

toward tautomerization becomes apparent, the dibromocarbinol existing in the two modifications, benzenoid and quinonoid.

4. The free radical *o*-methyl-*p*-carboethoxytriphenylmethyl has been proved to be capable of existence in solution. While apparently more stable than the corresponding free radical, *p*-carboethoxytriphenylmethyl, it is, none the less, sufficiently prone toward polymerization or isomerization to a non-reversible isomer to preclude the possibility of its isolation by the ordinary means at present in use.

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IX. THE ELECTRONIC FORMULA OF BENZENE AND THE MOLECULAR VOLUMES OF THE CHLOROBENZENES.¹

BY HARRY SHIPLEY FRY.

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Most of the papers of this series² have dealt with the interpretation of substitution reactions in the benzene nucleus, and other stereochemical problems, in terms of the electronic formula of benzene. Hence the evidence for the electronic formula of benzene has been found chiefly in chemical reactions rather than in particular physical properties, with the exception of the development of a relationship in the nature of a linear function between the systems of dynamic equilibria of the electromers of benzene and the oscillation frequencies of the seven bands which characterize the absorption spectrum³ of benzene solutions.

The present paper is an attempt to show that other relationships may exist between the electronic formula of benzene and certain physical properties, notably, the molecular volumes of mono-, di-, tri-, tetra-, penta- and hexa-chlorobenzenes.

The distinctive feature of an electronic formula is the designation of the polarities of certain atoms or radicals constituting the compound. Such designations should not be arbitrary: they are based chiefly upon definite reactions⁴—hydrolyses, oxidations, reductions, etc.—which indi-

¹ This paper constitutes Part IX of the series "Interpretations of Some Stereochemical Problems in Terms of the Electronic Conception of Positive and Negative Valences." Read by title at the 53rd meeting of the American Chemical Society, New York City, September 27, 1916.

² Fry, *THIS JOURNAL*, 36, 248, 262, 1035 (1914); 37, 855, 863, 883, 2368 (1915); 38, 1323, 1327, 1333 (1916). See also Fry, *Z. physik. Chem.*, 76, 385, 398, 591 (1911); 80, 29 (1912); 82, 665 (1913); 90, 458 (1915).

³ Fry, "Dynamische Formeln und das Ultravioletabsorptionsspektrum des Benzols," *Z. physik. Chem.*, 76, 398 (1911).

⁴ Fry, *Loc. cit.*; W. A. Noyes, *THIS JOURNAL*, 23, 460 (1901); Stieglitz, *Ibid.*, 23, 796 (1901) and "Qual. Chem. Anal.," Chaps. XIV and XV of Vol. I; Jones, *Am. Chem. J.*, 50, 414 (1913).

cate that certain atoms or radicals function positively while others function negatively. Hence, the employment of an electronic formula is justified when it will correlate or interpret reactions and properties which cannot be explained in terms of our ordinary structural formulas. What principles, then, are involved in the correlation of the electronic formulas of compounds and their respective molecular volumes?

Apropos to this question consider the remarkable anomaly first noted by Staedel¹ that β -halogen compounds always possess smaller molecular volumes than their isomeric α -halogen compounds. For instance, the molecular volume of $\text{CH}_3\text{CHXCH}_2\text{X}$ is about three units less than that of $\text{CH}_3\text{CH}_2\text{CHX}_2$. Thus, two structurally similar molecules may possess different molecular volumes, and there is nothing in the ordinary structural formulas of these isomers to account for, or to correlate, these differences.

Le Bas² has proposed an explanation of some of these anomalies in his hypothesis of partial or incomplete rings, and his examination of the molecular volumes of numerous compounds has led to the following results³ which must be considered in this paper: (a) If a paraffin compound be substituted by a halogen atom or other unsaturated substituent more than once, the volume of the compound is normal, or subject to the additive rule, provided that the substituents be attached to a single carbon atom. (b) If they are distributed among several carbon atoms, there are always contractions of a constituent nature. It matters not how many hydrogen atoms of the terminal carbon are substituted, the contractions are dependent upon the number substituted in the β -position. (c) For one substitution in the β -position the contraction is a little over three units. For two substitutions in the β -position the contraction is about six units, or nearly double the first. Substitutions in the γ -position always involve greater contractions than substitutions in the β -position; and it is conceivable that substituents in the δ -position would result in still greater contractions.

