taining 0.1 F tetramethylammonium perchlorate at -34 °C and the potential was -1.5 V. Only the 1-bromonorbornane that was initially added could have been recovered, because none is generated by reduction of the dibromide; actually, 95% of the monobromide was recovered, inasmuch as a small amount is reduced to norbornane because the foot of the reduction wave for the monobromide occurs at a potential close to -1.5 V. If 1-bromonorbornane were an intermediate in the formation of norbornane from 1,4-dibromonorbornane, the monobromide (HnbBr, where nb = norbornyl) would presumably arise from the reaction sequence $\mathrm{BrnbBr} + e^- \rightarrow \cdot\mathrm{nbBr} + \mathrm{Br}^-$ and $\cdot\mathrm{nbBr} + \mathrm{H}\cdot \rightarrow \mathrm{HnbBr}$. Then, one can propose that $\mathrm{HnbBr} + \cdot\mathrm{nbBr} \rightarrow \mathrm{Hnb}\cdot + \mathrm{BrnbBr}$ will be followed by $\mathrm{Hnb}\cdot + e^- + \mathrm{H}^+ \rightarrow \mathrm{HnbH}$. Taken together, these processes should, in the electrolysis of the dibromide with added monobromide, cause the yields of norbornane and bis(1-norbornyl)mercury to increase and decrease, respectively, compared with those in an electrolysis of the dibromide without added monobromide and, in addition, significantly <100% of the added monobromide should be recovered. However, these effects were not observed; so we rule out the intermediacy of the monobromide.

(25) If it is assumed that the 1,4-dihalonorbornane which cannot be accounted for undergoes an electron-transfer reaction having only a single n value, we can calculate this n from the relationship n = (tabulated overall n value) $- \{\Sigma[(n_i)$ (yield of i)/100]$\}$, where n_i is the number of electrons involved in forming product i from the starting material and where "yield of i" is the tabulated percentage yield of product i.

(26) In our study, mass spectra revealed that this norbornyl adduct of dimethylformamide has a molecular weight of 167, but we have not been able to distinguish between $HCON(CH_3)(CH_2C_7H_{11})$ and $C_7H_{11}CON(CH_3)_2$. In work by Wiberg, Bailey, and Jason,[3] a species reported to be the first of these two adducts was obtained, but NMR data included no resonance assignable to the formyl proton.

(27) For electrolyses performed in organic solvents containing salts of tetraalkylammonium cations [except $(CH_3)_4N^+$], Hofmann elimination has been taken as prima facie evidence for the presence of carbanions. However, hydroxide ion has been demonstrated to cause Hofmann elimination at room temperature in dimethylformamide containing tetraethylammonium bromide; see Reed, R. C. Ph.D. Thesis, Wesleyan University, Middletown, Conn., 1971. Hydroxide ion may be formed by abstraction of a proton from water (an impurity in the organic solvent) by any strong bases; these bases include fragmentation products of deprotonated dimethylformamide as well as carbanions themselves.

(28) Stohrer, W.-D.; Hoffmann, R. *J. Am. Chem. Soc.* **1972,** *94,* 779–786.

(29) Direct cyclization of species **2** cannot be ruled out; this reaction would yield propellane and an iodine atom. After reduction of this iodine atom to iodide, however, the n values and products for this process would be identical with those derived from cyclization of **6.** These two processes are indistinguishable.

(30) It is conceivable that 1,3-dimethylenecyclopentane, the product of a ring-cleavage reaction of [2.2.1]propellane (see ref 3) might be the source of the polymeric material, although this ring-opening is theoretically disallowed (see ref 28). Moreover, the absence of an alkene stretching band argues against this possibility in the present work.

(31) Electrochemical reduction of a propellane is unprecedented, although direct experimentation on the more reactive of such species is obviously difficult. Wilcox and Leung (Wilcox, C. F., Jr.; Leung, C. *J. Org. Chem.* **1968,** *33,* 877–880) reduced 1,4-dichloronorbornane with lithium metal and obtained only 1,4-dilithionorbornane and no 4-chloro-1-lithionorbornane. This reaction might involve reduction of the dichloride to propellane and reduction of propellane by lithium metal to achieve the dianion.

