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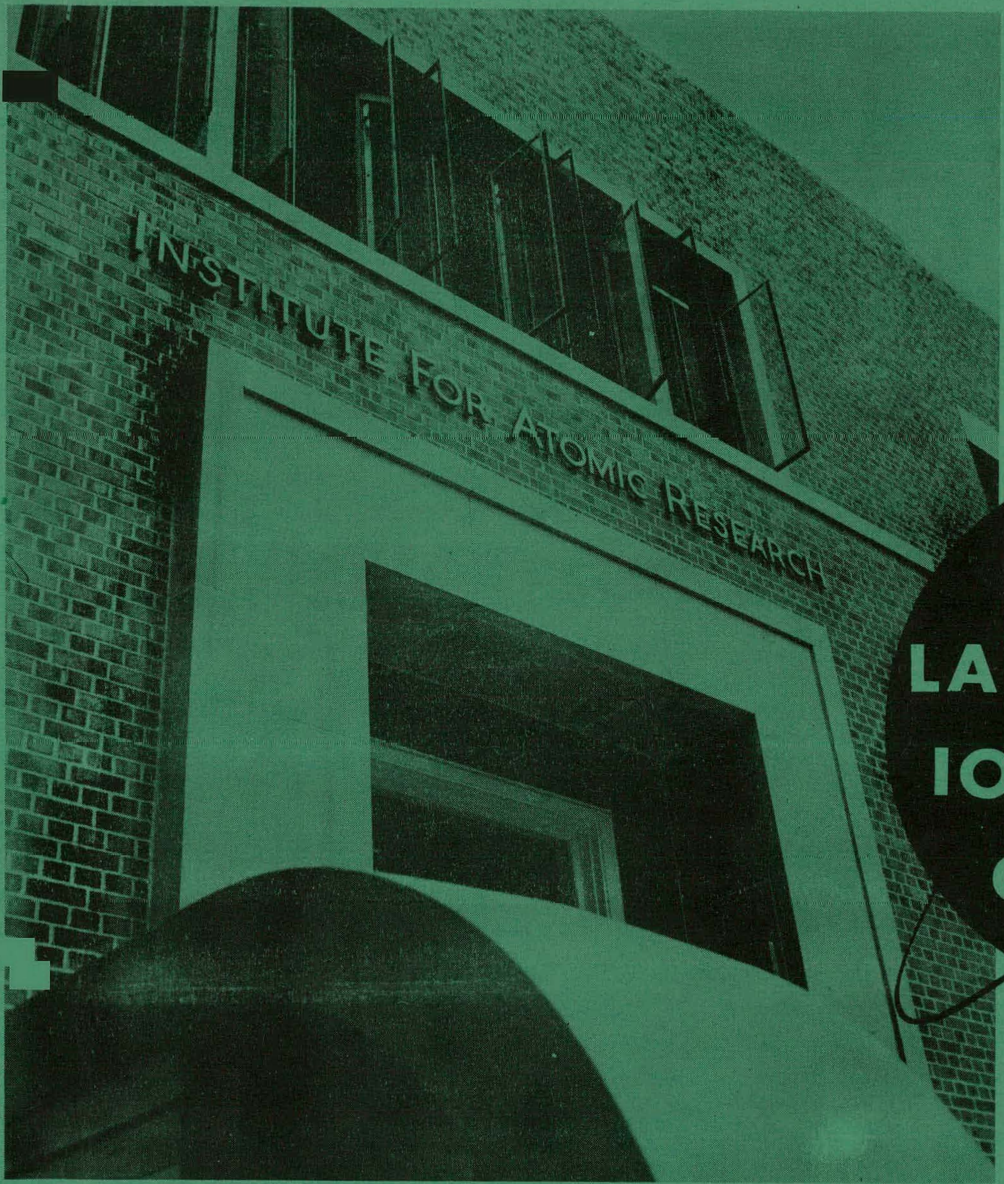

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THE INFRARED SPECTRA OF AROMATIC COMPOUNDS. II. EVIDENCE CONCERNING THE INTERACTION OF π -ELECTRONS AND σ -BOND ORBITALS IN C-H OUT-OF-PLANE BENDING VIBRATIONS.