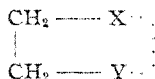
In explanation of these results Le Bas states⁴ that intermediate between open and closed chain compounds are what are known as partial or incomplete rings. "In order that they may be formed, it is necessary that two atoms or groups, which may be supposed to possess residual affinity, occur in a hydrocarbon chain attached to different carbon atoms. If the carbons are near to each other, there is no need to suppose any variation from structure usually considered when the tetrahedral arrangement of the valency links of carbon is understood. The additional feature of curvature of the hydrocarbon chain may also be the normal condition of things. In the case of saturated compounds the plane formulas are figured thus:

¹ *Ber.*, **15**, 2559 (1882).

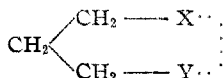
² "The Molecular Volumes of Liquid Chemical Compounds," by Gervaise Le Bas (Longmans, Green and Co., 1915).

³ Le Bas, *Phil. Mag.*, [6] **27**, 978 (1914).

⁴ Le Bas, *Loc. cit.*, p. 245.



If the two attracting groups are united to carbons not in the immediate neighborhood of each other, we must suppose that they are brought near by the curvature of the hydrocarbon chain, or the alternative supposition just given is true. In any such case, such a structure affects the molecular volumes of compounds." Thus:

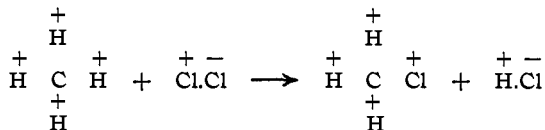


It is not the purpose of this paper to disparage or discredit the explanation of Le Bas, but, rather, to propose a new explanation based upon the electronic conception of positive and negative valences, as follows: Halogen atoms (and other substituents) may function positively or negatively as indicated in the typical scheme $\overset{-}{\text{Cl}} \cdot \overset{+}{\text{Cl}} + \overset{+}{\text{H}} \cdot \overset{-}{\text{O}} \cdot \text{H} = \overset{+}{\text{H}} \cdot \overset{-}{\text{Cl}} + \overset{-}{\text{O}} \cdot \overset{+}{\text{H}} \cdot \text{Cl}$. Halogen atoms substituted in the α -position alone or in the β -position alone cause no contraction; but each of the halogen atoms in the β -position occasions a contraction of about three units provided one or more halogen atoms are present in the α -position. May we not assume, then, that the differences or contractions in the molecular volumes of the isomers are due to differences in the polarities of the halogen atoms or substituents, in the α - and β -positions respectively? Further, may we not assume that differences in polarity are directly related to differences in the relative atomic volumes of the halogen atoms or substituents? For purposes of illustration, suppose that the halogen atoms in the α -position function positively while those in the β -position function negatively (evidence will be presented shortly), and that the atomic volume of $\overset{+}{\text{X}}$ is greater than that of $\overset{-}{\text{X}}$. Then, electronic formulas, such as $\overset{+}{\text{C}}\text{H}_3\overset{+}{\text{C}}\overset{+}{\text{H}}\overset{-}{\text{C}}\overset{-}{\text{H}}\overset{+}{\text{X}}\overset{-}{\text{X}}$ and $\overset{+}{\text{C}}\text{H}_3\overset{-}{\text{C}}\overset{-}{\text{H}}\overset{+}{\text{C}}\overset{+}{\text{H}}\overset{-}{\text{X}}$, correlate the fact that the molecular volume of the α -disubstituted compound is greater than that of the isomeric α, β -disubstituted compound, the difference in the molecular volumes being due to differences in the atomic volumes of $\overset{+}{\text{X}}$ and $\overset{-}{\text{X}}$.¹ Such a correlation cannot be shown by employing the ordinary structural formulas of the compounds in question.

