Summary

A general method has been developed for the determination of halogens in organic compounds, based upon oxidation of the substance by fuming sulfuric acid and distillation of the halogen formed. If the compound to be analyzed contains arsenic, antimony or bismuth, these metals, in addition to the halogen, may be determined in the same sample very easily.

The method of analyses requires only a short time and possesses decided advantages over the Carius and the Lemp and Broderson modification of the Pringsheim–Parr procedure.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ILLINOIS]

THE STEREOISOMERISM OF DIPHENYL COMPOUNDS. IV[1]

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Although the evidence for the obstacle theory to explain the optical isomerism possible in certain types of substituted diphenyl compounds is increasing, much more experimental work is necessary before an entirely satisfactory analysis of this phenomenon may be expected. Previous work[1b] from this Laboratory has demonstrated that compounds having all four groups in the 2,2′,6,6′-positions the same, may be resolved into optical antipodes provided each of the two rings is unsymmetrical in itself. This is substantial evidence against the theory that interference is due merely to the relative electrostatic charges on the substituted groups. The question as to how important may be the relative size of the groups in the 2,2′,6,6′-positions requires further study. This investigation has involved a careful consideration of the probable interfering forces of such groups from x-ray data.

From x-ray data it is possible to calculate the distance between the two connecting carbon atoms in diphenyl as 1.45 Å. In the same manner and by assuming the usual angles in the benzene ring, the vertical distance between the 2,2′-carbon atoms in the benzene rings may be estimated as 2.90 Å. Also by x-ray data the relative distances between the centers of the carbon atoms in the benzene ring and of the atoms or groups attached to the benzene ring may be obtained. A question for which, at the present time, there is no experimental attack and which, therefore, cannot be settled, is the angle at which the substituting group in a benzene ring is attached. This angle must depend upon electrostatic forces

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[1] Previous papers in this series are (a) Hyde and Adams, THIS JOURNAL, **50**, 2499 (1928); (b) Moyer and Adams, *ibid.*, **51**, 630 (1929); Stanley and Adams, *Rec. trav. chim.*, [4] **48**, 1035 (1929).

in the molecule, and hence will be affected by the position and character of the other substituting groups present. The values which have been estimated for the distances between the centers of the carbon atoms and of the attached groups are given below.

ATOMIC DISTANCES IN Å.

Values from x-ray data for aliphatic compounds		Aromatic compounds (calcd.)
C–H	1 to 1.1	0.94 to 1.04
C–N (amino)	1.48	1.39
C–C (methyl)	1.54	1.45
C–I	2.2 to 2.5	2.06 to 2.35
C–Br	2.1 to 2.4	1.97 to 2.26
H–I	1.5	....
H–Br	1.42	....
H–Cl	1.28	....
H–F	0.94	....
H–H	0.42 to 0.48	....
H–OH	1.11	..
C–Cl	2.01 (calcd.)	1.89
C–F	1.48 (calcd.)	1.39
C–COOH	1.67 (calcd.)	1.56
C–OH	1.62 (calcd.)	1.54
C–NH$_2$	1.66 (calcd.)	1.56
C–CH$_3$	1.84 (calcd.)	1.73
C–NO$_2$	2.05 (calcd.)	1.92
C–CH	..	1.90
C–CO	..	2.45

The first eleven atomic distances in the left-hand column determined by x-ray data were taken from the "Handbuch der Physik."[2] They represent the distances between atomic kernels, as derived from the study of aliphatic compounds. Since an aromatic carbon atom is similar in size to the carbon atoms in graphite, it is reasonable to suppose that the distances between benzene carbon atoms and the centers of the substituting groups will be somewhat smaller than in aliphatic compounds. This difference amounts to about 6%, since the diameter of an aliphatic carbon is generally given as 1.54 Å. and the diameter of an aromatic carbon atom as 1.45 Å. Therefore, 94% of the distances for the aliphatic compounds are taken as the distances involved in aromatic compounds. The distances C–Cl and C–F were calculated by extrapolation of the values determined for C–I and C–Br compared to the values determined for H–I, H–Br, H–Cl and H–F. The results obtained for C–Cl are essentially the same whether calculated through the C–I or C–Br distance. This is also true of the C–F values.

The values for C–COOH, C–NH$_2$, C–OH, C–CH$_3$, C–CH= and C–NO$_2$ were estimated from additional x-ray data. The length of the acetic acid molecule has been found to be 3.33 Å.[3] This represents the overall distance of a methyl group in combination with the carboxyl group. Since the sum of the radii of the two groups is taken as the distance between the centers of the two groups, the distance C–COOH is approximately 1.67 Å.

The C–NH$_2$ value was calculated from the distance between the kernel of a carbon atom and the kernel of a nitrogen atom in an amino group.

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[2] Grim, "Handbuch der Physik," Vol. 24, p. 539.

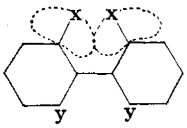
[3] Gibbs, *J. Chem. Soc.*, **125**, 2622 (1924).

It was assumed that the increase in size of the NH_2 due to the two hydrogen atoms is less than one-half of the effective diameter of a hydrogen atom or, perhaps, 0.18 Å. The total distance C–NH_2 then becomes 1.66 Å.