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The Infrared Spectra of Aromatic Compounds

II. Evidence Concerning the Interaction of π-Electrons and σ-Bond Orbitals in C-H Out-Of-Plane Bending Vibrations

by

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The Infrared Spectra of Aromatic Compounds
II. Evidence Concerning the Interaction of π-Electrons and σ-Bond Orbitals in C-H Out-Of-Plane Bending Vibrations

R. D. Kross, V. A. Fassel, and M. Margoshes

Abstract

In certain mono- and para-disubstituted benzenes the frequency of one of the C-H out-of-plane bending vibrations falls outside of the characteristic frequency range usually assigned to that vibration. The phenomenon is ascribed to bond rehybridization accompanying the out-of-plane vibrations, whereby the C-H σ-bonds of the benzene nucleus overlap with the π-electrons of the molecules and tend to form sp^3 hybrids. The rehybridization results in decreased effective force constants for the vibrations. The extent of rehybridization depends on the concentration of the π-electrons around the benzene ring, which in turn is dependent on the nature of the substituent. Nitro and carboxyl groups deplete the ring of π-electronic charge so that the σ-bonds undergo a smaller rehybridization. This leads to greater effective force constants, and higher frequencies for the C-H out-of-plane vibrations as compared with compounds in which the substituent is relatively inert with respect to the ring. Bond rehybridization also provides an explanation for the smaller relative intensities of the C-H out-of-plane bending vibrations of compounds such as nitrobenzene

as compared with the vibrations of compounds falling in the normal frequency range. Other anom~~o~~alous spectra are adequately explained on the same basis.

* * *

Various observations[1,2,3] have indicated that the frequencies of one of the out-of-plane C-H bending vibrations in monosubstituted benzenes falls outside of the characteristic frequency range for compounds such as benzoic acid, sodium benzoate, benzoyl chloride, and nitrobenzene. It has also been observed that in para-disubstituted benzenes the same substituents give rise to anomolous shifts in frequency. The purpose of this paper is to discuss certain other observations on the frequencies of these vibrations and to present a self-consistent explanation for this effect.

Experimental

All the spectra were recorded under the same conditions as were described in the first paper of this series.[1]

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(1) M. Margoshes and V. A. Fassel, Spectrochim. Acta, 7, 14 (1955).

(2) M. St. C. Flett, J. Chem. Soc. (London), 962 (1951).

(3) L. J. Bellamy, The Infrared Spectra of Complex Molecules, John Wiley & Sons, Inc., New York, p. 68.

Evidence Indicating the Interaction of π-Electrons and Aromatic C-H Bonds

In paper I of this series[1] it was shown that certain substituent groups caused a shift of the out-of-plane C-H bending vibrations in monosubstituted benzenes at 725-775 cm^{-1} outside of the frequency range generally assigned to this vibration. Spectra of a typical group of monosubstituted benzenes in which the frequency falls in the normal range below 775 cm^{-1} are shown in the upper portion of Figure 1, whereas the spectra of the group of compounds in the lower portion of Figure 1 all exhibit a shift of this frequency above 775 cm^{-1}. A pronounced decrease in intensity with the shift to higher frequency is also generally observed, although a low intensity may also be observed with a normal frequency, as in ethylbenzene.

To illustrate the shifts in frequency caused by the same substituent groups in para-disubstituted benzenes, Table II summarizes the frequencies of the 12 micron band in several para-disubstituted benzenes and the related compound, p-quinone. For the substituted toluenes and dihalobenzenes, the characteristic absorption band is between 800 and 820 cm^{-1}. In each of the compounds in which one of the substituents is a nitro or carboxyl group this band is displaced to 840-855 cm^{-1}. If both of the substituents are nitro or carboxyl groups there is an additional displacement to about 880 cm^{-1}; Finally in p-quinone the shift is to 895 cm^{-1}.