The above assumptions may now be correlated with a number of facts which are readily interpreted in terms of the electronic conception of

¹ It should be noted that when different atoms, such as chlorine and carbon, are united, a change in the polarity of one, involving a change in the polarity of the other, would concomitantly alter the atomic volumes of both atoms, but the atomic volume of each atom would not be altered to the same extent. Accordingly, the molecular volume data under consideration in this paper is regarded as a measure of certain additive and constitutive effects involving the polarity and the atomic volume of certain atoms.

positive and negative valences. It has been noted that when a paraffin compound undergoes substitution more than once, the molecular volumes of the substitution products are normal, *i. e.*, subject to the additive rule, provided that the substituents are linked to a single carbon atom. In this connection, consider the direct substitution of chlorine in methane which may be represented thus:



Successive substitution of positive chlorine atoms would result in the formation of compounds of formulas $\text{CH}_2(\text{Cl})_2$, $\text{CH}(\text{Cl})_3$ and $\text{C}(\text{Cl})_4$. If we tabulate the molecular volumes (V_m) of these compounds and the volumes of their hydrocarbon groups, the differences between these values will give the volumes of their chlorine atoms which are indicated under ($n\text{Cl}$) in the following table, n being the number of chlorine atoms in the respective compounds:

Compound.	(V_m).	Vol. of hydrocarbon group.	($n\text{Cl}$).
CH_2Cl_2	65.1	22.1	2×21.5
CHCl_3	84.5	18.5	3×22.0
CCl_4	103.7	14.8	4×22.2

The data show a slight increase in the atomic volumes of the chlorine atoms as they accumulate in the molecule. The electronic schemes for the substitution reactions (in the absence of intramolecular oxidation-reduction reactions)¹ indicate that the substituted chlorine atoms function positively. The molecular volume data indicate that the average atomic volume of these positive chlorine atoms is very nearly equal to 22.0.

The next question to be considered naturally relates to the atomic volume of the chlorine atoms which function negatively. An extension of the hypothesis to the constitution and molecular volumes of ethylene and ethylidene dichlorides leads to some interesting conclusions. The data with respect to these isomers are as follows:

Compound.	(V_m).	Vol. of hydrocarbon group.	($n\text{Cl}$).
CH_2CHCl_2	88.9	44.5	2×22.2
$\text{CH}_2\text{ClCH}_2\text{Cl}$	85.3	44.5	2×20.4

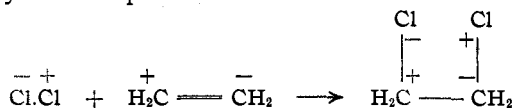
From the data it appears that the average atomic volume of the chlorine atom in ethylidene dichloride is 22.2; in ethylene dichloride, 20.4. To correctly interpret this constitutive effect, account must be taken of the

¹ L. W. Jones, *Am. Chem. J.*, 50, 414 (1913); Fry, *Z. physik. Chem.*, 76, 387 (1911).

fact that in the majority of the aliphatic compounds of the type RCl in which only one chlorine atom is substituted on a carbon atom, the average atomic volume of this single chlorine atom is 21.5. Since the chlorine atoms in ethylene dichloride are singly attached to separate carbon atoms and their total volume is 40.8, the volume of each cannot be 21.5. Consequently, it follows that if one of these chlorine atoms has the usual volume of 21.5, then the volume of the other chlorine atom must be 19.3, *i. e.*, the difference between their total volumes, 40.8 and 21.5. While none of these values is absolute, the data indicate a possible correlation of molecular volume data and electronic formulas. Thus, if the α -chlorine atom has a greater atomic volume than the β -chlorine atom and functions positively, then, in contradistinction, the β -chlorine atom would be assumed to function negatively. The correlation of the electronic formulas and atomic volumes of the chlorine atoms of ethylidene and ethylene dichlorides may be summarized thus:

