

Biltz's¹⁰ skeptical attitude seems justified, for Weiser and Porter¹¹ have concluded that the lakes in question are not definite compounds at all, being held together merely by adsorption forces.

The spectrophotometric evidence as interpreted here shows that hafnium and alizarin form a definite compound, held together by valence forces, the combining ratio being 1/1. There appears to be little or no adsorption of excess dye. The conditions investigated, however, are not those of mordant dyeing.

The definitive formula of the hafnium-alizarin lake cannot be adduced from the evidence available. But formula D, analogous to formula B, is extremely plausible for the following reasons. (1) The combining ratio: that alizarin and hafnium should combine in equimolar amounts contrasts with the evidence for other lakes; *e. g.*, three moles of alizarin combine with one of ferric ion.⁵ Consequently, different types of chelate rings could be involved in the two cases, the "inner complex" type (formula C) being characteristic of the latter. (2) Type of bond: the strong tendency of hafnyl ion to combine with anions (*e. g.*, HSO_4^- , F^-) indicates that its salt-forming (coulombic) characteristics are strong relative to its coordinating (homopolar) tendency; ferric ion, being derived from a transition element, should show a relatively greater tendency toward coordination. (3) Acid stability: the failure of hydrogen ion to decompose the alizarin lake of hafnium (or zirconium) contrasts sharply with its effectiveness toward the lakes of most metals, which suggests that the two classes be assigned

(10) Biltz, *Ber.*, **38**, 4143 (1905); especially the last paragraph.

(11) Weiser and Porter, *J. Phys. Chem.*, **31**, 1824 (1927).

different formulas. It is logical to assume that the ferric lake, for example, is thus decomposed because formula A is a more stable structure than are inner complex rings like formula C; this points to formula D for the hafnium-alizarin compound.

Because of its tendency to form inner complex salts, cupric ion was recently selected by Calvin and Wilson¹² for a study of the stability of this type of ring. (A parallel investigation of zirconyl or hafnyl ion would be very interesting.) The curves in ref. 1, Fig. 7, show that the solvated cupric ion (absorption near 7000 Å.) exists in acid solution beside the zirconium-alizarin lake; though the amount of copper greatly exceeded that of zirconium, there was no evidence that it contributed to lake formation (the yellow cupric chloride complex did, of course, form; *cf.* curve D near 7000 Å.). This contrast in the behavior of cupric and zirconyl ions reinforces the argument for formula D.

Summary

Spectrophotometric evidence has been obtained to show that the hafnium-alizarin lake is a definite chemical compound, the two constituents being combined in equimolar amounts. There appears to be little or no adsorption of excess dye.

Under some conditions, lake formation is incomplete.

On the basis of the evidence available, the hafnium lake has been assigned a chelate-ring formula different from the "inner complex" type of chelate ring usually assumed for the lakes (such as that of ferric ion) unstable toward acid.

(12) Calvin and Wilson, *THIS JOURNAL*, **67**, 2003 (1945).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Electric Moments of Ortho-substituted Phenols and Anisoles. III. Nitriles and Anils¹

BY COLUMBA CURRAN^{1a} AND E. P. CHAPUT

The electric moments of *o*-halophenols in carbon tetrachloride² have been interpreted as revealing the presence of intramolecular OH---X bonds, some of which are broken when these compounds are dissolved in dioxane. The intramolecular OH---O bonds in such compounds as guaiacol and salicylaldehyde appear to remain unbroken in dioxane, indicating that in ortho-substituted phenols the O—H---O bridge is stronger than the O—H---X bridge.³ In the ortho-substituted anisoles studied to date the methoxy group

appears to be locked in a configuration having the methyl group *trans* to the ortho substituent.

In the present investigation the O—H---N bridge in five and six-membered rings was studied by analyses of the electric moments of salicylonitrile and substituted salicylideneanils and their methyl ethers. The bond angles and bond moments assumed in earlier investigations were again used in obtaining moments calculated for various configurations, and additional moments selected from the literature are indicated in the discussion.

Experimental

Preparation and Purification of Compounds.—Salicylonitrile was prepared by treating salicylaldehyde with hydroxylamine hydrochloride to form the oxime, refluxing

(1) Presented before the Physical and Inorganic Division at the Detroit meeting of the American Chemical Society, April, 1943.