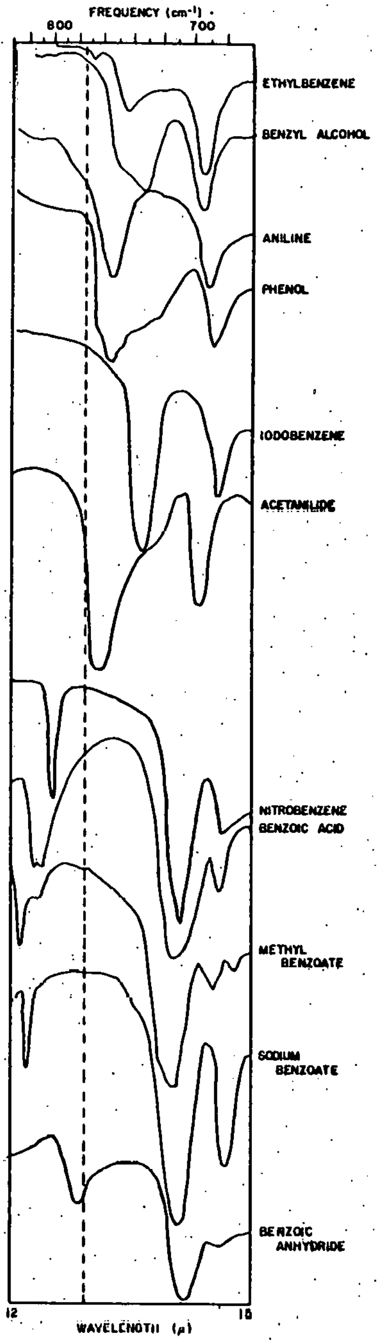

Fig. 1 - Normal and abnormal frequency patterns in monosubstituted benzenes.

It is well known[4-7] that the infrared spectra of many compounds show sharp differences in frequency and intensity as the compounds are measured in solid, liquid, and solution states. Some of the complex factors underlying these spectral changes are now well understood[4-7], but a complete understanding is not yet available. In order to interpret the change in frequency of the out-of-plane C-H bending vibrations, it is of primary importance to establish whether intra- or intermolecular interactions are responsible. Since intermolecular forces between solute molecules are destroyed in dilute solutions of the compounds in non-polar solvents, the spectra of dilute solutions of many of the compounds were studied. The data summarized in Table I and II show that the increase in frequency caused by certain groups is basically an intramolecular interaction.

It is not unreasonable to expect that the π-electrons located above and below an unsaturated chain or ring can exert a direct effect upon the vibrations of hydrogens perpendicular to that chain or ring. This influence can be inferred from C-H bond moment determinations. A convenient method for obtaining bond moments is based on measurement of the intensities of C-H bending vibrations, which are directly related to the dipolar nature of a bond.

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(4) R. E. Richards and H. W. Thompson, Proc. Royal Soc. (London) A195, 1 (1948).

(5) R. E. Richards and H. W. Thompson, J. Chem. Soc. 1947, 1248.

(6) T. A. Kletz and W. C. Price, J. Chem. Soc. 1947, 644.

(7) T. T. Harding and S. C. Wallwork, Acta Cryst. 6, 791 (1953).

Table I

Characteristic Frequencies for Various Substituent Groups in Monosubstituted Benzenes in Various States

Compound	Substituent Group	Frequency (cm^{-1}) Liquid	Solid	Dilute Sol'n.
Toluene	$-CH_3$	728		729
Aniline HCl	$-NH_3^+$		741	
Benzyl Alcohol	$-CH_2OH$	736		735
Ethylbenzene	$-C_2H_5$	747		
Phenylacetate	-OOCR	752		
Phenol	-OH		753	750
Sodiumbenzenesulfonate	$-SO_3Na$		754	
Aniline	$-NH_2$	755		
Benzenesulfonylchloride	$-SO_2Cl$	757		
Anisole	$-OCH_3$	756		753
Triphenylmethane	-CH		762	
Benzonitrile	-CN	758		756
Acetophenone	-COR	761		757
Trans-stilbine	$-C^{=}$		767	
Benzamide	$-CONH_2$		771	
Benzoylchloride	-COCl	779		
Benzoic Anydride	-COOCO		779	
Nitrobenzene	$-NO_2$	794		790
Benzoic Acid	-COOH		808	
Ethyl Benzoate	-COOEt		782 or 806	780 or 804
Sodium Benzoate	$-COO^-$		820	

All solution spectra were obtained using CS_2 as solvent.

