TABLE V

$h\,k\,l$	Expected d, Å.	d found, Å.
1 1 1	2.94	
0 0 2	2.88	
2 0 0	2.44	2.48
2 0 2	1.85	1.83
2 2 0	1.72	
1 1 3	1.68	
3 1 1	1.49	1.51
2 2 2	1.47	
2 0 4	1.24	1.27
4 0 0	1.22	

A faint line with d = 2.17 could not be accounted for; however, it was observed that this line occurred also with medium intensity in samples of pure magnesium, and hence was a line foreign to the sample.

of the alkaline earths are CaO_2, SrO_2, and BaO_2. As the radius of the cation decreases, the stability of the corresponding peroxide falls off also. The peroxide of magnesium is usually written as $MgO \cdot MgO_2$ which readily loses oxygen.

It is hoped that more work on the carbides of magnesium will be done by this author in the future.

Acknowledgments

The author desires to express his sincerest thanks to Professor J. C. W. Frazer for his continued interest and guidance in this work. He also wishes to express his gratitude to the Hynson, Westcott and Dunning Fund for financial assistance, which helped to make this work possible.

Results

1. It has been shown that the acetylide MgC_2 is a compound unstable at elevated temperatures, thereby liberating free carbon and Mg_2C_3, which upon hydrolysis gives methylacetylene. By all conceivable tests, Mg_2C_3 must be a pure substance. The concept that Mg_2C_3 contains a three-membered carbon chain in its crystal lattice appears to be correct.
2. Magnesium acetylide has been prepared from magnesium diethyl and acetylene.
3. An X-ray powder has been obtained of MgC_2. The data are compared with those expected for the tetragonal CaC_2 structure having the predicted axes a_0 = 4.86 Å., c_0 = 5.76 Å.
4. An explanation is proposed for the observed instability and reactivity of MgC_2.

BALTIMORE, MD. RECEIVED NOVEMBER 19, 1942

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Electric Moments of Ortho-substituted Phenols and Anisoles. I. Halogen Derivatives[1]

BY W. F. ANZILOTTI[2] AND B. COLUMBA CURRAN

Electric moments of ortho-substituted phenyl ethers are of interest in the study of the effects of steric hindrance between an alkoxy group and an ortho substituent on the configuration of these molecules. An analysis of the moments of the corresponding phenols permits a comparison of the extent and strength of intramolecular hydrogen bonding in these compounds. Interpretation of the observed moments of substituted phenols and anisoles must be based on values calculated for all possible configurations. These calculations require a knowledge of bond moments and of bond angles obtained from diffraction measurements. No diffraction data are available for alkyl phenyl ethers. The average oxygen valence angle reported from X-ray analyses[3] of resorcinol crystals is about 117°. This deviation from the tetrahedral angle may be partly due to intermolecular hydrogen bonding. A value of 118° has been assigned[4] to the oxygen bond angle in di-p-iodophenyl ether from electron diffraction measurements on the vapor. From these data, and from a consideration of steric and resonance effects, the authors have assumed an oxygen valence angle of 115° in substituted phenols, and of 120° in substituted anisoles.

The ring-to-oxygen moment in these compounds cannot be evaluated directly. The corresponding moment in diphenyl ether may be calculated from the moment[5] of this compound in benzene,

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[1] Presented in part at the Detroit meeting of the American Chemical Society, September, 1940.

[2] Present address: E. I. du Pont de Nemours and Co., Louisville, Ky.

[3] Robertson, *Proc. Roy. Soc.* (London), **A157, 79** (1936): **A167,** 122 (1938).

[4] Maxwell, Hendricks and Mosley, *J. Chem. Phys.*, **3,** 699 (1935).

[5] Appendix Tables, *Trans. Faraday Soc.*, **30,** App. (1934). Unless otherwise indicated, electric moments in this paper are taken from this source, and are in Debye units.