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(2) Anzilotti and Curran, *THIS JOURNAL*, **65**, 607 (1943).

(3) Curran, *ibid.*, **67**, 1835 (1945).

the oxime with excess acetic anhydride, hydrolyzing, saponifying, and acidifying the sodium salt. The product was crystallized from a mixture of carbon tetrachloride and dioxane; m.p. 95–96°. *o*-Methoxybenzoxime was prepared from *o*-anisidine and cuprous cyanide by the Sandmeyer reaction. The product was steam distilled, extracted with ether, and purified by fractional distillation. Fractions having a constant index of refraction were used in preparing solutions; b.p. 114° (6 mm.); d^{25}_4 1.0933; n^{25}_D 1.5445. The anils were prepared by condensation of the aldehydes with aniline and *p*-substituted anilines in alcohol solution in the presence of a small amount of acetic acid. The products were crystallized from alcohol and dried by passing a stream of dry air or nitrogen over the crystals for a few hours. The benzene and dioxane were purified as in previous work. Carbon tetrachloride was distilled over phosphorus pentoxide.

Measurements and Calculations.—The measurements of dielectric constants and densities and the calculation of solute polarizations at infinite dilution have been described previously.⁴ As the $\Delta\epsilon/c_2$ ratio for benzene solutions of salicylonitrile increased sharply with increasing solute concentration, an extrapolated rather than an average value for this ratio was used in the calculation. The electronic polarization of salicylonitrile was calculated from the observed molar refraction of *o*-methoxybenzoxime. The molar refractions of the anils were taken from, or calculated from, the values reported by De Gaouck and Le Fevre⁵ for anils in benzene solution. Electric moments

TABLE I
DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS AT 25°

c_2	ϵ	d
Carbon tetrachloride-salicylonitrile		
0.00000	2.233	1.5850
.00104	2.248	1.5845
.00149	2.253	1.5843
.00167	2.255
Benzene-salicylonitrile		
0.00000	2.274	0.8734
.00179	2.322
.00705	2.488
.00925	2.566	.8766
.01129	2.643	.8771
.01175	2.668	.8774
Dioxane-salicylonitrile		
0.00000	2.218	1.0281
.01253	2.669	1.0305
.01540	2.775	1.0310
.01699	2.843	1.0312
Benzene- <i>o</i> -methoxybenzoxime		
0.00000	2.274	0.8728
.00907	2.583	.8759
.01238	2.702	.8768
.02291	3.081	.8802
.02340	3.102	.8805
Benzene-salicylideneaniline		
0.00000	2.274	0.8734
.01176	2.381	.8797
.01575	2.422	.8816
.01926	2.453

(4) McCusker and Curran, *THIS JOURNAL*, **64**, 614 (1942).
(5) De Gaouck and Le Fevre, *J. Chem. Soc.*, 741 (1938).

Dioxane-salicylideneaniline		
0.00000	2.213	1.0278
.01126	2.333	1.0304
.01347	2.359	1.0309
.01601	2.383
Benzene-salicylidene- <i>p</i> -toluidine		
0.00000	2.274	0.8730
.01185	2.401	.8792
.01673	2.456	.8823
.02015	2.494	.8832
Dioxane-salicylidene- <i>p</i> -toluidine		
0.00000	2.210	1.0277
.01018	2.333	1.0298
.01400	2.376	1.0307
.01578	2.398	1.0308
Benzene-salicylidene- <i>p</i> -chloroaniline		
0.00000	2.274	0.8732
.01453	2.398	.8842
.01460	2.398	.8841
.01784	2.424	.8871
Dioxane-salicylidene- <i>p</i> -chloroaniline		
0.00000	2.210	1.0277
.01096	2.320	1.0315
.01319	2.341	1.0323
.01790	2.389
Benzene- <i>o</i> -methoxybenzylidene- <i>p</i> -chloroaniline		
0.00000	2.273	0.8732
.00935	2.477	.8806
.01103	2.515	.8819
.01418	2.585	.8842