Table II

Out-Of-Plane C-H Bending Frequencies for Some Para-disubstituted Benzenes

Compound	Frequencies (cm^{-1}) Liquid	Solid	Dilute Solution
p-Xylene	794		793
p-Iodotoluene	800		
p-Bromotoluene	803		800
p-Chlorotoluene	809		804
p-Dibromobenzene		811	809
p-Chloroiodobenzene		811	809
p-Tolunitrile	814		
p-Chlorobromobenzene		816	
p-Fluorotoluene	818		
p-Dichlorobenzene		820	817
p-Hydroquinone		827	
p-Nitroaniline		837	845*
p-Nitrobromobenzene		839	839
p-Nitrochlorobenzene		843	847
p-Aminobenzoic acid		841	848**
p-Toluic acid		843	
p-Chlorobenzoic acid		853	
p-Bromobenzoic acid		853	
p-Hydroxybenzoic		856	
p-Dinitrobenzene		870	867
p-Nitrobenzoic acid		874	
Terephthalic acid		882	
p-Quinone		895	

All solution spectra were obtained using CS_2 as solvent except those marked *-in N,N-dimethylformamide **-in acetone

Thorndike, Wells, and Wilson,[8] using both the in-plane and out-of-plane C-H bending vibrations in ethylene, found that the bond moment value obtained from the 950 cm^{-1} out-of-plane mode was almost twice that obtained from the 1444 or 995 cm^{-1} in-plane bands. The values calculated from the latter modes were approximately equal to the bond moment value usually associated with C-H bonds.

Recently, a theory has been proposed which can be directly applied to the anomalous bond moments in ethylene as well as to the interpretation of the frequency and intensity variance of C-H out-of-plane bending vibrations in substituted benzenes. This theory concerns the variation of bond hybridization with molecular deformation,[9,10,11] by which the bonding orbitals of the central atom change their hybridization in such a manner as to follow the outer atoms during the vibration. The greater the change in hybridization the greater will be the reduction in effective force constant for the particular vibration.

In ethylene, the in-plane bending vibrations of sp^2 C-H bonds are not affected by the π-electron bond, which has a node in the

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(8) A. M. Thorndike, A. J. Wells, and E. B. Wilson, Jr., J. Chem. Phys. 15, 157 (1947).

(9) C. A. Coulson, V. Henri Mem. Nol., Desoer, Liege, 1948, p. 15.

(10) J. Duchesne, Bull. Acad. roy. Belg. 38, 197 (1952).

(11) J. W. Linnet and P. J. Wheatley, Nature, 161, 971 (1948); Trans. Faraday Soc. 45, 33 (1949).

plane of the ethylene molecule. However, in vibrating perpendicular to the plane, the C-H bonds enter the field of the π-bond and through overlap tend to become sp^3 hybrids.[10] Since it is known that the bond moments of sp^2 and sp^3 hybrids differ,[12] the theory explains the ethylene anomoly. It should be noted that bond moment calculations from out-of-plane vibrations are of no real physical significance, since the bond moments are constantly changing with the degree of penetration into the π-bond. The value obtained from any calculation using an out-of-plane C-H mode is, at most, a time average. The difference between this "bond moment" and one calculated from an in-plane mode merely points up the role played by the π-electrons.

The degree of transformation of an sp^2 bond into an sp^3 bond depends, of course, on the concentration of π-electrons above the atom in question. For benzenoid systems, the π-electron density depends upon the nature of the substituents, i.e., whether they increase, decrease, or have no effect upon the π-electrons of the ring. The force constant, and thus the frequency, of the out-of-plane C-H bending vibrations of the benzene ring therefore depends on the sp^3 bond tendency, and thus the concentration of π-electrons above and below the ring. The smaller the concentration, the higher the frequency, and vice versa (other factors being equal).

Electrophilic groups, such as nitro or carboxyl, when coplanar with the aromatic ring, resonate with the ring with a resultant

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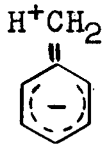
(12) C. A. Coulson, Trans. Faraday Soc., <u>38</u>, 433 (1942).

withdrawal of π-electrons to themselves. This lowers the concentration of π-electrons above and below the ring and, in accord with the above theory, the smaller change of hybridization results in higher C-H out-of-plane bending vibrations.

