2. Polymerization to dicyandiamide takes place quantitatively in alkaline solution up to *P*H 10.

3. The velocity of dicyandiamide formation is a function of the hydrogen-ion concentration. It reaches a maximum at *P*H 9.6 and decreases rapidly below or above this *P*H.

4. Above *P*H 12 cyanamide is hydrolyzed quantitatively to urea.

5. The rate of hydrolysis is independent of alkalinity in the range studied.

535 FIFTH AVENUE, NEW YORK CITY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE POLARITIES AND THE ORIENTING INFLUENCES OF SUBSTITUTES IN THE BENZENE RING

BY WENDELL M. LATIMER AND C. W. PORTER

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More than fifty years ago it was observed that certain groups, when substituted for hydrogen in benzene, direct the next entering group to the meta position and that other groups direct to the ortho and para positions. There have been many attempts to classify atoms and groups on the basis of this behavior.[1] The most successful theory (proposed by Lapworth[2] and Stieglitz[3] and supported and amplified by many others) assumes alternate polarities in the carbon atoms of the benzene ring, induced by the electronegative or electropositive character of the first substituted group. The theory is based upon arbitrary qualitative estimates of polarity.

We wish to present in this paper a system which gives at least a semi-quantitative basis for determining polarity and which may, therefore, serve as a means of classifying groups exerting different orienting influences.

Our plan is to estimate, from considerations of electronic configurations, the residual charge on the atom attached to the ring. When a pair of electrons is shared between two atoms, we assume, except in the case of hydrogen, that the electrons are quantized in respect to the field between the atoms and that the effect of their charges is distributed between the atoms in the ratio of the positive charges on the two kernels. Thus we consider a pair of electrons between carbon and nitrogen as contributing $2 \times 4/9$ electron charges to the carbon atom and $2 \times 5/9$ electron charges to the nitrogen.

The bond between hydrogen and another atom cannot be so treated, as

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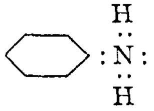
[1] The following are important references to the earlier literature: (a) Hübner, *Ber.*, **8**, 873 (1875); (b) Noelting, *ibid.*, **9**, 1797 (1876); (c) Armstrong, *J. Chem. Soc.*, **51**, 258 (1887); (d) Crum-Brown and Gibson, *ibid.*, **61**, 367 (1892); (e) Flürscheim, *J. prakt. Chem.*, **66**, 32 (1902); (f) Fry, THIS JOURNAL, **38**, 1323 (1916).

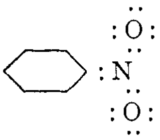
[2] Lapworth, *J. Chem. Soc.*, **121**, 1391 (1922).

[3] Stieglitz, THIS JOURNAL, **44**, 1299 (1922).

the moments of inertia of hydrides, obtained from band spectra, indicate that the hydrogen ion is within the electron shell or at least very close to the position of maximum electron density. Hence in this case we consider that two electrons and one proton are so close together that their resultant charge is minus one.

On this basis we may calculate, as an example, the resultant charge on the nitrogen of aniline  $:\underset{\underset{\displaystyle H}{\cdot\cdot}}{\overset{\overset{\displaystyle H}{\cdot\cdot}}{N}}:$ The positive charge on the nitrogen kernel is five. This is reduced by two unshared electrons, four electrons shared with hydrogen and two shared with carbon. The residual charge then is

$$+5 - 2 - (4 \times 1/2) - (2 \times 5/9) = -0.11$$

Dealing with nitrobenzene,  $:\underset{\underset{\overset{\cdot\cdot}{\underset{\cdot\cdot}{:O:}}}{\cdot\cdot}}{\overset{\overset{\overset{\cdot\cdot}{\underset{\cdot\cdot}{:O:}}}{\cdot\cdot}}{N}}$, in the same way, we have for the residual charge

$$+5 - (4 \times 5/11) - (2 \times 5/9) = +2.07$$

Similar calculations for a large number of groups and atoms are summarized in Table I.