(32) Kashin, A. N.; Ershler, A. B.; Strelets, V. V.; Butin, K. P.; Beletskaya, I. P.; Reutov, O. A. *J. Organomet. Chem.* **1972,** *39,* 237–243.

(33) Brown, O. R.; Thirsk, H. R.; Thornton, B. *Electrochim. Acta* **1971,** *16,* 495–503.

(34) Casanova, J. P.; Rogers, H. R. *J. Am. Chem. Soc.* **1974,** *96,* 1942–1944.

(35) Wood, D. E.; Bailey, W. F.; Wiberg, K. B.; Pratt, W. E. *J. Am. Chem. Soc.* **1977,** *99,* 268–269.

Completion of Koerner's Proof That the Hydrogens of Benzene Are Homotopic. An Application of Group Theory

J. Michael McBride

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06520. *Received November 29, 1979*

Abstract: For more than a century Koerner's elegant proof of the equivalence of the hydrogens in benzene has been almost totally ignored. The logic of the last step in his argument is faulty, but reformulation of the problem in the language of permutation groups show that his evidence was sufficient for the proof. Definitions necessary for applying group theory to abstract chemical structure discussions are proposed, and the following statement is proven: If a group of equivalence permutations **P** is transitive on a set of p chemical locations, where p is a prime number greater than 2, and **P** includes an element which exchanges two chemical locations, the number of isomers involving disubstitution among these equivalent locations is at most $(p - 1)/2$. Analogous arguments may prove useful in discussing the structure of fluxional molecules.

Wilhelm Koerner is remembered in most organic chemistry textbooks because of his method for systematic identification of the relative positions of multiple substituents on the benzene nucleus. This method applies only if the six substituent sites of the carbon core are equivalent, and Ladenburg's paper of 1874 is most often cited for proof of this equivalence.[1] Koerner had published his own equivalence proof 5 years earlier, but in an Italian journal so obscure that then, as now, his contribution was ignored.[2] His proof required only three pages in a 45-page paper entitled "Facts to Serve in Determining Chemical Position in Aromatic Substances". The only subsequent mention of this proof seems to have been in some of Koerner's later papers, in his obituaries,[3] and in a 1917 German translation of the Italian paper.[4]

The Koerner proof is as logically elegant as van't Hoff's discussion of tetrahedral carbon or Fischer's proof of the configuration of glucose. In a way it is superior to these because, not being tied to a geometric model, the arguments are as applicable to a vibrating or fluxional molecule as to a rigid structure.

Given the neglect of Koerner's proof, it may not be surprising that no one has noted a fault in the last step of his argument, where he retreated from an abstract to a geometric model. Below we summarize Koerner's discussion and then show, by recasting it in the language of permutation groups, that the proof can be completed rigorously using the evidence he cited. This completion vindicates Koerner's intuition that his evidence constituted a proof of the equivalence of the hydrogens in benzene, and we hope that the group-theoretical approach used to reformulate his arguments may prove useful in discussing more subtle structural questions for which rigid models are inappropriate.

Koerner's Proof

Koerner published his proof in 1869, 5 years before the van't Hoff-Le Bel hypothesis of tetrahedral carbon. In the positivist view of many established chemists geometric models of molecules were not subject to experimental test and were thus both inappropriate and insidious.[5] Introducing his paper Koerner wrote "The dogma of the impossibility of determining the

0002-7863/80/1502-4134$01.00/0

atomic constitution of substances, which until recently was advocated with such fervor by the most able chemists, is beginning to be abandoned and forgotten; and one can predict that the day is not far in the future when a sufficient collection of facts will permit determination of the internal architecture of molecules. A series of experiments directed toward such a goal is the object of this paper." Still, because of the intellectual atmosphere, he designed a proof that would be appropriate to abstract "chemical" space rather than being limited to three-dimensional "physical" space.

