[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NEW MEXICO HIGHLANDS UNIVERSITY]

Ultraviolet Absorption Spectra of Acetanilides[1]

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Absorption spectra have been determined for 36 acetanilides and related compounds. The intensities and wave lengths of the maxima are interpreted in terms of electronic and steric effects of the substituents.

Acetanilide and most of the substituted acetanilides have two bands above 200 mμ which are related to the benzene transitions at 203.5 and 255 mμ[3] and resemble the absorption bands in the corresponding anilines. The acetylation of aniline causes an extension of the conjugated system and therefore an increased absorption (and red shift) of the high intensity (primary) band.[4] It also diminishes the tendency of the nitrogen electrons to migrate into the ring, which decreases the absorption intensity of the weak (secondary) transition and causes it to shift to shorter wave lengths.[5]

The absorption spectrum of acetanilide is affected by replacing the methyl hydrogens of the acetyl group by methyl or by fluorine (Tables I and III). Trimethylacetanilide has a secondary band identical with acetanilide but its primary band is less intense and shifted slightly toward shorter wave lengths. The substitution of the methyl hydrogens in the acetyl group by fluorines produces a red shift of the primary band and a decrease in absorption intensity. The secondary band is so completely fused that it is no longer recognizable.

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA OF ALKYLACETANILIDES

Compound	λ_{max}, mμ[a]	ε	λ_{max}, mμ[b]	ε
Acetanilide	242	14,400	280	500
Trimethylacetanilide	241	12,900	280	500
o-Methylacetanilide	230	6,280	280[c]	210
o-*t*-Butylacetanilide	Infl.[d]			
m-Methylacetanilide	245	14,000	282[c]	640
m-*t*-Butylacetanilide	244	13,400	281	531
p-Methylacetanilide	245	14,850	286[c]	610
p-*t*-Butylacetanilide	245	16,100	282[c]	620

[a] First primary band. [b] Secondary band. [c] Shoulder. [d] ϵ_{230} 3,280.

In acetanilides with one nuclear substituent the absorption spectrum depends on the type of substituent and its position. *p*-Disubstituted benzene derivatives with opposite types of substituents (electron donors and acceptors) generally have larger dipole moments than the vector sums of the moments of the respective monosubstituted compounds. Similarly, their bathochromic shifts (compared to benzene) are larger than the sums of the shifts due to the single substituents.[6] For selected *p*-substituted acetanilides with electron-acceptor substituents and the corresponding anilines, the bathochromic shifts are greater, the greater the shifts of the substituent groups (Table II).

TABLE II

BATHOCHROMIC SHIFTS OF ACETANILIDES WITH ELECTRON-ATTRACTING SUBSTITUENTS IN Mμ[a]

C_6H_5X[b] X		C_6H_5Y[b] Y		*p*-XC_6H_4Y Sum[c]	Found	Difference
AcNH	38.5	SO_2NH_2	14.5[d]	53.0	55.5	2.5
NH_2	30.5	SO_2NH_2	14.5	45.0	58.5[e]	13.5
AcNH	38.5	COOH	24.5	63.0	66.5	3.5
NH_2	30.5	COOH	24.5	55.0	84.5[e]	29.5
AcNH	38.5	NO_2	56.5	95.0	112.5	17.5
NH_2	30.5	NO_2	56.5	87.0	171.5[e]	84.5

[a] All values for ethanol solutions. [b] Shift of the primary band in benzene (at 203.5 mμ) due to the substituents X and Y. [c] Sum of the group displacements. [d] λ_{max} 218 mμ (ε 8,970). [e] W. D. Kumler, THIS JOURNAL, **68**, 1184 (1946).

In each case the differences between found and calculated shifts, indicative of group interaction, are greater for the anilines than for their amides. The comparison of the shifts permits the conclusion that the resonance in anilines and acetanilides is similar but that the acetamino group has less tendency to release electrons.

