THE ULTRAVIOLET ABSORPTION SPECTRA
OF SOME SUBSTITUTED ACETOPHENONES

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THE ULTRAVIOLET ABSORPTION SPECTRA
OF SOME SUBSTITUTED ACETOXYPHENONES

A Thesis

By

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Memorial University of Newfoundland

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Note.

The abbreviation J. A. C. S. used throughout this thesis refers to the J. Am. Chem. Soc.

W. A. Mueller.
ABSTRACT

In order to investigate more fully the steric influences in the B-band of the ultraviolet spectrum, several acetophenones were prepared, giving molecules in which the angle between the planes of the electron rich centers varied. It was found that the light absorption maximum moved to shorter wavelengths as the amount of hindrance about the carbonyl group was increased, (i.e., as the interplanar angle was increased), and that steric hindrance increased in the order hydrogen atom < ortho-methylene group of the cyclopentyl ring < ortho-methyl group < ortho-methylene group of the cyclohexyl ring < an ortho-methyl group "buttressed" by a methyl group in the adjacent meta-position.

The carbonyl group becomes less readily accessible as steric interference is increased, as shown by the inability of the highly hindered ketones to form the ordinary ketone derivatives. In the highly hindered ketones, conjugation is inhibited to such an extent that the main peaks closely correspond to those of the substituted benzenoid hydrocarbons.
The spatial orientation of the compounds is discussed by interpreting the spectra in terms of the electronic and steric effects of the substituents.

The 2,4-dinitrophenylhydrazones of the unsubstituted compounds, and some of the substituted compounds are included, and it was found that the amount of steric hindrance can sometimes be estimated by color, i.e., as conjugation increases, the colors tend from yellow to red.

A recent example from the literature on the spectra of substituted hydroxybenzoic acids is included, and it was found possible to correlate nicely the observed spectra by means of the theories of steric and electronic effects.

In the experimental part, the syntheses of the ketones are described, along with the reaction of $\beta$-chloropropionyl chloride with tetralin, and an attempt to prepare 2,3,5,6-tetraethylbenzene.
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INTRODUCTION

The entire range of electromagnetic radiation can interact with matter, but that range in the visible and ultra-violet region of the spectrum is of particular interest to the chemist, since interaction in this region is dependent on the electronic structure of the molecule, and hence is closely related to chemical reactivity.

Absorption in the ultra-violet and visible region produces changes intermediate between the high energy required for complete photo-ionization of the molecule, and the relatively low energy of the infra-red region, which gives rise to rotational and vibrational changes. Absorption in the ultra-violet region is ascribed to a change in the electronic patterns of the non-bonding π electrons, and may also involve the p-electrons of single atoms. This type of absorption is found in molecules containing centers of unsaturation, such as the styrenes, diphenyls, benzamidines, benzaldehydes, etc.
Acetophenone itself has an intense absorption band at 240 m\(\mu\), \(\varepsilon = 13,000\). Methyl substituents cause rather small wavelength displacements (\(\Delta \lambda = 10\) m\(\mu\)). In the benzaldehyde system, meta- and para- groups cause a small increase in absorption probability (\(\varepsilon\)), while ortho- groups cause a small decrease in \(\varepsilon\). With acetophenones, meta- and para- substituents produce a similar increase in \(\varepsilon\), but ortho- groups give rise to a marked decrease. The propiophenones exhibit a like effect. The differences between the aldehyde and ketone are undoubtedly due to the fact that whereas the steric overlap between the ortho-methyl group of the benzene ring and the aldehyde-hydrogen atom is small, replacement of the latter by a methyl group causes appreciable interference.

It is instructive to compare the difference in spectral properties between the acetophenones and the diphenyls. Thus in the case of the diphenyls, ortho-methyl groups cause a considerable hypsochromic shift of the band, together with a pronounced loss in \(\varepsilon\). This type of effect has been ascribed\(^1\) to transitions involving non-planar ground states and

non-planar excited states. In the case of acetophenone, however, the absence of any remarkable changes in the band means that the transition energy remains almost unchanged. Transition in this region corresponds to an energy change of about 80 kcal/mol. The changes in wavelength in the acetophenone series correspond to an energy difference of 2-4 kcal/mol, which is approximately that required for vibrational transitions in a polyatomic molecule. Therefore, this type of steric effect found in acetophenones has been postulated as due to the restriction, caused by steric hindrance, of the number of ground state molecules having a sufficiently planar configuration permitting transition to a uniplanar excited state, thereby causing a reduction in the intensity of absorption.

In the case of acetophenone the allowed transition may be represented as a change from a non-ionic ground state to a polar excited state as follows:

\[
\text{\textcircled{C-O}} \rightarrow \text{\textcircled{C-O}^-}
\]

The introduction of an ortho-methyl group will raise the energy level of the ground state relative to the unhindered compound, due to the additional
steric strain. In the postulated polar excited state, the phenyl-carbon link will have increased double bond character. Now, due to the fact that considerably more energy is required to twist a double bond than a single bond, and further that since the interplanar angle cannot change during a transition due to the fact that the time required for a transition is much less than that required for a change in configuration (Franck-Condon principle), the increase in energy of the excited state will be raised even more than that of the ground state, thus causing the hypsochromic shift of the band. Transitions of this type may be ascribed to changes between non-planar ground states and planar excited states, and have been shown to exist in conjugated systems, where one unhindered or weakly hindered configuration is possible.

