of the type, Ph-NR-$CH(CH_3)_2$.

Camphor anil has been prepared by the action of sulfur on isobornylacetanilide and also by the dehydrogenating action of alkyl disulfides on isobornylaniline.

Under the reaction conditions, the anils have been found to undergo scission by hydrogen sulfide, spontaneous aldolization, and reduction by mercaptans in a mercaptan–disulfide–anil–amine equilibrium.

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The Electron Diffraction Investigation of Seven Chlorobenzenes

BY L. O. BROCKWAY AND K. J. PALMER

Introduction

The effect of conjugation on bond length was demonstrated a few years ago in the case of diacetylene and cyanogen,[1] in which the single carbon bond lying between two triple bonds, as the structures are ordinarily written, is 0.11 Å. shorter than a single bond in an unconjugated system. This bond shortening was explained as the effect of some double bond character introduced by the resonance of the molecules among several electronic structures including some having a double bond in the position of the single bond in the ordinary structure. This effect is well illustrated by the benzene molecule in which resonance chiefly between the two Kekulé structures shortens the single bonds in the individual structures by 0.15 Å.

More recently in an investigation of the chloroethylenes[2] a conjugated system of a similar type was found to exist when a single bond lies between two atoms, one of which has an unshared pair of electrons and the other is connected by a double bond to a third atom. In this case similar resonance possibilities arise; and the carbon–chlorine bonds in the chloroethylenes were found to be from 0.03 to 0.09 Å. shorter than they are in the chloromethanes. At that time it was suggested that in the halogen substituted benzenes also the carbon–halogen bonds would probably be affected; and the present investigation was begun to measure the effect and to test the possible influence of the number and position of the substituent atoms. We are now reporting the results of the electron diffraction investigation of the vapors of hexachlorobenzene, 1,2,4,5-tetrachlorobenzene, 1,3,5-trichlorobenzene, *o*-, *m*-, and *p*-dichlorobenzenes, and monochlorobenzene.

Experimental

The materials used were obtained from the Eastman Kodak Co. Because of their relatively low vapor pressures at room temperature it was necessary to use a sample holder and gas nozzle which could be heated to about 300°. This consisted of a cylinder of monel metal about an inch (2.5 cm.) long and one-half inch (1.27 cm.) in diameter. The upper end was fitted with a removable cap which gave access for charging the holder with the sample. In the cap was a copper plug containing a 0.016″ (0.41-mm.) hole through which the vapor passed to meet the electron beam just above the top surface of the cap. The flow of vapor was controlled by a needle-pointed rod seated into the hole in the copper plug. The lower end of the monel cylinder was closed by a plate through which a sleeve passed for supporting the valve needle. The movement of this needle was controlled from the outside through a siphon connection. A resistance wire wound on the monel cylinder with mica insulation heated the

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[1] L. O. Brockway, *Proc. Nat. Acad. Sci.*, **19**, 868 (1933).

[2] L. O. Brockway, J. Y. Beach and L. Pauling, THIS JOURNAL, **57**, 2693, 2705 (1935).

whole arrangement to temperatures which were followed by a thermocouple on the top of the removable cap. This style of high temperature nozzle has the advantage that vapor flows into the apparatus only at the time the exposure is being made.

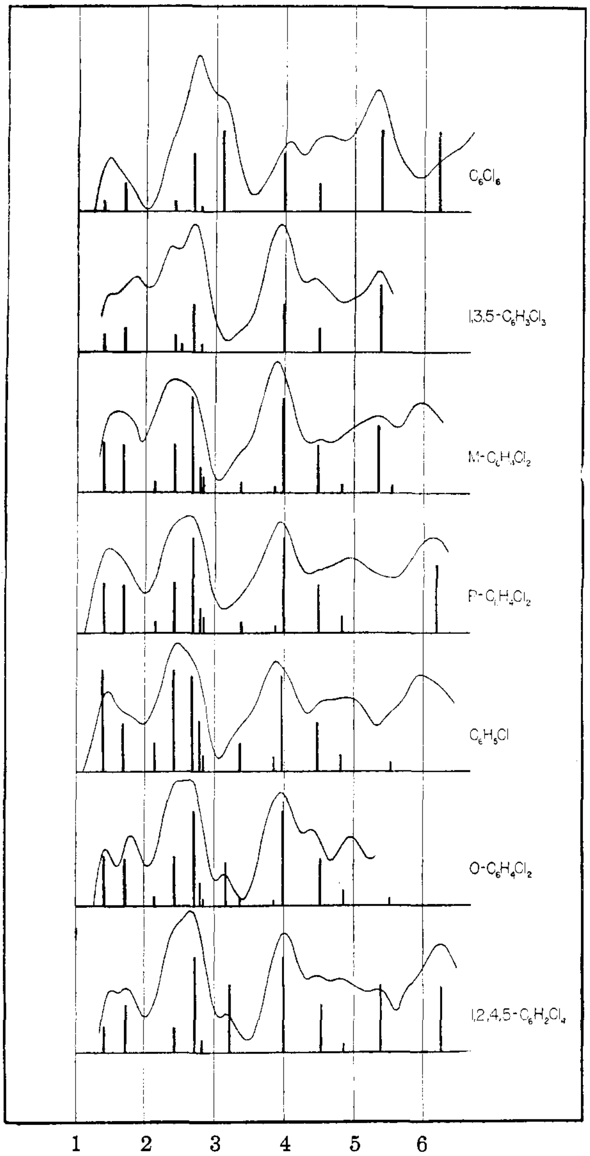

Fig. 1.—Curves showing the observed radial distributions of scattering matter in the chlorobenzenes. The heavy vertical lines indicate the values of the interatomic distances determined with the aid of theoretical scattering curves; the relative heights of the lines for each substance are proportional to the scattering power associated with the respective atomic separations.