Assumptions. Koerner's only assumptions were those which are indispensable when using chemical transformations in structure proof: (1) direct replacement and (2) experimental distinguishability of different substances. In 1867 he had stated these assumptions as follows: (1) "If one grants that in simple transformations the new substituent assumes the position of the element displaced . . ." and (2) ". . . most of the demonstrations are based on establishing the identity or difference of several substances of the same composition, but obtained by different reactions . . ."[7] The first assumption, that chemical locations persist through reactions, is reminiscent of the pre-1850 type theory of Laurent, Dumas, and Gerhardt. The first authentic examples of cine aromatic substitution, for which this assumption is not valid, were reported by von Richter 2 years after publication of Koerner's proof.[8] The second assumption is only plausible when the experimenter's skill and the chemical and physical methods used are adequate to distinguish different substances. Koerner's passion for preparing samples in a state of extreme purity and for testing them exhaustively is evident in his published work and has been noted previously.[3,9] In applying this assumption to macroscopic experimental results one must assume further that pure substances are composed of identical molecules, so that problems from inseparable mixtures (such as racemates) do not arise.

Chemical Evidence. Koerner used only the following five sets of experimental observations in his proof.

(A) There are three distinct isomers of hydroxybenzoic acid. These are "salicyclic acid", "hydroxybenzoic acid", and "parahydroxybenzoic acid".

(B) The phenols obtained by decarboxylating these three isomers are indistinguishable (and thus identical).

(C) The benzoic acids obtained by reductive removal of the hydroxyl group from these three isomers are indistinguishable.

(D) Substituting Br for NH_2 and Cl for NO_2 in "Arppe's nitroaniline" gives a product which is indistinguishable from that obtained by substituting Cl for NH_2 and Br for NO_2. "Arppe's nitroaniline" can be related to "hydroxybenzoic acid" where NH_2 has taken the OH position and NO_2 the COOH position.

(E) Among the nitration products of the bromophenol which is related to salicylic acid by having Br in place of COOH is found a bromodinitrophenol. This compound is indistinguishable from one obtained after a two-step bromination-nitration of the nitrophenol which is related to salicylic acid by having NO_2 in place of COOH.

Koerner's Argument. Evidence (B) and (C) showed that the isomeric hydroxybenzoic acids do not differ either in the absolute positions of their hydroxyl groups or in the absolute positions of their carboxyl groups, but only in the relative positions of these groups. Koerner named the position occupied by hydroxyl in these three compounds ω. He then used (A) and (C) to establish the existence of three positions, x, y, and z, which differ in relation to ω, but are equivalent in that, in the absence of hydroxyl, the presence of COOH in any of them gives the same benzoic acid.

Evidence (D) showed that there is no intrinsic difference between ω and y, the positions of the hydroxyl and carboxyl groups in "hydroxybenzoic acid", and thus that ω should be included in the set of equivalent positions together with x, y, and z.

Evidence (E) showed that there are two positions on the benzene nucleus which are, in Koerner's words, "symmetrical with each other with respect to the hydroxyl" of salicylic acid. In the bromodinitrophenol in question one of these positions is occupied by bromine, the other by a nitro group. Since one of these positions is x, the position of the carboxyl group in salicylic acid, Koerner called the second such position x'. He had thus established the existence of five equivalent positions on the benzene nucleus.

To establish equivalence of the sixth position with the previous five, Koerner used the following geometric argument instead of additional chemical evidence.

"Finally from the existence in metanitrophenol[10] of two positions of equal value and symmetrical with respect to the hydroxyl we can deduce that the sixth position must also have an equal value to the others, because if we imagine a plane passing through the hydroxyl which is perpendicular to the line joining the two symmetrical positions x and x', this plane, in order to satisfy the relation between the two positions, must necessarily divide the molecule into two equal and symmetrical parts. Now if instead the sixth position had a value different from the others, it would create a disturbance in the symmetry and in the equivalence of these two parts of the molecule and thus of the two positions x and x'. On the contrary we can conclude that *the six positions occupied by hydrogen in the benzene molecule are of equal value.*"

Criticism. Not only is the last of Koerner's arguments geometric, where the others are abstract; it is also wrong. It may not have occurred to him that a pentagonal pyramid would have a sixth, apical, position which would not disturb the symmetry plane and the equivalence of the other five positions. He was obviously thinking in terms of Kekulé's hexagon structure for benzene, since he had come to Palermo in 1867 from Ghent, where he had been Kekulé's assistant and secretary during the development of this structural hypothesis.[3]