ULTRAVIOLET ABSORPTION SPECTRA

Unsubstituted Ketones

Benzaldehyde has an intense absorption band at 244 mµ, $\epsilon = 13,000$, which is typical of $\pi-\pi$ conjugation. Acetophenone, as compared with benzaldehyde, absorbs at a slightly shorter wavelength
with slightly less intensity. In this case the replacement of the aldehyde-hydrogen atom by the larger methyl group causes a slight increase in steric hindrance. This trend continues with propiophenone, since the larger ethyl group would be expected to give rise to a slight additional strain as compared to the methyl group. \(n\)-Butyrophenone has a spectrum similar to that of propiophenone, which is to be expected, since the additional methyl group is presumably too far removed to give rise to any additional hindrance. The spectrum of iso-butyrophenone indicates a slight additional amount of strain. This is explained by the fact that the replacement of two hydrogen atoms of the acetophenone methyl group by two methyl groups would be expected to set up an increasing order of steric interference.

Substituted Ketones

**Molecular Configuration of 2-methylacetophenone and 2-methylpropiophenone.**

Upon examining the spectra, it will be noticed that the change in spectral properties between 4-methyl- and 2-methylacetophenone is almost identical with the change observed between 4-methyl- and 2-methylpropiophenone. For the first pair, there is
a bathochromic shift of 10 mµ, and the ratio of extinction coefficients is 0.57 (8500/15,000). For the second pair, the bathochromic shift is 9 mµ, and the ratio is also 0.57 (9000/14,000). This points to the fact that the geometrical configuration of the two molecules is similar, since the replacement of the methyl group in acetophenone by the ethyl group in propiophenone would increase the hindrance, thus giving rise to a greater difference in the shift between the two. Thus we may conclude that the preferred configuration is IA rather than IB. Examination of the spectra of penta-methyl- and pentaethylacetophenones indicates that the replacement of the methyl group by the more bulky ethyl group does cause additional steric effect, thus fortifying the argument.

The Electronic Effect of Substituents

Examination of the data show the 4-methyl- and 2-methylbenzaldehyde absorb at identical wavelengths,
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$ (m$\mu$)</th>
<th>$\epsilon_{\text{max}}$</th>
<th>$\lambda_{\text{max}}$ (m$\mu$)</th>
<th>$\epsilon_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzaldehyde</td>
<td>244</td>
<td>13,000</td>
<td>279</td>
<td>950</td>
</tr>
<tr>
<td>Acetophenone</td>
<td>240</td>
<td>12,500</td>
<td>276</td>
<td>1000</td>
</tr>
<tr>
<td>Propiophenone</td>
<td>240</td>
<td>12,000</td>
<td>276</td>
<td>1000</td>
</tr>
<tr>
<td>$n$-Butyrophenone</td>
<td>240</td>
<td>11,500</td>
<td>276</td>
<td>1000</td>
</tr>
<tr>
<td>Isobutoyrophenone</td>
<td>240</td>
<td>10,500</td>
<td>276</td>
<td>850</td>
</tr>
<tr>
<td>4-Methylbenzaldehyde (1)</td>
<td>251</td>
<td>15,000</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2-Methylbenzaldehyde (1)</td>
<td>251</td>
<td>13,000</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2-Methylacetophenone (1)</td>
<td>242</td>
<td>8500</td>
<td>283</td>
<td>1250</td>
</tr>
<tr>
<td>4-Methylacetophenone (1)</td>
<td>252</td>
<td>15,000</td>
<td>278</td>
<td>850</td>
</tr>
<tr>
<td>2,4-Dimethylacetophenone (1)</td>
<td>251</td>
<td>13,000</td>
<td>282</td>
<td>1250</td>
</tr>
<tr>
<td>2,6-Dimethylacetophenone (2)</td>
<td>241</td>
<td>2100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2,4,6-Trimethylacetophenone (2)</td>
<td>245</td>
<td>2300</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2,3,5,6-Tetramethylacetophenone</td>
<td>212</td>
<td>11,500</td>
<td>277</td>
<td>850</td>
</tr>
<tr>
<td>2,3,4,5,6-Pentamethylacetophenone</td>
<td>216</td>
<td>12,000</td>
<td>280</td>
<td>600</td>
</tr>
<tr>
<td>2,3,4,5,6-Pentaethylacetophenone</td>
<td>218</td>
<td>14,000</td>
<td>280</td>
<td>500</td>
</tr>
<tr>
<td>4-Methylpropiophenone</td>
<td>249</td>
<td>14,000</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2-Methylpropiophenone</td>
<td>240</td>
<td>8000</td>
<td>282</td>
<td>1200</td>
</tr>
<tr>
<td>4-Acetylhydrindacene (II)</td>
<td>252</td>
<td>7000</td>
<td>308</td>
<td>3000</td>
</tr>
</tbody>
</table>
### TABLE I (cont'd)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$</th>
<th>$\epsilon_{\text{max}}$</th>
<th>$\lambda_{\text{max}}$</th>
<th>$\epsilon_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Acetyl-5,6-dimethylindane (III)</td>
<td>246</td>
<td>3000</td>
<td>280</td>
<td>1700</td>
</tr>
<tr>
<td>9-Acetyloctahydroanthracene (IV)</td>
<td>220</td>
<td>10,000</td>
<td>282</td>
<td>1500</td>
</tr>
<tr>
<td>5-Acetyl-6,7-dimethyltetralin (V)</td>
<td>218</td>
<td>11,000</td>
<td>278</td>
<td>1100</td>
</tr>
<tr>
<td>2,3,5,6-Tetramethylbenzene</td>
<td>214</td>
<td>8500</td>
<td>268</td>
<td>600</td>
</tr>
</tbody>
</table>


