Laue and rotation patterns. An improvement in the reported procedure, however, resulted in the production of better crystals than had been obtained previously.

7. In an attempt to prepare PbO_2 having the theoretical oxygen content, the effect of sulfamic acid on PbO_2 was studied. It was found that sulfamic acid extraction lowers the active oxygen content in proportion to the length of treatment. X-Ray examination showed the presence of Pb_3O_4 in the extracted samples.

8. Black PbO, which has been reported by several investigators, was prepared and subjected to X-ray examination. The black color is apparently a surface phenomenon, as claimed by Appleby, since no lattice could be detected, except that of the expected yellow PbO.

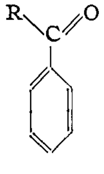
URBANA, ILLINOIS RECEIVED OCTOBER 23, 1940

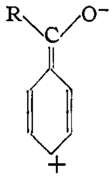
[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

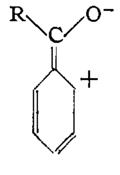
The Steric Inhibition of Resonance in Aromatic Carbonyl Compounds

BY RICHARD G. KADESCH AND SOL W. WELLER*

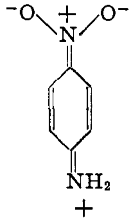
According to resonance theory aromatic carbonyl compounds are best represented as combinations of the classical structure I and quinonoid structures such as II and III.

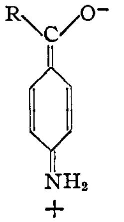

I

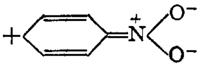

II

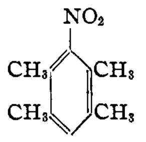

III

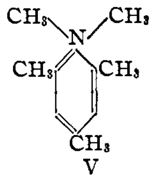
In addition to accounting for the meta-directing properties of such groups, it is the contributions of such quinonoid structures to the normal state of the molecule which lead to larger dipole moments for aromatic compounds of this type than for the corresponding aliphatic molecules. A further manifestation of the contributions from quinonoid structures of the above type is the abnormally high dipole moment of molecules which contain an electron-donating group para to the original electron-accepting group; examples of this are *p*-nitraniline and *p*-aminoacetophenone.[1] These abnormally high moments have been explained[2] as being due to contributions of the following type to the normal state of the molecule





If, for any reason, the contributions of structures II and III should be made less important, the dipole moment of the molecule should be lessened and should approach the value for the corresponding aliphatic type. It was first pointed out by Birtles and Hampson[3] that one should expect to accomplish this with the nitro group by the introduction of methyl groups ortho to it. This should reduce the contribution of  because of the steric hindrance to the oxygen atoms which must become coplanar with the benzene ring in such a structure. Birtles and Hampson confirmed this prediction when they found that the dipole moment of nitrodurene (IV) was only 3.39 *D* as compared with that of nitrobenzene (3.95 *D*) whereas aliphatic nitro compounds have moments of about 3.1 *D*. Subsequently Ingham and Hampson[4] found that the dimethylamino group in dimethylmesidine (V) is also hindered from attaining the coplanar configuration of the quinonoid structure. It is seen that the use of compounds of the type of IV and V permits a direct comparison of the moment with that of the corresponding non-methylated compound since the resultant moment of the ring methyl groups is zero in either case. The inhibition of resonance of the nitro[5] and dimethylamino[6] groups by ortho


IV


V

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* Present address: Chemistry Department, New York University.

[1] Sidgwick, *et al.*, "Table of Dipole Moments," *Trans. Faraday Soc.*, **30**, 904 (1934).

[2] Marsden and Sutton, *J. Chem. Soc.*, 599 (1936); Bergmann and Weizmann, *Trans. Faraday Soc.*, **32**, 1318 (1936).

[3] Birtles and Hampson, *J. Chem. Soc.*, 10 (1937).

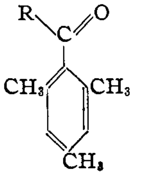
[4] Ingham and Hampson, *ibid.*, 981 (1939).

