52 cm.$^{-1}$ in the two compounds. The difficulty with this interpretation is the absence of a difference tone $\nu_6 - 2\nu_{14}$ in either spectrum. However, a similar difficulty arises with structures of lesser symmetry, including a non-linear Si–O–Si model, in which the band could be attributed to $\nu_6 + \nu_{14}$. Possibly the absence of a difference band may be due to a slightly bent structure in the vibrationless ground state, which becomes linear on the average when the Si–O–Si bending mode is excited to the first quantum state above ground. On this basis the summation tone might be much more intense than the corresponding difference tone. In this event ν_{14} would be placed at 112 cm.$^{-1}$ in disiloxane and at 105 cm.$^{-1}$ in disiloxane-d_6.

The other combination bands in the infrared spectra are readily explicable (Tables I and II) on the basis of D_{3d} selection rules, with the exception of the 1710 band in disiloxane-d_6. It is possibly due to an impurity.

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Cambridge, Mass.

[Contribution No. 428 from the Institute for Atomic Research and Department of Chemistry, Iowa State College]

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[1]

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

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In certain monosubstituted and *para*-disubstituted benzenes the frequency of one of the C–H out-of-plane bending vibrations falls above the characteristic frequency range assigned to that vibration. A property common to all of the substituents which cause this positive shift in frequency is that they are electrophilic in nature, *i.e.*, they tend to deplete the aromatic nucleus of π-electronic charge. These experimental observations are consistent with the theory of orbital following during molecular vibrations. The depletion of π-electron density of the aromatic nucleus by electrophilic substituents leads to a decreased ability of the carbon bonding orbitals to follow the out-of-plane movement of the hydrogen atoms. This results in higher bending vibration frequencies because the vibrations occur with greater difficulty as orbital overlap decreases. Applications of this theory to other spectral anomalies are also discussed.

Various observations[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 anomalous 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.[1,2a]

I. Results

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 Fig. 1, whereas the spectra of the group of compounds in the lower portion of Fig. 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. The same groups which give rise to the shifts in monosubstituted benzenes also cause corresponding shifts in the *para*-disubstituted benzenes (Table II). When both *para*-positions are occupied by one of these groups, the shift from the normal frequency range is even larger. The data summarized in Tables I and II show that the increase in frequency caused by certain groups is basically an intramolecular interaction, since there is no significant frequency difference between spectra obtained from the solid state and from dilute solutions.

II. Discussion

A. Orbital Rehybridization during C–H Out-of-plane Bending Vibrations.—A characteristic common to all of the substituents which cause a positive shift in C–H out-of-plane bending frequencies in both mono- and *para*-disubstituted compounds is that they are electrophilic in nature, *i.e.*, the substituents tend to deplete the aromatic nucleus of π-electronic charge. This suggests that the π-electrons located above and below the plane of the benzene ring exert a significant influence on the out-of-plane C–H bending vibrations. Independent supporting evidence for this interaction resides in the theory of the variation of bond hybridization during molecular deformations.[4-6] This theory has provided an explanation for the anomalously large C–H bond moments obtained from the

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[1] Work was performed in the Ames Laboratory of the Atomic Energy Commission.

[2] (a) M. Margoshes and V. A. Fassel, *Spectrochim. Acta*, **7**, 14 (1955); (b) M. St. C. Flett, *J. Chem. Soc.*, 962 (1951).

[3] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., p. 68.

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TABLE I

CHARACTERISTIC FREQUENCIES FOR VARIOUS SUBSTITUENT GROUPS IN MONOSUBSTITUTED BENZENES IN VARIOUS STATES[a]

Compound	Substituent group	Frequency (cm.$^{-1}$) Liquid	Solid	Dilute soln.
Toluene	$-CH_3$	728		729
Aniline·HCl	$-NH_3^+$		741	
Benzyl alcohol	$-CH_2OH$	736		735
Ethylbenzene	$-C_2H_5$	747		
Phenyl acetate	-OOCR	752		
Phenol	-OH		753	750
Sodium benzenesulfonate	$-SO_3Na$		754	
Aniline	$-NH_2$	755		
Benzenesulfonyl chloride	$-SO_2Cl$	757		
Anisole	$-OCH_3$	756		753
Triphenylmethane	-CH		762	
Benzonitrile	-CN	758		756
Acetophenone	-COR	761		757
trans-Stilbene	-C=		767	
Benzamide	$-CONH_2$		771	
Benzoyl chloride	-COCl	779		
Benzoic anhydride	-COOCO		779	
Nitrobenzene	$-NO_2$	794		790
Benzoic acid	-COOH		808	
Ethyl benzoate	-COOEt		782 or 806	780 or 804
Sodium benzoate	$-COO^-$		820	

[a] All solution spectra were obtained using CS_2 as solvent.