![Structural formulas](attachment:image.png)
and that the ratio of extinction coefficients is 0.87 (13,000/15,000). Thus in aceto-and propiophenone the intensity is almost halved by the introduction of an ortho-methyl group, whereas in benzaldehyde it remains almost constant. In o-methylbenzaldehyde a bathochromic shift of 7 mp is observed, while in acetophenone the corresponding shift is only 1 mp. In addition, the shift between benzaldehyde and 2-methylbenzaldehyde is almost identical with that between benzaldehyde and 4-methylbenzaldehyde. In the later case, there is little steric strain, and the shift is clearly caused by the electronic influence of the substituent. It may also be noted that 4-methylbenzaldehyde, 4-methylacetophenone, and 4-methylpropiophenone all show substantially similar spectral properties.

The introduction of a methyl group in the para-position of acetophenone causes a bathochromic shift of 12 mp, with an increase in ε of 2500. Assuming the absence of any steric effect, we may justifiably assume an entirely similar spectrum for ortho-methylacetophenone, since the mesomeric effect is approximately the same for the ortho- and para-positions, and the difference in inductive effect between the two positions is small by
comparison. Observing the actual spectrum of 2-methylacetophenone, it becomes apparent that the steric effect causes a hypsochromic shift of about $10 \text{ m\mu}$, with an attendant decrease in $\epsilon$ of 6500. Propiophenone has a corresponding shift of $9 \text{ m\mu}$, and the loss in intensity is 6000. To fully appreciate the effect of steric interference, the hindered ortho-compound should be compared with the para-analogue, rather than with the parent compound. This effect becomes apparent in o-methylbenzaldehyde, where steric influences are small, and in 4-acetylhyindacene (II), where the introduction of a second methylene group causes a bathochromic shift of about $10 \text{ m\mu}$.

The sensitivity of the band to para-substituents has led to the assumption of electronic transitions associated with para-resonance forms of type IC (3).

It can be seen from Figure 2 that a decrease

FIGURE 1

ABSORPTION SPECTRA OF PROPIOPHENONE AND 2-METHYLPROMETHYLPHENONE IN ETHANOL
in the interplanar angle, caused by an increase in amount of double bond character between the phenyl-carbon link, due to the introduction of the para-substituent, will lower the energy barrier between the ground and excited states, thus giving rise to the observed bathochromic shift, and by increasing the number of molecules having near-planar vibrational states permitting of transition to the excited state, increase the overall transition probability. Hence it is seen that the ortho-methyl group has a greater steric effect than apparent at first glance, since it must also overcome resonance forms of this type.

![Figure 2](image-url)
Spatial Orientation of Hindered Ketones.

The spectra of 2-methylacetophenone and 2-methylpropiophenone have been discussed previously (cf. page 5), and it has been shown that the preferred configuration is one in which the carbonyl oxygen atom is adjacent to the ortho-methyl group.

In the case of 2,6-dimethylacetophenone, the molecule can no longer take up a favorable steric configuration, i.e., two methyl groups must now be adjacent. Hence, the interplanar angle is increased considerably, and conjugation is almost completely inhibited.

The introduction of a third methyl group in the para-position of 2,6-dimethylacetophenone gives rise to an increase of para-resonance forms of type IC. This causes an increase in the double bond character between the phenyl group and the carbonyl group, which lessens the interplanar angle, thus increasing the transition probability and causing the observed bathochromic shift. A similar difference occurs between 2,3,5,6-tetramethyl- and 2,3,4,5,6-pentamethylacetophenone.

4-Acetylhydrindacene (II)

In the case of 4-acetylhydrindacene, there is
no preferred spatial orientation, and we may compare its spectrum to that of 2,6-dimethylbenzaldehyde and 2,6-dimethylacetophenone. The absorption maximum at 252 μ is similar to that of 2,6-dimethylbenzaldehyde. The intensity of absorption indicates a slight amount of steric strain corresponding to the usual decrease in the number of planar ground states. There is a decrease of intensity with respect to acetophenone, and an increase relative to 2,6-dimethylacetophenone. This indicates that the ortho-methylene group of the cyclopentyl ring offers steric resistance intermediate between an ortho-hydrogen atom and an ortho-methyl group. This is to be expected, and is reinforced by an examination of scale models.