Steric effects can occur in acetanilides with bulky *ortho* substituents in which there is a significant shift of the electron density center from the amino nitrogen to the nucleus.[7] In such compounds the acetamino group is twisted out of the plane of the ring with resultant decrease in the total absorption intensity and simultaneous blue shifts of the accessible bands.[8]

An effect of this sort is observed in *o*-methyl- and *o*-*t*-butylacetanilide (Table I) by comparison with acetanilide, with the corresponding *meta* and *para* compounds, and the anilines from which they are derived. *o*-Methylacetanilide has a maximum of decreased intensity (λ_{max} 230 mμ, ε 6,280) while *o*-toluidine absorbs at 233 mμ (ε 11,500).[9] *o*-*t*-Butylacetanilide only has an unresolved maximum in the 230 mμ region (ϵ_{230} 3,280). The experimental values agree qualitatively with previous determinations for some of the compounds by Morton and McGookin[9] and with the work of Grammaticakis,[10] who found steric effects in the *ortho* alkylated ani-

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(3) Additional high intensity bands occur in acetaminobenzoic acids and in nitroacetanilides at short wave lengths. These are believed to correspond to the benzene transition at 183 mμ.

(4) The bands are classified in accordance with the notations of L. Doub and J. M. Vandenbelt, THIS JOURNAL, **69**, 2714 (1947), and **71**, 2414 (1949).

(5) *Cf.* J. P. Picard and A. F. McKay, *Can. J. Chem.*, **31**, 897 (1953).

(6) L. N. Ferguson, "Electron Structures of Organic Molecules," Prentice-Hall, Inc., New York, N. Y., 1952, p. 277.

(7) This is apparently not the case in certain dyes investigated recently by I. I. Levkoev, N. N. Sveshnikov and N. S. Barvyn, *Doklady Akad. Nauk. S.S.S.R.*, **85**, 805 (1952).

(8) H. B. Klevens and J. R. Platt, THIS JOURNAL, **71**, 1716 (1949).

(9) R. A. Morton and A. McGookin, *J. Chem. Soc.*, 903 (1934).

(10) P. Grammaticakis, *Bull. soc. chim.*, [5] **16**, 134 (1949).

line derivatives $C_6H_5NR_2$, C_6H_5NHAc and C_6H_5NRAc.

Steric effects are also observed in the halogen acetanilides. The *ortho* compounds have decreasing absorption intensities in the order F > Cl > Br > I if the approximate absorption due to iodine is subtracted (Table III). At 246 mμ, where the iodobenzene absorption is at a minimum (ε 592), the *o*-haloacetanilides have the following molar absorptivities: F (ε 10,700), Cl (ε 9,460), Br (ε 6,700), I (ε 5,700).[11] The iodo compound no longer has a maximum in the 240 mμ region and its primary band appears only as a weak shoulder. As the atomic weights of the halogens increase the absorption bands of the *ortho* compounds are also shifted slightly toward longer wave lengths. The spectra of the *meta* isomers differ little with changes in the halogen and the small shifts of the maxima are in the same direction. More pronounced differences occur in the *p*-halogen acetanilides which are shifted bathochromically and hyperchromically from fluorine to iodine (Table III). The *o*-halogen anilines, chloro-, bromo- and iodoaniline show distinct absorption bands which increase rather than decrease in intensity in this order with little change in the wave lengths of the maxima.[12,13] It is therefore proposed that the *ortho* effects in the halogen acetanilides are primarily steric in nature although other factors may operate. An analogous steric effect has been determined in 2-acetylamino-3-iodofluorene[14] by comparison of its spectrum with those of the 7-iodo isomer and 2-acetylaminofluorene.[15]

TABLE III

ULTRAVIOLET ABSORPTION SPECTRA OF HALO ACETANILIDES

Acetanilide	λmax,[a] mμ	ε	λmax,[b] mμ	ε	λmax,[c] mμ	ε
Trifluoro	245	11,000				
o-Fluoro	239	12,600			278	1060
m-Fluoro	242	15,100	273	2070	279	1630
p-Fluoro	240	13,100			278	1230
o-Chloro	240	10,400				
m-Chloro	245	14,900	278	1100	286	890
p-Chloro	249	17,800				
o-Bromo	234	7,600				
m-Bromo	246	14,000	278	1100	286	850
p-Bromo	252	18,700				
o-Iodo	Shoulder[d]					
m-Iodo	246	13,600	281	1250	289	1000
p-Iodo	254	22,900				

[a] First primary band. [b] First secondary band. [c] Second secondary band. [d] ϵ_{234} 10,700; second primary band, λ_{max} 218 mμ, ε 17,700.