TABLE II

OUT-OF-PLANE C–H BENDING FREQUENCIES FOR SOME *para*-DISUBSTITUTED BENZENES[a]

Compound	Frequencies cm^{-1} Liquid	Solid	Dilute soln.
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[b]
p-Nitrobromobenzene		839	839
p-Nitrochlorobenzene		843	847
p-Aminobenzoic acid		841	848[c]
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	

[a] All solution spectra were obtained using CS_2 as solvent except those marked. [b] In N,N-dimethylformamide. [c] In acetone.

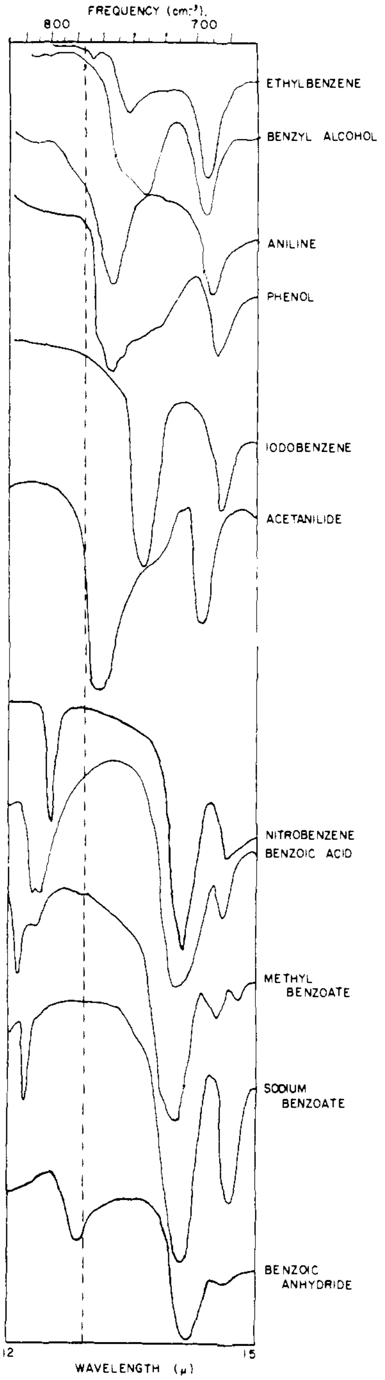

Fig. 1.—Normal and abnormal frequency patterns in monosubstituted benzenes.

intensities of C–H vibrations associated with these deformations,[7,8] and also appears to provide a consistent explanation for not only the observed frequency shifts but also the pronounced decrease in intensity generally accompanying these shifts.

In all bending vibrations, the bonding orbital of the central atom tends to follow the direction of the outer atom. This tendency can be most completely fulfilled for out-of-plane C–H bending vibrations in unsaturated systems because the carbon sp^2 bond, in following the hydrogen atom, enters the field of the π-electrons and, through overlap with these electrons, is transformed into a hybrid containing some sp^3 character. The more the carbon bond-

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

(8) R. P. Bell, H. W. Thompson and E. A. Vago, *Proc. Roy. Soc.* (*London*), **A192**, 498 (1948).

ing orbital is able to follow the movement of the hydrogen atom by changing its hybridization, the more easily the vibrations will occur, and hence relatively lower vibration frequencies should result. In benzenoid systems, this following tendency is a maximum in compounds having a maximum π-electron density associated with the ring. When the π-electron concentration is depleted by electrophilic substituents, there is less tendency for the carbon bonding orbitals to follow the attached hydrogen atoms during a bending vibration. Thus, the effective force constant for the vibration is not sensibly reduced, and relatively higher out-of-plane C–H bending frequencies should result.

