LIGHT ABSORPTION STUDIES

PART I. THE ULTRAVIOLET ABSORPTION SPECTRA OF SOME NITROBENZENES.

PART II. THE ULTRAVIOLET ABSORPTION SPECTRA OF SOME BENZALDEHYDES.

J. C. DEARDEN

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A THESIS

by

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PART I. THE ULTRAVIOLET ABSORPTION SPECTRA OF SOME NITROBENZENES

ABSTRACT

The electronic spectra of nitrobenzenes are discussed in terms of previously proposed hypotheses relating electronic interactions and ultraviolet absorption data. A previously suggested order of mesomeric interaction of the halogens is confirmed, and it is shown that the mesomeric effect of the nitro-group is greater than that of the acetyl-group.

PART I

THE ULTRAVIOLET ABSORPTION SPECTRA OF SOME NITROBENZENES

PREFACE

It has been suggested (for example, 9, 10, 11) that the ultraviolet absorption bands designated by Moser and Kohlenberg (30) as B- and C-bands are determined mainly by mesomeric and steric interactions, and only to a lesser extent by other factors. It is proposed here to extend the previously proposed hypotheses to include the spectra of nitrobenzenes and benzaldehydes. Since the nitro-group exerts a strong negative mesomeric effect, it would be anticipated that the spectra of the nitrobenzene series of compounds would be comparable with the previously studied acetophenones (8, 14).

The spectra of nitrobenzenes have recently been discussed by a number of workers (for example, 3, 23, 32, 35, 37), and have been noted to give rise to several anomalies (5, 6; cf. also the greater ethylenic stretching frequency at 1600 cm^{-1} in nitrobenzene (2a), and the absence of the usual correlations for C-H bending vibrations in the region 1000 - 650 cm^{-1} (2c)).

ULTRAVIOLET ABSORPTION SPECTRA

Nitrobenzene

The ultraviolet absorption spectra of nitrobenzene in different solvents are listed in Table I.

TABLE I

ABSORPTION MAXIMA OF NITROBENZENE IN DIFFERENT SOLVENTS[1]

Solvent	B-BAND λmax(mμ)	ε max	C-BAND λmax(mμ)	ε max
Gas phase	239.9	7600[2]		
Naphtha	251	9200[3]		
Hexane	252	9000	ca.285	1500
Iso-octane	252	8620[4]		
Ethanol (concn. = 70 mg/1)	257	8100	-	-
Ethanol (concn. = 1.75 mg/1)	258	7700	-	-
95% aqueous ethanol	260	8000[5]		
Dioxane (concn. = 90.5 mg/1)	257-258	8400	-	-
Dioxane (concn. = 1.81 mg/1)	259	7400	-	-
50% aqueous dioxane	263-265	7850	-	-
Water (concn. = 2.4 - 95 mg/1)	265-266	7900	-	-
N̄ NaOH	266	6900[6]	ca.304	2000[6]
0.1N̄ HCl	266	7800[6]	-	-[6]
conc. H_2SO_4	287.5	8600[6]	ca.302	7200[6]

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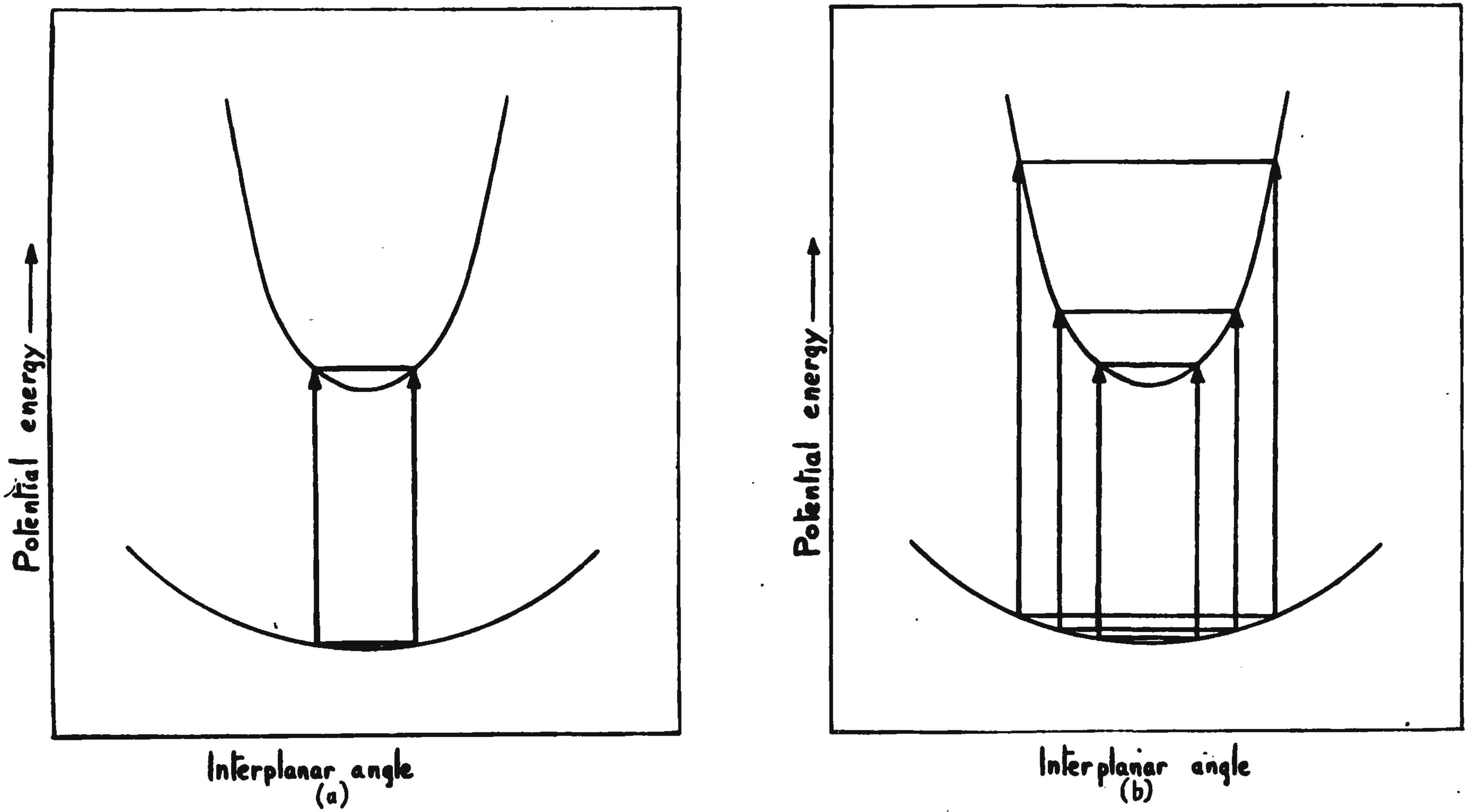
[1] Values underlined represent inflections in this and subsequent tables.

[2] Ref. 33 [3] Ref. 31 [4] Ref. 3 [5] Ref. 26 [6] Ref. 15



(a)

(b)

Fig. 1. Schematic representation of electronic transitions of nitrobenzene in:
(a) an inert liquid, and (b) the gas phase.

A broad symmetrical absorption band, structureless even in the gas phase (32), occurs near 260 mμ, and is classified as the B-band, by analogy with the B-band near 240 mμ in acetophenones (8). The bands are of comparable intensity and undergo similar changes on altering the dielectric constant or polarity of the solvent. The nitrobenzene band at 260 mμ will also be shown to be highly susceptible to steric effects, which cause hypsochromic shifts and reduced absorption intensities, and which is characteristic of the B-band in acetophenones and benzoic acids (14).

No appreciable concentration dependence has been discerned for various nitrobenzene solutions. This indicates that nitrobenzene is apparently not appreciably associated in solution within the investigated concentration range (see Table I). The hypsochromic displacement observed in the gas phase compared with the solution spectra for both nitrobenzene and acetophenone may be partly caused by an increased population of the higher vibrational levels of the ground state. This is illustrated in Fig. 1.

The observed bathochromic wavelength displacement of the B-band of nitrobenzene with increased dielectric constant of the solvent is parallel to that observed for acetophenone, but is more pronounced. This suggests increased solvent stabilisation, and may be related to the greater contribution of dipolar excited states in nitrobenzene. Change of pH of the solution does not cause any additional wavelength shift, which emphasises the importance of the dielectric constant (compared with the hydrogen ion concentration) in determining the location of the B-band.

Further, the B-band of nitrobenzene lies at considerably longer wavelength than that of acetophenone. Since the B-band of monosubstituted benzenes is determined predominantly by mesomeric interaction (12), it follows that, in the absence of other considerations, the nitro-group would be expected to exert a greater negative mesomeric effect than the acetyl-group. It may be noted that the large mesomeric effect of the nitro-group can also be used to explain the large frequency shift of the C-H bending vibration in nitrobenzene (27), the extremely high intensity of the $R-NO_2$ stretching vibration (2 f), and the increased intensities of the aromatic bands at 1660-1560 cm^{-1} (2 b), since absorption intensities in the infrared region are probably largely proportional to resonance interaction (1, 25).

The C-band in nitrobenzene is identified only with difficulty. This is explained by the hypothesis (14) that a large mesomeric effect causes a low intensity C-band. There is little doubt that this band corresponds to the band in benzene at *ca.*260 mμ (14, 30).

Para-Substituted Nitrobenzenes

The ultraviolet absorption spectra of some para-substituted nitrobenzenes are listed in Table II.

