[CONTRIBUTION FROM THE PHYSICAL SCIENCES LABORATORY, MELPAR, INC.]

Ultraviolet Spectra of 1,2,3-Trisubstituted Aromatic Compounds

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The ultraviolet spectra of some 1,2,3-trisubstituted aromatic compounds were compared with the spectra of the corresponding reference compounds. The extensive hypsochromic and hyperchromic shifts noted are discussed in terms of steric interaction and hydrogen bonding.

In the course of another research program, it became desirable to determine the ultraviolet spectrum of 2-hydroxy-3-methoxybenzoic acid. Comparison of this spectrum with the spectra of benzoic acid, 2-hydroxybenzoic acid, 3-methoxybenzoic acid and 2-methoxyphenol indicated the following:

1. The absorption maximum of *ortho-* or *meta-*substituted benzoic acid is at a longer wave length than is benzoic acid itself.
2. The absorption maximum of the B-band of 2-hydroxy-3-methoxybenzoic acid is at a shorter wave length than any of the other reference compounds listed above.
3. The extinction coefficient of the B-band of 2-hydroxy-3-methoxy benzoic acid is considerably higher than the extinction coefficient of any of the reference compounds. In view of this observation, it was decided to examine the spectra of other 1,2,3-trisubstituted aromatic compounds to determine if this were a general phenomenon.

In selecting the compounds to be studied, the following criterion was established: the compound must contain two *ortho* functional groups which might react through hydrogen bonding. A series of sixteen such compounds was obtained and the spectra compared to the spectra of the corresponding reference compounds (Table I). It was evident that in each case (with two exceptions) the maximum was shifted to a shorter wave length, and in each case (with two exceptions) the extinction coefficient was increased.

These exceptions were 3-methyl-2-hydroxybenzoic acid and 2,3-dimethoxybenzoic acid. One other compound, 3-chloro-2-hydroxybenzoic acid apparently gave no significant shift, either of wave length or of extinction coefficient. Although a much more limited sample of disubstituted benzaldehydes and phenols was studied, they too, exhibited the same shift.

The nomenclature of the absorption bands is that of previous workers.[1,2] This assigns the alphabetical order of A, B, and C to the bands proceeding from slightly below 200 mμ to longer wave lengths. The B-band normally lies between 200–320 mμ whereas the C-band is normally found in the 260–370-mμ region.

Forbes and Mueller[3] in a recent publication discuss the "buttressing effect" of the interaction occurring due to a *m*-substituent exerting an indirect steric effect on the *o*-substituent; in this way a *m*-substituent may alter the steric interaction of the other two vicinal substituents. A large number of examples were given of *m*-disubstituted benzenes and in most cases, the extinction coefficient was decreased; also when a shift was observed, it was usually to a slightly longer wave length.

Forbes and Mueller[3] further postulate that "the introduction of large *m*-substituents appears to inhibit some of the conjugation, as shown by the decreased absorption intensity or disappearance of the B-band."

If, as Forbes and Mueller[3] suggest, large *m*-substituents have an effect on the *o*-hydrogen interaction with the other vicinal functional group, then similar, and even larger effects should be noted, as in the example of 2-hydroxy-3-methoxybenzoic acid. However, the effect is exactly reversed. The wave length and absorption coefficient are shifted in the opposite direction as predicted when considering the "buttressing effect." The reference compound, 3-methoxybenzoic acid and indeed, all of the other 3-substituted reference compounds in this study, show the effects predicted by Forbes and Mueller. The major difference in the compounds in this study and those studied by Forbes is in the 2- position. All the compounds studied herein contain hydroxyl, methoxy, or nitro groups whereas all of Forbes's compounds have a hydrogen in that position. It is probable that these functional groups have hydrogen bonding tendencies. The steric effect of a bulky 3-substituent could possibly enhance this hydrogen bonding through a "buttressing effect."