1.14, the observed oxygen valence angle, 118°, and the assumption of a H–C moment of 0.3. The calculated ring-to-oxygen moment is 0.8. This checks the value of the C–O moment in dimethyl ether, and indicates very little double bond character. We are of the opinion that the ring-to-oxygen moment in phenols and anisoles is much lower than this value. The latter is not consistent with the observed moments of para-substituted anisoles, and it is affected by steric inhibition of resonance in diphenyl ether. The electric moment studies of Higashi and Uyeo[6] reveal that the two rings in the disubstituted diphenyl ethers are not in the same plane.

We have chosen to calculate the ring-to-oxygen moment in anisole from the observed moment of *p*-bromoanisole in benzene, 2.2. The C–Br moment is taken as 1.2, the difference between the moments of bromobenzene and the H–C bond. The value of the methyl carbon-to-oxygen bond moment most consistent with the moments of anisole and *p*-bromoanisole is 1.0. Assuming these bond moments, and an oxygen valence angle of 120°, the value calculated for the ring-to-oxygen moment by a simple vector treatment is zero. This is more correctly the sum of the C–O dipole plus the resultant of the C–C dipoles resulting from the interaction of oxygen with the ring. The calculated zero moment indicates that this interaction, the contribution of structures of the type $R{-}O^+{=}C_6H_5^-$ to the normal anisole molecule, is appreciable, giving the oxygen-to-ring bond a large double bond character. The short carbon-to-oxygen distance in resorcinol, 1.36 Å.,[3] compared to the value reported[7] for dimethyl ether, 1.44 Å., supports this interpretation. Chemical reactions likewise indicate strong resonance between the methoxy group and the ring; the methoxy group promotes a higher electron density at the para carbon atom in anisole than does the methyl group in toluene.[8]

The moment of *p*-bromophenol cannot be analyzed in the same manner as that of *p*-bromoanisole because some of the phenol molecules are associated. Freezing-point determinations for the *p*-bromophenol–benzene solutions listed in Table III indicate that the solute is about 7% associated at these concentrations. Further evidence for this association is apparent in the sharp rise in solute polarizations at very low concentrations observed by Williams and Fogelberg[9] for solutions of *p*-bromophenol and *p*-chlorophenol in benzene. In calculating the moments of halogenated phenols in various configurations a ring-to-oxygen moment of zero is assumed, and the H–O bond moment is taken as 1.7.

The calculated moments listed in Table I were obtained with the aid of the moments of chlorobenzene, 1.55, and of fluorobenzene, 1.4, in addition to the bond moments and bond angles previously discussed. The *cis*- and *trans*-configurations correspond to structures in which the methyl carbon or hydroxyl hydrogen is closest to and farthest removed from the halogen atom. The moments corresponding to free rotation about the phenyl carbon-to-oxygen bond were calculated according to the method of Fuchs,[10] using the formula $\mu^2 = m_1^2 + m_2^2 + m_1m_2 \cos \theta$, in which m_1 is the moment of phenol or anisole, m_2 the moment of the halobenzene, and θ is the angle that the phenol or anisole moment makes with the ring-to-oxygen bond. Assuming the bond moments and bond angles previously mentioned, this angle for the anisole moment is calculated to be 107°. This angle may be calculated from the observed moments of anisole, bromobenzene and *p*-bromoanisole without the assumption of any bond angle or bond moments by substitution in the equation $\mu^2 = m_1^2 + m_2^2 - 2m_1m_2 \cos \theta$ in which μ is the moment of *p*-bromoanisole. This calculation yields a value of 108.5°. The agreement between these two values supports the accuracy of the calculated moments listed in Table I. The second decimal places in these moments were included only to show relative values for the different compounds.

TABLE I

CALCULATED MOMENTS OF ORTHO-SUBSTITUTED PHENOLS AND ANISOLES

	cis	*trans*	Free rotation
o-Bromoanisole	0.43	2.45	1.78
o-Chloroanisole	.47	2.50	1.82
o-Fluoroanisole	.35	2.37	1.71
o-Bromophenol	.43	2.85	2.04
o-Chlorophenol	.40	2.90	2.07

Experimental

Preparation and Purification of Compounds.—The *o*-bromoanisole, *o*-chlorophenetole and *o*-chlorophenol were obtained from the Eastman Kodak Co. and purified by distillation. The *o*-chloroanisole was prepared from *o*-

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(6) Higashi and Uyeo, *Bull. Chem. Soc. Japan*, **14**, 87 (1939).