For the C–OH value the experimental data necessary for calculation are very meager. Caspari,[4] after a study of amino and hydroxyl derivatives of benzene comes to the conclusion that on the basis of atomic domains, the spaces occupied by hydroxyl and amino groups cannot differ greatly from each other. Judging from the C–NH_2 value of 1.66 Å., a C–OH value 1.62 Å. should be approximately correct, inasmuch as the hydroxyl ion has been shown to be somewhat smaller than an amino ion. A value for C–OH may also be calculated by a comparison of the length of octadecylbenzene[5] (24.6 Å.) and octadecylphenol (25.6 Å.), which will give the effective diameter of an oxygen atom in a hydroxyl on a benzene ring as 1.0 Å. Owing to the fact that the value obtained by studying such large molecules is probably too small and that in an aliphatic compound the substituent is larger, 0.15 Å. was added to the determined value for the oxygen atom. The total value of 1.15 Å. together with the diameter of a hydrogen atom, 0.45 Å., gives a final value of 1.60 Å. for the C–OH, which is essentially the same as the previously estimated value.

The distance C–CH_3 was calculated by assuming the three hydrogen atoms to increase the length of the C–C by at least two-thirds of the diameter of a hydrogen atom, or 0.30 Å., the distance C–CH= by assuming the hydrogen to increase the size of the aromatic CH= group by the effective diameter of the hydrogen atom, the distance C–NO_2 by assuming the two oxygen atoms to increase the length of C–N by at least one-half the effective diameter of an oxygen atom. The distance C–CO in a quinone ring was estimated by assuming the oxygen to increase the aromatic C–C value by the effective diameter of an oxygen atom on a benzene ring.

It is interesting to note that the calculated distance between an aromatic carbon atom and substituents are of the same order as the diameters of the corresponding ions of the substituents.



The relative values given in the table should not be considered as representing merely a linear effect. The forces around a group which might interfere with the forces around another group are certainly three dimensional in character. If these forces are assumed to be effective in an area of the character of an irregular ellipsoid (see diagram), as might be expected in view of the particular linking of carbon atoms in the diphenyl molecule, the shortest distance between the 2,6- or 2′,6′-carbon atoms in diphenyl would be included in the effective areas and the table values would, therefore, have significance as far as determining the

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[4] Caspari, *Phil. Mag.*, **4**, December (1927).

[5] Shearer, *J. Chem. Soc.*, **123**, 3152 (1923).

relative degree of collision that occurs in the various types of substituted diphenyl compounds. It seems probable, however, that the area of the forces might vary somewhat with the character of the group, and only by experiment may this be determined.

The amount of interference caused by several combinations of 2,2′,6,6′-substituted groups has been calculated by subtracting from the sum of the distances between C–X and C–Y, the 6,6′-substituted groups, the vertical distance between the 6,6′-carbon atoms, 2.90 Å. Compounds with just two different kinds of groups in the 2,2′,6,6′-position were selected since these are by far the most readily prepared and include those already described. The calculations based on the internuclear distances previously estimated are given in the following table.

CALCULATIONS BASED ON INTERNUCLEAR DISTANCES

Groups in positions		Sum of internuclear distances of 2,2′-groups in Å.	Interference over 2.90 Å., vertical distance between 2,2′-carbon atoms	Groups in positions		Sum of internuclear distances of 2,2′-groups in Å.	Interference over 2.90 Å., vertical distance between 2,2′-carbon atoms
2,2′	6,6′			2,2′	6,6′		
CH_3	CH_3	3.46	0.56	COOH	F	2.95	0.05
CH_3	NH_2	3.29	.39	F	Cl	3.28	.38
COOH	Cl	3.45	.55	F	F	2.78	− .12
COOH	CH	3.46	.56	F	OH	2.93	.03
COOH	CO	4.01	1.11	F	NH_2	2.95	.05
OH	CH	3.44	0.54	F	CO	3.91	1.01
COOH	NO_2	3.48	.58	OH	OH	3.08	0.18
COOH	Cl	3.45	.55	OH	NH_2	3.1	.20

Compounds representing the first eight combinations listed in the above table have been previously prepared and resolved into optical antipodes. None of the optically active forms of these compounds could be readily racemized. From these data it can be concluded that a difference of at least 0.39 Å. or more is sufficient to prevent practically complete rotation of the benzene nuclei into the same plane, provided this interfering effect is the only one involved.

Kenner[6] and Kuhn[7] have prepared the 2,4′-dinitro-6,6′-dicarboxydiphenyl and the 2,4,4′-trinitro-6,6′-dicarboxydiphenyl. Both of these compounds are readily racemized in alkaline solution. They are the only representatives yet prepared and resolved which have merely three substituents in the 2,2′,6,6′-positions. Those compounds with four groups present have at least two points of collision to aid in resisting racemization. Such tetrasubstituted compounds and especially those representatives which have two pairs of similar groups present in the proper positions are essentially symmetrical in regard to electrostatic or mechanical forces. In

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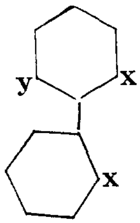
[6] Christie and Kenner, *J. Chem. Soc.*, **121**, 614 (1922); 470, 671 (1926).