An alternate and perhaps more plausible suggestion could be that these spectral changes are entirely due to the effect of steric conformation, rather than due to increased hydrogen bonding. These three adjacent functional groups could sterically interact and therefore influence the spectrum.

The effect of *ortho* substituents on the spectra of

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(1) C. M. Mosher and A. I. Kohlenberg, *J. Chem. Soc.*, 804 (1951).

(2) W. J. Forbes, W. A. Mueller, A. S. Ralph, and J. F. Templeton, *Can. J. Chem.*, **35**, 1049 (1957).

(3) W. F. Forbes and W. A. Mueller, *J. Am. Chem. Soc.*, **79**, 6495 (1959).

benzaldehyde, acetophenone and benzoic acid has been extensively studied.[4,5] An "*ortho*" effect has been postulated that effectively explains the observed phenomenon.

Maximum electronic interaction requires that *ortho* substituents be effectively planar. *ortho* Substituents which have radii large enough to inhibit this planarity raise the energy of the excited state more than the energy of the ground state—*i.e.*, the transition energy increases and the λ_{max} is shifted to shorter wave lengths.[6] *ortho* Hydroxyl groups also produce a steric reduction in the absorption intensity accompanied by a rather large bathochromic shift.[7] Hydrogen bonding, no doubt, also comes into play and accounts in part, for the large spectral differences in the hydroxy and methoxy substituted ketones.

The shift of λ_{max} of the B-band to a shorter wave length for the spectra of the compounds studied in this laboratory is in accord with expectations. The steric requirements of three functional groups is presumed to cause some steric hinderance to planarity, thus increasing the transition energy and shifting the maximum to shorter wavelengths. The sharp increase in the extinction coefficient is probably due to a combination of two factors.

1. The low wave lengths for λ_{max} are probably situated on the lower portion of the tail of a very strong A-band. This tail would contribute a very significant portion of the total absorption in this region.
2. The summation of two bands with a partial overlap is additive. Thus when these two bands are recorded, and when one of the bands has an extremely high extinction coefficient (10^5 for A-bands) there is a tendency for the λ_{max} of the B-band to shift in the direction of the much higher A-band.

Because of these two factors, and the unknown position of the A-band maximum, it is very difficult to measure the exact magnitude of the shift. The only readily ascertainable fact is that the shift is in the expected direction.

Two types of spectral effects are recognized in studying steric interactions. In type (1), the extinction coefficient is reduced without significant change of λ_{max}.[8] In type (2), both the extinction coefficient is changed and a hypsochromic shift is observed.[8] Type (1) is encountered where steric inhibition is rather weak and type (2) effects are usually encountered where steric inhibition is comparatively strong. The compounds used in this study appear to undergo a type (2) effect.

Although previous workers are not in complete agreement as to the effect of hydrogen bonding on the B-band[9-11] no such disagreement is evident in discussions concerning the effect of hydrogen bonding on the C-band. The C-band is comparatively insensitive to small steric effects but is useful for detecting hydrogen bonding, as hydrogen bonding gives rise to a more pronounced band at a longer wave length. A comparison of the spectra of 2-hydroxy- and 2-methoxy-substituted benzoic acids and acetophenones shows that the hydroxyl substituted compounds absorb at longer wave lengths. This has been rationalized in two ways. It may be due to increased planarity of the molecule[10] or to increased polarization.[11]

Examination of the spectra of the compounds used in this study shows that in most cases, the λ_{max} of the C-band has been shifted to longer wave lengths. Several significant discrepancies to the preceding statement may be observed; notably those compounds where the *ortho* substituent is a methoxy group. This would largely eliminate the the effect of hydrogen bonding.