9-Acetyloctahydroanthracene (IV)

In this molecule, the ortho-methylene group is held in a position where steric interference is considerably enhanced. This agrees with the findings of Arnold and Craig who found from reactivity differences and in part from an interpretation of carbonyl Raman frequencies, that the steric hindrance decreases around the carbonyl group in the order \( V \succ IV \succ III \succ II \). The methylene group causes a con-

siderable increase in the interplanar angle, thus increasing the transition energy and giving rise to the hypsochromic shift. Comparing with the spectra of 2,3,5,6-tetramethylacetophenone, it may be deduced that the ortho-methylene group in the cyclohexyl ring offers slightly less steric resistance than the ortho-methyl group in the tetra-substituted acetophenone, the latter methyl group offering in turn considerably more resistance than the ortho-methyl group in 2,6-dimethylacetophenone. This difference may be explained by the so-called "buttressing effect" of the meta-positioned methyl group in the tetramethylacetophenone, i.e., the meta-positioned methyl groups prevent the "bending away" of the ortho-methyl group, thus causing the latter to interfere to a greater degree with the keto-group, and preventing the attainment of a sterically favorable position.

4-Acetyl-5,6-dimethylindane (III)

For this compound, two structures (IIIA and IIIB, cf. page 8) are possible. It is possible that the ortho-methylene group in this molecule, by taking up the sterically most favorable position, i.e., one in which the two ortho-hydrogen atoms would form a saddle, could contribute to the co-
FIGURE 3

- - - - - - 4-ACETYL-5,6-DIMETHYLINDANE

--- 9-ACETYLOCTAHYDROANTHRACENE

- - - - - - - - 4-ACETYLHYDRINDACENE

Absorption Spectra of 4-ACETYLHYDRINDACENE, 9-ACETYLOCTAHYDROANTHRACENE, and 4-ACETYL-5,6-DIMETHYLINDANE in Absolute Ethanol
planarity of the molecule. This effect, together with the tendency toward uniplanarity due to the para- resonance forms, will be opposed by the usual steric effect.

If structure IIIA predominates, the spectrum would be expected to be similar to that of 2,6-dimethyl acetophenone, with modifications. Thus the amount of steric effect caused by the ortho-methyl group would be increased due to the previously described "buttressing effect" of the meta-methyl group. This in turn would tend to be offset by the substitution of the other ortho-methyl group by the ortho-methylene group of the cyclopentyl ring, which, as seen before, offers considerably less steric interference than an ortho-positioned methyl group. Since the steric effect has been shown to arise mainly due to the interference of the keto-methyl group with the ortho-methyl group of the benzene ring, the "buttressing effect" of the meta-methyl group in IIIA would not be expected to have a pronounced influence, because of the smallness of the carbonyl oxygen atom. Therefore, in structure IIIA one would predict that the total steric effect should be less than in the case of 2,6-dimethylacetophenone.
Concerning structure IIIB, the "buttressing effect" of the ortho-methyl group should have a considerable effect, as previously discussed in the comparison of 2,6-dimethylacetophenone with the tetramethyl acetophenone, and therefore the spectrum should resemble that of the tetra-methylacetophenone. From the data, it will be seen that only structure IIIA is reasonable from the above conclusions. This is indeed what would be expected from overall steric considerations, and is also borne out by the consideration of scale models.

5-Acetyl-6,7-dimethyltetralin (V)

In this example, two structures, VA and VB (see page 8) are possible. If structure VB were correct, the spectrum would resemble that of tetramethylacetophenone, since the buttressed ortho-methyl group in the tetra-substituted acetophenone presumably would offer only slightly more steric resistance to the small keto-oxygen molecule than would the ortho-methylene group of the cyclohexyl ring. If VA were the correct structure, then the spectrum should resemble that of 9-acetyloctahydroanthracene, with allowance for the fact that the buttressed methyl group might interfere slightly
FIGURE 4

--- 5-ACETYL-6,7-DIMETHYLTETRALIN
--- --- 2,3,5,6-TETRAMETHYLBENZENE

Wavelength in μ

ABSORPTION SPECTRA OF 5-ACETYL-6,7-DIMETHYL-TETRALIN AND 2,3,5,6-TETRAMETHYLBENZENE IN ABSOLUTE ETHANOL
with the keto-oxygen atom. The data seem to point
to structure VA rather than VB, which is what one
might expect from overall steric considerations.
Absorption in this region, however, is due prin-
cipally to the "tetramethyl benzene" band, and
since in these highly hindered compounds, the
interplanar angle approaches 90°, the probability
in favor of structure VA over VB is at best a
slight one.