Isomers.	(π Cl).	
$\overset{+}{\text{C}}\text{H}_3\text{.}\overset{+}{\text{C}}\text{HCl}\overset{+}{\text{C}}\text{HCl}\dots\dots\dots$	44.4	$\overset{+}{(2\text{Cl}} = 2 \times 22.2 = 44.4)$
$\overset{-}{\text{C}}\text{H}_2\overset{+}{\text{C}}\text{H.}\overset{-}{\text{C}}\text{H}_2\overset{+}{\text{C}}\text{H}\dots\dots\dots$	40.8	$(\overset{-}{\text{Cl}} + \overset{+}{\text{Cl}} = 19.3 + 21.5 = 40.8)$

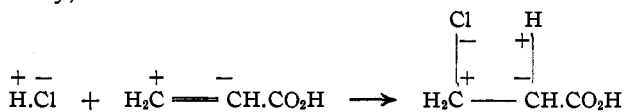
From this point of view, the difference between the molecular volumes of ethylidene and ethylene dichlorides is not dependent on the idea of the formation of a partial ring, as assumed by Le Bas in the case of ethylene dichloride, but is due to a difference in the atomic volumes of the α - and β -chlorine atoms which are assumed to function positively and negatively, respectively. Further evidence for the assumption of this difference of polarity is found in the union of chlorine with ethylene. The hydrolysis of chlorine (previously indicated) yielding hydrogen chloride ($\overset{+}{\text{H}}\overset{-}{\text{C}}\text{H}$) and hypochlorous acid ($\overset{-}{\text{H}}\overset{+}{\text{O}}\overset{-}{\text{C}}\text{H}$) indicates that the chlorine molecule may yield $\overset{+}{\text{Cl}}$ and $\overset{-}{\text{Cl}}$ on dissociation. Accordingly, the addition of chlorine to ethylene is represented thus:



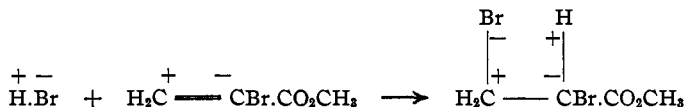
The "opening" of the double bond of ethylene may be regarded as the simultaneous development of a free positive valence on the one carbon atom and a free negative valence on the other, which valences, respectively, bind the negative and positive chlorine atoms. In other words, the chlorine atoms in the α - and β -positions are of opposite polarity.

An analogous situation, indicating that the α -substituent tends to function positively while the β -substituent is negative, is found in the addition

of hydrogen chloride ($\overset{+}{\text{H}}\cdot\overset{-}{\text{Cl}}$) to acrylic acid yielding β -chloropropionic acid exclusively,¹ thus:



Note also in this connection the addition of hydrogen bromide to α -bromo acrylic ester. Again the positive substituent unites with the α -carbon atom while the negative substituent assumes the β -position, thus:



This compound, α,β -dibromopropionic ester, is also the product of the addition of bromine ($\overset{+}{\text{Br}}\cdot\overset{-}{\text{Br}}$) to acrylic ester, and in view of the preceding facts the α - and β -bromine atoms are, respectively, positive and negative. Now the molecular volume of α,β -dibromopropionic ester is 3.9 units less than that of its isomer, the α,α -compound. Thus it appears that the α -substituents have a greater atomic volume than the β -substituents and a relationship exists between the electronic formulas of these isomers and their molecular volumes which is summarized as follows:

$\overset{+}{\text{C}}\text{H}_2\cdot\overset{+}{\text{C}}\text{H}\cdot\text{CO}_2\text{CH}_3$	$V_m = 156.3$
$\overset{+}{\text{C}}\text{H}_2\text{Br}\cdot\overset{-}{\text{C}}\text{H}\cdot\text{CO}_2\text{CH}_3$	$V_m = 152.4$
Difference (V. Br—V. Br)	= 3.9

The preceding facts and their correlation with the electronic formulas lead to the assumption that the atomic volume of the positive halogen substituent is greater than that of the negative halogen substituent. Consequently, the differences between the molecular volumes of the isomers in question is related in some way (to be considered later) to differences in the polarities of the substituents in the α - and β -positions. This hypothesis may now be extended to the explanation of the remarkable anomalies met with in the atomic volumes of the chlorine atoms in the several chlorobenzenes, especially hexachlorobenzene. The existence of a relationship between the molecular volumes of the chlorobenzenes and the electronic formula of benzene will be definitely indicated.