By application of similar criteria it is also certain that there are no steric effects in *o*-methoxyacetanilide for, although its primary band is somewhat less intense than that of the *meta* isomer, the anisidine spectra bear a similar relationship (Table IV), the order of intensities is reversed for the secondary bands and the wave lengths of corresponding bands in the *ortho* and *meta* isomers are virtually identical.[16]

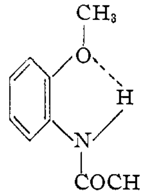
TABLE IV

ULTRAVIOLET ABSORPTION SPECTRA OF METHOXY- AND PHENOXYANILINES AND ACETANILIDES

Compound	λmax, mμ[a]	ε	λmax, mμ[b]	ε
o-Methoxyaniline	236	7,400	286	2940
o-Phenoxyaniline	236	9,100	277	2990
m-Methoxyaniline	236	7,780	286	2510
p-Methoxyaniline	235	9,400	300	2230
o-Methoxyacetanilide	244	10,400	280	4550
o-Phenoxyacetanilide	225[c,d]	10,000	271	1800
m-Methoxyacetanilide	245	11,700	280	3120
p-Methoxyacetanilide	249	14,900	[e]	

[a] First primary band. [b] Secondary bands; only the most intense band is given. [c] Shoulder. [d] Diphenyl ether absorbs at 225 mμ,[c] ε 10,300 and 271 mμ, ε 1,800. [e] ϵ_{280} 2,200.

The absence of an *ortho* effect in the methoxyacetanilides is explained by assuming that the groups are preferentially oriented so that the acetyl group is turned away from the methoxy group



This configuration could be stabilized by the weak hydrogen bond which is said to exist in this compound[17] and by the electrostatic repulsion between ether oxygen and carbonyl oxygen.[18]

The substituents are chromophorically active in this case and exert considerable resonance interaction of their own. Since the groups are electron donors, this will be in competition with the amine resonance, hence the 240 mμ bands are less intense in the methoxyanilines than in aniline itself. Some decrease occurs also in the corresponding bands of the methoxyacetanilides compared to acetanilide, particularly in the *o*-isomer.

Unlike *o*-methoxyacetanilide, the corresponding phenoxy compound is an example of steric inhibition of resonance, as is the case for the analogous 2-acetaminodiphenyl sulfide.[19] The absorption curve of 2-phenoxyacetanilide coincides with that of di-

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[11] The spectral effects of aromatic iodines have been discussed by T. M. Dunn and T. Iredale, *J. Chem. Soc.*, 1592 (1952); J. Ferguson and T. Iredale, *ibid.*, 2959 (1953); and H. E. Ungnade, THIS JOURNAL, **76**, 1601 (1954).

[12] J. E. Purvis, *J. Chem. Soc.*, **103**, 1638 (1913).

[13] More recent determinations for the chloro compounds have been reported by P. Grammaticakis, *Bull. soc. chim.*, [5] **16**, 761 (1949); **18**, 535 (1951), who also measured the spectra of the chloroacetanilides.

[14] E. K. Weisburger, J. H. Weisburger and F. E. Day, *J. Org. Chem.*, **16**, 1698 (1951).

[15] J. H. Weisburger, E. K. Weisburger and H. P. Morris, THIS JOURNAL, **74**, 4540 (1952); see also R. B. Sandin, *et al.*, *ibid.*, **74**, 5073 (1952).