TABLE II

ABSORPTION MAXIMA OF PARA-SUBSTITUTED NITROBENZENES

		B-BAND		C-BAND	
Substituent	Solvent	λmax (mμ)	ε max	λmax (mμ)	ε max
Amino-	2$\overline{N}$ HCl	258	8,700[1]	-	-[1]
Nitro-	methanol	258	14,700[2]		
Acetyl-	ethanol	261	14,000[3]	(ca.298 (ca.312	2200[3] 1200
Carboxyl-	0.1$\overline{N}$ HCl	264.5	12,400[11]		

TABLE II (continued)

		B-BAND		C-BAND	
Substituent	Solvent	λmax (mμ)	ε max	λmax (mμ)	ε max
Carboxyl-	$\overline{N}$ NaOH	274	10,600[11]		
Formyl-	ethanol	*ca.*265	11,400[4]	-	-[4]
Fluoro-	iso-octane	256	7,600[5]		
Fluoro-	95% aqueous ethanol	*ca.*263	7,900[6]	-	-[6]
Chloro-	95% aqueous ethanol	*ca.*272	10,000[6]	-	-[6]
Chloro-	pH 6	280	10,300[1]		
Bromo-	95% aqueous ethanol	*ca.*276	11,100[6]	-	-[6]
Iodo-	95% aqueous ethanol	*ca.*295	11,700[6]	-	-[6]
Methyl-	iso-octane	264	10,250[7]	-	-[7]
Methyl-	pH 6	285	9,250[1]		
i-Propyl-	iso-octane	265	10,430[7]	-	-[7]
t-Butyl-	iso-octane	265	10,720[7]	-	-[7]
Hydroxy-	naphtha	286	10,600[8]		
Hydroxy-	ethanol	314	13,000[9]		
Hydroxy	pH3	317.5	10,000[1]		
Hydroxy-	$\overline{N}$ NaOH	402.5	19,200[1]		
Methoxy-	ethanol	305	13,000[9]	-	-[9]

TABLE II (continued)

Substituent	Solvent	B-BAND λmax (mμ)	ε max	C-BAND λmax (mμ)	ε max
Amino-	naphtha	320	14,600[8]		
Amino-	ethanol	371	15,500[10]		
Dimethylamino-	ethanol	387	18,300[2]		

[1]Ref. 5 [2]Ref. 26 [3]Ref. 14 [4]Ref. 36 [5]Ref. 21 [6]Ref. 35
[7]Ref. 3 [8]Ref. 31 [9]Ref. 4 [10]Ref. 34 [11]Ref. 15

Para-disubstituted compounds provide a good method of studying mesomeric interactions, because inductive and steric effects are likely to be small (12). To investigate this mesomeric interaction, the data in Table II may be divided into two groups. Thus, the first several values in Table II indicate no appreciable mesomeric interaction. This is ascribed either to acid conditions inhibiting mesomeric interaction, as is the case with p-nitroaniline in acid solution, or to deactivation by two para-substituents inhibiting mesomeric interaction, as in p-dinitrobenzene. This latter is also suggested by other data. For example, the carbonyl stretching frequencies in dilute chloroform solution for p-nitrobenzaldehyde (ν max 1721 cm^{-1} (2d)) and p-nitroacetophenone (ν max 1700 cm^{-1} (12)) are considerably displaced from those of benzaldehyde (ν max 1709 cm^{-1}) and acetophenone (ν max 1691 cm^{-1}) (12). This indicates that at least some of the conjugation which, because of the aromatic nucleus, causes the initial shift to lower frequency, is no longer

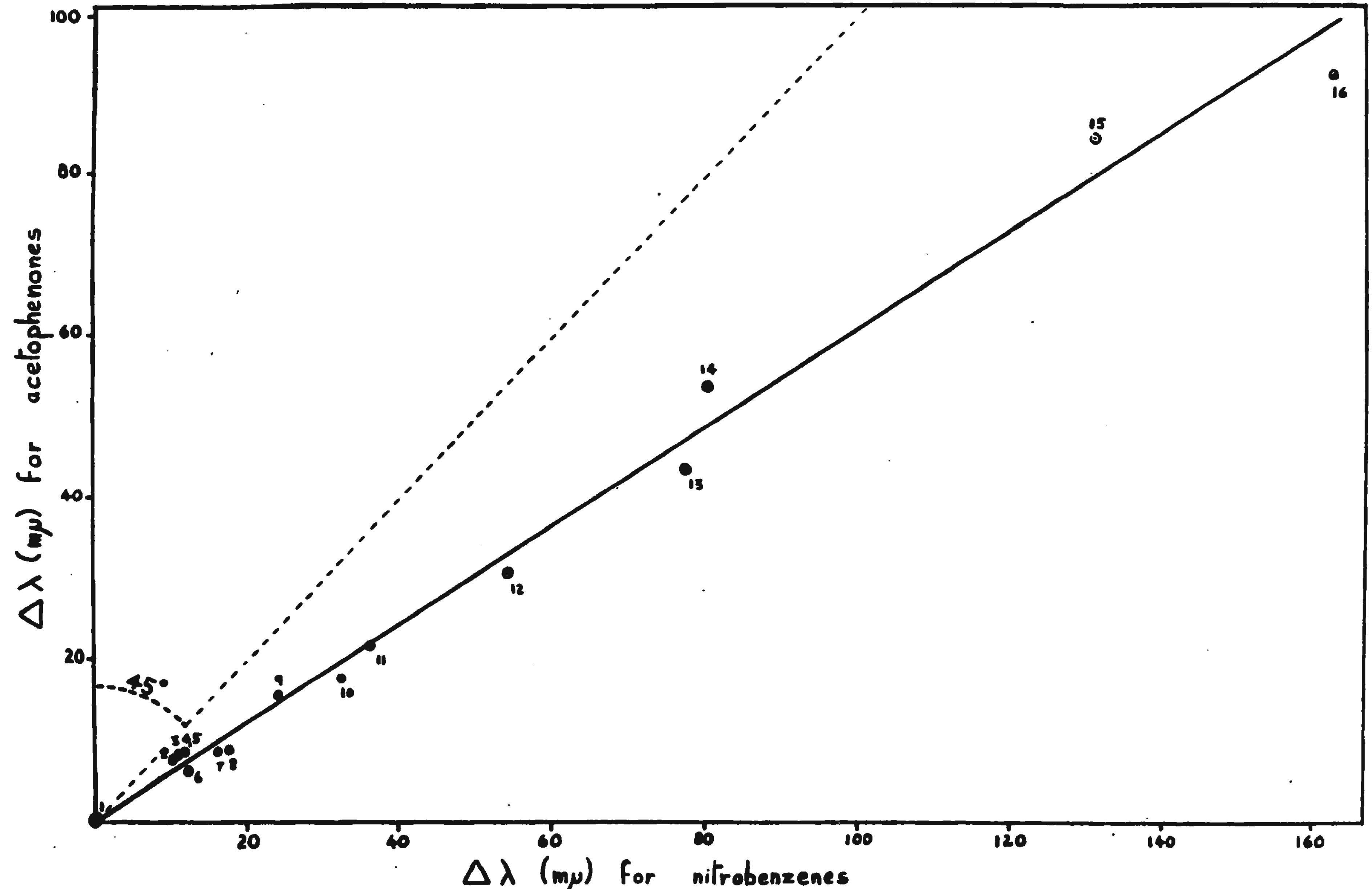


Fig. 2. Wavelength displacements (Δλ) of the B-band obtained on introducing a para-substituent in nitrobenzene and acetophenone. (1) -H (gas phase); (2) -Me (gas phase); (3) -Et (gas phase); (4) -iPr (gas phase); (5) -tBu (gas phase). (6) -H (hexane); (7) -F (iso-octane); (8) -H (ethanol); (9) -Me (iso-octane); (10) -Cl (95% ethanol); (11) -Br (95% ethanol); (12) -I (95% ethanol); (13) -OH (pH3); (14) -NH_2 (naphtha); (15) -NH_2 (ethanol); (16) -OH ($\bar{N}$ NaOH). (Values from Table II and refs. 8-12.)

available. Next, the supposed absence of mesomeric interaction may also be related to Hammett's observation (22) that for nitrobenzenes two different substitution constants must be used (cf. also 20). Thirdly, decreased mesomeric interaction implies reduced force constants of the bonds linking substituents to the benzene ring. Evidence for such a reduced force constant is in fact provided from the R-NO_2 stretching vibration of nitro-compounds at 1560-1500 cm^{-1} , since this is displaced towards lower frequency in compounds where a strongly electronegative group is substituted in the para-position (2e). Ultraviolet data also indicate a reduced force constant, since an increased extinction coefficient (as is observed in the first-listed examples in Table II, relative to nitrobenzene) has been ascribed to a reduced force constant (16). This latter may, incidentally, explain the more pronounced C-band in compounds like p-nitroacetophenone (see Table II and Ref. 14) compared with the C-band in nitrobenzene.

For the remaining data in Table II, the mesomeric interaction which affects predominantly the excited state is suggested as the main factor determining the maximal wavelength of the B-band. In support of this hypothesis, the following evidence is cited. Firstly, an increased dielectric constant in these para-substituted nitrobenzenes causes bathochromic shifts parallel to those observed for nitrobenzene itself (see Tables I and II). This suggests that the displacements are caused predominantly by the same (i.e. mesomeric) interaction. Secondly, Fig.2 shows that the wavelength displacements for acetophenones and nitrobenzenes are directly proportional to each other whenever mesomeric interaction is assumed to determine the B-band. This again indicates that both wavelength displacements are proportional to one electronic interaction, which is probably mesomeric in character. Since the slope of the straight line obtained in Fig. 2 is inclined at an angle of less than 45° to the nitrobenzene ~~ordinate~~ abscissa, a mesomeric action in nitrobenzenes greater than that in the acetophenones is indicated. This is ascribed to increased resonance contributions of dipolar excited states in nitrobenzenes because of the stronger electron-withdrawing tendency of the nitro-group. Two additional points may be noted. Firstly, although the concept of resonance structures is implied in this discussion, molecular orbital theory provides, qualitatively at least, a similar picture (cf. 30). Secondly, comparison of the extinction coefficients of para-substituted compounds and unsubstituted compounds is less suitable than wavelength changes in the study of mesomeric interaction. This is because not only may overlapping of absorption bands interfere with the quantitative estimation of absorption intensities, but also because intensity values are more sensitive to other effects, such as slight changes in the force-constant of the N-nuclear bond caused by solvent-solute interactions.

Meta-Substituted Nitrobenzenes

The spectra of the meta-substituted isomers of nitrobenzene are listed in Table III.