Photographs were obtained of the seven substances mentioned above by the usual technique[3] using a camera distance of 10.87 cm. and an electron wave length of 0.0611 Å. From seven to ten maxima were measured for each compound and the corresponding values of s_0 (equal to 4π (sin θ/ 2)/λ) are listed in Tables I–VII. These were combined with visually estimated intensities to give the observed radial distributions of scattering matter[4] shown in Fig. 1. The positions of the stronger peaks in these curves were taken into account in determining the interatomic distances in the respective molecules.

For the calculation of theoretical scattering curves models were used in which the benzene ring was taken as a regular hexagon with an edge of 1.39 Å., the distance found in benzene[5] and in mesitylene and hexamethylbenzene.[6] The carbon–chlorine bonds in all of the compounds except *o*-dichlorobenzene and 1,2,4,5-tetrachlorobenzene were assumed to make 120° angles with the sides of the carbon hexagon, and the different carbon–chlorine bonds in a single molecule were assumed to be equal in length. Wherever carbon–hydrogen bonds occurred, the distance 1.06 Å. was used. All interference terms except those of hydrogen–hydrogen were included in the calculations. Various carbon–chlorine distances were assumed, but on account of the greater scattering power of chlorine compared with carbon it was found that the curves for the molecules containing several chlorine atoms were not affected by small changes in the relative size of the benzene ring. Only in the case of chlorobenzene could the carbon–carbon distance be determined directly. A value for the sum of the carbon–carbon and carbon–chlorine bond distances was obtained in each case, and the latter distance was fixed with the aid of assumed values for the C–C separation. For reasons discussed in the final section of this paper the carbon–carbon distance in some of the compounds (as indicated in the following paragraphs) was assumed to be 0.01 Å. larger than in benzene.

Hexachlorobenzene.—Three curves calculated for hexachlorobenzene, with carbon–chlorine distances of 1.68, 1.70, and 1.76 Å., respectively, show excellent qualitative agreement with the observed ten-maximum diffraction pattern. The second of these is reproduced in Fig. 2 with the

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[3] L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

[4] For the procedure used in obtaining these curves see L. Pauling and L. O. Brockway, This Journal, **57**, 2684 (1935); also W. Schomaker and C. Degard, to be published in This Journal.

[5] L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

[6] L. Pauling and L. O. Brockway, This Journal, **59**, 1223 (1937).

positions of the measured maxima and minima marked. From the data in Table I the ortho chlorine–chlorine distance is fixed at 3.11 ± 0.03 Å., the same value being obtained from the other two models. This is equal to the sum of the carbon–carbon and carbon–chlorine bond distances; and with the former assumed to be 1.41 Å., the latter is given as 1.70 ± 0.03 Å.

TABLE I

HEXACHLOROBENZENE

Max.	Min.	I	s_0	s^a	s/s_0
1		8	2.82	2.57	(0.912)
	2		4.00	3.85	(.963)
2		10	4.98	4.96	.996
	3		5.67	5.77	1.017
3		2	6.30	6.33	1.005
	4		6.77	6.77	1.000
4		3	7.33	7.31	0.998
	5		7.85	7.78	0.991
5		6	8.44	8.45	1.001
	6		9.08	9.18	1.011
6		4	9.83	(10.00)	
7		2	12.21		
	8		13.61	13.78	1.012
8		5	14.35	14.56	1.014
9		1	16.49	16.66	1.011
10		2	18.87	19.15	1.014
				Average	1.006
				Cl–Cl (ortho)	3.11 Å.

[a] Calculated for C–C = 1.39 Å. and C–Cl = 1.70 Å.

1,3,5-Trichlorobenzene.—Carbon–chlorine distances of 1.70, 1.72, and 1.76 Å., respectively, were used in calculating theoretical intensity curves for 1,3,5-trichlorobenzene. Because they lead to the same result the first one only is reproduced in Fig. 2. The qualitative agreement with the photographs is again very good. A small change in the scale of this curve is required by the quantitative comparison in Table II, which leads to the value Cl–Cl (meta) = 5.38 ± 0.05 Å. The sum of the C–C and C–Cl distances is then 3.10 ± 0.03 Å.; and with C–C = 1.41 Å., we obtain the final value C–Cl = 1.69 ± 0.03 Å.

TABLE II

1,3,5-TRICHLOROBENZENE

Max.	Min.	I	s_0	s^a	s/s_0
1		8	3.41		
2		10	5.22	5.05	(0.968)
3		4	7.29	7.40	1.015
	4		7.84	7.88	1.005
4		4	8.48	8.42	0.993
	5		9.09	9.12	1.004
5		6	9.86	9.83	0.997
6		5	11.72	11.87	1.013
	7		12.39	12.60	1.017
7		2	13.03	13.08	1.004
	8		13.68	13.72	1.003
8		5	14.34	14.50	1.011
9		1	16.55	16.58	1.002
10		2	19.04	19.18	1.007
			Average		1.006
			Cl–Cl (meta) =		5.38 Å.