TABLE II
POLARIZATIONS AND ELECTRIC MOMENTS

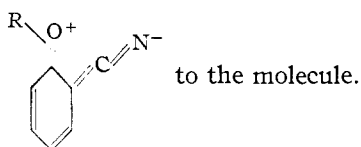
	$P_{2\infty}$	MR_D	μ
<i>o</i> -Methoxybenzoxime	546.9	38.5	4.97
Salicylonitrile (carbon tetrachloride)	251	33.5	3.2
Salicylonitrile (benzene)	427.3	33.5	4.38
Salicylonitrile (dioxane)	553.6	33.5	5.03
Salicylideneaniline (benzene)	187.5	66.4	2.40
Salicylideneaniline (dioxane)	205.8	66.4	2.57
Salicylidene- <i>p</i> -toluidine (benzene)	215.3	71.0	2.63
Salicylidene- <i>p</i> -toluidine (dioxane)	227.4	71.0	2.74
Salicylidene- <i>p</i> -chloroaniline (benzene)	180.2	71.4	2.27
Salicylidene- <i>p</i> -chloroaniline (dioxane)	201.6	71.4	2.49
<i>o</i> -Methoxybenzylidene- <i>p</i> -chloroaniline	383.5	76.0	3.85

in debye units were calculated from the relation $\mu = 0.0128 \sqrt{(P_{2\infty} - 1.05MR_D)T}$.

Discussion of Results

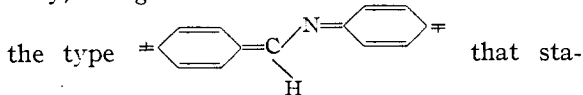
The moment calculated for *o*-methoxybenzoxime, taking 3.9 as the moment of benzonitrile, is 2.7 for a molecule having the methyl group in the *cis* position, and 4.8 for a molecule having a *trans* configuration. The observed moment in benzene, 4.97, indicates that the methoxy group is locked in a *trans* configuration. The difference, 0.2, between the observed and calculated moment

is attributed to the contribution of the structure



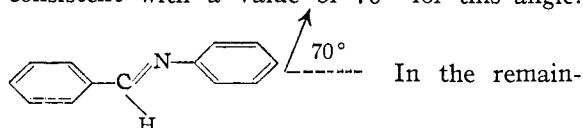
The calculated moment for salicylonitrile molecules having a *trans* configuration is 5.2. Adding 0.2 for resonance interaction between the hydroxy and nitrile groups gives a value of 5.4. The calculated moment for a *cis* molecule is 2.5. Assuming that all molecules have either of these two configurations, the observed moment of salicylonitrile in carbon tetrachloride, 3.2, corresponds to a mixture of 83% *cis* and 17% *trans* molecules, in qualitative agreement with the interpretation of infrared absorption spectra.⁶ The moment of salicylonitrile in benzene, 4.38, corresponds to about 57% *trans*, assuming no solute association, indicating that the benzene molecules interact with the *trans* molecules, causing a shift in the *cis-trans* equilibrium. This is somewhat surprising, as benzene has no highly negative atoms to attract the positive hydroxyl hydrogen. When *o*-chlorophenol is transferred from carbon tetrachloride to benzene the proportion of *trans* molecules is increased from 13 to 18%. The much larger increase observed for salicylonitrile, 17 to 57%, indicates that the O—H...N bridge in salicylonitrile is much weaker than the O—H...Cl bridge. As has been previously pointed out by other authors, this is probably due to the large distance, 3.5 Å., between the oxygen and nitrogen atoms in the *cis* form of salicylonitrile. The $\Delta\epsilon/c_2$ ratio for salicylonitrile in benzene increases from 26.9 at a solute mole fraction of 0.00167 to 33.4 at a concentration of 0.01175, suggesting that some of the *trans* molecules are associated in this solvent. The moment of salicylonitrile in dioxane, 5.03 reveals that almost all of the solute molecules have a *trans* configuration, due to the formation of O...HO bonds with this solvent.