TABLE III

ABSORPTION MAXIMA OF META-SUBSTITUTED NITROBENZENES

Substituent	Solvent	B-BAND λ max (mμ)	B-BAND ε max	C-BAND λ max (mμ)	C-BAND ε max
Nitro-	96% aqueous ethanol	235	17,400[1]		
Nitro-	water	241.5	16,300[2]	305	11,000[2]
Acetyl-	cyclohexane	(224 (254	23,000[3] 7,000	(288 (298	1,100[3] 750
Acetyl-	ethanol	(227 (ca.261	22,000[4] 6,600	-	-[4]
Formyl-	cyclohexane	(225 (242 (252	26,000 11,000 6,800	287 298	1,050 750
Formyl-	ethanol	265	11,700[4]	-	-[4]
Carboxyl-	cyclohexane cont. 2% ether	250-251	7,400[3]	(285 (296	1,150[3] 650
Carboxyl-	ethanol	255	7,000[3]	-	-[3]
Fluoro-	iso-octane	246	7,400[5]	284	1,700[5]
Fluoro-	95% aqueous ethanol	ca.255	7,700[6]	ca.300	1,900[6]
Chloro-	95% aqueous ethanol	ca.258	7,200[6]	ca.300	1,700[6]
Chloro-	water	(224 (264	6,800[2] 7,100	313	1,300[2]
Bromo-	95% aqueous ethanol	ca.259	6,200[6]	ca.303	1,200[6]
Iodo-	light petroleum	ca.260	6,200[7]	ca.308	1,000[7]
Iodo-	95% aqueous ethanol	ca.262	6,400[6]	ca.315	1,000[6]

TABLE III (continued)

Substituent	Solvent	B-BAND λ max (mμ)	B-BAND ε max	C-BAND λ max (mμ)	C-BAND ε max
Methyl-	iso-octane	256.5	8,160[8]	ca.292	1,500[8]
t-Butyl-	iso-octane	258	8,220[8]	ca.292	1,500[8]
Methoxy-	ethanol	268	6,400[9]	325.2	2,400[9]
Methoxy-	water	(228 (273.5	8,900[2] 6,000	330	2,050[2]
Hydroxy-	ethanol	270.5	6,900[9]	332.2	2,700[9]
Hydroxy-	pH3	(228.5 (273.5	7,900[2] 6,000	333	1,960[2]
Hydroxy-	0.1$\overline{N}$ NaOH	(251.5 (291	11,000 ~~14,500~~[2] 4,500	392	1,500[2]
Amino-	ethanol	233	18,000[10]	375	1,600[10]
Amino-	0.1$\overline{N}$ NaOH	(246 (280	10,700[2] 4,800	358	1,450[2]
Dimethyl-) amino-)	ethanol	246	23,000[10]	400.3	1,350[10]

[1] Ref. 26 [2] Ref. 6 [3] Ref. 14 [4] Ref. 36 [5] Ref. 21 [6] Ref. 35
[7] Ref. 7 [8] Ref. 3 [9] Ref. 4 [10] Ref. 29

In meta-substituted nitrobenzenes primary mesomeric interaction between the two substituents is theoretically impossible, and hence the observed B-bands would be expected to correspond to the B-bands of the two monosubstituted parent compounds. This accounts for the frequent occurance of two distinct B-bands in a meta-disubstituted benzene derivative (see Table III). It may be noted that this second B-band is sometimes designated as a "secondary primary band" (6). For example, the maximal absorption of m-nitrophenol at 251.5 mμ is assumed to be a secondary primary band, whereas the ascription proposed here is that of phenolic B-band absorption.

However, the observed B-bands will not necessarily correspond closely to the B-band of a monosubstituted parent compound, since a secondary interaction occurs between the two substituents in meta-substituted compounds. This latter interaction is thought to be inductive in effect (15), and, since it is a short-range interaction, operates in both ortho- and meta-isomers.

Various data exemplifying the effect of a meta-nitro substituent on the B-band of a monosubstituted benzene derivative are given in Table IV, which show that the meta-nitro substituent indeed affects the B-band, usually giving rise to a considerable displacement. This displacement is positive or negative depending on the dipolar forms contributing to the electronic excited state. In this way a nitro-group causes a negative wavelength displacement (hypsochromic) on chromophores such as acetophenone, or benzoic acid, but a positive displacement on chromophores like aniline, or phenol. This, incidentally, illustrates the general principle that a B-band is not, even within one group of compounds, consistently determined by one and the same electronic excited state.

The different effects of the nitro-group in meta-disubstituted benzene derivatives may be illustrated by structures I and II (below) which indicate how a nitro-group in the meta-position may either facilitate or hinder electronic excitation.

TABLE IV

THE B-BANDS OF META-SUBSTITUTED NITROBENZENES, WITH RESPECT TO THE MONO-SUBSTITUTED BENZENE DERIVATIVE, AND OTHER SUITABLE REFERENCE COMPOUNDS

Solvent	*m*-Substituted Nitrobenzene	λ max(mμ)	ε max	Reference Compound	λ max(mμ)	ε max	Δ λ
96% aqueous ethanol	*m*-dinitrobenzene	235	17,400	nitrobenzene	260	8,000	-25
Water	*m*-dinitrobenzene	241.5	16,300	nitrobenzene	265-266	7,900	-24
Cyclohexane	*m*-nitroacetophenone	224	23,000	acetophenone	238.5	12,000	-14.5
Ethanol	*m*-nitroacetophenone	227 ~~226~~	22,000 ~~22,500~~	acetophenone	240	12,500	-16
Cyclohexane	*m*-nitrobenzaldehyde	225	26,000	benzaldehyde	241	14,000	-14
0.1N NaOH	*m*-nitrophenol	251.5	11,000	phenol	234	10,500	+16.5
pH3	*m*-nitrophenol	228.5	7,900	phenol	210	6,000	+18.5
0.1N NaOH	*m*-nitroaniline	246	10,700	aniline	230	7,000	+16
Water	*m*-nitroanisole	228	8,900	anisole	217	4,300	+11

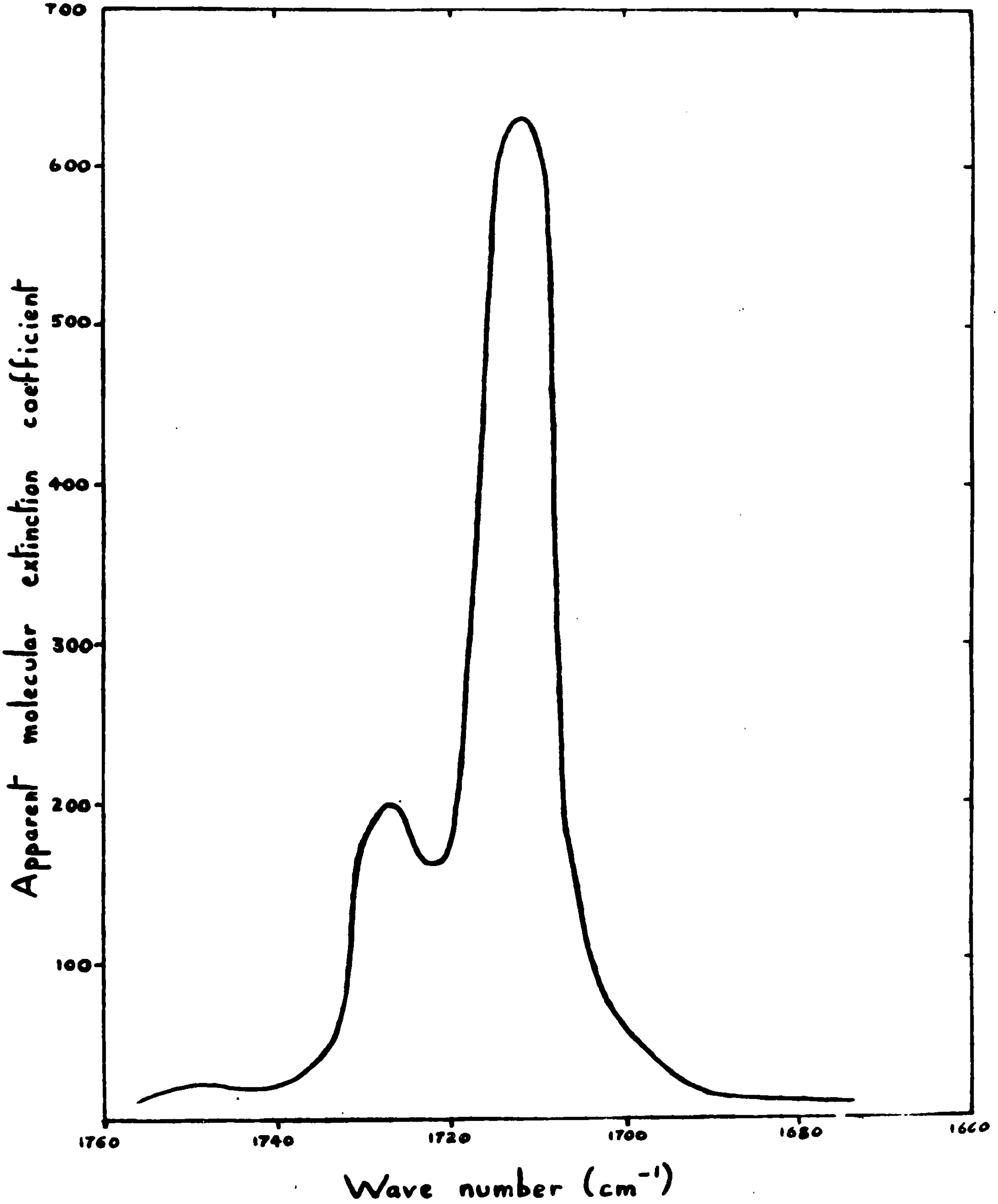
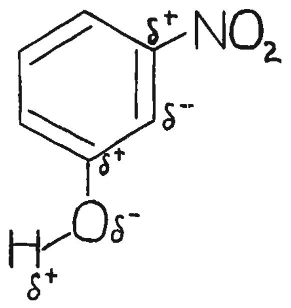


Fig. 3. The carbonyl stretching frequency absorption band of m-nitrobenzaldehyde in CCl_4 solution.