Of course a pentagonal pyramid would be inconsistent with the other evidence. It would allow only two basal disubstituted isomers, neglecting enantiomers. Under the assumption of distinguishability, enantiomers are excluded by evidence (D), since interchange of two basal substituents in a pentagonal pyramid would interconvert enantiomers. Still, it would be pleasing if the proof could be completed with a generality and rigor consistent with the rest of the proof, so that one could be assured that *no* other structure, geometric or abstract, would be consistent with inequivalence of the sixth position.

Group Theoretical Formulation of Koerner's Argument

Chemical Location. A molecule of n atoms[11] may be described by associating with each atom a chemical location. Chemical location could specify the position of an atom in physical space, but more generally it denotes the relation between an atom in the location and atoms in other locations of the molecule as, for example, in molecules of fluxional structure. Thus a molecule can be denoted by a list of its chemical locations and the atoms which occupy them as

atom	a b c d . . .
chemical location	1 2 3 4 . . .

For example, methanol could be denoted

$$\begin{array}{ccccc} OH & H & H & H & C \\ 1 & 2 & 3 & 4 & 5 \end{array}$$

where a detailed relationship among locations 1-5 is assumed but not specified.

Chemical Substitution. A statement of Koerner's first assumption (direct replacement) in terms of chemical location is that the only difference in description of a molecule before and after chemical substitution is that the new atom assumes the chemical location of the atom displaced. Thus substitution of Br for NH_2 in nitroaniline could be written

$$\begin{array}{ccccccccc} \mathrm{NO_2} & \mathrm{NH_2} & \mathrm{H} & .. & \mathrm{H} & \mathrm{C} & .. & \mathrm{C} \\ 1 & 2 & 3 & .. & 6 & 7 & .. & 12 \end{array} \rightarrow \begin{array}{ccccccccc} \mathrm{NO_2} & \mathrm{Br} & \mathrm{H} & .. & \mathrm{H} & \mathrm{C} & .. & \mathrm{C} \\ 1 & 2 & 3 & .. & 6 & 7 & .. & 12 \end{array}$$

Equivalence Permutations and Experimental Indistinguishability. Koerner's second assumption may be reformulated in the following way. Two chemical locations in a molecule or in separate molecules may be said to be *equivalent* when they are identically related to corresponding sets of locations occupied by indistinguishable sets of atoms. Atoms of the same element occupying equivalent locations may also be said to be equivalent.

If, and only if, two molecules with different descriptions have experimentally indistinguishable properties, it is assumed that they have equivalent sets of chemical locations and of atoms *and* that some permutation of equivalent locations among atoms to interconvert the descriptions of the two molecules is an *equivalence permutation.* When chemical location is taken to denote position in physical space, an equivalence permutation corresponds to a rigid rotation of the molecule, but to speak more generally we denote by

$$\begin{pmatrix} 3 & 5 & y \\ x & 2 & z \end{pmatrix}$$

a permutation which carries location 3 of a molecule into location x, location 5 into location 2, and location y into location z. Similarly by

$$\left(\begin{matrix} 3 & 5 \\ x & 2 \end{matrix}\right.$$

we can denote a permutation which carries 3 into x and 5 into 2, and permutes the remaining locations in an unspecified manner.

When molecules each contain no more than one atom of any one type, experimental indistinguishability determines an equivalence permutation uniquely. For example, if the molecules

$$\begin{array}{ccccc} \mathrm{Br} & \mathrm{Cl} & \mathrm{CH_3} & \mathrm{H} & \mathrm{C} \\ 1 & 2 & 3 & 4 & 5 \end{array} \qquad \begin{array}{ccccc} \mathrm{Br} & \mathrm{Cl} & \mathrm{CH_3} & \mathrm{H} & \mathrm{C} \\ 3 & 2 & 1 & 4 & 5 \end{array}$$