The effect of electron donating groups on the C-H out-of-plane bending vibrations can also be considered from the π-electron viewpoint. Thus, although the amino group is generally considered as a stronger donor than the methyl group, the latter can hyperconjugate with the ring to give a structure in which the π-electrons are concentrated above and below the five ring C-H bonds, thus



The frequency of toluene is therefore lower (728 cm^{-1}) than aniline (755 cm^{-1}).

The difference in the C-H out-of-plane bending frequencies of benzonitrile (756 cm^{-1}) and nitrobenzene (790 cm^{-1}) lends support to the arguments of this paper. Although the nitrile and the nitro groups are of approximately equal strength as meta-orienting substituents, the two groups have different effects upon the π-electron distribution of the benzene ring. The nitro group has mainly a mesomeric influence upon the ring, because it readily conjugates with the aromatic system and depletes it of π-electrons. The nitrile group, on the other hand, basically exerts an inductive effect on the benzene ring by modifying the potential acting on the π-electrons.[13] Consequently, the π-electron

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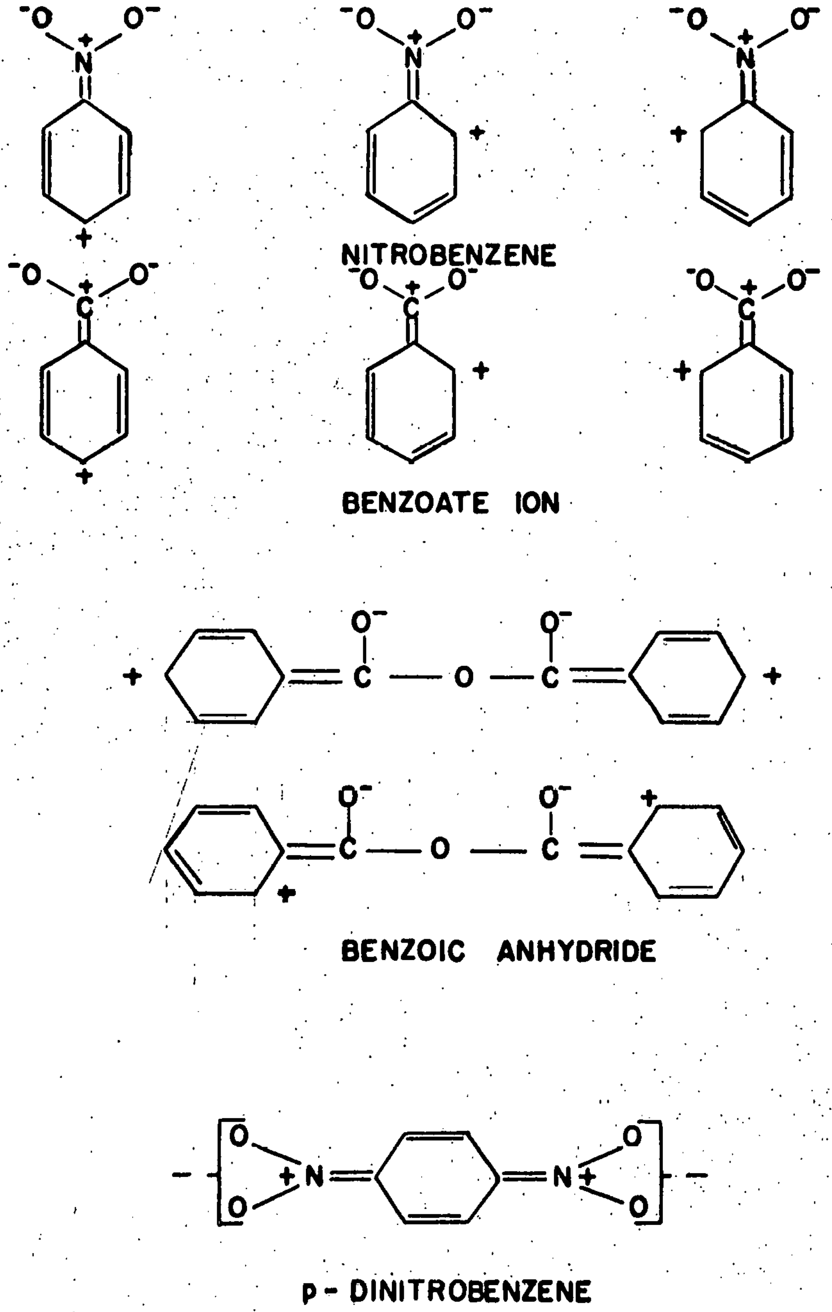
(13) J. N. Murrel and H. C. Longuet-Higgins, Proc. Phys. Soc., A68, 329 (1955).