[a] Calculated for C–C = 1.39 Å., C–Cl = 1.70 Å., and C–H = 1.06 Å.

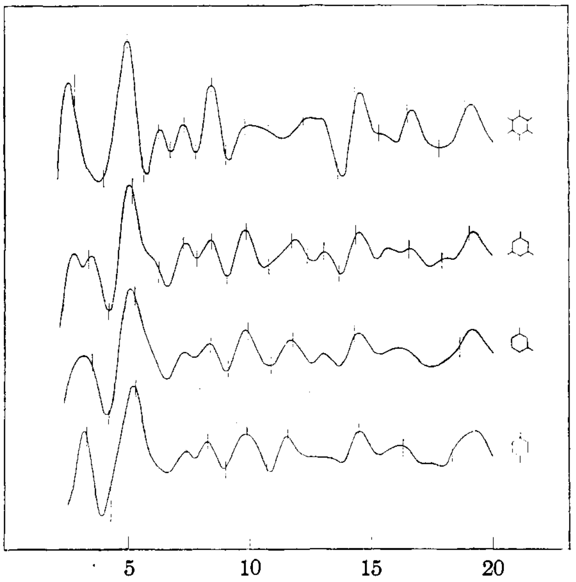

Fig. 2.—Theoretical electron scattering curves for hexachlorobenzene, 1,3,5-trichlorobenzene, *m*-dichlorobenzene, and *p*-dichlorobenzene. The positions of the maxima and mimima measured on the photographs are shown for each substance.

***m*-Dichlorobenzene.**—Ten maxima were observed on the photographs of *m*-dichlorobenzene, but the last two were too faint for reliable measurements of their diameters to be made. In choosing molecular models to be considered those involving a distortion of the C–Cl bond angles were neglected because the interaction of two chlorine atoms separated by more than 5 Å. is scarcely great enough to bend the bonds. The undistorted models give curves which reproduce the observed pattern satisfactorily. The three theoretical curves, calculated for C–Cl distances of 1.68, 1.70, and 1.76 Å., respectively, show slight qualitative differences; but in the quantitative comparisons with the s_0 values from the photographs the same value for the meta chlorine–chlorine separation is obtained, namely, 5.35 ± 0.05 Å. (Table III). Accordingly, it is impossible also in this case to make a direct determination of the size of the benzene ring. With the sum of the C–C and C–Cl distances equal to 3.09 ± 0.03 Å. the separate distances are given the values C–C = 1.40 Å. and C–Cl = 1.69 ± 0.03 Å.

TABLE III

m-DICHLOROBENZENE

Max.	Min.	I	s_0	s^a	s/s_0
1		8	3.46	3.28	(0.948)
2		10	5.34	5.13	(.961)
3			(7.02)	7.39	
4		4	8.28	8.34	1.007
	5		9.07	9.07	1.000
5		5	9.91	9.86	0.995
	6		10.86	10.79	.993
6		4	11.77	11.73	.996
7			13.07	13.06	.999
8		2	14.33	14.50	1.012
9			(16.47)	16.10	
10		1	(18.64)	19.15	
				Average	1.000

Cl–Cl (meta) = 5.35 Å.

[a] Calculated for C–C = 1.39 Å. and C–Cl = 1.70 Å.

***p*-Dichlorobenzene.**—The three theoretical curves for *p*-dichlorobenzene with C–Cl equal to 1.68, 1.70, and 1.76 Å., respectively, do not show significant differences, and on comparison with the photographs each of them gives a value for the para chlorine–chlorine separation of 6.18 ± 0.06 Å. (Table IV). The sum of C–C and C–Cl, accordingly, is 3.09 Å., so that with a C–C distance of 1.40 Å., the C–Cl distance is 1.69 ± 0.03 Å.

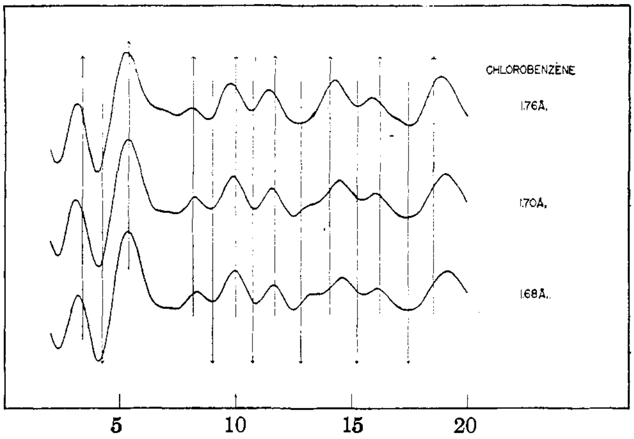

Fig. 3.—Theoretical scattering curves for three molecular models of chlorobenzene.

TABLE IV

p-DICHLOROBENZENE

Max.	Min.	I	s_0	s^a	s/s_0
1		5	3.38	3.25	(0.961)
2		10	5.33	5.27	0.989
3		2	8.27	8.30	1.004
	4		9.05	8.98	0.993
4		3	9.89	9.90	1.001
	5		10.77	10.86	1.008
5		3	11.57	11.58	1.001
6		2	14.38	14.53	1.011
7		1	16.30	16.24	0.996
				Average	1.000

Cl–Cl (para) = 6.18 Å.