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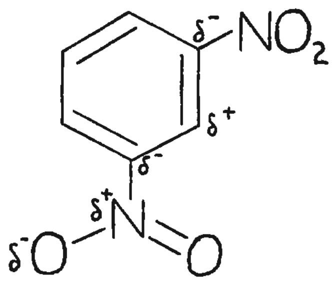
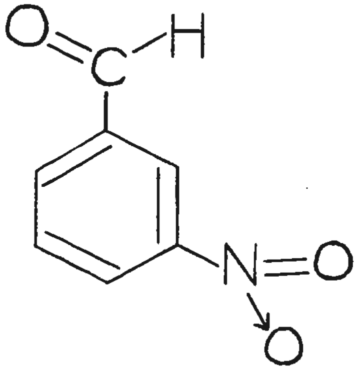
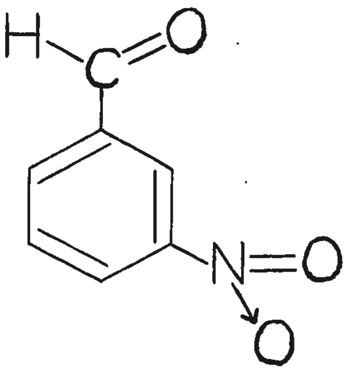


II

Assuming an inductive type mechanism, as shown, it is evident how the formation of a positive or negative charge near the meta-nitro-group may have opposite effects for the two examples, m-nitrophenol and m-dinitrobenzene. The relatively large extinction coefficient which is frequently noted in the B-band of the meta-substituted nitrobenzenes listed in Table IV is tentatively ascribed to the reduced force constant due to the electron-withdrawing effect of the nitro-substituent (cf. 16). Next, a buttressing effect would be expected to occur in meta-substituted nitrobenzenes (cf. 13), and this effect would be expected to be greatest for m-dinitrobenzene.. Thus, the buttressing effect may contribute to the variations in the observed wavelength displacements (see Table IV). This hypothesis receives support from the infrared spectra of certain carbonyl bands which can be shown to exist as doublets. Fig. 3, for example, shows the observed doublet for the spectrum of m-nitrobenzaldehyde. By analogy with published data (25), the band at 1712 cm^{-1} is ascribed to structure III, and the less intense band at 1727 cm^{-1} to structure IV.



III



IV

Since this type of compound may thus be assumed to exist in both *s*-*cis* and *s*-*trans* conformations, the greatly reduced extinction coefficient in *m*-nitroacetophenone, compared with that of *m*-nitrobenzaldehyde is satisfactorily accounted for (see 13). That is, a buttressing effect is assumed to account, at least partly, for the difference in the spectra of *m*-nitroacetophenone and *m*-nitrobenzaldehyde (see Table III). The mechanism proposed is that compounds like *m*-nitroacetophenone exist in more than one conformation, but only some of these conformations contribute appreciably to the observed absorption intensity in the ultraviolet region. Consequently a typical type I steric effect (cf. 12) is observed - that is, the absorption intensity is decreased, but there is no appreciable wavelength displacement. In *m*-iodonitrobenzene also, the nitrobenzene B-band is appreciably reduced in intensity, whereas the C-band is more pronounced than in other meta-halogensubstituted nitrobenzenes (cf. Table III and Ref. 35). Generally, it is noted that the C-band in meta-substituted nitrobenzenes is usually more pronounced than in the corresponding para-isomer, which has been explained (14) by increased p-π electronic interaction due to the buttressing effect.

Ortho-Substituted Nitrobenzenes

The ultraviolet absorption spectra of ortho-substituted nitrobenzenes are listed in Table V.

TABLE V

ABSORPTION MAXIMA OF ORTHO-SUBSTITUTED NITROBENZENES

Substituent	Solvent	B-BAND λmax(mμ)	 ε max	C-BAND λmax(mμ)	 ε max
Acetyl-	ethanol	257	6,000[1]	-	- [1]
Acetyl-	cyclohexane	254	6,000[1]	-	- [1]
Formyl-	ethanol	252	4,700[2]	270	3,600[2]
Formyl-	cyclohexane	247	7,000	282	1,750
Carboxyl-	cyclohexane	-	- [1]	ca.278	1,350[1]
Carboxyl-	ethanol	ca.250	3,500[1]	-	- [1]
Fluoro-	iso-octane	242	7,250[3]	278	1,850[3]
Fluoro-	95% aqueous ethanol	ca.250	6,900[4]	ca.285	2,200[4]
Chloro-	95% aqueous ethanol	ca.252	3,500[4]	ca.290	1,200[4]
Chloro-	water	(228 (260	4,400[5] 4,000	310	1,400[5]
Bromo-	95% aqueous ethanol	ca.255	3,000[4]	ca.292	1,300[4]
Iodo-	95% aqueous ethanol	ca.260	3,500[4]	ca.310	1,500[4]
Methyl-	iso-octane	250	5,950[6]	ca.290	1,500[6]

TABLE V (continued)

Substituent	Solvent	B-BAND		C-BAND	
		λmax(mμ)	ε max	λmax(mμ)	ε max
i-Propyl-	iso-octane	247	3,760[6]	ca.290	1,300[6]
t-Butyl-	iso-octane	-	- [6]	ca.275	700[6]
Methyl-	water	266	5,300[5]	325	1,300[5]
Hydroxy-	ethanol	273	6,600[7]	343.5	3,600[7]
Hydroxy-	pH3	(230 (278.5	3,900[5] 6,600	351	3,200[5]
Hydroxy-	0.1N̄ NaOH	(250 (282	5,000[5] 4,300	416	4,800[5]
Methoxy-	ethanol	258.5	3,450[7]	317.2	2,850[7]
Amino-	ethanol	275.2	5,100[8]	403.6	5,400[8]
Amino-	0.1N̄ NaOH	(245 (282.5	7,000[5] 5,400	412	4,500[5]
Dimethylamino-	ethanol	245.5	21,500[8]	416	2,950[8]

[1] Ref. 14 [2] Ref. 36 [3] Ref. 21 [4] Ref. 35 [5] Ref. 6 [6] Ref. 3
[7] Ref. 4 [8] Ref. 29

The ortho-effect of alkyl-groups in nitrobenzenes has previously been ascribed to steric inhibition of resonance (3), and it was noted that the decreased absorption intensity is qualitatively related to the increased size of the substituent i.e. t-butyl > i-propyl > methyl. For alkylnitrobenzenes in iso-octane solution a hypsochromic shift is also observed, compared with the wavelength of maximal absorption in the meta-isomer. This

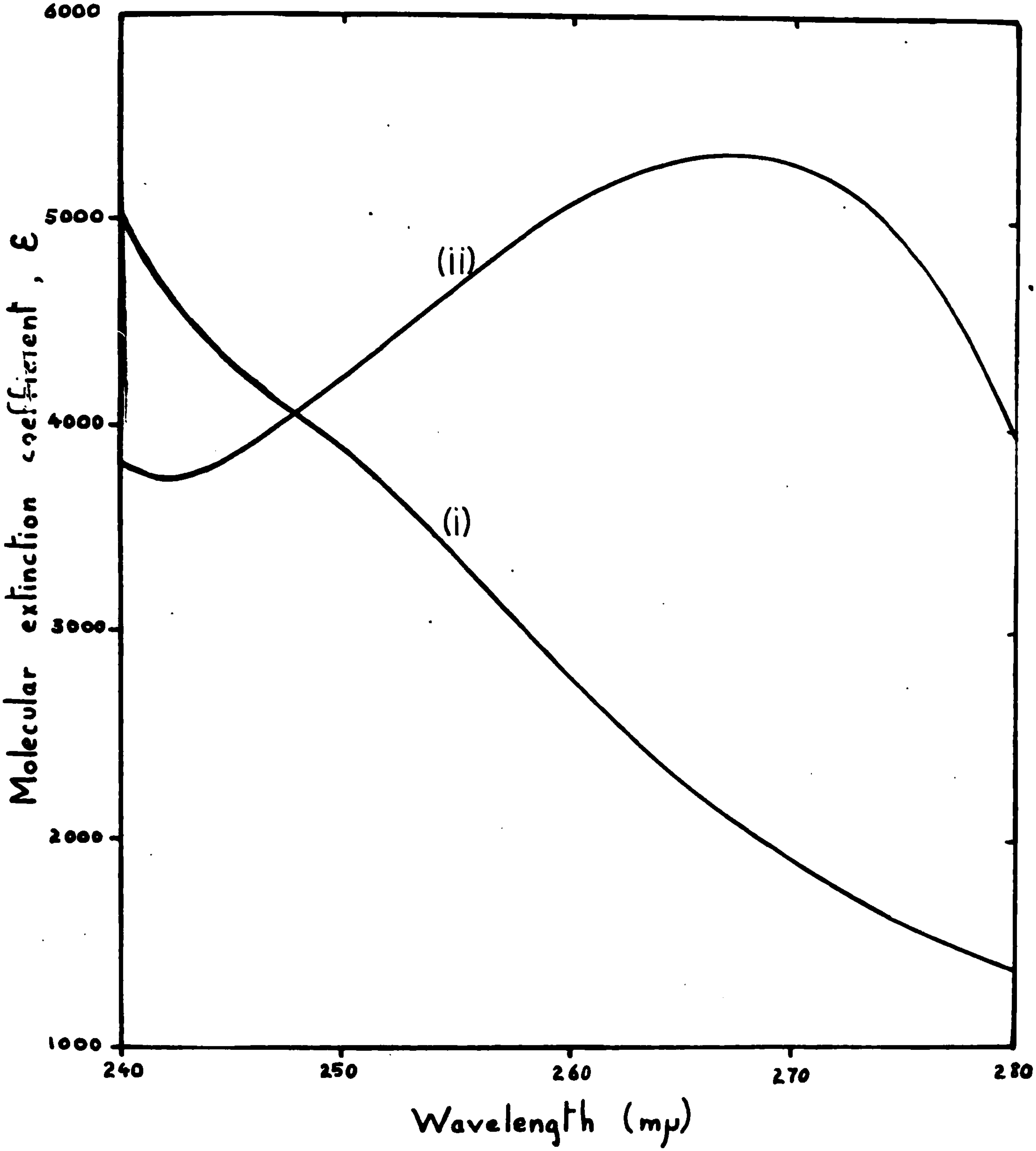


Fig. 4. The B-band (corresponding to nitrobenzene absorption) of o-nitrobenzoic acid in (i) cyclohexane containing 2% ether; (ii) water.

can be explained by assuming that, in ortho-isomers, not only is the alkyl-group forced out of the plane of the benzene ring, in this way failing to contribute appreciably to mesomeric interaction between the two substituents, but in addition the vicinal alkyl-group causes the nitro-group to rotate about the N-nuclear bond. Consequently, absorption in the ortho-isomer frequently occurs at shorter wavelength, and usually with decreased absorption intensity (cf. 15).