¹ Addition reactions involving the two types of double bonds, *diplex* ($\overset{+}{\text{C}}=\overset{-}{\text{C}}$), and *contraplex* ($\overset{-}{\text{C}}=\overset{+}{\text{C}}$) (Fry, *Z. physik. Chem.*, 76, 400 (1911)), renders possible an interpretation of many of the anomalous addition reactions studied by Michael from the standpoint of his "chemical neutralization" theory.

In previous papers of this series numerous facts have been presented and interpreted by means of the electronic formula of benzene (Fig. 1). A substitution rule has been developed showing that when substituents are of the same sign or polarity they will occupy positions which are meta to each other, but if two substituents are of opposite sign or polarity they will occupy either ortho or para positions to each other. The development of this rule depended upon the fact that the electronic formula of benzene is the only formula which presents conjointly a structural basis and an

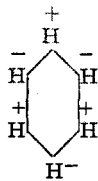


Fig. 1.

electronic interpretation of the relations between ortho and para positions and substituents in contradistinction to meta positions and substituents. Now, if the electronic formula of benzene is subject to correlation with the molecular volumes of the chlorobenzenes, the following conditions must be fulfilled: (1) Substituted chlorine atoms occupying ortho or para positions to each other must be of opposite polarity while those occupying meta positions to each other must be of the same polarity. (2) It has been indicated that chlorine atoms which function positively possess a greater atomic volume than those which function negatively. Consequently, positive chlorine atoms in the benzene nucleus must possess greater atomic volumes than the negative chlorine atoms in the corresponding para or ortho positions. These conditions would be fulfilled completely if it is shown that, for instance, in hexachlorobenzene (Fig. 2) the positive chlorine atoms in Positions 1, 3 and 5 possess greater atomic volumes than the negative chlorine atoms in Positions 2, 4 and 6. To this end, consider, first, the electronic schemes for the formation of the six chlorobenzenes whose molecular volumes present the remarkable anomalies that demand an explanation.

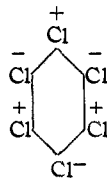
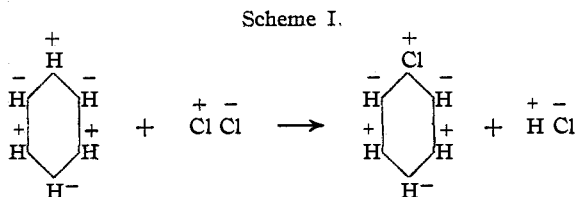


Fig. 2.

The direct substitution of chlorine in the benzene nucleus,¹ generally effected with the aid of halogen carriers, corresponds to the following simplified Scheme I:

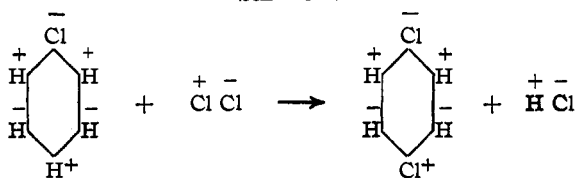


in which positive chlorine is introduced. The extended substitution of chlorine yields the several di-, tri-, tetra-, penta- and hexa-chlorobenzenes. Direct substitution, as indicated, effects the introduction of a positive substituent but the electronic formula of benzene requires that polysubsti-

¹ Fry, *THIS JOURNAL*, 36, 1035 (1914).

tuted derivatives embody negative substituents as well. The existence of the negative substituents depends upon the electronic tautomerism¹ (for example, $\overset{-}{\text{C}_6\text{H}_5\text{Cl}} \rightleftharpoons \overset{+}{\text{C}_6\text{H}_5\text{Cl}}$) of some of the derivatives which in turn undergo further substitution. With reference to the formation of paradichlorobenzene, or any other disubstituted derivative, recall that if a given substituent in the benzene nucleus is positive, the entering positive substituent will occupy the meta position, but if the monosubstituent is negative, the entering positive substituent will occupy para or ortho positions. The chlorination of monochlorobenzene yields chiefly paradichlorobenzene. Consequently, electromer $\overset{+}{\text{C}_6\text{H}_5\text{Cl}}$ (and not electromer $\overset{-}{\text{C}_6\text{H}_5\text{Cl}}$) undergoes substitution according to Scheme II:

Scheme II.