Table I

Residual Charge and Directing Influence of Substituent Groups in Benzene

Group	Residual charge	Principal orienting influence	Group	Residual charge	Principal orienting influence
—OR	−0.4	*p* + *o*	$-CHX_2$	+0.55	*p* + *o*
—X (halogen)	−0.27	*p* + *o*	$-CBr_2NO_2$	+0.65	*m*
—OH	−0.2	*p* + *o*	$-CX_3$	+0.82	*m*[a]
$-NH_2$	−0.11	*p* + *o*	$-\overset{+}{N}H_3$	+0.88	*m*
$-NH_2COR$	−0.11	*p* + *o*	$-\overset{+}{N}R_3$	+0.88	*m*
$-N=N-C_6H_5$	−0.11	*p* + *o*	—NHOH	+1.0	*m*
$-CH_3$	0	*p* + *o*	—CHO	+1.20	*m*
$-C_nH_{2n+1}$	0	*p* + *o*	$-COCH_3$	+1.20	*m*
$-C_6H_5$	0	*p* + *o*	—C=N	+1.2	*m*
$-CH_2COOH$	0	*p* + *o*	$-CONH_2$	+1.32	*m*
$-CR_2NO_2$	+0.11	*p* + *o*	—CONHR	+1.32	*m*
$-CHRNH_2$	+0.11	*p* + *o*	—COCl	+1.38	*m*
$-\underset{\substack{\mid \\ O-CH_3}}{C}=CH_2$	+0.2	*p* + *o*	—COOH	+1.4	*m*
—N=O	+0.2	*p* + *o*	$-SO_3H$	+1.8	*m*
$-CH_2X$	+0.27	*p* + *o*	$-NO_2$	+2.1	*m*

[a] *p* and *o* in chlorinations and *m* in nitrations.

It will be observed that if the residual charge on the atom attached to the ring has a high positive value, the substituent directs to the meta position.

If the value is negative or zero, the group directs to the ortho and para positions. As the rule represents only a first approximation to a true solution of the problem, the line of division is not sharp and in general values between +0.1 and +0.6 lead to mixtures of para, ortho and meta compounds with large percentages of each.

An obvious inaccuracy in the method is the failure to take into account the decrease in the effective positive charge of the kernels by distortion or shielding effects of the orbits of electrons not directly involved in the bond. Thus actually there must be a difference between the residual carbon charges in CF_3, CCl_3, CBr_3 and CI_3: the distortion of the electron shells in the larger ions will tend to decrease the effective positive charge on their kernels making the carbon in CI_3 more negative than in CF_3, though in the case of the lighter elements such effects are probably not large.

In the case of unsaturated compounds it is especially arbitrary to assign positions to the electrons since we do not know how many electrons are in the bonds. In Table I we have used the ordinary symbol for double bond, =, as indicating four electrons shared; in all other cases the bond is considered as a single pair. In the so-called carbon–oxygen double bonds of carboxyl, aldehyde, etc., we have assumed a single electron pair in the belief that the large difference in the electronegative character of oxygen and carbon renders it unlikely that the carbon can pull four electrons into the bond. This is also in agreement with the symmetrical arrangement of the oxygen atoms about carbon in solid carbonates. For the same reason we assume for the structure of the cyanide ion, $:\mathrm{C}::\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}}$, rather than a six electron bond. However, the nature of an unsaturated nitrogen–oxygen bond is more uncertain, as oxygen is not much more electronegative than nitrogen. In these cases we have assumed a double electron bond in the NO_2 group where there are two oxygen atoms competing with a single nitrogen atom, but a four electron bond in the NO group. Actually these represent limiting conditions and our values for nitro, carboxyl, aldehyde, etc., are probably somewhat too positive and for the nitroso group too negative.