(7) Sutton and Brockway, THIS JOURNAL, **57**, 473 (1935).

(8) Hammett, *ibid.*, **59**, 96 (1937).

(9) Williams and Fogelberg, *ibid.*, **52**, 1356 (1930).

(10) Fuchs, *Z. physik. Chem.*, **14B**, 339 (1931).

anisidine by adding the diazonium chloride to a cuprous chloride solution. The *o*-fluoroanisole was prepared from *o*-anisidine by adding to the diazonium chloride a large excess of fluoroboric acid prepared from a 60% solution of hydrogen fluoride according to the method of Schiemann and Miau.[11] The *o*-fluorophenol was prepared by refluxing *o*-fluoroanisole with a 48% aqueous solution of hydrogen iodide for about fifty hours.[12] The *o*-bromophenol was prepared by Dr. F. L. Benton of this department by the cleavage of *o*-bromoanisole with boron tribromide.[13] The *p*-bromophenol was obtained from the Eastman Kodak Co. and purified by fractional freezing; m. p. 63–64°. Each liquid was purified by fractional distillation in an all-glass still, and fractions having a constant index of refraction were used in the preparation of solutions. The physical constants of these liquids are listed in Table II.

TABLE II

PHYSICAL CONSTANTS OF LIQUIDS

Compound	B. p. °C.	B. p. Mm.	d^{25}_4	$n^{25}\text{D}$
o-Fluoroanisole	67	23	1.1205	1.4947
o-Chloroanisole	92–93	20	1.1865	1.5433
o-Bromoanisole	107– 8	21	1.5037	1.5711
o-Chlorophenetole	97–98	15	1.1288	1.5284
o-Fluorophenol	78–79	62	1.2108	1.5107
o-Chlorophenol	90	50	1.2573	1.5563
o-Bromophenol	79–80	17	1.6328	1.5861

The solvents were purified in the following manner: C. P. benzene and practical dioxane were dried by refluxing over sodium. The benzene used to calibrate the dielectric cell was purified by repeated fractional freezings before drying. Carbon tetrachloride was dried over calcium chloride. All solvents were distilled in an all-glass still.

Measurements and Calculations.—The measurements of dielectric constants and densities and the calculations of solute polarizations at infinite dilution have been described

TABLE III

DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS AT 25°

c_2	ϵ	d
Benzene-*o*-Fluoroanisole		
0.00000	2.276	0.8734
.02150	2.435	.8775
.02225	2.446	.8799
.02471	2.459	.8814
.02927	2.495	.8859
Benzene-*o*-Chloroanisole		
.00000	2.276	.8734
.01437	2.403	.8799
.01853	2.441	.8815
.01943	2.449	.8822
Benzene-*o*-Bromoanisole		
.00000	2.276	.8734
.01520	2.410	.8870
.01743	2.429	.8892
.01938	2.446	.8910
Dioxane-*o*-Bromoanisole		
.00000	2.213	1.0282
.01110	2.319	1.0358
.01785	2.384	1.0404
.02613	2.462	1.0462
Benzene-*o*-Chlorophenetole		
.00000	2.276	0.8734
.00884	2.355	. .
.01673	2.425	.8791
.02113	2.466	.8802
Carbon tetrachloride-*o*-Fluorophenol		
.00000	2.230	1.5812
.01982	2.264	1.5732
.02355	2.270	1.5717
Dioxane-*o*-Fluorophenol		
.00000	2.230	1.0270
.01540	2.305	1.0303
.02619	2.359	1.0326
Carbon tetrachloride-*o*-Chlorophenol		
.00000	2.232	1.5856
.02123	2.272	1.5780
.02675	2.281	1.5759
.03040	2.289	1.5744
Benzene-*o*-Chlorophenol		
.00000	2.276	0.8733
.01212	2.308	0.8783
.01699	2.321	0.8805
.02919	2.351	0.8861
Dioxane-*o*-Chlorophenol		
.00000	2.227	1.0262
.01371	2.317	1.0304
.01550	2.331	1.0309
.01868	2.350	1.0324
Carbon tetrachloride-*o*-Bromophenol		
.00000	2.233	1.5856
.01714	2.266	1.5862
.02004	2.272	1.5864
.03031	2.292	1.5868
Dioxane-*o*-Bromophenol		
.00000	2.211	1.0282
.01235	2.311	1.0378
.01673	2.348	1.0413
.02691	2.438	1.0491
Benzene-*p*-Bromophenol		
.00000	2.277	0.8737
.01268	2.371	.8854
.01489	2.379	.8875
.02588	2.466	.8977
.02756	2.476	. .
Dioxane-*p*-Bromophenol		
.00000	2.212	1.0280
.01227	2.354	1.0376
.01739	2.406	1.0412
.02098	2.448	1.0442