Schemes I and II in conjunction with the principle of electronic tautomerism ($\overset{-}{\text{C}_6\text{H}_5\text{Cl}} \rightleftharpoons \overset{+}{\text{C}_6\text{H}_5\text{Cl}}$) show that a given positive substituent may, under certain conditions, function as a negative substituent, but in paradichlorobenzene the halogen atoms are of opposite polarity. This not only follows from the electronic formulas but is confirmed by experimental facts, notably the reactivity of the negative chlorine atom and the non-reactivity of the positive chlorine atom when paradichlorobenzene is heated with methyl alcohol solution of sodium methylate. The reaction conforms quantitatively to the electronic equation:

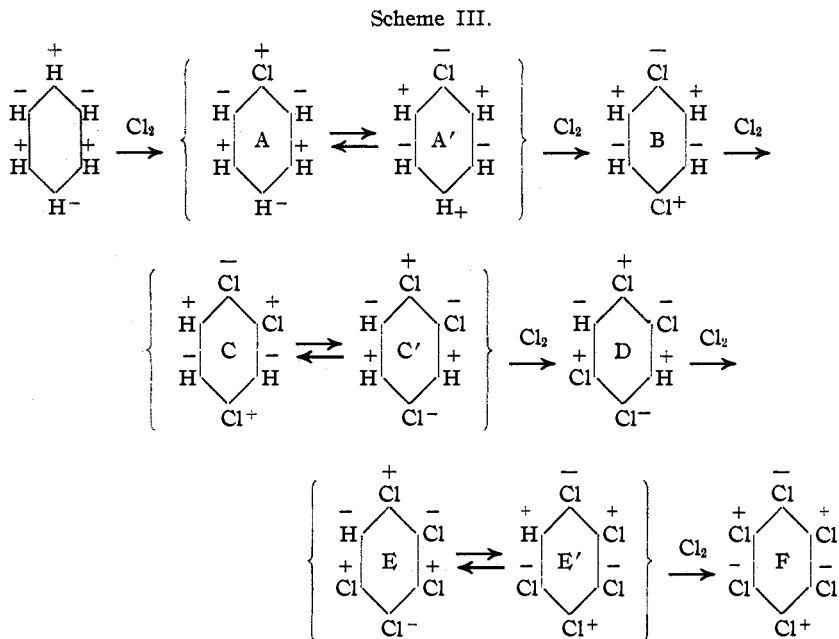


Another remarkable difference between the chlorine atoms in paradichlorobenzene will shortly be considered in connection with their atomic volumes.

In the complete scheme for the formation of the six chlorobenzenes in question, a number of systems of electronic tautomerism are involved, but in the following abbreviated Scheme III only those electronic formulas have been included which are directly related to the present investigation, namely, the correlation of the molecular volumes of mono-, 1:2 di-, 1:2:4 or 1:4:5 tri-, 1:2:4:5 tetra-, penta- and hexa-chlorobenzenes with their respective electronic formulas. The electronic formulas of these com-

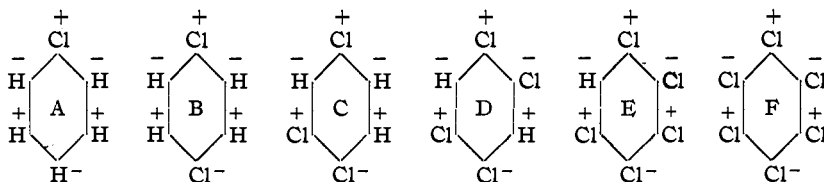
¹ Fry, *THIS JOURNAL*, 38, 1327 and 1333 (1916).