De Gaouck and Le Fevre⁵ have reported the dipole moments of some anils in benzene solution. The agreement between the moments of benzylideneaniline, 1.57, and *p*-chlorobenzylidene-*p*-chloroaniline, 1.56, led the authors to conclude that these are *trans* molecules. *cis* Molecules would be less stable because steric factors prevent coplanarity, ruling out the contribution of structures of



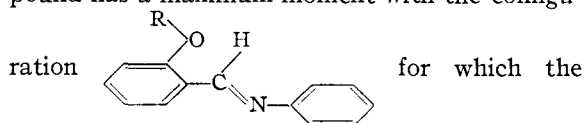
the type \equiv that stabilize the *trans* forms. From the moments reported by De Gaouck and Le Fevre for *p*-chlorobenzylideneaniline, 1.77; *p*-chlorobenzylidene-*p*-toluidine, 2.06, and for benzylideneaniline, 1.57, we have calculated the angle that the moment vector of benzylideneaniline makes with the ni-

trogen-to-ring bond. These three moments are consistent with a value of 70° for this angle.

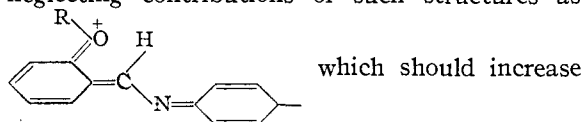


ing portion of the discussion we shall refer to the angle that the over-all moment vector makes with the nitrogen-to-ring bond as the *direction* of the moment.

These authors report a moment of 3.02 for the methyl ether of salicylideneaniline. This compound has a maximum moment with the configura-

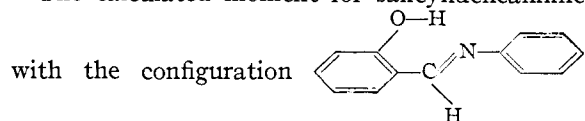


calculated moment is 2.7 with a direction of 60° neglecting contributions of such structures as

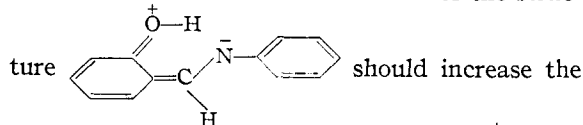


the moment to about the observed value, 3.0. This configuration is preferred to that in which the nitrogen atom is adjacent to the oxygen (μ calcd. = 1.5) because of the attraction between the oxygen atom and the H—C=N hydrogen. The calculated moment of the methyl ether of salicylidene-*p*-chloroaniline with the illustrated configuration is 4.0. The moment obtained for this compound is 3.85.

The calculated moment for salicylideneaniline

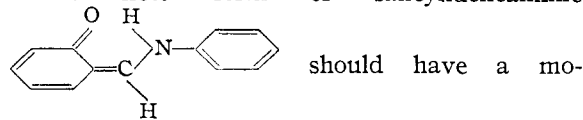


neglecting resonance interaction, is 2.15, with a direction of 118°. The contribution of the struc-



moment somewhat. We have obtained a moment of 2.40 for this compound in benzene. In order to determine the direction of this vector the moments of salicylidene-*p*-chloroaniline and salicylidene-*p*-toluidine were measured. The values obtained, 2.31 and 2.66, are consistent with angles of 114 and 120° for the direction of the salicylideneaniline moment, lending support to the above configuration.

The keto form of salicylideneaniline



ment of about 2.3 and a direction of 40°. The discrepancy between this angle and the angle con-

(6) Hendricks, Wulf, Hilbert and Liddel, *THIS JOURNAL*, 58, 1991 (1936).

sistent with the moments of the chloro and methyl derivatives, $117 \pm 3^\circ$, indicates that if tautomerism exists, the keto form is present in the tautomeric mixture to a very small extent.

If dioxane were to break the OH---N bonds in these anils, forming O---HO bonds, the solvated salicylideneaniline molecules should have a configuration similar to that of the methyl ether, with a moment of about 3.6. The calculated moments of salicylidene-*p*-toluidine and salicylidene-*p*-chloroaniline with this configuration in dioxane are 3.3 and 4.6. Assuming no rupture of the OH---N bonds, the moments of these anils should be about 0.15 unit higher in dioxane than in benzene, a portion of this increase being due to the interaction of dioxane with the H—C=N hydrogen atoms. The addition of this increment gives values of 2.55, 2.78 and 2.42, respectively, for the calculated moments of salicylideneaniline, salicyl-

idene-*p*-toluidine and salicylidene-*p*-chloroaniline. The moments obtained for these three compounds in dioxane are 2.57, 2.74 and 2.49, indicating that dioxane does not break the OH---N bonds in the anils.