Although the discussion has so far considered only disubstituted benzoic acids, it was found that several disubstituted benzaldehydes and several disubstituted phenols also seem to undergo the same type of shifts (Table I). The λ_{max} is at a much lower wave length than is any of the reference compounds and the extinction coefficient of the B-band is considerably higher. The λ_{max} of the C-band of the 3-methoxysalicylaldehyde is 15 mμ higher than is that of salicylaldehyde itself. However, the λ_{max} of the C-band of 2,3-dimethoxybenzaldehyde is the same as that of 2-methoxybenzaldehyde.

Insufficient examples were available for a more thorough investigation of the generality of this phenomenon.

EXPERIMENTAL

Commercial samples of chemicals were of the highest available purity and were recrystallized from appropriate solvents until the melting points agreed with, or exceeded literature values. The ultraviolet spectra were run in Spectro grade methanol (Matheson, Coleman, and Bell) using a Bausch and Lomb ultraviolet spectrophotometer, Model 505 with 1-cm. matched silica cells. The concentration varied from $6 \times 10^{-5}M$ to $1.5 \times 10^{-4}M$.

Preparation of 3-methoxysalicylic acid. A suspension of freshly prepared silver oxide (0.4 mole) in 500 ml. of water

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(4) See E. A. Braude and co-workers, *J. Chem. Soc.*, 1945–1956, for extensive references.

(5) See W. F. Forbes and co-workers, *Can. J. Chem.*, 1955, to present.

(6) E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3754 (1955).

(7) See leading references in (6) above.

(8) E. A. Braude, F. Sondheimer, and W. F. Forbes, *Nature*, 117 (1954).

(9) R. A. Morton and A. L. Stubbs, *J. Chem. Soc.*, 1347 (1946).

(10) W. F. Forbes and W. A. Mueller, *Can. J. Chem.*, **34**, 1340 (1956).

(11) A. Burawoy, M. Cais, J. T. Chamberlain, F. Liversedge, and A. R. Thompson, *J. Chem. Soc.*, 3727 (1955).

(12) I. A. Pearl, *J. Am. Chem. Soc.*, **68**, 431 (1946).

TABLE I
Ultraviolet Spectra of 1,2,3-Trisubstituted Aromatic Compounds^a

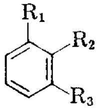
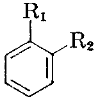
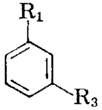
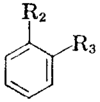
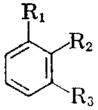
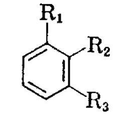
Disubstituted Benzoic Acids					Reference Compounds											
																