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(11) Schiemann and Miau, *Ber.*, **66**, 1183 (1933).

(12) Schiemann and Kuhne, *Z. physik. Chem.*, **156A**, 417 (1931).

(13) Benton and Dillon, THIS JOURNAL, **64**, 1128 (1942).

previously.[14] The electric moments were calculated from the equation $\mu = 0.0128\sqrt{P_{2\infty} - MR_D}$. The molar refraction of *p*-bromophenol was assumed to be equal to that of *o*-bromophenol. Freezing points were measured for benzene and the three most dilute solutions of *p*-bromophenol in benzene listed in Table III. The freezing point constant for the benzene was determined by measuring the freezing point of a dilute solution of *o*-bromoanisole in benzene. These measurements yielded a molecular weight of 185 ± 2 for *p*-bromophenol. If association results in the formation of dimers, this molecular weight corresponds to 7% association.

TABLE IV

POLARIZATIONS AND ELECTRIC MOMENTS

	$P_{2\infty}$	MR_D	μ
o-Fluoroanisole	142.1	32.79	2.31
o-Chloroanisole	165.7	37.95	2.50
o-Bromoanisole (benzene)	165.4	40.86	2.47
o-Bromoanisole (dioxane)	174.7	40.86	2.56
o-Chlorophenetole	174.6	42.73	2.54
o-Fluorophenol (CCl_4)	55.3	27.72	1.16
o-Fluorophenol (dioxane)	97.0	27.72	1.84
o-Chlorophenol (CCl_4)	59.8	32.89	1.15
o-Chlorophenol (benzene)	69.1	32.89	1.33
o-Chlorophenol (dioxane)	123.6	32.89	2.11
o-Bromophenol (CCl_4)	62.5	35.57	1.15
o-Bromophenol (dioxane)	149.3	35.57	2.36
p-Bromophenol (benzene)	139.2	35.6	2.25
p-Bromophenol (dioxane)	193.7	35.6	2.78

Discussion of Results

The difference in the moments of *o*-bromoanisole in dioxane and benzene, 0.09, may be taken as a rough measure of the increase in moment to be expected when the dioxane exerts no specific chemical action on the solute. The moment of *p*-bromophenol in dioxane, 2.78, compares to a calculated value for non-associated molecules in benzene of 2.5. A portion of this difference is probably due to the dipole introduced by the formation of the O---H bond between the dioxane and the acid hydrogen of the phenol. The $\Delta\epsilon/c_2$ ratios for the solutions of *p*-bromophenol in benzene listed in Table III increase with increasing solute concentration, indicating association. The average ratio for the three most dilute solutions was used in calculating the moment of the solute.