[a] Calculated for C–C = 1.39 Å. and C–Cl = 1.70 Å.

Chlorobenzene.—The three theoretical curves calculated for chlorobenzene are shown in Fig. 3. Of these the first (C–Cl = 1.76 Å.) is less satisfactory than the other two because it fails to show the shelf observed in the photographs on the inner side of the sixth maximum (near s = 14.4). In Table V it is seen that the "1.76" model leads to a carbon–carbon distance of 1.37 Å., which is 0.02 Å. less than that in benzene. For these two reasons the "1.76" model is rejected. The other models are equally good, and the average results given by them are C–Cl = 1.69 ± 0.03 Å. and C–C = 1.39 ± 0.02 Å.

***o*-Dichlorobenzene.**—Theoretical intensity curves were calculated for three undistorted models of *o*-dichlorobenzene; model A, C–Cl = 1.76 Å.; model B, C–Cl = 1.70 Å.; and model C, C–Cl = 1.68 Å. Model C is in definite disagreement with the photographs, since it shows two equal maxima at s = 11.6 and 13.0, respectively, where a strong maximum and a weak shelf are observed (Fig. 4). Model B is unsatisfactory for the same reason. Model A, on the other hand, shows good qualitative agreement with the photographs with respect to the relative intensities of successive maxima. From the data of Table VI model A gives an ortho Cl–Cl separation of 3.11 Å., a C–Cl distance of 1.74 Å., and a C–C distance of 1.37 Å. This value for the C–C distance smaller than in benzene is probably not correct, however, and the possibility of distortion of the carbon–chlorine bonds was considered.

The satisfactory qualitative appearance of curve A required that only very small changes be made in the relative lengths of the more important interatomic separations. The group of carbon–chlorine terms is responsible for more than half of the total scattering, and their relative contributions were held practically constant by choosing new models having the value for the sum of the carbon–carbon and carbon–chlorine distances required by model A, that is, 3.11 Å. With this restriction three additional models were considered in which the chlorine–

TABLE V

CHLOROBENZENE

Max.	Min.	I	s_0	s_A	s_A/s_0	s_B	s_B/s_0	s_C	s_C/s_0
1		6	3.41	3.18	(0.932)	3.08	(0.903)	3.14	(0.921)
2		10	5.42	5.37	.991	5.34	.985	5.29	.976
3		3	8.17	8.33	1.020	8.24	1.008	8.10	.991
	4		9.01	8.97	0.996	8.95	0.994	8.83	.980
4		4	10.00	9.95	.995	9.91	.991	9.78	.978
	5		10.75	10.88	1.012	10.85	1.010	10.67	.993
5		3	11.67	11.63	0.997	11.58	0.993	11.44	.980
	6		12.81	12.49	(.975)	12.50	(.976)	12.65	.987
6		3	14.06	14.60	(1.038)	14.50	(1.031)	14.28	1.015
	7		15.28	15.50	1.015	15.46	1.012	15.25	0.998
7		1	16.24	16.10	0.991	16.05	0.989	15.87	.978
				Average	1.002		0.998		0.988
				C–Cl, Å.	1.684		1.696		1.739
				C–C	1.393		1.387		1.374

s_A: calculated for C–C = 1.39 and C–Cl = 1.68.
s_B: calculated for C–C = 1.39 and C–Cl = 1.70.
s_C: calculated for C–C = 1.39 and C–Cl = 1.76.

TABLE VI

o-DICHLOROBENZENE

Max.	Min.	I	s_0	s_A	s_A/s_0	s_D	s_D/s_0
1		8	3.35	3.05	(0.911)	3.05	(0.911)
2		10	5.24	5.03	(.960)	5.12	(.977)
3		2	(7.00)	6.78		6.79	
4		4	8.31	8.18	0.984	8.29	.998
	5		9.18	8.98	.978	9.10	.991
5		6	10.03	9.88	.985	10.01	.998
	6		10.86	10.70	.985	10.88	1.002
6		4	11.74	11.45	.976	11.67	0.994
	7		13.37	13.36	.999	13.50	1.010
7		6	14.39	14.35	.997	14.50	1.008
	8		15.43	15.31	.993	15.44	1.000
8		1	16.35	16.03	.980	16.20	0.991
	9		17.57	17.55	.999	17.53	0.998
9		3	18.80	18.84	1.002	19.00	1.011
		Average			0.989		1.000
		Cl–Cl (ortho) Å.			3.115		3.150
		Sum of C–C and C–Cl			3.115		3.110

s_A: calculated for C–C = 1.39 Å., C–Cl = 1.76 Å., Cl–Cl = 3.15 Å.—undistorted. s_D: calculated for C–C = 1.39 Å., C–Cl = 1.72 Å., Cl–Cl = 3.15 Å.—C–Cl angles bent through 0°48′.

chlorine distance is increased above that in the undistorted molecule but with the chlorine atoms still in the plane of the benzene ring: model D, Cl–Cl = 3.15 Å.; model E, Cl–Cl = 3.30 Å.; and model F, Cl–Cl = 3.30 Å. In the curve for model F (Fig. 4) the third maximum observed on the photographs is entirely missing, and the shelf observed on the outside of the sixth maximum (at s = 11.6) does not appear. In curve E these features are a little better, and in curve D the representation is entirely satisfactory. The quantitative comparison from curve D is the most consistent, and it is shown in Table VI. In the final result the ortho chlorine–chlorine separation is 3.15 ± 0.03 Å. and the sum of the carbon–carbon and carbon–chlorine distances is 3.11 ± 0.03 Å. This latter distance is divided between C–C = 1.40 Å. and C–Cl = 1.71 ± 0.03 Å.