The Secondary Carbonyl Absorption Band

The secondary band, near 280 μ, is little
affected by the steric influences heretofore dis-
cussed. Examination of the data present two points
of interest. One is the fact that the introduction
of a para-methyl group in the acetophenone molecule
does not cause any remarkable occurrences, while
the introduction of a para-methyl group in the pro-
piophenone molecule causes the complete disappear-
ance of the secondary band. The other point of
interest is that in 4-acetylhydrindacene (II), there
exists a high degree of symmetry with relatively
little steric hindrance. The secondary band of this
molecule has undergone a bathochromic shift of about
28 μ. It would be presumptuous to draw any
conclusions on such nebulous data, and any explanation must await further experimental work, which is in progress. This work indicates that the band may concern itself with the angle of incidence of the photon.

2,4-dinitrophenylhydrazones

The absorption spectra of the 2,4-dinitrophenylhydrazones of some of the ketones, together with reference compounds, are listed in Table II.

Unsubstituted Compounds

Cyclohexanone 2,4-dinitrophenylhydrazone absorbs maximally at 362 μm. Since in this case there is no cross-conjugation possible, this maximum must be attributed to the C=N-NH-R group, (R = 2,4-dinitrophenylhydrazone chromophore). The spectrum of benzaldehyde, acetophenone, and propiophenone 2,4-dinitrophenylhydrazones indicate cross conjugation, as evidenced by a bathochromic shift and an increase of absorption intensity. The spectrum of isobutyrophenone 2,4-dinitrophenylhydrazone shows that the replacement of a hydrogen atom in propiophenone 2,4-dinitrophenylhydrazone by a methyl group causes a transition from a planar to a non-planar molecule. Para-resonance forms make their usual contribution by lowering the energy of the excited state more than that of the ground state, as is evidenced by the spectrum of 4-methylpropiophenone 2,4-dinitrophenylhydrazone. In 2-methylpropiophenone 2,4-dinitrophenylhydrazone, the introduction of the ortho-
methyl group causes a complete loss of conjugation, and
the spectrum is similar to that of cyclohexanone 2,4-
dinitrophenylhydrazone.

**TABLE II**

Absorption Spectra of 2,4-Dinitrophenylhydrazones of
Acetophenones and Related Compounds in Chloroform.

Wave-lengths and intensities of the main maxima.

<table>
<thead>
<tr>
<th>Carbonyl compound</th>
<th>$\lambda_{\text{max}}$ m$^\mu$</th>
<th>$\epsilon_{\text{max}}$</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzaldehyde</td>
<td>372</td>
<td>29,000</td>
<td>Red</td>
</tr>
<tr>
<td>Acetophenone</td>
<td>372</td>
<td>25,000</td>
<td>Red</td>
</tr>
<tr>
<td>Propiophenone</td>
<td>374</td>
<td>25,000</td>
<td>Red</td>
</tr>
<tr>
<td>4-Methylpropiophenone</td>
<td>380</td>
<td>25,500</td>
<td>Red</td>
</tr>
<tr>
<td>2-Methylpropiophenone</td>
<td>362</td>
<td>23,500</td>
<td>Red</td>
</tr>
<tr>
<td>Isobutyrophenone</td>
<td>362</td>
<td>23,500</td>
<td>Yellow</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>362</td>
<td>23,500</td>
<td>Yellow</td>
</tr>
<tr>
<td>4-Acetylhydrindacene</td>
<td>366</td>
<td>24,000</td>
<td>Orange</td>
</tr>
<tr>
<td>4-Acetyl-5,6-dimethylindane</td>
<td>362</td>
<td>22,000</td>
<td>Orange</td>
</tr>
</tbody>
</table>

The spectrum of 4-acetylhydrindacene 2,4-dinitro-
phenylhydrazone indicates an intermediate amount
of steric hindrance, and that of 4-acetyl-5,6-dimethyl-
indane 2,4-dinitrophenylhydrazone
shows a complete lack of coplanarity. 9-Acetyl-octahydroanthracene (IV), 5-acetyl-6,7-dimethyl-tetralin (V), tetramethyl-, pentamethyl-, and pentaethylacetophenones do not form 2,4-dinitrophenylhydrazones, oximes, or semicarbazones under the usual conditions. The amount of steric hindrance may sometimes be estimated from the color of the 2,4-dinitrophenylhydrazones. (See Table II).

Substituted Benzoic Acids

An interesting example of the relation of spectra to electronic and steric effects is provided by a recent paper on the spectra of various tri-substituted benzenes. In this work, the authors attempt to correlate the spectra of the tri-substituted compounds with those of the corresponding di-substituted compounds. They choose β-resorcylic acid as a representative example of a tri-substituted benzene, and report the data listed in Table III.

The authors state that the primary band of salicylic acid has no analogue in the spectrum of β-resorcylic acid, and further that the first pri-

mary band of the tri-substituted compound may be related to the most displaced band of the component di-substituted compounds. They point out that the first primary bands of the di-substituted compounds frequently do not occur in the tri-substituted compound, and in concluding add that steric effects are usually small in absorption spectra.