[5] Spitzer and Wheland, THIS JOURNAL, **62**, 2995 (1940).

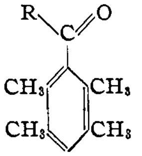
[6] Brown, Widiger and Letang, *ibid.*, **61**, 2597 (1939).

substituents also has been deduced from chemical evidence.

It has been the purpose of the present investigation to apply the method of Birtles and Hampson to compounds of the types VI and VII by comparison of their dipole moments with that of



VI



VII

the corresponding non-methylated compound I. If the methyl groups hinder the attainment of coplanarity of the —COR group in structures II and III as they do for the nitro and dimethylamino groups, the dipole moments of both VI and VII should be lower than that of I. The magnitude of the maximum effect which is to be expected may be estimated from a comparison of the dipole moments for the corresponding aromatic and aliphatic compounds:

TABLE I

	Aromatic	Aliphatic	Difference
Ketone	2.87[1]	2.72[1]	0.15
Aldehyde	2.96[7]	2.5-2.6[7]	0.4
Acid Chloride	3.33[8]	2.5-2.6[8]	0.8

Experimental

Preparation of Materials

Benzene.—Baker C. P. thiophene-free benzene was thoroughly shaken twice with concd. sulfuric acid, washed with water three times and dried over phosphorus pentoxide. The benzene was decanted, fractionally distilled from a fresh portion of phosphorus pentoxide and stored over sodium.

Acetophenone.—Acetophenone (m. p. 19–20°) was fractionally frozen twice, dried over sodium sulfate and fractionated under reduced pressure through a short column: b. p. 91.5–92.0° at 19–20 mm., d^{25}_4 1.0238, n^{25}_{D} 1.5318.

Acetylmesitylene.—Prepared from mesitylene and acetyl chloride. After distillation the product was dried over sodium sulfate and twice fractionated under reduced pressure through a short column: b. p. 121.5–123° at 18–19 mm., d^{25}_4 0.9717, n^{25}_{D} 1.5143.

Acetyldurene.—Durene was prepared according to the method of v. Braun and Nelles,[9] m. p. 77–79°. Acetyldurene was prepared from durene and acetic anhydride by the method of Noller and Adams,[10] yield 86%. The product was distilled *in vacuo*, recrystallized twice from ether and then recrystallized repeatedly from aqueous methanol, m. p. 72.5–73.5°.[11]

Benzaldehyde.—Reagent grade benzaldehyde was fractionated under reduced pressure through a short column, b. p. 73.7° at 21 mm., n^{25}_{D} 1.5432.

Mesityl Aldehyde.—Prepared from mesitylene, carbon monoxide and hydrogen chloride in the presence of aluminum chloride according to the method of Gattermann,[12] yield 40%. After purification through the mesitylidene aniline followed by distillation the aldehyde was fractionated twice under reduced pressure through a short column, b. p. 105–106° at 8 mm., d^{25}_4 1.0154, n^{25}_{D} 1.5490.

Benzoyl Chloride.—Mallinckrodt analytical benzoyl chloride (m. p. 0–2°, b. p. 195–198°) was fractionated under reduced pressure through a short column, b. p. 49–50° at 2.5–3 mm., d^{25}_4 1.2070, n^{25}_{D} 1.5508.

2,4,6-Trimethylbenzoyl Chloride.—The Grignard compound from bromomesitylene[13] was converted to 2,4,6-trimethylbenzoic acid by carbonation.[14] The acid was recrystallized from ligroin and treated with thionyl chloride. The excess of thionyl chloride was removed at the water pump and the acid chloride distilled twice under reduced pressure from a modified Claisen flask, b. p. 115.5–116.5° at 18 mm.,[15] d^{25}_4 1.0967, n^{25}_{D} 1.5263.

Benzophenone.—Eastman Kodak Co. benzophenone was recrystallized twice from aqueous alcohol, m. p. 48°.