The very good check between the observed moments of *o*-chloroanisole and *o*-bromoanisole, 2.50 and 2.47, and the values calculated for *trans*-configurations, 2.50 and 2.45, indicate that very probably all of these molecules have the methoxy groups locked in the *trans*-position. This is further evidence of the strong double bond character of the ring-to-oxygen bond. The *cis*-configuration is not possible in these compounds because of the steric repulsion between the methyl groups and the halogen atoms. The small difference, 0.06, between the observed and calculated *trans*-moments for *o*-fluoroanisole is probably not significant, although the small size of the fluorine atom makes the *cis*-configuration less improbable for this compound than for the other *o*-haloanisoles.

The infrared absorption spectrum of a dilute solution of *o*-chlorophenol in carbon tetrachloride obtained by Wulf and Liddel[15] has been interpreted by Pauling as revealing that 91% of the solute molecules have a *cis*-configuration due to intramolecular hydrogen bonding.[16] Assuming the calculated moments for the *cis*- and *trans*-forms of *o*-chlorophenol listed in Table I, the observed moment of this compound in carbon tetrachloride, 1.15, corresponds to a mixture of 86% *cis*- and 14% *trans*-molecules. Atomic polarizations were neglected in calculating the moments listed in Table IV. If the atomic polarization is taken as 10% of the molar refraction, the molecular polarization of *o*-chlorophenol in carbon tetrachloride amounts to 23.6 cc., corresponding to a mixture of 88% *cis*- and 12% *trans*-molecules. The similarity in the observed moments of *o*-fluoro-, *o*-chloro- and *o*-bromophenol in carbon tetrachloride reveals that the per cent. of *cis*-molecules is about the same for all three compounds in this solvent. The moment of *o*-chlorophenol in benzene indicates the presence of about 82% *cis*-molecules.

The large moments obtained for the substituted phenols in dioxane indicates that this donor solvent forms hydrogen bonds with the *trans*-molecules and thus causes a shift in the *cis–trans* equilibrium. A comparison of the moments of *o*-bromophenol, 2.36, *o*-chlorophenol, 2.11, and *o*-fluorophenol, 1.84, reveals that the H---Br bonds are more readily broken than the H---Cl and H---F bonds. This order prevails despite the fact that the valence electrons of the halogen atom are closer to the hydroxyl hydrogen in *o*-bromophenol than in the other two compounds. The shift in the *cis–trans* equilibrium from carbon tetrachloride to dioxane cannot be evaluated quantitatively from the electric moment data because a portion of the increase in moment is due to the

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[14] McCusker and Curran, THIS JOURNAL, **64**, 614 (1942).

[15] Wulf and Liddel, *ibid.*, **57**, 1464 (1935).

[16] Pauling, *ibid.*, **58**, 94 (1936).

formation of the O---H bonds. It appears to the authors that more than 50% of the *o*-bromophenol molecules in dioxane have the *trans*-configuration, compared to about 12% in carbon tetrachloride.

Summary

A comparison of the observed electric moments of *o*-fluoroanisole, *o*-chloroanisole, *o*-bromoanisole and *o*-chlorophenetole in benzene solution with values calculated for various configurations reveals that the double bond character of the ring-to-oxygen bond is sufficient to lock these molecules in a *trans*-configuration.

The moments obtained for *o*-fluorophenol, *o*-chlorophenol and *o*-bromophenol in carbon tetrachloride show that between 85 and 90% of these molecules have the hydroxyl group in the *cis*-position, due to intramolecular hydrogen bonding. The large moments of these compounds in dioxane have been interpreted as indicating that dioxane forms hydrogen bonds with the *trans*-molecules and thus brings about a shift in the *cis–trans* equilibrium. The order of bond strength in the substituted phenols is revealed to be H---F > H---Cl > H---Br.