were indistinguishable

$$\begin{pmatrix} 1 & 2 & 3 & 4 & 5 \\ 3 & 2 & 1 & 4 & 5 \end{pmatrix}$$

must be an equivalence permutation. But indistinguishability of the molecules

$$\begin{array}{ccccc} \mathrm{Br} & \mathrm{H} & \mathrm{CH_3} & \mathrm{H} & \mathrm{C} \\ 1 & 2 & 3 & 4 & 5 \end{array} \qquad \begin{array}{ccccc} \mathrm{Br} & \mathrm{H} & \mathrm{CH_3} & \mathrm{H} & \mathrm{C} \\ 3 & 2 & 1 & 4 & 5 \end{array}$$

proves only that at least one of

$$\begin{pmatrix} 1 & 2 & 3 & 4 & 5 \\ 3 & 2 & 1 & 4 & 5 \end{pmatrix} \text{ and } \begin{pmatrix} 1 & 2 & 3 & 4 & 5 \\ 3 & 4 & 1 & 2 & 5 \end{pmatrix}$$

must be an equivalence permutation, that is that an equivalence permutation exists which contains

$$\left(\begin{matrix} 1 & 3 & 5 \\ 3 & 1 & 5 \end{matrix}\right.$$

According to the assumption of direct replacement, if a particular permutation has been shown to be an equivalence permutation in a molecule, it must also be an equivalence permutation in the molecule in which all monovalent atoms have been substituted by hydrogen. The set of equivalence permutations of such a "parent" molecule constitutes a mathematical group.[12]

The Problem. On the basis of observations (A)-(E) Koerner wished to prove that the chemical locations of the six hydrogen atoms of benzene are equivalent. In the language of group theory the proposition is that the group of equivalence permutations of benzene is transitive on the set of hydrogen locations, that is, that the group contains elements which will carry any one hydrogen location into any of the other five hydrogen locations.

Restatement of the Evidence. We can begin numbering the hydrogen positions of benzene arbitrarily so that the locations of OH and COOH of "hydroxybenzoic acid" are 1 and 2, respectively. The OH and COOH positions of "salicylic acid" can be denoted i and j, respectively; and those of "parahydroxybenzoic acid", r and s, respectively. Evidence (A)-(E) can then be formulated as follows.

(A) There is no equivalence permutation which contains any of the permutations **A1–A3.**

$$\mathbf{A1}\left(\begin{matrix} 1 & 2 \\ i & j \end{matrix}\right. \qquad \mathbf{A2}\left(\begin{matrix} 1 & 2 \\ r & s \end{matrix}\right. \qquad \mathbf{A3}\left(\begin{matrix} i & j \\ r & s \end{matrix}\right.$$

(B) There is an equivalence permutation which contains **B1**, and one which contains **B2.**

$$\mathbf{B1}\left(\begin{matrix} 1 \\ i \end{matrix}\right. \qquad \mathbf{B2}\left(\begin{matrix} 1 \\ r \end{matrix}\right.$$

(C) There is an equivalence permutation which contains **C1**, and one which contains **C2.**

$$\mathbf{C1}\left(\begin{matrix} 2 \\ j \end{matrix}\right. \qquad \mathbf{C2}\left(\begin{matrix} 2 \\ s \end{matrix}\right.$$

(D) There is an equivalence permutation which contains **D.**

$$\mathbf{D}\left(\begin{matrix} 1 & 2 \\ 2 & 1 \end{matrix}\right.$$

(E) There is an equivalence permutation which contains **E**, where x is not j.

$$\mathbf{E}\left(\begin{matrix} i & j \\ i & x \end{matrix}\right.$$

Koerner's Proof That Five Positions Are Equivalent. Let the inverse of permutation **B1** be called $\mathbf{B1}^{-1}$. The inverse of the equivalence permutation which contains **B1** must be a member of the group of equivalence permutations and must contain $\mathbf{B1}^{-1}$. This inverse carries i into 1 and j into a point we may call k. Because i and j must be distinct (they are occupied by different groups in "salicylic acid"), k cannot be 1; k also cannot be 2, or else **A1** would be contained in an equivalence permutation. Thus we can replace k by 3 and expand **B1.**