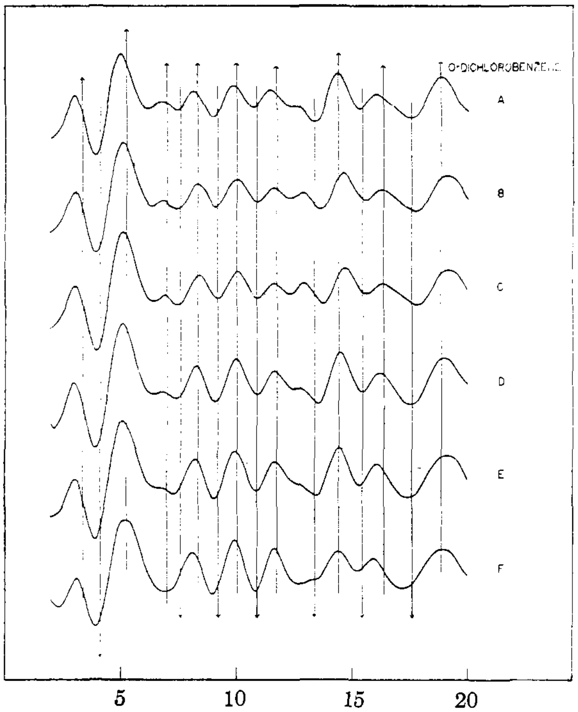

Fig. 4.—Theoretical scattering curves for various models of *o*-dichlorobenzene.

1,2,4,5-Tetrachlorobenzene.—Five molecular models of 1,2,4,5-tetrachlorobenzene were used in calculating theoretical intensity curves. The first two were undistorted, *i. e.*, with all C–Cl bonds directed toward the center of the benzene ring and with C–Cl = 1.70 and 1.76 Å., respectively.

Both curves failed to reproduce the diffraction pattern in the region between $s = 5$ and 8, and the maximum near $s = 10$ is too small relative to the maxima on either side. The second of these curves is shown as A in Fig. 5. The following distorted models similar to those of *o*-dichlorobenzene were calculated: model B, C–Cl = 1.72 Å., Cl–Cl (ortho) = 3.18 Å.; model C, C–Cl = 1.72 Å., Cl–Cl (ortho) = 3.20 Å.; and model D, C–Cl = 1.72 Å., Cl–Cl (ortho) = 3.30 Å. It may be noted that the ratios of the meta and ortho chlorine–chlorine separations in the four models have the respective values: 1.732, 1.685, 1.662, 1.593. Model D is eliminated because the fourth measured maximum (at $s = 10.0$) is too strong relative to the third and fifth; moreover, no suggestion of the small maximum at $s = 13.4$ appears on the photographs. Models B and C give better qualitative representations of the photographs, and the quantitative consistency of the data in Table VII is better than for model D. The final values taken as intermediate between the results from models B and C are known with a little less certainty than in the foregoing substances: Cl–Cl (ortho) = 3.20 ± 0.04 Å., Cl–Cl (meta) = 5.37 ± 0.06 Å., Cl–Cl (para) = 6.25 ± 0.07 Å. The sum of C–C and C–Cl is accordingly 3.12 ± 0.04 Å., which is divided between C–C = 1.40 Å. and C–Cl = 1.72 ± 0.04 Å.

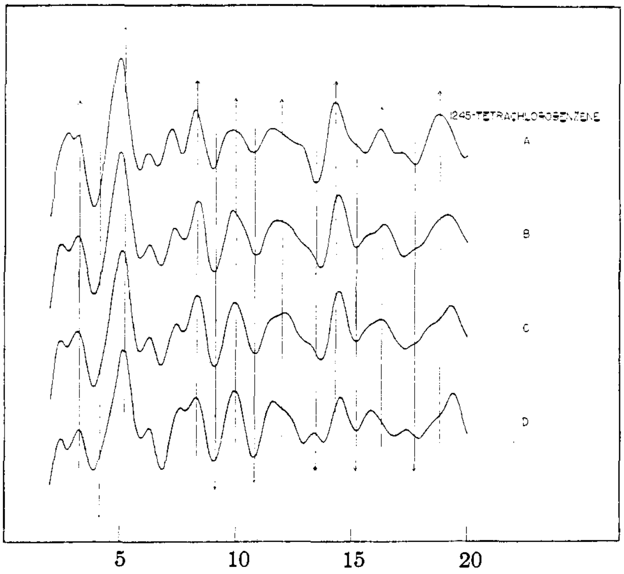

Fig. 5.—Theoretical scattering curves for various models of 1,2,4,5-tetrachlorobenzene.

The foregoing results may be compared with the results of previous investigations. The only other electron diffraction investigation is that of de Laszlo[7] on hexachlorobenzene, for which he reports an ortho Cl–Cl distance of 3.10 Å., a value supported by our result of 3.11 ± 0.03 Å.