By considering the two types of B-bands in ortho-isomers (cf. preceding section) changes in the B-bands can be related with the ease of dislodging a particular group from the plane of the benzene ring. For example, in o-nitrophenol in basic solution, the band corresponding to nitrobenzene occurs at λ max 282 mμ , ε 4,300, which is similar in intensity to the band in m-nitrophenol at λ max 291 mμ , ε 4,500. The other B-band, which occurs in the meta-isomer at λ max 251.5, ε max 14,500, and which is ascribed to the phenolate ion, occurs in the ortho-isomer as only an inflection, at 250 mμ , ε = 5,000. This suggests that the -ONa group is more readily dislodged from the plane of the benzene ring than is the nitro-group. More data can be obtained from the spectra of a number of other ortho-substituted nitrobenzenes where, in contrast to the meta-isomer, only the nitrobenzene band is evident. Examples of this are provided by the spectra of o- and m-nitroacetophenone in ethanol (36) and in cyclohexane (see Tables III and V). It is concluded that, of the two substituents, the nitro-group is again the less readily dislodged.

The ease of dislodging a particular group from the plane of the benzene ring may also depend on the solvent used. This is illustrated in Fig. 4 by the B-band of o-nitrobenzoic acid, which shows that the nitrobenzene band in aqueous medium is more pronounced, and hence more easily recognised. This has some application from an analytical point of view (see next section). The phenomenon can be explained by assuming that in aqueous and ethanolic solution the nitrobenzene band is strengthened at the expense of benzoic acid coplanarity, because of solvent-solute interaction. This hypothesis is supported by the fact that there is an appreciable wavelength displacement observed for nitrobenzene absorption on changing the solvent from hexane to ethanol or water, since this also suggests interaction between the solvent and the nitro-group. This implies that in ethanolic or aqueous solutions ortho-substituted nitrobenzenes will normally give rise to type I steric effects (for classification of steric effects, see Ref. 12 and references cited there), whereas in hexane other steric effects will frequently be observed.

Steric interaction in ortho-substituted nitrobenzenes are also evident from a number of other physical data. For example, whilst the characteristic Raman frequency of the nitro-group is around 1367 cm^{-1}, in nitrobenzene the interaction of the nitro-group with the aromatic nucleus causes a frequency drop to 1341 cm^{-1}. In o-nitrotoluene some of this interaction is destroyed, and absorption again occurs at higher frequency (1345 cm^{-1}). In nitromesitylene the interaction is almost completely destroyed, and absorption occurs at 1363 cm^{-1}, close to the frequency of the unconjugated nitro-group (31; cf. also 19,28). This latter absorption may be compared with the ultraviolet absorption of nitromesitylene (31), which also indicates the virtual absence of conjugation.

Apart from steric interactions, the operation of other forces - in particular intramolecular hydrogen bonding - would be expected to be evident in ortho-substituted nitrobenzenes. For example, whilst the B-bands of m-nitrophenol and m-nitroanisole absorb maximally within 3 mμ (see Table III), the B-band of o-nitrophenol shows a bathochromic shift of 14.5 mμ with respect to that of o-nitroanisole (see Table V). This wavelength displacement is qualitatively similar to that observed in the corresponding acetophenones (14). Intramolecular hydrogen bonding in nitrobenzenes is also suggested by infrared data (cf. 2d, 18).

The C-band in ortho-substituted nitrobenzenes is again more pronounced than in the corresponding para-isomers, and tends to disappear when steric inhibition of resonance is great (14).

Applications

Since the negative mesomeric effect is large for a nitro-group, the mesomeric interaction in nitrobenzene will be large, and not easily inhibited by steric interactions. Consequently the prerequisite for a type I steric effect is available; namely, the electronic excited state, where mesomeric interaction is presumed to be greater than in the ground state, remains at a similar energy level for the prevalent conformations in both the sterically hindered and the reference compounds. Steric effects of type I are in fact observed, and are found to occur more frequently in ethanolic or aqueous solution, where solvent-solute interactions will facilitate mesomeric interaction.

Thus, irrespective of the complexity of a molecule, the nitrobenzene chromophore will often be evident, by reason of the characteristic band near 260 mμ in ethanolic or aqueous solution. Conversely, the occurrence of a band near 260 mμ under those conditions, for a compound containing a nitro-group, will indicate the presence of the nitrobenzene chromophore. It should be noted, however, that for ortho- or meta-substituted nitrobenzene chromophores more than one band may occur in this region, and that for certain para-substituents the band may be considerably displaced towards longer wavelength (see Table II).

If a definite absorption band occurs near 260 mμ , the absorption intensity of the band can be used to estimate steric effects. This type of spectral analysis has recently been employed in the discussion of the structure of 2-carboxy - 4, 5, - dimethoxy - 2' - nitrobiphenyl, and 2-carboxy - 4, 5, - dimethoxy -2' - nitro -3' - methylbiphenyl (13), and of 6, 6' - dinitro -2, 2' - di - (2, 4 - dimethylbenzoyl) - biphenyl (17). Qualitative spectral examination of the nitro-group is also possible in the infrared region (2e, 24), since the nitro-group shows typical bands near 1550 cm^{-1} and in the region 1360-1300 cm^{-1}. Thirdly, the B-band in the ultraviolet region appears to be well suited to the quantitative determination of compounds containing the nitrobenzene chromophore, as the observed extinction coefficients obey Beer's law fairly accurately; in addition, the absorption is not particularly sensitive to slight changes in pH. Thus the method may offer advantages in, for example, the study of reaction mechanisms involving a nitro-substituent.

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PART II

THE ULTRAVIOLET ABSORPTION SPECTRA OF SOME BENZALDEHYDES

ABSTRACT

The electronic spectra of benzaldehydes are recorded and discussed in terms of previously proposed hypotheses. The formyl-group is shown to endow benzene derivatives with similar properties to those of nitro- and acetyl-substituted derivatives, save that the effects of steric interactions and hydrogen bonding are slightly modified. An order of mesomeric interaction $-NO_2 > -CHO > -COCH_3 > -COOH$ is proposed.

PART II

ULTRAVIOLET ABSORPTION SPECTRA OF BENZALDEHYDES

PREFACE

The benzaldehyde series of compounds is of interest because it provides additional examples in the study of the various interactions which determine electronic spectra. As the formyl-group exerts a negative mesomeric effect, the spectra would be anticipated to be similar to the previously discussed nitrobenzenes, (Part I of this thesis), and also acetophenones (6, 10, 11) and benzoic acids (7).

The spectra of some benzaldehydes have previously been recorded (2, 3, 4, 16, 17) but wherever it proved convenient spectra were re-determined in order to obtain data under near-identical conditions.

THE SPECTRUM OF BENZALDEHYDE

The absorption maxima of benzaldehyde in different solvents are listed in Table I.

TABLE I

ABSORPTION MAXIMA OF BENZALDEHYDE IN DIFFERENT SOLVENTS

Solvent	B-BAND Concn.(mg./l)	λmax(mμ)	ε max	C-BAND λmax(mμ)	ε max
Cyclohexane	(1.01	241	14,000[1]	277-278	1,200
	(	247	11,500	287	1,000
	(				
	(40.5	241	14,500		
	(	247	12,500		
Dioxane	(1.03	243	8,000[1]	278-279	1,200
	(41.2	243	12,500		
50% Aqueous dioxane	(1.01	247	10,500[1]	279-280	1,350
	(41.2	247	12,500		
Water	(0.98	248	12,000[1]	278-279	1,400
	(39.1	248	12,500		
$\bar{N}$ NaOH	(1.02	248	10,000[1]	ca.279	1,200
	(40.8	248	10,100		
0.1$\bar{N}$ HCl	(1.03	249	13,300[1]	280	1,500
	(41.2	249	13,400		
conc. H_2SO_4		293	21,000[2]	ca.330	2,000[2]

---

[1] Intermediate values for extinction coefficients were obtained at intermediate concentrations.

[2] Ref. 13

Benzaldehyde in cyclohexane solution appears to exhibit a slight concentration dependence, which may be due to intermolecular hydrogen bonding (14). Unfortunately, the changes in the extinction coefficients are not sufficiently large to permit any valid conclusions to be drawn. Extinction coefficients are also altered on varying the solute concentrations in dioxane solutions (see Table I), the concentration dependence decreasing with increasing water content of the solutions.

The concentration dependence indicates that hydrogen bonding probably occurs between solute molecules, giving rise to a higher extinction coefficient at greater concentration; that is, where there is more possibility of solute-solute association. The decrease of concentration dependence with increase of the dielectric constant of the solvent suggests that both solute-solute and solvent-solute associations occur, the latter predominating in a solvent of high dielectric constant owing to the polar nature of the solute molecules in the electronic excited state.

The bathochromic wavelength displacements of the absorption maxima of benzaldehyde in various solvents, referred to the wavelength of maximal absorption in cyclohexane solution, also indicate solvent-solute hydrogen bonding, which is greatest in aqueous solution.

None of the C-bands listed in Table I shows concentration dependence within the accuracy of the experiments.

The wavelength displacements observed on changing the dielectric constant and acidity of the solvent for solutions of benzaldehyde, acetophenone, and nitrobenzene are listed in Table II.