R_1	R_2	R_3	λ_{max}	ϵ	R_1	R_2	λ_{max}	ϵ	R_1	R_3	λ_{max}	ϵ	R_2	R_3	λ_{max}	ϵ
CO_2H	OH	OCH_3	221	12,300^{a,b}	CO_2H	OH	236	8,900^c	CO_2H	OCH_3	230	6,800^c	OH	OCH_3	274	2,600^d
			244	5,200			306	3,700			293	2,500				
			312	3,700												
CO_2H	OH	NO_2	228	12,400	CO_2H	OH	236	8,900^c	CO_2H	NO_2	260	6,200	OH	NO_2	272	6,000^e
			334	4,000			306	3,700			356	120			346	3,200
CO_2H	OH	CH_3	241	7,900	CO_2H	OH	236	8,900^c	CO_2H	CH_3	232	8,900^c	OH	CH_3	275	2,000^d
			308	4,700			306	3,700			279	1,000				
CO_2H	OH	Cl	230	8,700	CO_2H	OH	236	8,900^c	CO_2H	Cl	230	8,300^c	OH	Cl	278	2,400^f
			315	3,300			306	3,700			284	960				
CO_2H	OH	Br	228	18,000	CO_2H	OH	236	8,900^c	CO_2H	Br	225	8,300^c	OH	Br	279	2,800^f
			324	3,300			306	3,700			280	830				
OCH_3	CO_2H	OCH_3	205	27,000^c	CO_2H	OCH_3	230	6,200^c	OCH_3	OCH_3	274	2,800^g	—	—	—	—
			282	1,800			291	2,700			284	2,400				
CO_2H	OCH_3	OCH_3	240	3,100^{a,h}	CO_2H	OCH_3	230	6,200^c	CO_2H	OCH_3	230	6,800^c	OCH_3	OCH_3	274	2,800^g
			293	2,900			291	2,700			293	2,500			284	2,400
OH	CO_2H	OH	222	15,800	CO_2H	OH	236	8,900^c	OH	OH	274	1,900^i	—	—	—	—
			255	9,200			306	3,700								
			303	3,400												
			~320	2,400												
CO_2H	NO_2	CH_3	222	9,300	CO_2H	NO_2	~253	2,500	CO_2H	CH_3	232	8,900^c	NO_2	CH_3	260	6,300^j
			278	1,600							279	1,000			340	200
			287	1,500												
CO_2H	NO_2	OCH_3	215	8,900	CO_2H	NO_2	~253	2,500	CO_2H	OCH_3	230	6,800^c	NO_2	OCH_3	259	3,500^g
			298	2,100							293	2,500			317	2,600
CO_2H	NH_2	CH_3	221	20,000	CO_2H	NH_2	248	6,600	CO_2H	CH_3	232	8,900^c	NH_2	CH_3	284	2,100
			~242	6,600			334	4,900			279	1,000				
			332	4,300												
CO_2H	OH	C_6H_5	229	25,000	CO_2H	OH	236	8,900^c	CO_2H	C_6H_5	250	16,500^k	OH	C_6H_5	245	8,000^l
			318	6,300			306	3,700							285	4,500
																
CHO	OH	OCH_3	219	19,000	CHO	OH	255	10,000^m	CHO	OCH_3	253	8,300^m	OH	OCH_3	274	2,600^d
			265	9,700			325	3,000			315	2,800				
			340	2,800												
CHO	OCH_3	OCH_3	221	18,100	CHO	OCH_3	253	11,800^m	CHO	OCH_3	253	8,300^m	OCH_3	OCH_3	274	2,800^g
			260	8,000			320	4,300			315	2,800				
			320	2,300											284	2.400

TABLE I (*continued*)

Substituted Phenols



R_1	R_2	R_3	λ_{max}	ϵ	R_1	R_2	λ_{max}	ϵ	R_1	R_3	λ_{max}	ϵ	R_2	R_3	λ_{max}	ϵ
OH	NO_2	CH_3	216 271	10,000 1,900	OH	NO_2	272 346	6,000[e] 3,200	OH	CH_3	275	2,000[d]	NO_2	CH_3	260 340	6,300[j] 200
OH	NO_2	OH	218 280 310	9,200 2,300 3,300	OH	NO_2	272 346	6,000[e] 3,200	OH	OH	274	1,900[i]	—	—	—	—

[a] Data obtained in this laboratory, unless otherwise noted. [b] I. A. Pearl, *J. Am. Chem. Soc.*, **63**, 2331 (1949) reports λ_{max} 247, 250 and 318 mμ. [c] C. M. Mosher and A. I. Kohlenberg, *J. Chem. Soc.*, 804 (1951). [d] A. Kiss *et al.*, *Bull. Soc. Chim.*, **16**, 275 (1949). [e] W. A. Schroeder *et al.*, *Anal. Chem.*, **23**, 1740 (1951). [f] A. Burawoy and J. T. Chamberlain, *J. Chem. Soc.*, 2310 (1952). [g] R. Adams, C. H. Cain and H. Wolff, *J. Am. Chem. Soc.*, **62**, 733 (1940). [h] H. Unganade, E. E. Picket, L. Rubin, and E. Youse, *J. Org. Chem.*, **16**, 1318 (1951) report λ_{max} 262, 294, mμ, ε 700, 2600.[i] H. H. Hodgson, *J. Chem. Soc.*, 380 (1943). [j] Landolt-Bornstein, *Physikalische-chemische Tabellen*, Julius Springer, Berlin. [k] W. Baker, M. P. V. Boarland, and J. W. F. McOmie, *J. Chem. Soc.*, 1476 (1954). [l] R. A. Friedel, M. Orchin, and C. Riggel, *J. Am. Chem. Soc.*, **70**, 199 (1940). [m] R. A. Morton and A. L. Stubbs, *J. Chem. Soc.*, 1347 (1946).