R. Schoppe[8] obtained X-ray diffraction photographs of the vapors of chlorobenzene, *o*-, *m*-, and *p*-dichlorobenzenes, and 1,2,4-trichlorobenzene. He reports the distances C–Cl = 1.65 ± 0.03 Å., Cl–Cl (ortho) = 3.30 ± 0.05 Å., Cl–Cl (meta) = 5.35 ± 0.08 Å., and Cl–Cl (para) = 6.10 ± 0.09 Å. with an assumed C–C distance of 1.42 Å. The procedure used in fixing on the reported distances is not entirely clear, but it seems probable that the observed agreement between theory and experiment would not be affected if values outside of the ranges given by the investigator were used. In particular, the chlorine–chlorine distance in *o*-dichlorobenzene cannot be greater than 3.20 Å. because of the definite disagreement (pointed out in the above discussion of this compound) between our electron-diffraction photographs and theoretical diffraction patterns based on models having distances greater than 3.20 Å. This disagreement is not marked in the region out to $s = 8$ observed by Schoppe but is unmistakable in our photographs extending to $s = 19$. His value for the meta chlorine–chlorine distance, 5.35 Å., is supported by our results; but the para distance of 6.10 Å. is about 0.10 Å. too small. The distance 1.42 Å. which he used for the carbon–

Table VII

1,2,4,5-Tetrachlorobenzene

Max.	Min.	I	s_0	s_B	s_B/s_0	s_C	s_C/s_0
1		8	3.26	3.18	(0.976)	3.15	(0.966)
2		10	5.20	5.07	(.975)	5.07	(.975)
3		6	8.31	8.33	1.002	8.33	1.002
	4		9.11	9.07	0.996	9.05	0.993
4		5	9.95	9.85	.990	9.92	.997
	5		10.82	10.87	1.005	10.85	1.003
5		3	11.86	11.80	0.994	12.11	1.021
	6		13.44	13.62	1.014	13.65	1.016
6		5	14.29	14.47	1.014	14.43	1.010
	7		15.18	15.22	1.003	15.20	1.002
7		1	16.27	16.35	1.005	16.25	0.999
8		2	18.82	19.12	1.016	19.30	1.026
		Average			1.004		1.007
		Cl–Cl (ortho) Å.			3.193		3.222
		Cl–Cl (meta)			5.380		5.357
		Cl–Cl (para)			6.26		6.25
		Sum of C–C and C–Cl			3.12		3.125

s_B: calculated for C–C = 1.39 Å., C–Cl = 1.72 Å., and Cl–Cl (ortho) = 3.18 Å.

s_C: calculated for C–C = 1.39 Å., C–Cl = 1.72 Å., and C–Cl (ortho) = 3.20 Å.

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(7) H. de Laszlo, *Proc. Roy. Soc.* (London), **A146**, 662 (1934).

(8) R. Schoppe, *Z. physik. Chem.*, **B34**, 461 (1936).

carbon distance was originally observed in graphite and is 0.02 or 0.03 Å. larger than the distance in benzene and its derivatives. With this correction Schoppe's carbon–chlorine distance becomes 1.67 or 1.68 Å., as compared with our values of 1.69 to 1.71 Å.

An X-ray investigation of hexachlorobenzene was made by Kaiser,[9] who obtained an ortho chlorine–chlorine separation of 3.35 ± 0.05 Å. Pierce[10] investigated chlorobenzene and *o*- and *p*-dichlorobenzenes and reported ortho Cl–Cl = 3.0 Å. and para Cl–Cl = 6.25 Å.

Hendricks[11] obtained a para chlorine–chlorine separation of 6.2 Å. (our result—6.18 Å.) in an X-ray investigation of crystalline *p*-dichlorobenzene. Mrs. Lonsdale[12] studied crystalline hexachlorobenzene; and while she did not obtain a complete set of parameter values for the atomic positions, the average of the minimum values suggested by her for the carbon–chlorine bond distances is 1.71 Å., in good agreement with the result of the present investigation.

Discussion

Carbon–Chlorine Distances.—The carbon–chlorine bond distances in the seven chlorobenzenes investigated all lie in the range from 1.69 to 1.71 Å., inclusive (with the exception of the value 1.72 Å. observed with less certainty in tetrachlorobenzene). As was remarked by de Laszlo[7] this is 0.06 Å. less than the carbon–chlorine distances observed in saturated aliphatic chlorine compounds. That such a difference might be expected on the basis of a characteristic difference in the radii of aliphatic and aromatic carbon atoms was suggested by Mrs. Lonsdale[13] in her investigation of hexamethylbenzene. A recent more complete analysis[6] of hexamethylbenzene, however, leads to the same value for the length of the bond C_{ar}–C_{al} which is observed for the bond C_{al}–C_{al} in many aliphatic compounds.

We suggest that the situation which gives rise to the shortening is entirely analogous to the situation in the chloroethylenes.[2] If we consider the various Lewis electronic structures which make appreciable contributions to the normal state of *o*-dichlorobenzene, for example, the first two (Fig. 6) are the Kekulé structures of the benzene ring. In addition we can write a set of three others in which one of the chlorine atoms is connected to the ring by a double bond, and an unshared pair of electrons appears on one of the three carbon atoms ortho or para to the first. A second set of three structures exists in which the other chlorine atom is double bonded. If each of these sets of three makes a 10% contribution to the normal state of the molecule, the observed shortening of 0.05 Å. below the value 1.76 Å. found in the chloromethanes is just accounted for on the basis of the empirical relation which has been developed between bond length and double bond character.[2,6] A contribution of this magnitude is not unreasonably large, and similar formulations can be made for the other chlorobenzenes. Variations in the degree of double bond character might be expected with variations in the number and positions of the chlorine atoms attached to the ring, but the effect on the bond distances is evidently less than the experimental error. The small variations which are observed in the distances bear no definite relation to the number or positions of the chlorine atoms, although the shortest distances are obtained in the four compounds not containing chlorine atoms attached to adjacent carbon atoms.