[7] Kuhn and Albrecht, *Ann.*, **455,** 272 (1927); **458,** 221 (1927).

the trisubstituted compounds, however, there may be only one point of collision at any one instant and, at the same time, much less symmetry in the molecule. Hence the possibility is greater that a distortion of the molecule, due either to electrostatic forces or to other factors, may take place and aid racemization. In other words, the assumption is that during racemization, at the instant when the two rings move through the same plane, there may be a tendency in the trisubstituted compound for the rings to be bent toward each other on the side where the one substituting group and the hydrogen are present (see diagram). This decreases the effective interfering forces on the other side of the molecule and racemization takes place readily. It may be that such distortion is greater in 6,6′-dicarboxy compounds when the carboxyl groups are ionized, due particularly to the strongly repelling electrostatic forces of the ions.



With these assumptions it is possible to make predictions as to diphenyl compounds which might not be resolved, to others which could be resolved but which would racemize readily, and to still others which could not be racemized at all. It will be noticed from the table that in the case of the 2,2′-difluoro-6,6′-dicarboxydiphenyl, the interfering values amount only to 0.05 Å., and consequently the active forms of this compound should show a much greater tendency to racemize than the active forms of those compounds previously studied. In a communication published several years ago Kenner[8] mentioned that he intended to prepare 2,2′-difluoro-6,6′-dicarboxydiphenyl and in a recent letter (January, 1930), stated that he had already started this problem. On the other hand, a tetrafluorodiphenyl with the proper substitution to make each ring unsymmetrical in itself could not be resolved if the values mentioned have any significance, since the 2,6-fluorine atoms would fail to reach the 2′,6′-fluorine atoms by 0.12 Å. The 2,2′-difluoro-6,6′-diaminodiphenyl or 2,2′-difluoro-6,6′-dihydroxydiphenyl derivatives should be like the 2,2′-difluoro-6,6′-dicarboxydiphenyl. They would probably resolve, but would be expected to racemize readily since the *o*-substituted groups would interfere by 0.05 and 0.03 Å., respectively. The acetylated derivatives, however, should perhaps racemize with much greater difficulty, inasmuch as the acetyl group would probably increase the interference. Other combinations such as a 2,2′,6,6′-tetrahydroxydiphenyl or 2,2′-dihydroxy-6,6′-diaminodiphenyl, having interferences of 0.18 and 0.20 Å., respectively, would be expected to racemize with greater difficulty than either of the above-mentioned combinations, and with less difficulty than any of the first eight combinations listed in Table II. Representatives of these compounds are now being studied with a view to determine how reliable the conclusions from x-ray data may be. Of even more interest is the de-

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[8] Kenner, *Chemistry and Industry*, **46**, 218 (1927).

sirability of further study of the rather difficultly prepared 2,2′,6-trisubstituted diphenyls and their tendency to racemize. If the assumptions outlined are sound, it might be anticipated that trisubstituted compounds of all gradations of stability to racemization could readily be found. In fact, if the sum of the distances from the carbons to each of the three substituting groups and of the carbon to hydrogen is appreciably greater than twice the perpendicular distance between the α,α'-carbon atoms (2×2.90 Å.), no racemization should occur. If the sum is only slightly greater, the substances should racemize and if less, no resolution should be possible. Following out this plan of reasoning, it should even be possible to resolve merely a disubstituted α,α'-diphenyl provided the two groups were sufficiently large.

Slightly different methods of calculating interferences which are also based on x-ray data may be used, but the relative values are nearly the same. As a consequence the simplest method which involved the least amount of calculation was selected for discussion in this paper.

The authors wish to express here their appreciation to Dr. George L. Clark of the Chemistry Department of the University of Illinois for his assistance and advice in using the x-ray data.

Summary

A discussion is given of the expected isomerism of certain diphenyl compounds from a consideration of distances between the ring carbons and the centers of the substituting groups as deduced from x-ray data.

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

SOME DERIVATIVES OF DIPHENYL ETHER

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Raiford and Colbert[1] brominated 4-nitrodiphenyl ether and obtained a dibromo derivative that melted at 79°,[2] but the halogen atoms were not oriented. In the work now reported this structure was determined by two syntheses. When 4-nitrochlorobenzene was heated with the potassium salt of 2,4-dibromophenol,[3] as explained below, the ether melt-

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[1] Raiford and Colbert, THIS JOURNAL, **48**, 2652 (1926).

[2] This melting point is not recorded in the published report but is given in the typed thesis on file in the University Library.

[3] The material available was not pure. It contained 62.26% of bromine instead of 63.49% calculated. It was converted into the benzoyl ester which, after several crystallizations, melted at 96° [*Ber.*, **40**, 747 (1907)] and analysis for bromine indicated a pure product. The phenol obtained by hydrolysis melted at 35°. Körner [*Ann.*, **137**, 205 (1866)] reported 40°. while Peratoner [*Gazz. chim. ital.*, **16**, 402 (1886)] found 35–36°.