TABLE II

VARIATION OF ABSORPTION MAXIMA WITH DIELECTRIC CONSTANT AND ACIDITY

	BENZALDEHYDE		ACETOPHENONE		NITROBENZENE	
Solvent	λmax(mμ)	ε max	λmax(mμ)	ε max	λMax(mμ)	ε max
			B-BANDS			
Dioxane	243	10,000	239	12,000	257-259	8,000
50% Aqueous dioxane	247	11,500	243	12,000	264	8,000
Water	248	12,000	244	12,000	265-266	8,000
$\bar{N}$ NaOH	248	10,000	244	11,500	266	7,000
0.1$\bar{N}$ HCl	249	13,500	244	12,000	266	8,000
conc. H_2SO_4	293	21,000[1]			287.5	8,500[1]
			C-BANDS			
Dioxane	278	1,200	277	1,000		
50% Aqueous dioxane	279-280	1,350	278	1,150		
Water	278-279	1,400	276-278	1,250		
$\bar{N}$ NaOH	ca.279	1,200	277	1,250	ca.304	2,000
0.1$\bar{N}$ HCl	280	1,500	277	1,250		
conc.H_2SO_4	ca.330	2,000[1]			ca.302	7,200[1]

---

[1] Ref. 13

Table II shows that the changes ~~a~~occurring on changing the dielectric constant or acidity of the solvent are similar for benzaldehyde, acetophenone and nitrobenzene. The slightly greater wavelength displacement in the B-band of nitrobenzene for the dioxane-water series probably occurs because of the greater electron-withdrawing ability of the nitro-group. Although differences in the wavelength displacements are small (5 mμ for benzaldehyde and acetophenone compared with 8 mμ for nitrobenzene) they are significant, since differential wavelength measurements are accurate to ± 1 mμ. Absolute wavelength measurements, on the other hand, are accurate only to ± ca. 2 mμ (see Experimental).

A further difference between the benzaldehyde, the acetophenone, and the nitrobenzene spectra is that the benzaldehyde absorption in hexane solution occurs as a double band. This doublet formation is more pronounced for both B- and C- bands at lower temperatures (19), and disappears in dioxane, ethanolic and aqueous solutions. The B-band in acetophenone, in the gas phase and in heptane solution, is also reported to be slightly unsymmetrical and shows a small shoulder at about 7 mμ to the red of the peak. Again, in all other solvents this maximum was found to be symmetrical and the shoulder was absent. For nitrobenzenes, the B-band is structureless, even in the gas phase, and quite symmetrical about the maximum (11). Three possible explanations are put forward to account for this phenomenon. In the one case, the fine structure can be ascribed to benzenoid fine structure, which disappears if the resonance contribution is large, as in nitrobenzene or aniline. This does not, however, explain why the fine structure is much more pronounced for benzaldehyde than for acetophenone, but it accounts well for the fine structure of a number of other spectra, and for the lack of fine structure in the infrared carbonyl band of benzaldehyde (19).

A second explanation is that the fine structure is due to rotational isomerism of the formyl-group. Again, this does not account for the more pronounced fine structure in benzaldehydes, since, as will be shown later, the formyl-group exerts a greater negative mesomeric effect than the acetyl-group. However, the hypothesis is supported by the fact that the infrared carbonyl band of meta-nitrobenzaldehyde exists as a doublet (see Part I of this thesis, page 13), the absorption intensity of one peak being less than that of the other because of a buttressing effect.

A third explanation, which may be taken partly as a corollary to the second, is that hydrogen bonding occurs (cf. 21). It is probable, however, that no one explanation will account satisfactorily for the phenomenon.

The occurrence of the double band in the spectra of solutions of benzaldehydes in inert solvents is of some practical importance, since it frequently facilitates the identification of the benzaldehyde band not only in simple benzaldehydes, such as are discussed here, but also in more complicated molecules (cf. for example, 15).

Finally, in this section, it may be noted that the maximal absorption of the B-band of benzaldehyde occurs at longer wavelength than that of acetophenone. This suggests that the former exists, under the conditions employed, with a larger proportion of planar or near-planar forms. This hypothesis is supported by the fact that benzaldehydes are less susceptible to steric interactions (6, 8). Furthermore, whereas the carbonyl stretching frequency of benzaldehyde lies at 1709 cm^{-1} (Mean Integrated Absorption Intensity, $A = 2.56$ $mole.^{-1}$ $litre.$ $cm^{-2}.$ 10^{-4}), the corresponding

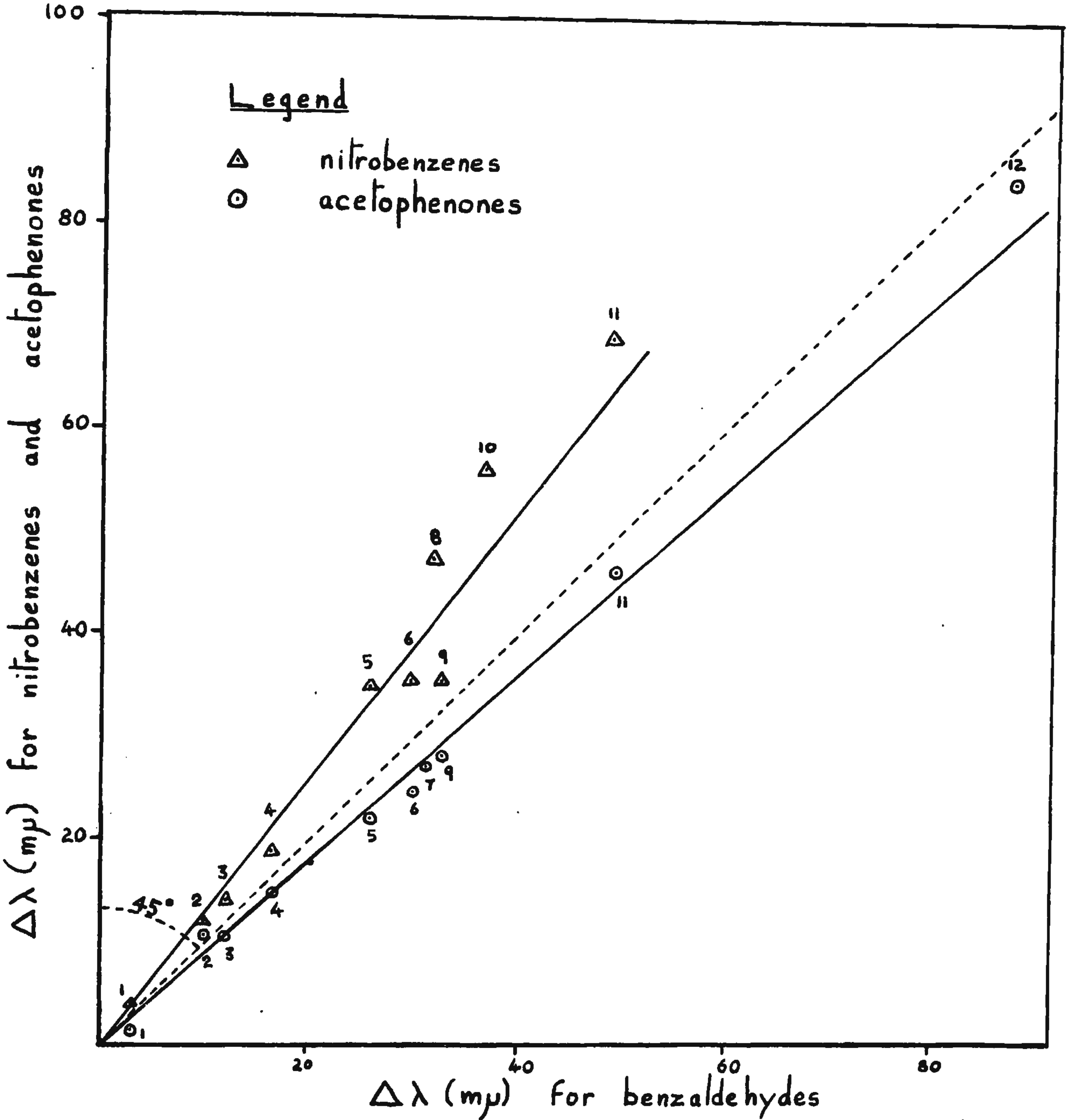

Fig. 1. Wavelength displacements (Δλ) of the B-band obtained on introducing a para-substituent in benzaldehyde, nitrobenzene and acetophenone, in n-hexane or cyclohexane solution. (0) – H; (1) – F; (2) – Me; (3) – Cl; (4) – Br; (5) – I (ethanol); (6) – I; (7) – OMe; (8) – OMe (ethanol); (9) – OH; (10) – OH (ethanol); (11) – NH_2; (12) – $-OH$ (alkaline ethanol). (Values from Table III).

frequency for acetophenone under identical conditions occurs at 1691 cm^{-1} (A = 2.20); that is, at longer wavelength (10). The wavelength shift is thus in the reverse order from that observed in the ultraviolet region. Since steric effects in the B-band are caused predominantly by the interactions between vicinal atoms in the electronic excited state (8, 9, 10), the observed opposite wavelength displacements may represent a type of steric effect previously noted (10), where a lowering of the ground state energy has the same effect (that of causing a hypsochromic shift) as a raising of the excited state energy. It may also be noted that the integrated absorption intensities (A) of the vibrational spectral bands of benzaldehyde and acetophenone relate to the observed wavelength changes in the electronic spectra. This is as anticipated, since the integrated absorption intensities have been related to the resonance energies of conjugation (1), which also predominantly determine the B-band in electronic spectra.

THE SPECTRA OF PARA-SUBSTITUTED BENZALDEHYDES

The spectra of para-substituted benzaldehydes are listed in Table III, together with wavelength shifts with respect to the parent compound. Similar wavelength shifts obtained in the acetophenone and nitrobenzene series are also listed (see also Fig. 1).