$$\mathbf{B1}\left(\begin{matrix} 1 & 3 \\ i & j \end{matrix}\right.$$

Similarly, the equivalence permutation containing $\mathbf{B2}^{-1}$ carries r into 1 and s into a position we may call t. The existence of "parahydroxybenzoic acid" together with **B2** shows that t is not 1; **A2** shows that t cannot be 2; a combination of **A3** and the expanded **B1** shows that t cannot be 3. Thus we can replace t by 4 and expand **B2.**

$$\mathbf{B2}\left(\begin{matrix} 1 & 4 \\ r & s \end{matrix}\right.$$

An equivalence permutation containing **C1** followed by one containing $\mathbf{B1}^{-1}$ carries 2 into 3, and an equivalence permutation containing **C2** followed by one containing $\mathbf{B2}^{-1}$ carries 2 into 4. Thus locations 2, 3, and 4 are equivalent, which we can express as $2 = 3 = 4$. Because an equivalence permutation containing **D** carries 1 into 2, we have $1 = 2 = 3 = 4$.

From the existence of equivalence permutations containing **B1** and **E,** we know that there is an equivalence permutation which leaves 1 unchanged but carries 3 into a location we can call z, which cannot be 3 and is obviously not 1. Since this equivalence permutation carries the pair 1 z into 1 3, a combination of $\mathbf{B1}$ and $\mathbf{A1}^{-1}$ shows that z cannot be 2. Similarly a combination of **B1, A3,** and $\mathbf{B2}^{-1}$ shows that z cannot be 4. We can replace z by 5 and write $1 \equiv 2 \equiv 3 \equiv 4 \equiv 5$.

Completion of the Proof

The foregoing shows that Koerner's proof of the equivalence of at least five hydrogen locations in benzene was rigorous. The existence of only six hydrogens in benzene had been established by vapor density determinations.[13] Thus the following proof that there are not *only* five equivalent locations proves the proposition that there are six equivalent positions.

The basis of this proof is that, if a group of equivalence permutations contains an element which exchanges two of the locations (the element is the equivalence permutation containing **D**), there can exist no more than two isomers of substances involving substituents in pairs of only five equivalent locations. This would contradict the evidence that there exist three hydroxybenzoic acids involving substitution within the set of equivalent positions (A). This assertion is a special case[14] of statement I.

I. "If a group of equivalence permutations **P** is transitive on a set of p chemical locations, where p is prime number greater than 2, and **P** includes an element which exchanges two chemical locations, the number of isomers involving disubstitution among these equivalent locations is at most $(p - 1)/2$."

Statement I can be proven by showing that the total number of distinct, ordered pairs of p chemical locations divided by the minimum number of pairs which can be interconverted by equivalence permutations is $(p - 1)/2$. A set of pairs which can be thus interconverted is called an *orbit* of pairs, and all of its members correspond to a single isomer. The proof involves the following five steps:

(1) If **G** is a permutation group which is transitive on a set of p elements, where p is prime, but is not doubly transitive (having all pairs in a single orbit), **G** contains no element which *fixes* a pair (leaves the position of two elements unchanged), other than the identity. This is a trivial synthesis of statements from Burnside[15] and Galois.[16]

(2) Under the assumptions of (1), every orbit of pairs has the same number of elements as **G**. If this were not so, two *different* elements of **G** would have the same effect on a pair, and one element followed by the inverse of the other would be an element of the group which would fix the pair without being the identity. This would be contrary to (1).

(3) The number of elements in the permutation group **P** is at least $2p$. By a theorem of Cauchy[17] a group which is transitive on a set with a prime number of elements (that is, a transitive group of prime degree) must contain a p cycle of p distinct elements, $s, s^2, s^3, \ldots, s^p =$ identity, where s is

$$\begin{pmatrix} 1\ 2\ 3 \ldots p \\ 2\ 3\ 4 \ldots 1 \end{pmatrix}$$

The permutations in this p cycle are distinct from the permutation, t, which exchanges two locations, and from all products of t with elements of the p cycle. Since these products are also distinct from one another, there must be at least $2p$ elements in **P**. Thus, from (2), the minimum size for an orbit of pairs is $2p$.