pounds are indicated in the following Scheme III by the letters A, B, C, D, E and F:



The scheme involves three systems of electronic tautomerism, namely, ($A \rightleftharpoons A'$), ($C \rightleftharpoons C'$), and ($E \rightleftharpoons E'$). Beginning with benzene, each of the six successive chlorinations introduces only one positive substituent, Cl, as has been illustrated in preceding Schemes I and II. Note that A', C', and E' (the respective electromers of A, C and E) yield on chlorination B, D and F, respectively. Compounds B, D and F do not possess electromers because they contain an *even* number of *symmetrically* substituted chlorine atoms. On the other hand, the electronic Formulas A, C and E are in tautomeric equilibrium with their respective electromers A', C' and E' since they embody an *uneven* number of substituted chlorine atoms and the number of their positive substituents is unequal to the number of their negative substituents.

Before tabulating the molecular volume data, it will facilitate comparisons if the electronic formulas of the six chlorobenzenes are rewritten in juxtaposition and with the positive substituents in Positions 1, 3 and 5, and the negative substituents in Positions 2, 4 and 6. Such an arrangement will not alter in the least the electronic formulas of these compounds as derived in the preceding scheme: the relative positions and polarities of the substituents remain the same.



This arrangement will serve as a key to the following table of molecular volume data.

Chlorobenzenes.		V_m .	V'_m .	$V_x\text{Cl}$.	Δ .
A Mono-	(odd).....	114.6	92.8	21.8	
B 1:4-Di-	(even).....	130.9	89.6	41.3	19.5
C 1:4:5-Tri-	(odd).....	149.1	86.4	62.7	21.4
D 1:2:4:5-Tetra-	(even).....	164.8	83.2	81.6	18.9
E 1:2:3:4:5-Penta-	(odd).....	183.9	80.0	103.9	22.3
F 1:2:3:4:5:6-Hexa-	(even).....	200.0	76.8	123.2	19.3

The first column embodies the names of the six chlorobenzenes, A to F, inclusive. The designation (odd) or (even) refers to the number of chlorine atoms in the respective compounds. The former are unsymmetrical in structure; the latter, symmetrical. The molecular volumes of the chlorobenzenes, originally determined by Jungfleisch,¹ and subsequently retabulated by Le Bas,² are given in the second column, V_m . The third column indicates the molecular volumes of the hydrocarbon groups of the compounds, V'_m . The difference between the molecular volume of a given chlorobenzene and its hydrocarbon group ($V_m - V'_m$) gives the molecular volume of its chlorine atoms, $V_x\text{Cl}$, column four. The last column is one of differences (Δ) between the total volumes of the chlorine atoms of the successive compounds. For example, the atomic volume of the chlorine atom in monochlorobenzene is 21.8. The combined atomic volumes of the two chlorine atoms in 1:4 dichlorobenzene is 41.3. The difference between these values, namely, 19.5, is, therefore, the volume of one chlorine atom while that of the other in the para position is 21.8. The electronic formula of benzene has shown that substituents para to each other are of opposite polarity. Since previous investigations have indicated that the positive chlorine atom may have a greater atomic volume than the negative chlorine atom, the correlation between the atomic volumes and the electronic formula is maintained in paradichlorobenzene. Further correlations are maintained throughout the series of the six chlorobenzenes since the column of differences (Δ) shows that

¹ "Jahresb. uber der Fortschritte der Chemie," 19, 551 (1866); 20, 36 (1867).