**TABLE III**

**ABSORPTION SPECTRA OF β-RESORCYLIC ACID AND RELATED COMPOUNDS IN ETHANOL**

<table>
<thead>
<tr>
<th>Compound</th>
<th>λmax (\mu)</th>
<th>εmax</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-Resorcylic Acid</td>
<td>256</td>
<td>13,600</td>
</tr>
<tr>
<td>Salicylic Acid</td>
<td>237</td>
<td>9000</td>
</tr>
<tr>
<td>Resorcinol</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>p-Hydroxybenzoic Acid</td>
<td>255</td>
<td>14,000</td>
</tr>
</tbody>
</table>

Application of steric and electrical effects as outlined above should prove of interest in this case.

**Benzoic Acid**

Benzoic acid absorbs maximally with smaller
intensity of absorption than acetophenone. As has been pointed out\(^6\), this may be ascribed to the fact that in the excited state the concentration of electrons in the carboxyl group is greater than that in the acetyl group. The two structures may be represented as follows:

\[
\text{CH}_3\text{C}^\cdot \text{O}^- \\
\text{H}^\cdot \text{C}^\cdot \text{S}^\cdot \
\]

It is seen that in the case of benzoic acid, there will be less double bond character in the excited state relative to acetophenone. Hence benzoic acid will be more sensitive to steric effects, since the carboxyl group may be twisted out of the plane of the benzene ring more easily than the acetyl group. The hindrance is presumed to occur mainly in the excited state, which accounts for the fact that the steric effect is manifested by a decrease in absorption intensity rather than by a pronounced hypsochromic shift of the band (compare acetophenone).

However, due to replacement of the methyl group in acetophenone by the hydroxy group in benzoic acid, the negative inductive effect of the hydroxy group will stabilize ground state resonance forms to a greater extent than in acetophenone. Also, in benzoic acid the excited state has a somewhat higher energy than acetophenone due to a larger charge separation. Hence the energy of transition in benzoic acid is greater than that of acetophenone, causing benzoic acid to absorb maximally at shorter wavelength with decreased intensity, (λmax 227 μm; εmax 11,000).5

p-Hydroxybenzoic Acid

The introduction of a hydroxy group in the para-position, due to the usual resonance stabilization, lowers the energy level of the excited state more than that of the ground state, thus causing the observed bathochromic shift and increased intensity of absorption, as in the acetophenones.

Salicylic Acid

In the case of salicylic acid, the purely electronic effect of the hydroxy group will be offset to some degree by steric interference of the carboxyl group with the ortho-hydroxy group. The resonance effect of the ortho-hydroxy group may
may be considered to be equal to that of the para-hydroxy group, but the inductive effect will be greater in the ortho-position. This will tend to stabilize polar excited states of type IE, thus giving a further bathochromic shift.

Hence the steric effect of the ortho-hydroxy group is somewhat larger than appears at first glance, since it must overcome this difference in inductive effect. Thus it can be seen that the steric effect causes a hypsochromic shift of 19 m\(\mu\), and a decrease in intensity corresponding to a ratio of extinction coefficients of 0.64 (9000/14,000), comparing with the para-compound.

\(\beta\)-Resorcylic Acid

If, now, another hydroxy group is introduced in the para-position of salicylic acid, the increased stabilization of the excited state relative to the ground state due to the resonance contributions will cause a further bathochromic shift and a
corresponding increase in absorption. In this case, and also in the case of 2-methyl- and 2,4-dimethylacetophenone, the increase in stabilization due to para-resonance forms is very closely equal to the decrease in stabilization due to steric interference. Thus $\lambda_{\text{max}}$ and $\varepsilon_{\text{max}}$ of the para-compound closely correspond to those of the 2,4-disubstituted compounds. The possibilities of dimer formation and hydrogen-bonding at the low concentrations used in spectral work are being investigated at this time, and present data do not permit a detailed discussion of these topics.

From the above discussion, it can be seen that an interpretation of the operative electronic and steric effects leads to a more precise correlation of the spectra in this particular example than is possible with empirical terms. An examination of spectral data available in the literature shows steric effects to be widely prevalent, and in any critical discussion of spectroscopic evidence, the importance of steric hindrance cannot be overlooked.
EXPERIMENTAL PART

The ultraviolet spectra were determined by standard methods using a Unicam SP 500 spectrophotometer. \( \varepsilon \) represents the molecular extinction coefficient defined by \( \varepsilon = \log_{10}(I_0/I) \cdot c \cdot l \), where \( I_0 \) and \( I \) equal the intensity of incident and transmitted light, respectively, \( c \) equals the concentration in moles/liter, and \( l \) equals the cell thickness in centimeters.

Melting points are uncorrected, and the analyses were carried out in the micro-analytical laboratory (Mr. F. H. Oliver) of the Department of Organic Chemistry, Imperial College, London, England.

Benzaldehyde, Acetophenone, Propiophenone, Iso-butyrophenone.