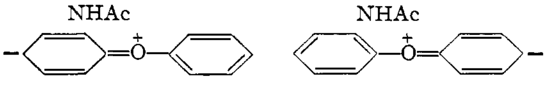
[16] These spectra have recently been reported by P. Grammaticakis, *Bull. soc. chim.*, [5] **18**, 220 (1951).

[17] A. E. Remick, "Electronic Interpretations of Organic Chemistry," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1949, p. 31.

[18] When both amino hydrogens in *o*-anisidine are substituted, as in *o*-methoxydimethylaniline, this condition no longer exists and one would therefore expect a steric effect instead. This seems to be the case. Grammaticakis has reported the primary band of *o*-methoxydimethylaniline at 245 mμ with approximately half the intensity of the corresponding band in the *m*-isomer, which occurs at 255 mμ. The values are estimated from the curves of P. Grammaticakis, *Bull. soc. chim.*, [5] **18**, 222 (1951).

[19] A. Mangini and R. Passerini, *J. Chem. Soc.*, 1168 (1952).

phenyl ether (except for the lack of fine structure), while 2-phenoxyaniline is shifted bathochromically and hyperchromically (Table IV).[20] It may be concluded that polar resonance forms such as



are the chief ionic structures contributing to the excited states.

The ultraviolet absorption spectra for the isomeric acetaminobenzoic acids, acetaminonitrobenzenes (Table V) and acetaminobenzenesulfonamides[21] show some similarity since in each case the secondary band of the *ortho* compound is more intense and occurs at longer wave length than the corresponding band in the *meta* isomer. This effect disappears when the amino hydrogens are both replaced by alkyl groups. It is no longer found in the dimethylaminobenzoic esters,[22] in the dimethylaminonitrobenzenes[21] and in the dimethylaminobenzenesulfonamides.[23] On the contrary, the spectra of methyl *o*-dimethylaminobenzoate[24] and *o*-dimethylaminonitrobenzene are shifted hypochromically and hypsochromically due to steric interference with coplanar resonance forms. The spectrum of N-methyl-*o*-nitroacetanilide resembles that of nitrobenzene, while the curves for di-N-acetyl-*o*-nitroaniline and nitrobenzene are quite similar. Likewise the absorption curve for N-methyl-*o*-acetylaminobenzoic acid does not have a maximum in the region under investigation and is shifted nearer the values for benzoic acid.[25]

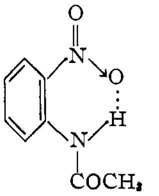
TABLE V

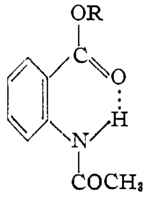
ULTRAVIOLET ABSORPTION SPECTRA OF ACETANILIDES WITH *meta*-DIRECTING SUBSTITUENTS

Acetanilide	λmax, mμ[a]	ε	λmax, mμ[b]	ε	λmax, mμ[c]	ε
p-Sulfonamido			259	22,200		
o-Carboxy	221	25,700	252	13,400	305	4650
m-Carboxy	222	27,700	245[d]	12,600	295	1600
p-Carboxy			270	21,200		
o-Nitro	233	17,000	270	4,200	340	2500
m-Nitro	242	22,500	270[d]	5,660	326	1510
p-Nitro	222	13,200	316	11,400		

[a] Second primary band. [b] First primary band. [c] Secondary band. [d] Shoulder.

The observed spectral effects in the acetamino compounds evidently depend on the presence of the NH hydrogen and are therefore ascribed to chelated structures such as





There is other evidence for hydrogen-bonded structures in the case of *o*-nitroacetanilide[26] and *o*-aminobenzoic acid.[27]

Experimental[28]