² *Loc. cit.*, p. 253.

the chlorine atoms successively substituted vary in their atomic volume values by an average difference of ≈ 2.6 units. This simultaneous variation in polarity and atomic volume is emphasized by the retabulations in the following table:

	Relative position.	Polarity.	Atomic volume (positive).	Atomic volume (negative).
A 1st chlorine atom.....	(1)	(+)	21.8	..
B 2nd chlorine atom.....	(4)	(-)	..	19.5
C 3rd chlorine atom.....	(5)	(+)	21.4	..
D 4th chlorine atom.....	(2)	(-)	..	18.9
E 5th chlorine atom.....	(3)	(+)	22.3	..
F 6th chlorine atom.....	(6)	(-)	..	19.3
			Mean values, 21.8	19.2
				$\Delta = 2.6$

It is, therefore, evident that a marked difference (average $\Delta = 2.6$) exists between the atomic volumes of the chlorine atoms in Positions 1, 3 and 5 and those in Positions 2, 4 and 6; and, since the electronic formula of benzene and the substitution rule has shown that substituents in Positions 1, 3, and 5 are opposite in polarity to those in Positions 2, 4 and 6, it follows that *a definite relationship exists between the electronic formulas of the six chlorobenzenes and their respective molecular volumes. The existence of this relationship may be regarded as additional evidence, from a physical point of view, for the electronic formula of benzene.*

Various facts presented in this paper seem to indicate that a change in the polarity of a halogen atom causes a variation in its atomic volume. Any attempts to explain this in the present state of our knowledge would plunge us fatally into the metaphysics of an atomic structure maelstrom. Notwithstanding the incomplete knowledge of the constitution of the atom as manifested by the many different hypotheses relative to the nature and disposition of "valence electrons," it is quite conceivable that variations in the relative positions of the valence electrons which determine the polarity of an atom may likewise cause variations in the atomic volume of the atom. This assumption may lead to an explanation of other anomalies in molecular volume relationships. For instance, in the compounds methylene dichloride, chloroform and carbon tetrachloride, previously noted, the average atomic volumes of the chlorine atoms are 21.5, 22.0, and 22.2, respectively. This small increase in the average volumes of the chlorine atoms as they accumulate about a given carbon atom may be due to the relative positions of the valence electrons between the carbon and chlorine atoms which may mutually alter the respective atomic volumes of these atoms. It has also been noted that for one substitution in the β -position of a compound the contraction in molecular volume is a little over three units while substitutions on the γ - and δ -positions result in even greater

contractions. These anomalies may also be related to differences in the relative positions of the valence electrons between the carbon atoms and the halogen atoms substituted in the α -, β -, γ - and δ -positions, thus causing varying differences in the degrees of contractions.

In conclusion, a quotation from Le Bas¹ should be noted:

"There is no doubt that in spite of the care taken, many parts of the present theory of molecular volumes may have to be altered later as data accumulate, and as our knowledge of the physical property increases. The identification and explanation of constitutive effects is not always easy. Some particular atomic values—generally those found in the homologous series R — X are taken as standard, and by the method of summation the value ΣnV_a is found. The difference, $V_m - \Sigma nV_a$, then measures the constitutive effect. Sometimes a mean atomic value is taken, and it then follows that no account is taken of variations. The great difficulty is to identify the effect with a particular atom or group. When this seems possible, it sometimes happens that other atoms or groups might equally well be identified with the effect in question. Only a careful examination of a large number of data can overcome these difficulties. It will generally be found that the constitutive effects are traceable to some modifications in particular atomic values, and a considerable advance is made when we are able to ascertain for certain which atoms are marked by the variation in question and by how much."

Appropos to the above quotation, and as a summary of the present paper, it has been shown that:

1. Halogen atoms which function positively appear to possess different atomic volumes from those which function negatively. Consequently, it is possible to correlate certain additive and constitutive effects apparent in the molecular volumes of certain compounds with their electronic formulas. These effects cannot be explained by means of the ordinarily employed structural formulas.
2. Definite relationships exist between the molecular volumes of six different chlorobenzenes and their respective electronic formulas. These relationships further confirm the electronic formula of benzene.
3. It is suggested that any variations in the relative positions of the valence electrons which determine the polarity of an atom may likewise cause variations in the atomic volume of the atom.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

STUDIES IN THE CYCLOPROPANE SERIES.

[SECOND PAPER.]

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The cyclopropane derivatives described in our first paper had the great advantage of being so closely related to known substances that the structure of their transformation products could be determined with certainty.

¹ *Loc. cit.*, p. 253.