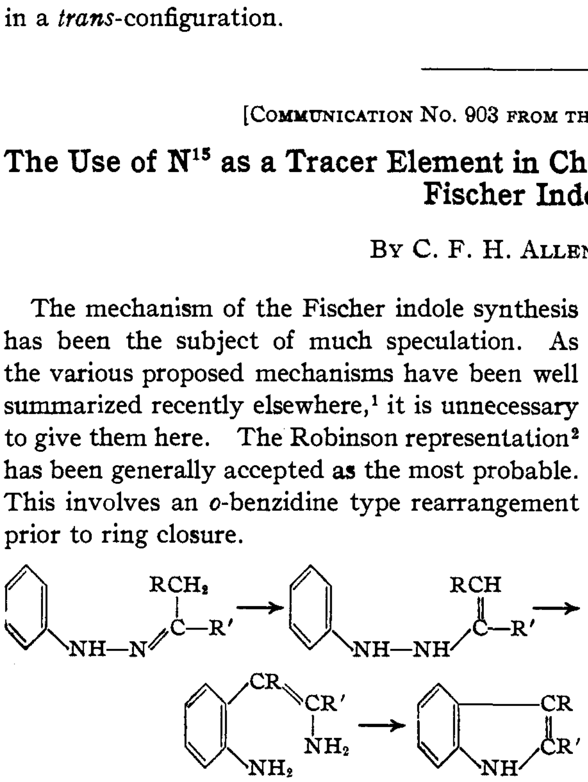
NOTRE DAME, INDIANA RECEIVED JANUARY 30, 1943

[COMMUNICATION NO. 903 FROM THE KODAK RESEARCH LABORATORIES]

The Use of N^{15} as a Tracer Element in Chemical Reactions. The Mechanism of the Fischer Indole Synthesis

BY C. F. H. ALLEN AND C. V. WILSON

The mechanism of the Fischer indole synthesis has been the subject of much speculation. As the various proposed mechanisms have been well summarized recently elsewhere,[1] it is unnecessary to give them here. The Robinson representation[2] has been generally accepted as the most probable. This involves an *o*-benzidine type rearrangement prior to ring closure.



A

The method of elimination of the ammonia has not been explained by any of the proposed mechanisms, but it has been generally accepted that it is the nitrogen atom farthest removed from the aromatic ring that is eliminated; this conclusion was based upon the observation that N-alkylindoles are produced when *as*-N-alkylphenylhydrazones are submitted to the Fischer reaction.[3,4] With the advent of heavy nitrogen, it has become possible to devise a series of reactions using it as a tracer element, and to obtain confirmation of this conclusion. Also, the opportunity has been taken to interpret the mechanism of the reaction in a slightly different way.

2-Phenylindole was used in the work described in this paper, being prepared by steps from benzamide N^{15}. The N^{15} was introduced into benzamide by treating benzoyl chloride with ammonium hydroxide containing N^{15}. The benzamide was degraded to aniline N^{15} by the Hofmann method; the N^{15} is thus attached to the ring in the aniline. Conversion of this to the hydrazine by the customary procedure gives a molecule in which the N^{15} is in the *alpha*-position, adjacent to the ring, but the ordinary nitrogen, introduced by nitrous acid, is in the *beta*-position. The acetophenone phenylhydrazone was then prepared, and used in the Fischer synthesis, giving 2-phenylindole; the latter should still contain the N^{15}, and analysis showed that such was, indeed, the case. Thus, the N^{15} has remained attached to the *Ar* ring throughout all the reactions. Conversely, the ordinary nitrogen has been eliminated; but the ordinary nitrogen is that farthest from the ring. Its elimination thus confirms the conclusions drawn from the use of *as*-alkylphenylhydrazones.

Our view of the mechanism is the same as the Robinsons' as far as the elimination of ammonia, which they represent as either a removal as such from both ends of a chain that are close together in space (A), or by a prior hydrolysis to hydroxyl,

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(1) Van Order and Lindwall, *Chem. Rev.*, **30**, 80 (1942).

(2) Robinson and Robinson, *J. Chem. Soc.*, **113**, 639 (1918); *ibid.*, 827 (1924).

(3) Fischer and Hess, *Ber.*, **17**, 559 (1884).

(4) Degen, *Ann.*, **236**, 151 (1886).