Measurements

The densities were determined at 25° with an Ostwald–Sprengel pycnometer. The refractive indices were determined at 25° using an Abbe refractometer.

The dielectric constants were determined using a Wyman apparatus[16] constructed by Mr. P. R. Bell of this Laboratory. The resonator used had a frequency of 36 mc. in air. Temperature control furnished some difficulty since the small available quantities of investigated substances required the use of a comparatively small volume of solution (250 cc.). The following procedure was adopted. The benzene solution to be measured, contained in a stoppered Erlenmeyer flask, was immersed for ten minutes in a bath at 25°. Following this, the solution was poured into a transparent dewar flask and the temperature measured; the resonator was then suspended in the solution, the resonance frequency observed and the temperature again determined. In general, the difference between the initial and final temperature readings was less than 0.2°; the average was used and was always within 0.8° of 25°. The dielectric constant obtained at temperature t°C. was corrected to 25° by using the relation $\Delta\epsilon = 0.0018(25 - t)$; this assumes that the temperature coefficients of the dilute solutions used are the same as that of pure benzene. The Wyman apparatus is, of course, an absolute instrument, the dielectric constant being given by $\epsilon = \gamma^2\theta/\gamma^2$ ($\gamma\theta$ is the resonance frequency in air and γ is the resonance frequency

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(7) Coomber and Partington, *J. Chem. Soc.*, 1444 (1938); see also Goebel and Wenzke, THIS JOURNAL, **59**, 2301 (1937).

(8) Martin and Partington, *J. Chem. Soc.*, 1175 (1936); see also Koehl and Wenzke, THIS JOURNAL, **59**, 1418 (1937).

(9) Von Braun and Nelles, *Ber.*, **67**, 1094 (1934).

(10) Noller and Adams, THIS JOURNAL, **46**, 1889 (1924).

(11) Baum and Meyer, *Ber.*, **28**, 3213 (1895); V. Meyer, *ibid.*, **29**, 847 (1896).

(12) Gattermann, *Ann.*, **347**, 374 (1906).

(13) "Organic Syntheses," Vol. XI, 1931, p. 24.

(14) *Ibid.*, Vol. XI, 1931, p. 80.

(15) Norris and Young, THIS JOURNAL, **57**, 1424 (1935); Nauta and Wuis, *Rec. trav. chim.*, **56**, 537 (1937).

(16) Wyman, *Phys. Rev.*, **35**, 623 (1930).

in the liquid being measured). The estimated error in ϵ is less than one part in 1000.

TABLE II

Benzene

$\epsilon = 2.272$, $P_1 = 26.61$, $d = 0.8732$

N_2	d	ϵ	P_2
	Acetophenone–		
0.0051044	0.8742	2.332	206.9
.015743	.8767	2.464	203.9
.021027	.8775	2.525	202.5
.024858	.8784	2.574	200.0
	Acetylmesitylene–		
.0054312	.8740	2.327	199.7
.010842	.8749	2.386	202.8
.021092	.8765	2.498	202.5
	Acetyldurene–		
.0049790	.8745	2.322	199
.0064717	.8748	2.341	207
	Benzaldehyde–		
.0098822	.8760	2.395	205.7
.021931	.8778	2.552	206.7
.034421	.8803	2.720	203.8
	Mesitylaldehyde–		
.0067533	.8748	2.358	231.0
.011725	.8758	2.422	227.1
.019948	.8776	2.536	229.1
	Benzoyl Chloride–		
.010260	.8779	2.435	259.5
.020310	.8821	2.602	257.5
.030308	.8864	2.763	250.0
	2,4,6-Trimethylbenzoyl Chloride–		
.0049790	.8753	2.331	224
.0087989	.8769	2.382	230
.010364	.8775	2.405	234
	Benzophenone–		
.0081360	.8772	2.379	236.8
.013748	.8796	2.452	234.6
.028110	.8857	2.647	232.6