(4) The number of distinct, ordered pairs among a set of p elements is $p(p - 1)$.

(5) The number of orbits of pairs is at most the number of distinct, ordered pairs divided by the minimum orbit size, that is, $p(p - 1)/2p = (p - 1)/2$.

Thus the maximum number of isomers that could be formed by disubstitution *within the set of five locations which Koerner had proved equivalent* would be $(5 - 1)/2 = 2$, unless the true set did not include only five equivalent locations. Since there were three hydroxybenzoic acids, there must have been another, that is, a sixth, location in the set.

The theorem of Burnside on which this proof is based was not proven until this century, so Koerner was obviously in no position to complete this proof rigorously by this means. Still it is worth noting that he was correct in thinking that no additional experimental evidence was necessary. Ladenburg's subsequent proof involved more experiments.[1]

Acknowledgments. I am deeply indebted to Professor George Seligman of the Department of Mathematics, Yale University, for his patient help in constructing the group theoretical argument. Professor K. Mislow and Dr. J. Nourse provided helpful comments on a preliminary manuscript. This work was supported in part by a Camille and Henry Dreyfus Teacher-Scholar Grant.

References and Notes

(1) Ladenburg, A. *Ber. Dtsch. Chem. Ges.* **1874,** *7*, 1684. Cited, e.g., in Wheland, G. W. "Advanced Organic Chemistry", 3rd ed.; Wiley: New York, 1960; p 71.
(2) Koerner, W. *G. Sci. Nat. Econ. Palermo* **1869,** *5*, 212.
(3) Anschütz, R. *Ber. Dtsch. Chem. Ges.* **1926,** *59*, 75. Cohen, J. B. *J. Chem. Soc.* **1925,** *127*, 2975.
(4) Bruni, G., Vanzetti, B. L., Translators. "Vier Abhandlungen von Wilhelm Koerner", Ostwald's Klassiker der Exacten Wissenschaften, No. 174; W. Engelmann: Leipzig, 1917.
(5) For example, Ladenburg wrote in 1876, ". . . Kekulé has shown repeatedly that arrangement in space is not to be understood [in discussions of symmetry] . . .";[6a] and in the 1877 reply to van't Hoff's criticism of his prism formula for benzene he wrote. "Van't Hoff brings into the formulae something which I, together with most other chemists, deliberately exclude. I mean arrangement in space." [6b]
(6) (a) Ladenburg, A. "Theorie der Aromatischen Verbindungen"; Friedrich Vieweg und Sohn: Braunschweig, 1876; p 10. (b) Ladenburg, A. *Ber. Dtsch. Chem. Ges.* **1877,** *10*, 1154.
(7) Koerner, W. *Bull. Acad. R. Belg.* **1867,** *24*, 166.
(8) von Richter, V. *Ber. Dtsch. Chem. Ges.* **1871,** *4*, 21, 459, 553. von Richter concluded correctly that conversion of *m*- and *p*-halonitrobenzenes to halobenzoic acids by heating with potassium cyanide involves rearrangement.
(9) Kekulé, A. *Bull. Acad. R. Belg.* **1867,** *24*, 111.
(10) Koerner used the names ortho, meta, and para for 1,4-, 1,2-, and 1,3-disubstituted benzenes, respectively. Although he, if anyone, could claim the right to name the isomers, the German usage (1,2, 1,3, and 1,4, respectively) became established.
(11) Wherever "atom" occurs in this discussion "atom or group of atoms" may be understood.
(12) If chemical location is interpreted as position in physical space, the set of equivalence permutations, that is, rigid-body rotations, will constitute a group. In the more general case this is a modest assumption.
(13) Reference 6, p 9.
(14) Burnside [Burnside, W. "Theory of Groups of Finite Order"; Dover Publications: New York, 1955; p 214] enumerates the orbits of pairs for a set of five equivalent locations.
(15) Huppert, B. "Endliche Gruppen", Vol. I; Springer-Verlag: West Berlin, 1967; p 609, Theorem 21.3.
(16) Reference 15, p 163, theorem 3.6, statements *b* and *d*.
(17) Reference 14, p 47, corollary II.