The commercially available compounds were re-distilled to constant refractive index and intensity of absorption. Light absorption in ethanol: see Table I. The 2,4-dinitrophenylhydrazones of these as well as of the other carbonyl compounds described below, were chromatographed over alumina from chloroform-benzene and crystallized, unless otherwise stated, from ethanol-ethyl acetate mixtures. Benzaldehyde 2,4-dinitrophenylhydrazone crystallized from glacial acetic acid as red needles, m.p. 241-
242°, (Johnson⁷ (J) gives m.p. 239-240°); acetophenone 2,4-dinitrophenylhydrazone crystallized from glacial acetic acid as red needles, m.p. 250°, (Johnson⁷ (J) gives m.p. 247-248°); propiophenone 2,4-dinitrophenylhydrazone crystallized as red plates, m.p. 196-197° (decomp.) (Johnson⁷ (J) gives m.p. 193-194°); isobutyrophenone 2,4-dinitrophenylhydrazone crystallized as yellow monoclinic prisms, m.p. 165-166° (Johnson⁷ (J) gives m.p. 161-162°).

Light absorption in chloroform: see Table II.

4-Methylpropiophenone

Anhydrous aluminum chloride (9.1 gm.) was added to toluene (100ml.) and propionyl chloride (6.3 gm.) was added dropwise with stirring at 0°C. After stirring for one hour, the mixture was hydrolyzed and isolated in the usual manner. The product distilled at 110°/12 mm., yield 5.5 gm. (55%), nD²².⁵ 1.5264. (Birch, et al.⁸ (J) give boiling point 135°/30 mm.; nD²⁰ 1.5278). Light absorption in ethanol: see Table I. The 2,4-dinitrophenylhydrazone crystallized from ethyl acetate as red monoclinic prisms, m.p. 209° (decomp.).


(Cullinane et al.\textsuperscript{9} give m.p. 201°). Light absorption in chloroform: see Table II.

2-Methylpropiophenone

2-Methylpropiophenone was prepared according to the method of Birch et al.\textsuperscript{9}(7), and was obtained as a colorless liquid, b.p. 100°/8 mm., \(n_D^2\) 1.5243 (Birch et al.\textsuperscript{9}(7) give \(n_D^2\) 1.5250), yield 9.2 gm., (62%). Light absorption in ethanol: see Table I. The 2,4-dinitrophenylhydrazone crystallized from ethanol as red plates, m.p. 115°. Anal.: Calc for C\(_{15}\)H\(_{14}\)O\(_4\)N\(_4\): C, 57.3; H, 4.5; N, 17.3. Found: C, 57.3; H, 4.5; N, 17.7%. Light absorption in chloroform: see Table II.

2,3,5,6-Tetramethylacetophenone

Durene (4 gm.), prepared from xylene by the method of Smith\textsuperscript{10}(3), was dissolved in carbon disulfide (40 ml.) at 0°. Aluminum chloride (4 gm.) was added to the stirred mixture in small portions followed by the dropwise addition of acetyl chloride (2.4 gm.) over a period of ten minutes. Stirring was continued for three hours at 0°, and the mixture was then allowed to stand overnight at room


temperature. It was then poured onto an ice-hydrochloric acid mixture and extracted with ether. After drying, removal of the ether afforded the acetophenone in 55% yield, which crystallized from petroleum ether (40-60°) as colorless plates, m.p. 75°. (Meyer \(\text{II}^{10}\) gives m.p. 73°). No oxime, semicarbazone, or 2,4-dinitrophenylhydrazone could be obtained under the usual conditions. Light absorption in ethanol: see Table I.

2,3,4,5,6-Pentamethylacetophenone

Pentamethylbenzene (2 gm.), prepared by the method of Smith \(\text{I}^{10}(\text{J})\), was dissolved in carbon disulfide (50 ml.) and treated with aluminum chloride (1.8 gm.) and acetyl chloride (1.1 gm.) as described above. The product, which crystallized from methanol as colorless needles, m.p. 87°, was obtained in 90% yield. Anal.: Calc. for \(\text{C}_{13}\text{H}_{18}\text{O}\): C, 82.1; H, 9.5%. Found: C, 82.1; H, 9.7%. No oxime, semicarbazone, or 2,4-dinitrophenylhydrazone could be obtained under the usual conditions. Light absorption in ethanol: see Table I.

2,3,4,5,6-Pentaethylacetophenone

Pentaethylbenzene (5.1 gm., \(n^D_{25} 1.5130\)),

prepared by the method of Smith and Guss, (11), was treated with aluminum chloride (3.2 gm.) and acetyl chloride (2.7 gm.) as described above. The product which crystallized from 95% ethanol as colorless needles, m.p. 143.5-144°, was obtained in 80% yield. Anal.: Calc. for C$_{18}$H$_{28}$O: C, 83.0; H, 10.9%. Found C, 83.0; H, 11.0%. No oxime, semicarbazone, or 2,4-dinitrophenylhydrazone could be obtained under the usual conditions. Light absorption in ethanol: see Table I.