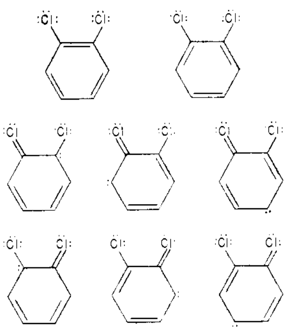

Fig. 6.—Figures representing the electronic structures of *o*-dichlorobenzene which make appreciable contributions to the ground state of the molecule. The C–H bonds are not shown: unshared electron pairs are indicated by pairs of dots.

The effect observed in the chlorobenzenes amounts to 16% double bond character for a C–Cl distance of 1.69 Å., decreasing to 10% for a distance of 1.71 Å. This is comparable in magnitude to the effect in the chloroethylenes, in which the C–Cl distances range from 1.69 to 1.73 Å. In these latter substances there is more certain evidence for an increase in the distance with increase in the number of chlorine atoms. This may be due to the fact that the number of chlorine atoms adjacent to the double bond ranges from one to four, whereas the corresponding number in the chlorobenzenes is either one or two. The range of the carbon–chlorine distances in the chlorobenzenes accordingly is less than in the chloroethylenes.

(9) R. Kaiser, *Physik. Z.*, **36**, 92 (1935).

(10) W. C. Pierce, *J. Chem. Phys.*, **2**, 1 (1934).

(11) S. B. Hendricks, *Z. Krist.*, **84**, 85 (1933).

(12) K. Lonsdale, *Proc. Roy. Soc.* (London), **A133**, 536 (1931).

(13) K. Lonsdale, *ibid.*, **A123**, 494 (1929).

A similar shortening of bond distance is expected for any other substituent atom having an unshared electron pair. This has been observed by de Laszlo[7] for bromobenzenes and iodobenzenes. Dibromoacetylene[14] also shows such an effect.

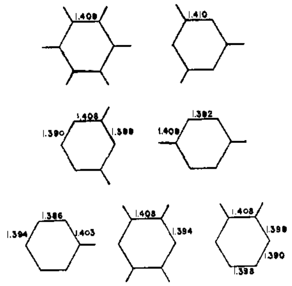

Fig. 7.—Expected values for the C–C bond distances in the chlorobenzenes based on the observed shortenings in the C–Cl bonds. The numbers represent the C–C bond lengths in Ångström units; the unmarked bonds are fixed by the symmetry of the molecule. The lines extending out from the ring show the positions of the attached chlorine atoms.

Distortion of the Benzene Ring.—The resonance situation described above changes the character of the bonds in the benzene ring. When only the two Kekulé structures are to be considered, each of the six carbon–carbon bonds has 50% double bond character and the distance 1.390 Å. observed in benzene itself. With the consideration of other structures required by the observations made on the carbon–chlorine distances the fraction of double bond character is changed and in different amounts for the several carbon–carbon bonds. For example, in the case of *o*-dichlorobenzene formulated in Fig. 6 the observed C–Cl distance corresponds to a 79% contribution of the two Kekulé structures with 10.5% for each of the two sets of structures with double-bonded chlorine atoms. Considering the carbon–carbon bond between the two atoms to which the chlorines are attached we see that of the eight structures in the figure only the first has a double bond in this position. Accordingly, the contribution of this single structure represents the degree of double bond character in the bond, namely, 39.5%, instead of the 50% which it has in benzene. This change affects the bond distance in accordance with the relation referred to above, and we expect 1.408 Å. in place of 1.390 Å. Consideration of the other five bonds in the same fashion leads to anticipated distances of 1.396, 1.390, 1.396, 1.390, and 1.396 Å., respectively. While the accuracy of the absolute values is affected by the uncertainty in the determination of the carbon–chlorine distance (from which the relative contributions of the resonating structures were determined), the directions and orders of magnitude of the changes are correct, and we believe that the benzene ring actually is distorted in this way. The average of the above distances is 1.40 Å., and this value was used in interpreting the photographs in preference to 1.39 Å.

Changes are expected in the carbon–carbon distances in the other chlorobenzenes, too; and the observed carbon–chlorine distances have been used to obtain the anticipated values shown in Fig. 7. The extended bonds mark the positions of the chlorine atoms. The numerals represent bond lengths in Ångström units; where a numeral is not shown the bond length is fixed by the symmetry of the molecule. In each case the average carbon–carbon distance for the ring was used in the structure determination, since the deviations from the average are too small to be detected in a diffraction experiment.

Distortion of the Ortho Chlorine Atoms.—In the two unsymmetrical compounds having chlorine atoms attached to adjacent carbon atoms, the chlorine–chlorine separation is larger than it would be if their bonds made a 60° angle. In *o*-dichlorobenzene the observed separation is 3.15 Å., while the "undistorted" separation would be 3.11 Å., an increase of 0.04 Å. In 1,2,4,5-tetrachlorobenzene the observed separation is 3.20 Å. and the "undistorted" 3.12 Å.; the greater experimental error in the investigation of this substance makes it uncertain that the increase is actually twice as great as in the former compound.