containing 1 mole of sodium hydroxide was heated to 55°. 3-Methoxy-2-hydroxybenzaldehyde (30 g.) was added in one portion and the suspension was stirred for 5 min. without external heating. The temperature rose to 80°. The suspension was filtered while hot, the filtrate was cooled and acidified with dilute hydrochloric acid. A solid gummy mass precipitated which when recrystallized from benzene and then from water gave yellow crystals (12 g.), m.p. 151–152°; lit. m.p.,[12] 150°.

Preparation of 2,3-dimethoxybenzaldehyde. A mixture of 3-methoxysalicylaldehyde (50 g.), dimethyl sulfate (75 g.), potassium carbonate (200 g.), and ethanol (500 ml.) was placed in a 1-l., round-bottom flask and stirred periodically over a period of 48 hr. The reaction was extremely exothermic during the first hour and required external cooling with an ice bath. After 48 hr., the mixture was filtered and concentrated under reduced pressure to remove the ethanol. The residue was recrystallized from methanol by cooling the solution in Dry Ice. 2,3-Dimethoxybenzaldehyde was obtained in 65% yield, m.p. 50–51°.[13]

Preparation of 2,3-dimethoxybenzoic acid. A suspension of freshly prepared silver oxide (0.4 mole) in 500 ml. of water containing 1 mole of sodium hydroxide was heated to 55°. 2,3-Dimethoxybenzaldehyde (25 g.) was added in one portion and the suspension was stirred for 5 min. while heating to 75°. The suspension was filtered while hot and the filtrate was cooled to room temperature. An oil separated and the aqueous layer was decanted from the oil. The aqueous solution was acidified with dilute hydrochloric acid and a white precipitate was obtained. Recrystallization from methanol gave a product (9 g.) which melted at 125–126°; lit. m.p.,[14] 125–126°.

Preparation of 3-chlorosalicylic acid.[15] *tert*-Butyl hypochlorite was prepared according to the procedure in Organic Syntheses.[16] *t*-Butyl hypochlorite (25 g.) was added to a suspension of salicyclic acid (25 g.) in 500 ml. of water containing a trace of ferrous sulfate. The suspension was stirred for 10 min. while protected from light. The reaction was very exothermic and was cooled with ice. The reaction was filtered and the white solid was recrystallized from a mixture of methanol and water (50/50), m.p. 183–183.5°.

Preparation of 3-bromosalicylic acid.[17] A solution of mercuric nitrate (32 g. in 300 ml. of water) was heated to boiling. A solution of salicylic acid (14 g. in 300 ml. of hot water) was added to the mercuric nitrate and a copious precipitate formed in a few minutes. The white solid was removed by filtration and dried overnight in a vacuum desiccator. The dry solid was suspended in 200 ml. of glacial acetic acid which was cooled in an ice bath. Bromine (15 g.) was dissolved in 50 ml. of glacial acetic acid and this bromine solution was slowly added, with stirring, to the cold suspension. The suspension dissolved. The solution was added to 500 ml. of water and the solid 3-bromosalicylic acid precipitated. Recrystallization from a methanol-water solution gave white crystals, m.p. 181–181.5°.

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(15) B. F. Clark, Jr., *Chem. News*, **143**, 265 (1931).

(16) R. T. Arnold, *Org. Syntheses*, **XXXII**, 20 (1952).

(17) C. K. Kanvinde *et al.*, *Current Sci.*, **11**, 397 (1942).