concentration of the benzonitrile ring is greater than the concentration in nitrobenzene and so the C-H out-of-plane bending vibrations of the latter are of higher frequency.

The pronounced intensity changes which accompany the shift in frequency of the out-of-plane C-H bending vibration can be directly correlated with the degree of rehybridization of sp^2 into sp^3 hybrids. For example, since C-H bond moments are greater for sp^3 bonds than for sp^2 bonds, the lower degree of rehybridization in nitrobenzene leads to smaller C-H bond moments than in phenol, where rehybridization is greater. Because infrared intensities are proportional to dipole moment changes during vibrations, the vibrations showing a frequency increase also exhibit the decrease in intensity. For compounds whose frequency falls in the normal range, the observed intensities are relatively great, indicating a high degree of rehybridization into sp^3 bonds.

The withdrawal of π-electrons from the ring can be directly associated with the contribution of quinoid structures to the ground states of the molecules. Thus, all the monosubstituted benzenes having C-H out-of-plane bending vibrations greater than 770 cm^{-1}, as listed in Table I, have electronic structures in which a quinoid form plays a considerable role. Sodium benzoate, having the highest frequency in the Table, undoubtedly has the greatest contribution of this structure due to the symmetrical nature of the resultant form. Figure 2 illustrates some contributing quinoid structures.

The large shifts observed for the para-disubstituted benzenes are also interpretable on the basis of bond rehybridization and



NITROBENZENE

BENZOATE ION

BENZOIC ANHYDRIDE

p-DINITROBENZENE

Fig. 2 - Contributing resonance structures.

quinoid resonance contributions. Figure 2 includes a major resonance form for p-dinitrobenzene, which accounts for the increased C-H out-of-plane bending frequency (listed in Table II). Carboxyl groups and other substituents which can contribute similar resonance structures affect the frequency similarly. If the para-disubstituted benzene contains only one substituent which is electrophilic the shift is approximately only half as great. A comparison of the C-H out-of-plane frequencies for p-dibromobenzene (811 cm^{-1}) and p-nitrobromobenzene (839 cm^{-1}) reveals that the introduction of one nitro group causes a shift of 28 cm^{-1}, while in p-dinitrobenzene (874 cm^{-1}) there is an additional shift of 35 cm^{-1}. The displacements to higher frequency in these compounds are therefore directly related to the per cent of quinoid structure making up the ground states of the various molecules.

p-Quinone and p-hydroquinone provide particularly strong confirming data for the role of the π-electrons. p-Quinone has almost a pure quinoid structure and shows the highest frequency in Table II (895 cm^{-1}), whereas p-hydroquinone, with a predominant benzenoid structure, has the corresponding vibration at 827 cm^{-1}.

The theory of orbital rehybridization provides a consistent explanation of anomolous frequency shifts in C-H out-of-plane bending vibrations which have come to the authors' attention. Take, for example, the isomeric compounds 2,4- and 2,5-dimethylbenzoic acid. Even though both are 1,2,4-trisubstituted, the 2,4-dimethylbenzoic acid has its characteristic band at 841 cm^{-1} while the 2,5-acid has its band at 822 cm^{-1}. Figure 3 shows that the 2,4-isomer can contribute a quinoid resonance structure to the ground state of the molecule through a hyperconjugation of the methyl