The system used in the calculations does not take into account atoms beyond those directly connected with the key atom, though these may in certain cases have considerable influence. An example of this, discussed by Flürscheim and Holmes,[4] is COOH which, in benzoic acid, directs meta, and COO^- which, in the benzoate ion, directs ortho and para, the latter being an exception to our rule. In the free acid the resultant field acting upon the benzene ring is positive, as determined by the residual charge upon the carbon of the carbonyl group. In the ion the negative field due to the unneutralized charge is superimposed to such an extent that the sign of the

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[4] Flürscheim and Holmes, *J. Chem. Soc.*, **128**, 1562 (1926).

resultant field is changed. Likewise the positive charges on NH_3^+ and on NR_3^+ probably render them more strongly meta orienting than indicated by our figures.

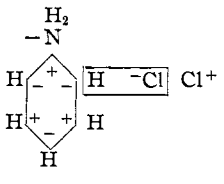
Ingold's[5] observation that the group $CH_3—O—\overset{|}{C}=CH_2$ directs to the ortho and para positions is in harmony with our system of classification. This was regarded as an exceptional case when the oxygen atom was used as the key atom in determining the position of induced positive charges in the ring; and in general the results obtained clearly indicated that the actual orienting influence of a group is determined by its positive or negative character, as given by this semi-quantitative treatment.

Holleman lists certain groups in the order of their meta directing capacities as follows:[6] COOH > SO_3H > NO_2. The order was determined with reference to the position taken by a third group in a ring containing two of these radicals. The presence of two groups complicates the problem by destroying the balance which normally exists in the benzene ring (see later discussion of this point). The more direct evidence based upon the percentages of ortho, meta and para derivatives formed from monosubstitution products is given below. The figures indicate the percentage of meta derivative obtained from each by treatment with nitric acid.

	C_6H_5COOH[7]	$C_6H_5SO_3H$[8]	$C_6H_5NO_2$[9]
% meta	82%	90%	93%
Charge (Table I)	+1.4	+1.8	+2.1

These values substantiate our order, although it is not to be expected that this type of evidence will in every case give agreement, especially when derived from very different experimental conditions.

While the effect of polarity upon orientation may be accepted as an experimental observation, the explanation of this behavior obviously depends upon a knowledge of the structure of the benzene ring. The theory proposed by Lapworth and by Stieglitz of induced polarity of opposite signs on alternate carbon atoms appears to make a satisfactory start. Thus the action of chlorine upon aniline was pictured as indicated. The chlorine molecule splits to give a negative chloride ion, which combines with a hydrogen ion. The positive chlorine combines with a negative carbon, in this case para and ortho, to the negative nitrogen. The same mechanism applies to all the other types of direct substitution, *i. e.*, Br, NO_2 or SO_3H, since all of these involve the



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[5] Ingold and Ingold, *J. Chem. Soc.*, **127**, 870 (1925).

[6] A. F. Holleman, "Die direkte Einführung von Substituenten in den Benzolkern," **1910**, p. 469.

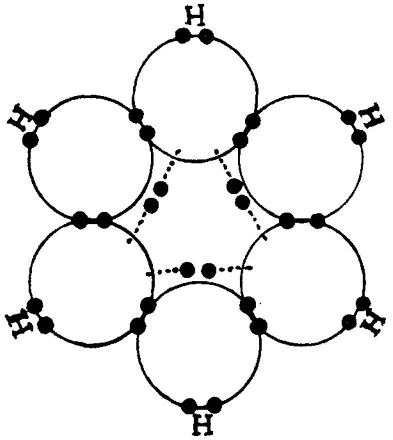
[7] "Annual Reports on the Progress of Chemistry," London, **1927**, p. 151.

[8] A. F. Holleman, Ref. 6, p. 75.

[9] "Annual Reports on the Progress of Chemistry," London, **1926**, p. 132.

splitting of the oxidizing agent into a negative ion which joins with a hydrogen ion and a positive ion which combines with a negative carbon.