Such increases in the separation of ortho-substituted atoms have been ascribed to the bending of the carbon–chlorine bonds due to the mutual repulsion of the chlorine atoms. A comparison may be made with dichloromethane, in which the 2.5° increase in bond angle above the value in the symmetrical tetrachloro derivative corresponds to an increase in the chlorine–chlorine separation from 2.87 to 2.92 Å. Since the repulsive potential is approximately proportional to the inverse ninth power of the separation, the increase in the "undistorted" chlorine–chlorine distance to 3.11 Å. in the chlorobenzene is accompanied by a decrease to less than half in the force acting between the chlorine atoms. Although the decrease in force is partly compensated by the more favorable direction in which it is applied to the atoms (due to the smaller angle between the bonds in chlorobenzene), we would expect an increase in the chlorine–chlorine separation in *o*-chlorobenzenes of

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(14) Unpublished work by Mr. Henri Lévy in these Laboratories.

about 0.02 or 0.03 Å. The increase observed is from 0.04 to 0.08 Å. Accordingly, an explanation in addition to the mutual repulsion of the atoms is necessary. The distortion of the benzene ring discussed above occurs in these unsymmetrical compounds in a manner which would increase the ortho chlorine atom separations from 0.02 to 0.04 Å. according to the deviations from 120° of the various ring angles. Although still other effects may be involved it seems probable that some of the increase is to be ascribed to distortions of the benzene ring.

It should be noted that even if a regular benzene ring is assumed the bending of the carbon–chlorine bonds is not large. In *o*-dichlorobenzene the bending calculated with a regular ring is less than 1°; in 1,2,4,5-tetrachlorobenzene it is 1.5°. The distortion of the bond angles is much less than has been estimated on the basis of dipole measurements, in the interpretation of which insufficient allowance was made for the interaction of the moments in the adjacent carbon–halogen bonds.

We are grateful to Professor Linus Pauling for his encouragement and advice during the course of this investigation.

Summary

The molecular structures of some of the chlorobenzenes have been investigated with the following results

Substance	Sum of C–C and C–Cl, Å.	C–C (assumed), Å.	C–Cl, Å.	Cl–Cl (ortho), Å.	Cl–Cl (meta), Å.	Cl–Cl (para), Å.
C_6Cl_6	3.11	1.41	1.70	3.11	5.39	6.22
1,3,5-$C_6H_3Cl_3$	3.10	1.41	1.69		5.38	
m-$C_6H_4Cl_2$	3.09	1.40	1.69		5.35	
p-$C_6H_4Cl_2$	3.09	1.40	1.69			6.18
C_6H_5Cl	3.08	1.39	1.69			
o-$C_6H_4Cl_2$	3.11	1.40	1.71	3.15		
1,2,4,5-$C_6H_2Cl_4$	3.12	1.40	1.72	3.20	5.37	6.25

The decrease of the carbon–chlorine distances below the value 1.76 Å. observed in the chloromethanes is due to the contribution of electronic structures which introduce a degree of double bond character in the carbon–chlorine bonds. The resonating structures involved produce distortions in the benzene ring amounting in some cases to an increase of 0.02 Å. in the carbon–carbon distances. The benzene ring distortion is responsible in part for the increased chlorine–chlorine separation observed in the unsymmetrical ortho substituted compounds. The distortion of the bond angles in the ortho positions is not as great as has been supposed previously; even with the assumption of a regular benzene ring the ortho bonds are bent to the order of 1°.

PASADENA, CALIF. RECEIVED AUGUST 17, 1937

[CONTRIBUTION FROM THE GEORGE HERBERT JONES CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

I. A Simple Accurate Film Balance of the Vertical Type for Biological and Chemical Work, and a Theoretical and Experimental Comparison with the Horizontal Type.
II. Tight Packing of a Monolayer by Ions

BY WILLIAM D. HARKINS AND THOMAS F. ANDERSON

Introduction

The importance of the determination of pressure–area relations of monomolecular films in biological problems and other work in surface chemistry makes the development of new methods for such investigations desirable. This is particularly true in view of the disadvantages of the "horizontal pull" film balance[1] now in use. This apparatus is too inaccurate in its crude form and too difficult to build and to operate in its precision form to be adopted widely by either biologists or chemists. Furthermore, it is difficult to avoid the use of metals in its construction and their presence makes the device unsuitable for a study of the effects of metallic ions on surface films.[2] It is also difficult to adapt the instrument for continuous compression of surface films. Continuous compression is highly desirable to simplify the mathematical theory of the observed effect of the rate of compression on the pressure–

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[1] So called because it measures a horizontal force. In the adaptation of the Wilhelmy surface tension balance for the study of surace films which is to be described here, a vertical force is measured. This latter device is therefore designated the "vertical pull" film balance.

[2] W. D. Harkins and H. Zollman, THIS JOURNAL, **48**, 69 (1926); I. Langmuir and V. J. Schaefer, *Science*, **34**, 379 (1936); Abstracts of Papers Presented before Div. of Phys. and Inorg. Chem. of Am. Chem. Soc. at 93rd Meeting, Chapel Hill, N. C., April 12, 1937; R. J. Myers and W. D. Harkins, *Nature*, **139**, 367 (1937); J. S. Mitchell, E. K. Rideal and J. H. Schulman, *ibid.*, **139**, 625 (1937).