TABLE III

ABSORPTION MAXIMA OF PARA-SUBSTITUTED BENZALDEHYDES AND THE EFFECT OF PARA-SUBSTITUENTS ON THE B-BAND FOR BENZALDEHYDES, ACETOPHENONES, AND NITROBENZENES IN n-HEXANE OR CYCLOHEXANE SOLUTION (WAVELENGTH DISPLACEMENTS FOR ETHANOL ARE GIVEN IN PARENTHESES)

	B-BAND			C-BAND		Wavelength shift with reference to parent compound in		
Benzaldehyde Substituent	λmax(mμ)	ε max	Mean λmax	λmax(mμ)	ε max	Benzal-dehydes	Aceto-phenones	Nitro-benzenes[8]
None	(241	14,000	244	(277-278	1,200	-	-	-
	(247	12,000		(287	1,000			
p-Methyl-	(251	15,000[1]	254	(279	1,200[1]	10	10.5[4]	12
	(257	12,500		(284	1,000			
p-Fluoro-	244	13,000[2]	244	Not given[2]		3	1.5[4]	4
p-Chloro-	(253	19,000	256	(276	1,500	12	10.5[4]	14
	(259	15,500		(286	1,000			
p-Bromo-	257.5	18,500[2]	257.5	Not given[2]		16.5	14.5[4]	18.5
p-Iodo-	(268	19,500	274	-	-	30	24.5[4]	35
	(275	16,000				(26)[6]	(22)[4]	(34.5)
	(280	14,500						
p-Methoxy-	(265	18,500	275	-	-	31	27[5]	
	(ca.272	16,000				(32)[7]		(47)
	(278	12,500						
	(286	5,500						
p-Hydroxy-	(265-266	19,000	277	-	-	33	28[5]	35
	(ca.274	15,500				(37)[7]		(56)
	(281	12,000						
	(288	6,000						
p-Amino-	(291	16,300	293.5	Not determined		49.5	46[4]	69
	(296	16,100						
p-~~Amino-~~ Hydroxy- in) alkaline) ethanol)	336	30,000[3]	336	-	-[3]	88[3]	84[3]	
p-Nitro-	[259	13,800]	259	ca.284	3,400			
				ca.295	2,100			
				ca.305	1,200			
p-Nitro in water	[266	14,400]	266	ca.301	3,000			
				ca.314	1,800			

TABLE III (continued)

	B-BAND			C-BAND		Wavelength shift with reference to parent compound in		
Benzaldehyde Substituent	λmax(mμ)	ε max	Mean λmax	λmax(mμ)	ε max	Benzal-dehydes	Aceto-phenones	Nitro-benzenes[8]
p-Carboxy-	(249 (257	17,100 15,200	253	(280 (288-289 (298-299	1,630 1,930 1,580			

[1] Ref. 2 [2] Ref. 4 [3] Ref. 2 0 [4] Ref. 11 [5] Ref. 5 [6] Ref. 4 [7] Ref. 3

[8] See Tables I and II, Part I of this thesis, for references.

[9] Cyclohexane containing ca.2% ether.

In compiling the wavelength displacements for Fig. 1 the mean maximal wavelengths of the B-band of the substituted benzaldehydes were used. As the wavelength displacement between the peaks was found to be usually 7 mμ ± 1 mμ , this does not introduce any appreciable error, and, in the cases where the B-band shows more than two maxima (see Table III), causes the displacements to lie more nearly on a straight line (see Fig. 1). Although most of the values in Table III were determined in hexane solution, some are for ethanolic solution. However, Fig. 1 shows that the wavelength displacements are still approximately proportional for each series of compounds, indicating that solvent-solute interactions are comparable for the compounds considered. Most of the values in Table III were obtained under identical conditions (see Experimental).

All the B-bands of para-substituted benzaldehydes show fine structure in hexane solution save that of p-nitrobenzaldehyde. This latter absorption may thus be ascribed to nitrobenzene absorption, which ascription receives support from the fact that the B-band exhibits properties characteristic of nitrobenzene absorption. For example, in aqueous solution the B-band undergoes the unusually large bathochromic shift associated with nitrobenzene absorption (see Part I of this thesis, page 3). These data suggest, therefore, that there is very little interaction in p-nitrobenzaldehyde, particularly in the excited state. The reverse phenomenon is noted in the spectrum of p-carboxybenzaldehyde, where the characteristic benzaldehyde doublet occurs, but where there is no absorption which may be ascribed to benzoic acid (14). The ascriptions can be rationalised in terms of competing mesomeric interactions, the suggested order being $-NO_2 > -CHO > -COOH$. A study of previous work (11) indicates that the acetyl-group exerts a stronger mesomeric effect than the carboxyl-group. This is supported by the fact that acetophenone absorbs at 237.5 mμ in hexane, compared with 230 mμ for benzoic acid.

Wherever appreciable interaction does occur in para-substituted benzaldehydes, the resulting bathochromic displacements are shown, in Fig. 1, to be directly proportional to corresponding displacements in the acetophenone and nitrobenzene series, which indicates that the displacements are proportional to one "basic" electronic interaction which acts along the extremities of a conjugated system and which is characteristic for each substituent. This interaction has already been associated with the usual mesomeric effect of a substituent, although in its assignment of the order for halogens ($I > Br > Cl > F$) this interpretation affords a different order from that usually accepted for the mesomeric interaction of the halogens (18). It must be remembered, however, that the above order applies to the excited state, whereas usually mesomeric effects are determined in the ground state.

The slope of the line in Fig. 1 relating wavelength displacements in para-substituted acetophenones and benzaldehydes is less than 45° (with benzaldehyde displacements on the abscissa), whilst that for corresponding nitrobenzenes and benzaldehydes is greater than 45°. This confirms the previously proposed order of mesomeric effect; that is, $-NO_2 > -CHO > -COCH_3$. Further support comes for the already established order (see Fig. 2, Part I of this thesis) of mesomeric interaction $-NO_2 > -COCH_3$. Thus the final order of negative mesomeric effect is $-NO_2 > -CHO > -COCH_3 > -COOH$, which agrees with the order determined from the wavelengths of maximal absorption for these compounds.

The C-band in the compounds listed in Table III could usually be identified only with difficulty. It disappeared in compounds where there is large interaction between the two para-substituents, which tendency has previously been noted (11).

THE SPECTRA OF META-SUBSTITUTED BENZALDEHYDES

The absorption maxima of meta-substituted benzaldehydes are listed in Table IV, together with wavelength displacements from the parent compound. Corresponding displacements are also listed for meta-substituted acetophenones and nitrobenzenes.

TABLE IV

ABSORPTION MAXIMA OF META-SUBSTITUTED BENZALDEHYDES AND THE EFFECT OF META-SUBSTITUENTS ON THE B-BAND FOR BENZALDEHYDES, ACETOPHENONES AND NITROBENZENES IN n-HEXANE OR CYCLOHEXANE SOLUTION (WAVELENGTH DISPLACEMENTS IN ETHANOLIC SOLUTION ARE GIVEN IN PARENTHESES).

	B-BAND			C-BAND		Wavelength shifts with reference to parent compound in		
Benzaldehyde Substituent	λmax (mμ)	ε max	Mean λmax	λmax (mμ)	ε max	Benzaldehydes	Acetophenones	Nitrobenzenes[6]
None	(241 (247	14,000 12,000	244	(277-278 (287	1,200 1,000	-	-	-
m-Methyl-	(245 (251	13,500[1] 12,000	248	(280 (290	1,000[1] 800	4	5[2] (4.5)[2]	4.5
m-Fluoro-	(238 246	12,800 11,600	242	(282-283 (290 (293	2,100 1,730 1,680	-2	-3.5[2] (-4)[2]	-6 (-5)
m-Chloro-	(241-242 (248	11,500 10,000	245	(288 (298	1,400 1,200	1	0.5[2] (0)[2]	(-2)
m-Bromo-							4[2] (0)[2]	(-1)
m-Iodo-	(244 (249 (251 (253	8,000 7,600 7,400 6,850	249	(295-296 (303	1,300 1,230	5	9.5[2] (10)[2]	(2)
m-Hydroxy-	(244 (250	10,000 9,500	247	(302-303 (ca.307	3,000 2,800	3 (9)[4]	7.5[3]	(12.5)
m-Methoxy-	(247 (ca.251	6,800 6,500	249	(304 (ca.313	3,000 2,700	5 (8)[4]	7.5[3]	(10)
m-Amino-	(ca.245 (ca.256	9,000[5] 7,500	250.5	Not determined		6.5	7.5[2] (15)[2]	
m-Nitro-	(225 ([ca.242 ([ca.252	26,000 10,900] 6,800	225	(287 (298	1,000 700	-19	-13.5[2]	
m-Nitro-	([265	11,700])[7]						

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[1] Ref. 2 [2] Ref. 11 [3] Ref. 5 [4] Ref. 3 [5] Cyclohexane containing ca.2% ether.

[6] See Tables I and III, Part I of this thesis, for references. [7] Value in constant-boiling ethanol. Ref. 23

Table IV shows that the effect of meta-substituents on the location of the benzaldehyde B-band is usually small, and similar to that in meta-substituted acetophenones and nitrobenzenes. Table IV also shows that meta-substituted benzaldehydes may have two quite distinct B-bands, as may meta-substituted nitrobenzenes (see Part I of this thesis, Table III, page 10). The second B-band corresponds to the absorption of the chromophore $-C_6H_4 - X$, where X is the meta-substituent, the formyl-group acting as the secondary substituent. These latter bands are indicated by square brackets in Table IV. Thus, in the spectrum of m-nitrobenzaldehyde in cyclohexane two bands occur, one at λ max 225 mμ , ascribed to benzaldehyde absorption, and a weaker absorption at ca.247 mμ ascribed to nitrobenzene absorption. This ascription is very tentative, and may be questioned on the grounds that the benzaldehyde band is appreciably displaced, and also because the band does not show the characteristic doublet of benzaldehyde in inert media. On the other hand, a nitro-group normally produces appreciable changes in the spectra of meta-disubstituted benzenes (see Part I of this thesis, page 11). The ascription receives further support from the spectrum of m-nitrobenzaldehyde in ethanolic solution (see Table IV), where the presence of ethanol would be expected to displace the nitrobenzene band to longer wavelength, and, in addition, cause a reinforced nitrobenzene absorption band (see Part I of this thesis, page 13). This corresponds to the experimental observation, since the weak inflection at about 245 mμ in cyclohexane becomes the maximal absorption band at 265 mμ in ethanolic solution. A similar phenomenon is observed for m-nitroacetophenone (11).

Steric effects in meta-substituted benzaldehydes would not be expected to be significant, since the formyl-group is relatively small. However, the fairly low extinction coefficient for the B-band of m-iodobenzaldehyde may be caused, partly at least, by a buttressing interaction.

Similarly, the exceptional wavelength displacements (see Table IV) for m-iodonitrobenzene compared with those for m-iodoacetophenone and m-iodobenzaldehyde also point to the operation of a buttressing effect in this type of compound (cf. 12).

The C-bands, as anticipated, are well defined for meta-substituted benzaldehydes (cf. 11).

THE SPECTRA OF ORTHO-SUBSTITUTED BENZALDEHYDES

The absorption maxima of ortho-substituted benzaldehydes are listed in Table V, together with those of ortho-substituted acetophenones.