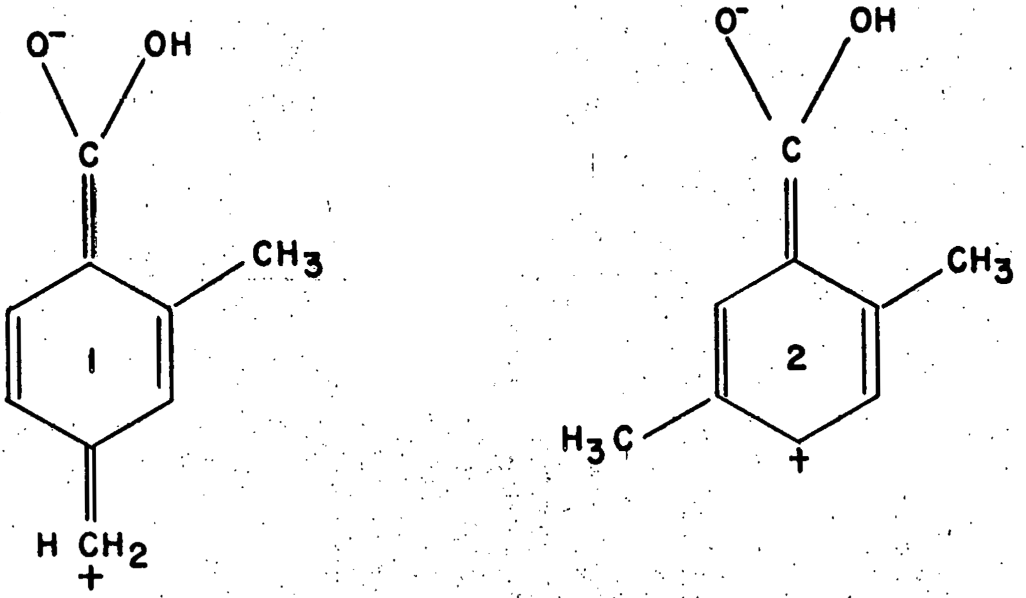


Fig. 3 - Resonance structures for 1) 2,4-dimethylbenzoic acid and 2) 2,5-dimethylbenzoic acid.

group in the 4-position with the benzene ring and the para carboxyl group. The 2,5-isomer cannot assume this extended form of conjugation, so that the π-electron structure of that molecule is less affected.

An additional case which is easily explained is found in the spectra of phenylacetic acid, diphenylacetic acid, and triphenylacetic acid, shown in the 13-14 micron region in Figure 4. It is seen that phenylacetic acid has a single absorption band at 13.27 microns (754 cm^{-1}), diphenylacetic acid has two absorption bands at 13.32 and 13.63 microns (750 and 734 cm^{-1}) of about equal intensity (notice that the lower frequency band is slightly less intense), and triphenylacetic acid has two absorption bands at 13.13 and 13.60 microns (761 and 735 cm^{-1}), with the latter about twice as strong as the former. Fisher-Taylor-Hirschfelder models of these compounds indicate that steric factors do not permit more than one phenyl ring to be coplanar with the carbonyl group. The coplanar phenyl group can form a conjugated system with the carbonyl group by assuming a quinoid structure, which gives rise to the higher frequency band at 755 cm^{-1}. Additional phenyl groups that are introduced onto the methyl carbon cannot interact with the conjugated system, and thus remain as benzenoid configurations. The latter give rise to the band at ca. 734 cm^{-1}, whose intensity depends on the number of benzenoid groups present.

Electrophilic groups must be coplanar with the aromatic ring for the full effect of resonance to take place. This is well illustrated for the case of a few ortho-disubstituted benzenes. In o-nitrophenol and o-nitroaniline, where intramolecular hydrogen