One interpretation of this picture in terms of an electronic structure of the benzene ring would be that alternate carbon atoms of the ring possess or share six and eight electrons, respectively. This, doubtless, is a limiting condition, the actual polarity being very much less. It appears probable in terms of our present ideas of molecular structure that the electrons not directly held in the bonds between carbon and carbon and between carbon and hydrogen are quantized in respect to the field of the molecule as a whole. For each atom the direction of this resultant field is a line drawn through the center of the atom and the center of the ring. A pair of electrons rotating about this line might be thought of as binding one atom to all the other atoms of the ring, especially those in the ortho and para positions, as indicated in the diagram.



It is not especially profitable to speculate in terms of hypothetical benzene models; still, we believe that attempts to explain these orienting effects should be based upon some such electronic picture. In the above model unsubstituted benzene would be very nearly non-polar as on an average the three pairs of unshared electrons would be distributed equally among the six carbons. The substitution of a polar group would upset this balance. If the group is negative, the carbons in the ortho and para positions become slightly more negative. If the group is positive, the carbon atoms in the meta positions become relatively negative.

It is then only necessary to assume that the hydrogen ion is more readily displaced by the positive ion of the oxidizing agent from its electron pair on the negative carbon than from the pair on the positive carbon. Whether this is a matter of energy or of rate, depending upon the ease of activation, is not easily determined. The fact that varying amounts of all of the products are obtained seems to indicate that the rate of some step in the process is the determinative factor and that the ratio of the quantities of the products formed is not a good measure of their relative energies of formation.

Summary

A semi-quantitative measure of the polarity of a group attached to the benzene ring has been proposed which correlates the directing influence of

various substituents. The polarity is discussed in terms of the electronic structure of benzene.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE PENNSYLVANIA STATE COLLEGE]

ELECTROMETRIC STUDIES ON THE 2-HYDROXYNAPHTHALENE SULFONIC ACIDS. PREPARATION OF PURE 2-HYDROXYNAPHTHALENE-6-SULFONIC ACID

BY KARL H. ENGEL AND A. WITT HUTCHISON

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The purpose of the investigation was to study the neutralization curves, as obtained by electrometric titrations, of the 2-hydroxynaphthalenesulfonic acids in order to characterize them as acids and to determine especially the effect on the second dissociation constant of the position of the sulfonic acid group.

Preparation of Pure 2-Hydroxynaphthalene-6-sulfonic Acid.—In the study of this acid an especially pure material was desired. Though the preparation of metallic salts of the acid in a pure state may be accomplished by repeated recrystallization from their solutions, this cannot be done with the free acid because of its extreme solubility in water, alcohol, acetone, ether, etc.

It was found that the free acid may be precipitated from its aqueous solution by the addition of hydrogen chloride. This permitted a complete separation of the acid from excess sulfuric acid remaining in the sulfonation mass and from any isomeric compounds that may have been formed.

Schaeffer[1] first prepared the free acid from the lead salt by means of hydrogen sulfide. He obtained a crystalline compound which, when dried over concentrated sulfuric acid, melted at 125°. Later Ebert and Merz[2] used the same method of isolation and found a melting point of 122° but accepted Schaeffer's higher value as the correct one. Analyses of the compounds were not given in either case.

Preparation of the Free Acid from Hydrogen Chloride Solutions.—A mixture of 100 g. of 2-hydroxynaphthalene (Merck's resublimed) and 100 g. of sulfuric acid (100%) was stirred for seventy-five minutes at a temperature of 85°. The sulfonation mass, which had begun to solidify, was poured into a mixture of 500 g. of ice and water.

An aliquot portion of the solution was made alkaline with sodium carbonate and titrated with a standard solution of 1-diazo-2-methylbenzene hydrochloride. It was found that the solution contained 70% of the theoretically possible amount of the 2-hydroxynaphthalene-6-sulfonic acid.

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[1] Schaeffer, *Ann.*, **152**, 296 (1869).

[2] Ebert and Merz, *Ber.*, **9**, 609 (1876).