B. Application of the Theory to Spectral Data. Monosubstituted Benzenes.—Substituent groups which donate π-electrons, through some mesomeric form, or which have little effect on the π-electron density of the ring show frequencies in the usual 725–775 cm.$^{-1}$ region (see Table I and Fig. 1). These frequencies are the result of a significant overlap of the σ-bonds and the π-electrons of the ring during the course of the C–H out-of-plane bending vibration. Substituent groups that are electrophilic with respect to π-electrons show the predicted higher frequencies, which result from the reduced ability of the carbon bonding orbitals to follow the ring hydrogens during the vibration. The difference in the C–H out-of-plane bending frequencies of benzonitrile (756 cm.$^{-1}$) and nitrobenzene (790 cm.$^{-1}$) is in full agreement with this argument. Although the nitrile and 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.[9] Consequently, the π-electron concentration of the benzonitrile ring is greater than the concentration in nitrobenzene, resulting in a significantly higher frequency for nitrobenzene.

An attempt was made to determine if the other C–H out-of-plane bending vibrations, which fall at higher frequencies, showed similar positive shifts as a result of the action of electrophilic substituents. However, because of the complexity of these higher frequency regions, the bands corresponding to these vibrations were not generally assignable.

***para*-Disubstituted Benzenes.**—In *para*-substituted toluenes and the *para*-dihalobenzenes the minimum depletion of π-electron density around the ring results in C–H bending frequencies in the usual range of 800–820 cm.$^{-1}$ for *para*-disubstituted benzenes (see Table II). Replacement of one inert substituent by an electrophilic group is manifested by the expected increase of the C–H frequencies to the 840–855 cm.$^{-1}$ region. Replacement of both inert substituents by electrophilic groups results in a further decrease in π-electron density, and thus gives rise to frequencies in the 870–885 cm.$^{-1}$ region. The shift is most pronounced in *p*-quinone (895 cm.$^{-1}$), which essentially has only four π-electrons associated with its ring, instead of the six π-electrons common to benzenoid systems (*cf.* *p*-hydroquinone, 827 cm.$^{-1}$).

***ortho*-Disubstituted Benzenes.—Role of Steric Influence.**—Electrophilic groups must be coplanar with the aromatic ring for the full effect of resonance to take place. In *o*-nitrophenol and *o*-nitroaniline, where intramolecular hydrogen 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*-chloronitrobenzene and *o*-bromonitrobenzene, where the steric influence of the 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.$^{-1}$, respectively, 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[10] (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).

Miscellaneous Compounds.—The theory of orbital rehybridization provides a consistent explanation of other anomalous frequency shifts in C–H out-of-plane bending vibrations which have come to the authors' attention. The isomeric compounds 2,4- and 2,5-dimethylbenzoic acid are a good example. Although 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 2 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 group in the 4-position with the benzene ring and the *para*-carboxyl group. This results in a decreased π-electron density on the ring and a lower out-of-plane C–H vibration frequency. The 2,5-isomer cannot assume this extended form of conjugation, so that the π-electron structure of that molecule is less affected.

The spectra of phenylacetic acid, diphenylacetic acid and triphenylacetic acid, shown in the 13–14 μ region in Fig. 3, are consistent with this theory. It is seen that phenylacetic acid has a single absorption band at 13.27 μ (754 cm.$^{-1}$), diphenylacetic acid has two absorption bands at 13.32 and 13.63 μ (750 and 734 cm.$^{-1}$) of about equal intensity (the higher frequency band is slightly less intense), and triphenylacetic acid has two absorption bands at 13.13 and 13.60 μ (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, which gives rise to the higher frequency band at 755 cm.$^{-1}$. Additional phenyl groups on the methyl carbon cannot interact with the conjugated system, so that

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[9] See, for example, J. N. Murrel and H. C. Loguet-Higgins, *Proc. Phys. Soc.*, **A68**, 329 (1955).

[10] W. Cochran, *Acta Cryst.*, **6**, 260 (1953).