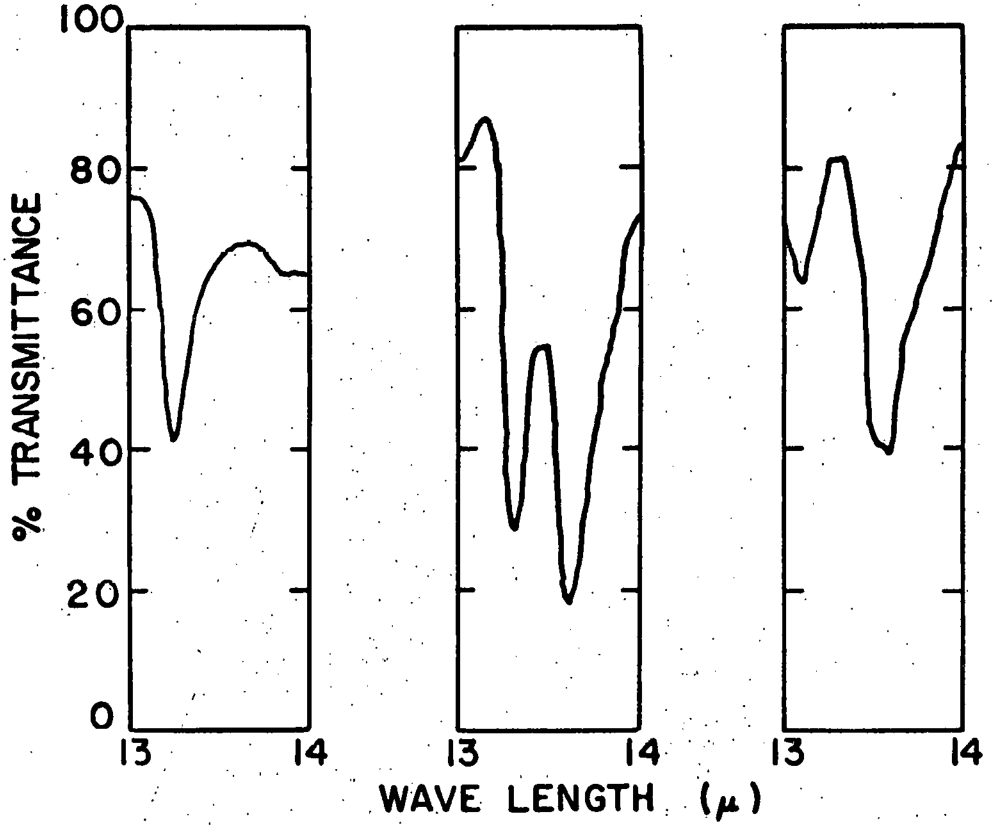


Fig. 4 - Spectra from 13-14 μ of (from left to right) phenylacetic acid, diphenylacetic acid, and triphenylacetic acid as mineral oil slurries.

bonding between the nitro group and the OH or NH_2 group stabilizes the nitro group in the plane of the ring, the C-H bending frequencies are 748 and 747 cm^{-1}, respectively. In o-chlorobenzene and o-bromobenzene, where the steric influence of the large halogen substituents causes rotation of the nitro groups out of the plane of the ring, the C-H bending frequencies are 732 and 731 cm^{-1}, indicating decreased withdrawal of π-electrons from the ring. Similarly, in the corresponding carboxylic acids the carboxyl group is in the plane of the ring in salicylic acid[14] (762 cm^{-1}) and may be assumed to be in the plane of the ring in anthranilic acid (755 cm^{-1}) and rotated out of the plane of the ring in o-chloro and o-bromobenzoic acid (744 cm^{-1} for both).

In a recent infrared study of picric acid molecular complexes by two of the authors,[15] it was shown that the C-H out-of-plane bending vibrations of picric acid molecules involved in π - π complexes were of lower frequency than the same vibration in pure picric acid. Since picric acid in the π - π complexes acts as the acceptor molecule, i.e., a π-electron is transferred to one of its vacant molecular orbitals, the π-electron density around that molecule is thereby increased. Accordingly, the C-H bonds vibrating perpendicular to the plane of the complexed picric acid

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(14) W. Cochran, Acta Cryst., 6, 260 (1953).

(15) R. D. Kross and V. A. Fassel, Submitted to this Journal for publication.

molecules undergo greater changes in hybridization than the equivalent C-H bonds in pure picric acid, resulting in lower frequencies of the out-of-plane bending vibrations. On the other hand the C-H out-of-plane bending vibrations in the electron donor molecules involved in the $\pi - \pi$ complexes with picric acid are observed at a higher frequency than in the pure molecule.