Summary

Electric moments reveal that about 83% of salicylonitrile molecules have a *cis* configuration in carbon tetrachloride, indicating a weak OH---N bond. Very many of these bonds are broken when this compound is dissolved in benzene, and almost all are broken in dioxane.

An analysis of the moments of several anils indicates the presence of an O—H---N bridge in salicylideneaniline which is not broken in dioxane. The keto form is present to a very small extent, if at all, in this compound.

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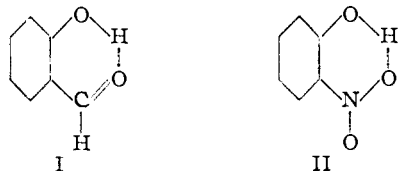
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY AND THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Dissociation of the Compounds of Trimethylboron with Pyridine and the Picolines; Evidence for the Steric Nature of the Ortho Effect¹

BY HERBERT C. BROWN AND GERALDINE K. BARBARAS

Ortho benzene derivatives often exhibit markedly different properties than the corresponding *meta* and *para* compounds. Numerous such observations by Victor Meyer and his collaborators led to the concept of steric hindrance.² According to this interpretation, the unusual effects of groups in the *ortho* positions of benzene derivatives are due to their steric requirements which hinder the near approach of other groups or molecules to the reactive centers.

In recent years, other explanations have been advanced to explain certain cases of unusual behavior in *ortho*-substituted compounds. Thus Sidgwick and Callow³ attribute the high volatility and non-polar character of such compounds as salicylaldehyde (I) and *ortho*-nitrophenol (II) to the formation of a six-membered "chelate" ring



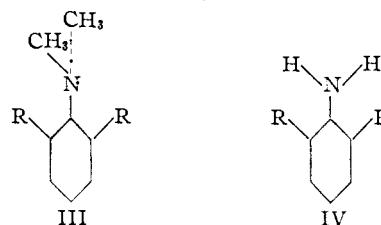
(1) Acid-Base Studies in Gaseous Systems. III. Paper no. X in the series Studies in Stereochemistry. For preceding paper, see *Science*, **103**, 385 (1946).

(2) Meyer, *Ber.*, **27**, 510 (1894); Meyer and Sudborough, *ibid.*, **27**, 1580 (1894). The literature on *ortho* effects and steric hindrance is too voluminous to be cited here. For an introduction to the literature on the subject, see Stewart, "Stereochemistry," Longmans, Green and Co., New York, 1907, pp. 314-443; Cohen, "Organic Chemistry," Edward Arnold and Co., London, 1928, 5th Ed., Vol. 1, Chapt. V; Anschütz, *Z. anorg. Chem.*, **41**, 691 (1928).

(3) Sidgwick and Callow, *J. Chem. Soc.*, **125**, 527 (1924).

involving hydrogen bonding of the hydroxyl group with the *ortho* substituent.

More recently, certain marked differences in the properties of *ortho* substituted dimethylaniline derivatives (III) as compared with those of the corresponding *ortho* substituted aniline compounds (IV), have been ascribed to inhibition of resonance in the dimethylaniline derivative.



According to this interpretation, the *ortho* substituents prevent the dimethylamino group, but not the smaller amino group, from assuming the position coplanar with the benzene ring that is most favorable for resonance interaction.⁴

These interesting developments in the field of *ortho* effects have resulted in drawing attention away from Victor Meyer's original, purely steric, interpretation of such effects and have led to attempts to explain the observed phenomena in other than steric terms. Probably the most

(4) Ingham and Hampson, *ibid.*, 981 (1939); W. G. Brown, Widiger and Letang, *THIS JOURNAL*, **61**, 2597 (1939), and subsequent papers in *THIS JOURNAL*, by W. G. Brown and his collaborators. For a recent review of this field, see Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, New York, N. Y., 1944, pp. 185-190, 272-279.