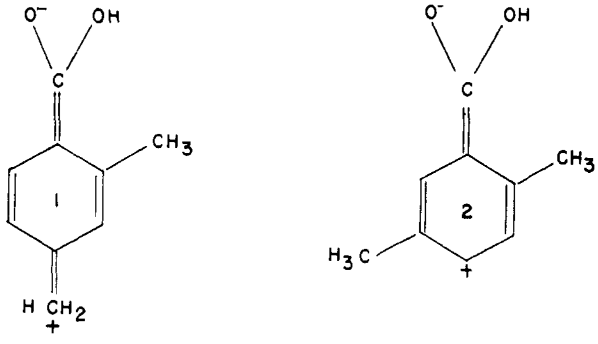

Fig. 2.—Resonance structures for: (1) 2,4-dimethylbenzoic acid and (2) 2,5-dimethylbenzoic acid.

the π-electron density associated with their rings is somewhat greater than that of the conjugated phenyl group. The non-conjugated rings give rise to the band at *ca.* 734 cm.$^{-1}$, whose intensity depends on the number of these groups present.

Intensity Changes Related to the Degree of Rehybridization.—The pronounced intensity change which accompanies the positive shift in frequency of the out-of-plane C–H bending vibration results directly from the decreased π-electron concentration around the ring. Eggers[11] has recently shown, on the basis of orbital following, that π-electrons give a dipole moment perpendicular to the molecular plane which is in addition to that produced by the C–H bonds vibrating normal to that plane. These two moments interact so that the total dipole moment change is manifested in the intensity of the C–H out-of-plane bending vibration bands. A decrease in π-electron concentration therefore gives rise to both a positive shift in frequencies and lower intensity bands.

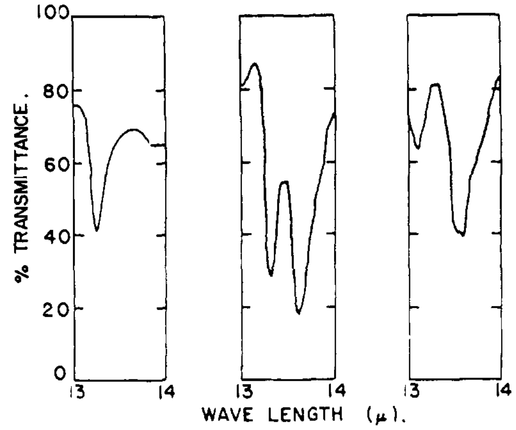

Fig. 3.—Spectra from 13–14 μ of (from left to right) phenylacetic acid, diphenylacetic acid and triphenylacetic acid as mineral oil slurries.

AMES, IOWA

[11] D. F. Eggers, Jr., *J. Chem. Phys.*, **23**, 221 (1955).

[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY OF CLARK UNIVERSITY]

Tetraphenylporphine and Some *para*-Substituted Derivatives[1,2]

BY DANIEL W. THOMAS AND ARTHUR E. MARTELL

RECEIVED SEPTEMBER 22, 1955

Tetraphenylporphine and its *para* methyl, methoxy, chloro and nitro derivatives have been synthesized by direct reaction of pyrrole with the corresponding aldehyde. Chlorins and other by-products were separated chromatographically and characterized by spectrophotometric analysis. The yields of main product decrease as the acceptor activity of the aldehyde carbonyl increases.

Since the early investigations of the preparation and properties of porphine by Fischer and Gleim[3] and by Rothemund,[4] the recent studies of tetraphenylporphine[5–7] and of other $\alpha,\beta,\gamma,\delta$-tetrasubstituted porphyrins[8,9] have provided further information and a greater understanding of the structure and internal bonding in chelate compounds derived from porphine. The purpose of this investigation was to prepare and study a number of derivatives of tetraphenylporphine in which the *para* positions have been substituted with polar groups having well-known inductive and resonance effects. This study is the first part of a more extensive investigation which includes a study of various metal chelates of these substituted tetraphenylporphines.

The synthesis of tetraphenylporphine has been reported previously[10–13] and the isolation of the *p*-methoxy derivative also has been reported by Rothemund.[8] None of the other derivatives of tetraphenylporphine prepared in this Laboratory have appeared in the literature.

Discussion of Results

Synthesis.—The method of synthesis which proved most satisfactory for the purposes of this investigation is the direct one-step procedure simi-

[1] This research was supported by the National Institute of Health of the U. S. Public Health Service under Grant No. G-3819(c).

[2] Abstracted from a dissertation submitted by Daniel W. Thomas to the Faculty of Clark University in partial fulfillment of the requirements for the degree of Master of Arts.

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