TABLE III

	R_D	$P_2\infty$	$\mu \times 10^{18}$
Acetophenone	36.32	209	2.88±0.03
Acetylmesitylene	50.25	203	2.71± .03
Acetyldurene	54.8 (calcd.)	204	2.68± .05
Benzaldehyde	32.11	209	2.92± .03
Mesitylaldehyde	46.39	230	2.96± .03
Benzoyl chloride	37.13	266	3.32± .06
2,4,6-Trimethylbenzoyl chloride	51.11	232	2.95± .06
Benzophenone	56 (calcd.)	238	2.96± .02

The molar refractions (R_D) for acetyldurene and benzophenone were calculated from the atomic refractions given by Swietoslawski.[17] In most cases the P_2^∞'s represent the values for P_2 extrapolated to infinite dilution; where the scattering of the data is great, it was considered preferable to take for P_2^∞ the weighted mean of the P_2's and correspondingly large estimates have been made in these cases for the uncertainty in the moment. The moments were calculated according to the following usual equations[18] which are due to Debye

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2}\,\frac{N_1M_1 + N_2M_2}{d}$$

$$P_2 = \frac{P_{12} - P_1}{N_2} + P_1$$

$$\mu = [0.0127\sqrt{298(P_2 - R_2)}] \times 10^{-18}$$

Discussion

It is seen from the experimental results that, as expected, the moment of acetophenone (2.88 *D*) has been reduced by the introduction of ortho methyl groups to 2.71 *D* in acetylmesitylene (VI, R = CH_3) and to 2.68 *D* in acetyldurene (VII, R = CH_3). The moments of these two latter compounds are very nearly the same as the value for aliphatic ketones (2.72 *D*) showing that the maximum possible reduction in moment was attained. These results indicate strongly that in these two acetophenone derivatives the stability of structures II and III has been decreased and their contributions to the overall state of the molecule thereby decreased also. The recent study by O'Shaughnessy and Rodebush[19] on the absorption spectra of acetylmesitylene and 2,4,6-tri-*i*-propylacetophenone leads these authors to the same conclusion. Thus, the physical evidence supports the existence of the steric inhibition of resonance as previously postulated by Baddeley[20] on the basis of the behavior of di-ortho substituted acetophenones in the Friedel and Crafts reaction.

It was thought that a comparison of the moments of acetyldurene and acetylmesitylene might be significant in view of the discrepancies previously observed between the moments of nitrodurene and nitromesitylene. Whereas Birtles and Hampson[3] found a value of 3.39 *D* for nitrodurene (IV), the moment of nitromesitylene has been reported as 3.65 *D*[21] and 3.67 *D*.[22] It has been suggested by Dr. G. W. Wheland that the

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[17] Swietoslawski, THIS JOURNAL, **42**, 1945 (1920).

[18] In spite of the recent criticism of the Debye theory by Rodebush and Eddy, *J. Chem. Phys.*, **8**, 424 (1940), it was considered advisable to calculate the moments by the Debye equations since most of the literature values have been obtained in this way.

[19] O'Shaughnessy and Rodebush, THIS JOURNAL, **62**, 2906 (1940).

[20] Baddeley, *Nature*, **144**, 444 (1939).

[21] Brown, de Bruyne and Gross, THIS JOURNAL, **56**, 1291 (1934).

[22] Hammick, New and Williams, *J. Chem. Soc.*, 29 (1934).

higher value for nitromesitylene may be due to a change in the valence angles of the ortho-methyl groups resulting from the repulsion between them and the nitro group. In nitrodurene this repulsion is opposed by the "buttressing effect" of the methyl groups in the 3- and 5-positions which enables the ortho methyl groups to more nearly maintain their true valence angles. Although our results show that acetyldurene has a slightly smaller moment than has acetylmesitylene, which is in accord with this explanation, the difference is too small to be considered significant. It is to be noted also that such discrepancies have not been observed between aminodurene[3] ($\mu = 1.39\ D$) and mesidine[4] ($\mu = 1.40\ D$) nor between bromodurene[3] ($\mu = 1.55\ D$) and bromomesitylene[21] ($\mu = 1.52\ D$). This is not surprising since the nitro group in the coplanar configuration would be expected to exert a greater repulsion toward methyl groups ortho to it than would either the bromo or amino groups.