Materials and Methods.—Two general methods were employed for the preparation of the acetamino compounds from the available nitro compounds. Catalytic hydrogenation with Raney nickel catalyst (3 g.) of 5 g. of nitro compound in 50 ml. of ethanol under 10 cm. of hydrogen furnished *o*-bromoaniline, *o*-methoxyaniline and *o*-phenoxyaniline. The catalytic hydrogenation of *o*-*t*-butylnitrobenzene was carried out according to Brown and Nelson.[29] *m*-Aminobenzoic acid was prepared by catalytic reduction of the nitro acid in 1% hydrochloric acid. These methods failed with *o*-iodonitrobenzene, and the reduction in this and other nitro compounds was effected by stannous chloride (14.25 g.) and hydrochloric acid (40 ml.) in ethanol (50 ml.) at 25°. The reaction mixture from 5 g. of nitro compound was worked up by adding 50 ml. of benzene and 100 ml. of 40% sodium hydroxide at such a rate, with cooling, that the temperature remained below 30°. The benzene solution was separated, washed with water, dried and distilled to remove the solvent. The crude amines were acetylated by refluxing for 2 hours with 50 ml. of acetic anhydride. The mixture was poured into 100 ml. of water and was brought to boiling. Most of the acetamino compounds crystallized on cooling. They were recrystallized from appropriate solvents and decolorized when necessary. The final products and melting points were as follows: *o*-iodoacetanilide, m.p. 108–109°; *m*-iodoacetanilide, m.p. 120–120.5°; *o*-bromoacetanilide, m.p. 98.5–99.5°; *o*-methoxyacetanilide, m.p. 84.5–85.5°; *m*-methoxyacetanilide, m.p. 79–80°; *o*-phenoxyacetanilide, m.p. 89–90°; *m*-acetylaminobenzoic acid, m.p. 245–246°; *o*-fluoroacetanilide, m.p. 78–79°; *m*-fluoroacetanilide, m.p. 86–87°; *p*-fluoroacetanilide, m.p. 152–153°; trifluoroacetanilide, m.p. 89–90°; *o*-*t*-butylacetanilide, m.p. 164–165°; and trimethylacetanilide, m.p. 131–132°.[30]

Absorption Spectra.—Ultraviolet absorption spectra were determined with a model DU Beckman spectrophotometer[31] at 2-mμ intervals or less and with a Cary recording spectrophotometer[32] in 1-cm. silica cells at 25° for alcoholic solutions in concentrations of 1×10^{-3} to 1×10^{-5} mole per liter. Hydrocarbon solvents were avoided because acetanilide is associated in such solvents.[33,34]

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(20) The absorption values of these compounds have been reported in a note by R. Passerini and G. Righi, *Boll. sci. fac. chim. ind. Bologna*, **10**, 163 (1952).

(21) P. Grammaticakis, *Bull. soc. chim.*, [5] 95 (1954).

(22) P. Grammaticakis, *ibid.*, [5] **18**, 222 (1951).

(23) P. Grammaticakis, *ibid.*, [5] 92 (1954).

(24) The acid in this case gives an abnormal spectrum resembling the betaine of *o*-trimethylaminobenzoic acid.[25]

(25) P. Grammaticakis, *ibid.*, [5] **17**, 160 (1950).

(26) M. E. Runner and E. C. Wagner, THIS JOURNAL, **74**, 2529 (1952); H. O. Chaplin and L. Hunter, *J. Chem. Soc.*, 375, 1034 (1938).

(27) L. Dede and A. Rosenberg, *Ber.*, **67**, 147 (1934).

(28) All temperatures uncorrected.

(29) K. L. Nelson and H. C. Brown, THIS JOURNAL, **73**, 5605 (1951).

(30) The author is indebted to Dr. H. C. Brown for samples of *m*- and *p*-*t*-butylacetanilide and *o*-*t*-butylnitrobenzene, to Dr. Glen C. Finger for a sample of *m*-fluoronitrobenzene and to Gene Schroll for a sample of *m*-anisidine.

(31) The author is indebted to James McDowell, Frida Lutz and Robert Smith for a number of the determinations.

(32) Cary recordings by Robert Curry, Purdue University.

(33) H. E. Ungnade, THIS JOURNAL, **75**, 432 (1953).

(34) For the complete spectra for the substances referred to in this paper order Document 4293 from ADI Auxiliary Publications Project. Photoduplication Service, Library of Congress, Washington 25, D. C., remitting $1.75 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $2.50 for photoprints readable without optical aid.