4-Acetyl-5,6-dimethylindane (III)

5,6-Dimethylindane (1.9 gm., $n_D^4$ 1.5318), prepared by the method of Arnold and Craig (4), in carbon disulfide (30 ml.) was treated with aluminum chloride (1.7 gm.) and acetyl chloride (1 gm.) as described above. Fractionation at 3 mm. afforded the indane as a pale yellow oil, which solidified on standing and crystallized from petroleum ether (40-60°) as monoclinic prisms, m.p. 42.5°. Arnold and Craig (4) report m.p. 43° for this compound. Light absorption in ethanol: see Table I. The 2,4-dinitrophenylhydrazone crystallized

from benzene as yellow plates, m.p. 196-197°. Anal.: 
Calc. for C_{19}H_{20}O_{4}N_{4}: C, 61.9; H, 5.5; N, 15.2%. Found: 
C, 61.9; H, 5.5; N, 15.1%. Light absorption in chloro-
form: see Table II.

4-Acetylhydridacene (II), 9-Acetyloctahydroanthracene 
(IV), and 5-Acetyl-6,7-dimethyltetralin (V).

These compounds were crystallized to constant melting 
point. Their preparation has been described (4, 13), and 
Professor Arnold kindly provided the required specimens. 
The last two compounds form no oximes, semicarbazones, or 
2-4 dinitrophenylhydrazones. The 2,4-dinitrophenylhydrazone 
of 4-acetylhydridacene crystallized from ethanol as orange 
needles, m.p. 185°. Anal.: Calc. for C_{20}H_{20}O_{4}N_{4}: C, 63.15; 
H, 5.3; N, 14.7%. Found: C, 63.2; H, 5.3; N, 14.6%. Light 
absorption in chloroform: see Table II.

The following experiments were performed in an attempt 
to synthesize 4-acetyltetrahydrobenz(f)indane and 2,3,5,6-
tetraethylacetophenone.

Reaction of β-Chloropropionyl Chloride with Tetralin.

Aluminum chloride (25 gm.) was placed in a flask 
with carbon disulfide (100 ml.). β-Chloropropionyl 
chloride (25 gm.) was added in portions

13. Arnold, R. T., and Røndestvedt, E. J., J.A.C.S., 
68, 2176. (1946).
through the condenser. The solution turned red, and was refluxed for 45 min., giving a liquid layer and a reddish-brown solid. The liquid and solid were added in portions to tetralin (14.5 gm.), which was cooled in an ice bath. After the addition was complete, the mixture was stirred for one hour, and poured onto ice. Extraction with ether, evaporation, and recrystallization from petroleum ether (40-60°) yielded 20.5 gm. of product (I) (49% based on tetralin), m.p. 65°. The 2,4-dinitrophenylhydrazone crystallized from glacial acetic acid as red needles, m.p. 207.5-208.5 (decomp.). Anal.: Calc. for C₁₉H₁₈N₄O₄Cl: N, 13.94%. Found: N, 13.79%.

Cyclization of (I).

Phosphoric acid (5 gm., sp. gr. 1.7), phosphorous pentoxide (5 gm.) and formic acid (5 gm., 91%) were mixed in a beaker, and the resulting cloudy suspension (10 gm.) was poured in a 50 ml. round-bottomed flask. (I) (1 gm.) was added in one lot, and the mixture (two layers) was heated (80-90°) on a water bath for two hours. It was allowed to cool, decomposed with ice, and extracted with ether. The residue (1 gm.) was dissolved in ethanol and 2,4-dinitrophenylhydrazine (equiv. amount) was
added, together with hydrochloric acid (2 ml., conc.). After heating, the precipitate was dissolved in chloroform, and chromatographed over alumina, using benzene as an eluent. The band was redissolved and chromatographed again. Only one band was obtained. Recrystallization from glacial acetic acid gave yellow needles, m.p. 247.5-248.5° (decomp.). Anal.: Calc. for C_{16}H_{16}O_{4}N_{4}: C, 58.53; H, 4.91; N, 19.09%. Found: C, 62.54; H, 5.10; N, 15.32%.

Ethylation of 1,3,5- and 1,2,4-triethylbenzenes.

To a mixture (16.2 gm., \(n_D^{21} 1.4950\)) of triethyl benzenes obtained from a Friedel-Crafts alkylation was added aluminum chloride (1 gm.). Ethyl bromide (8 gm.) was then added dropwise over a period of one hour, the mixture was stirred at room temperature for three hours, and allowed to stand overnight. Recovery and distillation at reduced pressure gave only starting material, (\(n_D^{21} 1.4950\)).

The above procedure was repeated, except the mixture was heated on a water bath for six hours. Recovery in the usual manner gave tetraethylbenzenes, (10.9 gm., \(n_D^{22} 1.5048\)), starting material (2.9 gm.), and approximately one gram of undistillable
residue, which showed a blue fluorescence.

The results of Smith and Guss\(^1\)\(^2\)\(^{(11)}\) in separating the tetraethylbenzene fraction into its respective isomers by sulfonation with chlorosulfonic acid, separation by fractional crystallization, and desulfonation by steam distillation from sulfuric acid could not be reproduced. No limiting value for the sulfuric acid concentration necessary for the Jacobsen rearrangement to take place could be found in the literature.