As contrasted with the effect in acetophenone, the introduction of ortho methyl groups into benzaldehyde produces no decrease in moment as shown by the value of 2.96 D for mesityl aldehyde (VI, R = H) when compared to 2.92 D for benzaldehyde. Use of the same type of reasoning as has been employed heretofore leads us to conclude that the —CHO group is not hindered appreciably by the ortho methyl groups in attaining the coplanar position. Construction of scale atomic models brings out clearly the reason for the different behavior of the —CHO and —COCH$_3$ groups; Fig. 1 is constructed using van der Waals radii for the atoms and groups. From Fig. 1 it is seen that the interference between carbonyl oxygen and the ortho methyl is comparatively small, whereas the interference between the methyl of the acetyl group and the ortho methyl is the main source of hindrance to the coplanar structure. In the —CHO group this source of hindrance has been removed since the small hydrogen atom no longer interferes appreciably with the ortho methyl group.

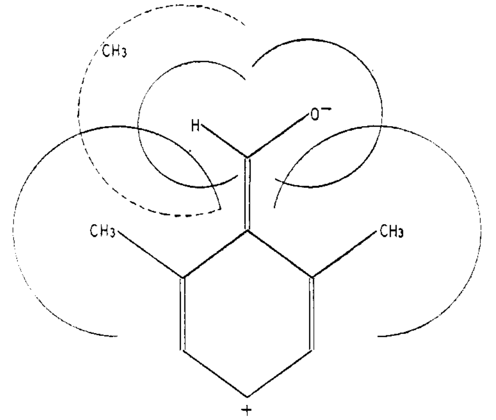

Fig. 1.—Model of aldehyde and ketone (superposed) using van der Waals radii: CH$_3$, 2.0 Å.; H, 1.2 Å.; O, 1.40 Å. Interatomic distances used were: C–C, 1.54; C=C, 1.33; C–H, 1.09; C–O, 1.43. Angles are according to the tetrahedral theory.

It might be expected that the introduction of two methyl groups ortho to the substituent in the benzene ring would alter the original moment of this substituent by virtue of inductive effects between the adjacent groups. Therefore, it might be argued that the observed differences in dipole moments between I and VI are due to such inductive effects rather than to the steric inhibition of resonance which has been postulated. We believe that this is unlikely. Such inductive effects should be of very nearly the same magnitude in two similiar groups such as —COCH$_3$ and —CHO. However, it has been shown that, after the introduction of two ortho methyl groups, the behavior of the —COCH$_3$ and —CHO groups is distinctly different and may be correlated with their sizes. It has been found that the moments of bromodurene[3] (1.55 D) and bromomesitylene[21] (1.52 D), in which hindrance of the cylindrically symmetrical bromine atom is impossible, lie very close to that of bromobenzene (1.52 D), thus demonstrating that inductive effects are negligible. Smyth and Lewis[23] have found from their study of the dipole moments of several other poly-substituted benzenes that, whereas the interaction between two adjacent chlorine atoms is appreciable, the effect of mutual induction between a methyl group and a negative ortho group such as chlorine is negligible.

Again in the case of trimethylbenzoyl chloride (VI, R = Cl) the moment (2.95 D) is found to be substantially less than that for benzoyl chloride itself (3.32 D). Such a result would be expected from a comparison of the moment of benzoyl chloride with those for aliphatic acid chlorides and from the size of the chlorine atom. Although the —COCl group is larger than the —COCH$_3$ group, the ortho methyls have caused the aromatic moment to be decreased only about half-way to the aliphatic value in the former case, whereas in the latter case the maximum reduc-

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[23] Smyth and Lewis, THIS JOURNAL, 62, 721 (1940).

tion to the aliphatic value was attained. We have no explanation of this fact.

It was suggested to us by Dr. W. G. Brown that the efficiency of ortho methyl groups in preventing coplanarity, and therefore resonance, should be temperature dependent. The higher the temperature, the more should the blocked-out group (*e. g.*, the acetyl methyl group in acetophenone) be able to force its way for a time into the region occupied by the ortho methyls and thus achieve coplanarity; the moment of the substituted compound should therefore increase with increasing temperature. This experiment was not tried, due to the smallness of the effects expected and to the fact that the solvent influence would, presumably, also change with temperature.

It is to be noted that resonating structures such as II and III should lead to a shortening in length of the bond connecting the —COR group with the ring and to an increase in the ring —C—R angle corresponding to double bond formation between ring and carbonyl carbon. We would also expect that the inhibition of these resonating structures by ortho methyls should tend to increase the bond distance and decrease the angle in question to the values predicted on the basis of structure I. Unfortunately, the direct determination of these quantities by X-ray or electron diffraction measurements is, as yet, not possible for such complicated molecules.

The authors wish to thank Drs. W. G. Brown and G. W. Wheland and Mr. N. R. Davidson for their kind assistance and many helpful comments during the course of this work.

Summary

1. By the method of Birtles and Hampson it has been shown from dipole moment measurements that the resonance of compounds of the type C_6H_5COR involving quinonoid structures may be inhibited by two ortho methyl groups.

2. This inhibition of resonance is purely a steric effect in which the ortho methyl groups block the attainment of the completely coplanar configuration necessary in the quinonoid structure.

3. The steric effect depends on the size of the —COR group, being absent in the small —CHO group while $—COCH_3$ and —COCl lead to readily observable effects.

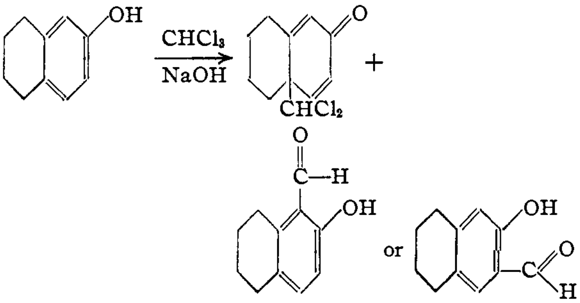
CHICAGO, ILLINOIS RECEIVED DECEMBER 18, 1940

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Reimer–Tiemann Reaction of β-Tetralol

BY RICHARD T. ARNOLD, HAROLD E. ZAUGG AND JOSEPH SPRUNG

In a valuable paper recently published, Woodward[1] made use of the Reimer–Tiemann reaction for the direct introduction of angular groups into polycyclic molecules. The neutral compound from β-tetralol is accompanied by a 50% yield of expected hydroxyaldehyde (m. p. 86–87°).[2]



I II

Previous work on the orientation of β-tetralol[3,4] led to the reasonable assumption that the aldehyde could be correctly formulated as (II).

β-Tetralol yields the same hydroxyaldehyde in the Gattermann synthesis.[5]

Numerous early attempts to prove the structure of the hydroxyaldehyde by direct oxidation or indirect conversion to the hydroxy acid failed.[5]

The importance of these substances to our investigation of the Mills–Nixon problem necessitated a complete proof of structure.

Using the basic fusion method of Kauffmann,[6] the hydroxyaldehyde was readily transformed into the corresponding acid (V). That the chief product of the Reimer–Tiemann reaction is (I) and not (II) as formerly supposed is proved by the

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(1) Woodward, THIS JOURNAL, **62**, 1208 (1940).

(2) We are indebted to Dr. R. B. Woodward for a highly purified sample of the aldehyde for purposes of comparison. Its melting point was originally given as 82°.[1]

(3) Schroeter, *Ann.*, **426**, 147 (1922).

(4) Robinson and Walker, *J. Chem. Soc.*, 1531 (1935).

(5) Thom and Kross, *Arch. Pharm.*, **265**, 336 (1927).

(6) Kauffmann, *Ber.*, **15**, 806 (1882).