TABLE V

ABSORPTION MAXIMA OF ORTHO-SUBSTITUTED BENZALDEHYDES AND ACETOPHENONES IN n-HEXANE OR CYCLOHEXANE SOLUTION

Substituent	BENZALDEHYDE				ACETOPHENONE	
	B-Band		C-Band		B-Band	
	λmax(mμ)	ε max	λmax(mμ)	ε max	λmax(mμ)	ε max
None	(241	14,000	(277-278	1,200	238-239	12,500[1]
	(247	12,000	(287	1,000		
o-Methyl-	(243	12,500[2]	291	1,700[2]	{ 237	11,500[5]
	(251	13,000			{ 245·5	9,060
o-Fluoro-	(240	13,300	(284	2,400	233	9,500[1]
	(ca.247	9,700	(291	2,000		
			(294	2,000		
o-Chloro-	(246	11,000	(292	1,750	235	5,700[1]
	(252	8,500	(302	1,400		
o-Bromo-					234-236	4,900[1]

TABLE V (continued)

	BENZALDEHYDE				ACETOPHENONE	
	B-Band		C-Band		B-Band	
Substituent	λmax(mμ)	ε max	λmax(mμ)	ε max	λmax(mμ)	ε max
o-Hydroxy-	(250	11,000	324-325	3,500	251	9,700[3]
	(257	11,500				
o-Methoxy-	(246	10,500	(306	4,600	246	8,000[3]
	(ca.253	8,500	(ca.314	4,200		
o-Amino-					252	5,500[1]
o-Carboxy-	(224	7,800	(269	770		
	(ca.231	6,700	(276	840		
			(ca.286	380		
o-Nitro-	(222	15,300	ca.282	1,800		
	(247	7,000				
	((252	4,700	270	3,600	256	4,800)[4]

[1] Ref. 11 [2] Ref. 2 [3] Acetophenone values in ether. Ref. 5

[4] Values in constant-boiling ethanol. Ref. 23 [5] Values in isopentane. Ref. 25

The B-bands of all benzaldehydes shown in Table V exist as doublets with the exception of that of *o*-nitrobenzaldehyde. Here there are two distinct bands, the one at 247 mμ being ascribed to nitrobenzene absorption, which is supported by the fact that the maximal absorption in ethanol occurs at 252 mμ. ε = 4,700 (23). The greatly reduced absorption intensity of the band, particularly in ethanolic solution, as compared with the meta-isomer, is ascribed to the increased steric interaction between the two ortho-substituents.

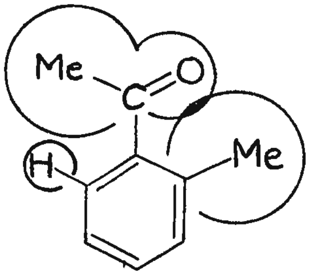
The data for nitrobenzaldehydes in ethanolic solution, as reported by Walker and Young (23), are also of value in understanding the nature of steric interaction. This is because it may be held that the frequently observed similarity between the spectra of ortho- and meta-isomers is inherent in the electronic configurations of disubstituted benzene derivatives, and is not caused by steric interaction (see 13). On the other hand it may be supposed that the similarity provides evidence for steric interactions. This latter argument assumes that in o-disubstituted benzene derivatives resonance is frequently inhibited because of steric interactions, primary resonance in m-disubstituted benzene derivatives being impossible by definition. Consequently the B-band spectra are often similar (cf. 13). However, if the secondary short range interaction is large in the meta-isomer, or if steric interactions in the ortho-ismer are sufficiently large to dislodge both vicinal substituents, the two spectra will not resemble each other. Furthermore, examples should exist where there is no primary resonance interaction in the para-isomer, because of two opposing electronic effects, and where there is consequently a similarity between the spectra of the meta- and para-isomers, rather than between those of the ortho- and meta-isomers. This is observed, in fact, for the nitrobenzaldehydes, which are reported (23) to exhibit the following B-bands in constant-boiling ethanol.

o-Nitrobenzaldehyde λmax 252 mμ; ε = 4, 700
m-Nitrobenzaldehyde λmax 265 mμ; ε = 11,700
p-Nitrobenzaldehyde λmax 265 mμ; ε = 11,400

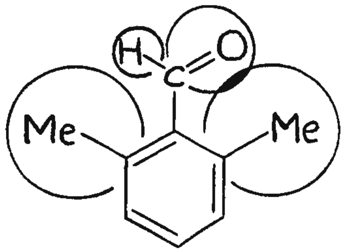
Interpretation of the ortho-effect can also be discussed by comparing the spectra of o-substituted benzaldehydes with those of the corresponding acetophenones (see Table V). At least three interpretations may be advanced for the ortho-effect and the data assist in deciding between these. The first interpretation is to ascribe the ortho-effect to intramolecular hydrogen bonding; the second is to ascribe it to steric interaction between vicinal atoms or groups with the molecule occupying only one ground state (2); and the third is to assume the ortho-effect is sometimes caused by the molecule existing in more than one conformation (e.g. *s-cis* and *s-trans*) which, however, need not all contribute to the observed absorption (8).

Examination of Table V shows that an explanation based on intramolecular hydrogen bonding is consistent with the observed similarity of the B-bands for the *o*-hydroxy and *o*-methoxy derivatives of benzaldehyde and acetophenone. On the other hand, this would not account for the generally decreased absorption intensities in the acetophenones, nor in particular for the *o*-methyl- and *o*-chloro-acetophenone B-band absorptions, which are much lower than those of the corresponding benzaldehydes. Intramolecular hydrogen bonding is not, then, the sole explanation for the observed ortho- effects.

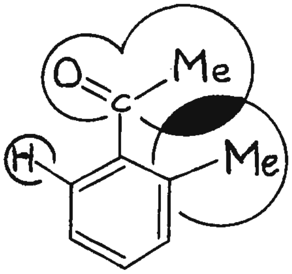
The second explanation, ascribing the ortho-effect to steric interactions whilst postulating only one ground state, is also not entirely satisfactory. For example, according to this explanation, *o*-methylacetophenone would be expected to exist in only one conformation (I), which must be non-planar since the extinction coefficient has been reduced from 15,000 (for the para-isomer, in ethanol) to 8,500 (11).



I[1]



II[1]



III[1]

[1] After Braude and Sondheimer (2)

At the same time, the degree of non-planarity would be expected to be similar for both o-methylacetophenone and 2, 6 - dimethylbenzaldehyde (II). Yet this is evidently not so, since the extinction coefficient of 2, 6 - dimethylbenzaldehyde is 12, 500 (2). That is, no appreciable decrease is observed with respect to the extinction coefficient of o-methylbenzaldehyde (13,000) or that of p-methylbenzaldehyde (15,000).

This objection can be accounted for by the third explanation, which assumes structures of type I to be planar or near-planar, but ascribes the reduced extinction coefficient to the existence of other non-planar s-cis or s-trans conformations (eg.III). These latter conformations are assumed to exist in the ground state, but are unable, because of their non-planarity, to contribute appreciably to the observed absorption (cf. 8).

The C-bands show the usual changes (see 11) although it may be noted that in o-tolualdehyde and salicylaldehyde the C-band does not occur as a doublet (see Table V). The occurrence of doublets in the B- and C-bands is of interest since this fine structure almost invariably occurs for the benzaldehyde bands in inert media, and as such can be used to identify the benzaldehyde chromophoric system (cf. 15). At the same time, the underlying physical reason for the occurrence of this fine structure remains in doubt (see section under "The spectrum of benzaldehyde"). It should be noted, however, that the fine structure occurs for all benzaldehyde B-bands described in this thesis, with the exception of the bands at 225 mμ and 222 mμ for m- and o-nitrobenzaldehyde respectively. A further point of interest is that, of the two peaks shown by the B-bands of benzaldehydes, the one at shorter wavelength is the one of higher intensity (see Tables I, III, IV and V) save in the case of o-hydroxybenzaldehyde. Since, in the latter compound and o-aminobenzaldehyde only, of the compounds considered, there is a possibility of intramolecular hydrogen bonding with the oxygen of the carbonyl group, this supports the hypothesis that the fine structure is caused, in part at least, by rotational isomerism.

EXPERIMENTAL

The ultraviolet absorption spectra were determined in duplicate, in a Unicam SP 500 spectrophotometer, using fused silica cells with 1 cm. path length. ε represents the molecular extinction coefficient defined by $\varepsilon = [\log (I_0/I)]/cl$, where I_0 and I are intensities of incident light and transmitted light respectively, c = concentration in moles/ litre, and l = cell length in centimetres. The errors of the instrument were calculated as: Extinction coefficient ± 3%; wavelength ± 0.5 mμ; absolute wavelength ± 2 mμ.

The general infrared spectrum of m-nitrobenzaldehyde was determined using a Perkin-Elmer Model 21 double beam infrared spectrophotometer, and the details of the carbonyl band were determined using a Perkin-Elmer 12 C single beam instrument converted to double pass. The solvent used was carbon tetrachloride and the spectrum was determined at three concentrations: 5.82×10^{-3}, 7.48×10^{-3} and 8.80×10^{-3} moles/litre. The integrated absorption intensities of the carbonyl band were calculated to be 2.33, 2.35, and 2.65 respectively, giving a mean of 2.44 $\text{mole}^{-1}.\text{litre.cm}^{-2} \times 10^{-4}$.

Physical constants of the purified compounds used in this work are recorded in Table VI.

TABLE V1

PHYSICAL CONSTANTS OF BENZALDEHYDES

Substituent	Published Values	Reported Values
None	b.p. 62/10 mm; $n^{17.6}$ 1.5463	b.p. 41/1 mm; $n^{22.5}$ 1.5444
m-Amino-	-	-
p-Amino-	m.p. 70-72	
o-Chloro-	b.p. 213-214; $n^{21.7}$ 1.5656	b.p. 213; n^{22} 1.5656
m-Chloro-	b.p. 213-214; $n^{20.2}$ 1.5650	b.p. 55/1 mm; $n^{25.8}$ 1.5613
p-Chloro-	m.p. 47.5	m.p. 47.5
o-Fluoro-	b.p. 175	b.p. 51/11 mm; n^{22} 1.5212
m-Fluoro-	b.p. 173	$n^{21.3}$ 1.5173
o-Hydroxy-	b.p. 196.5; $n^{19.7}$ 1.5736	b.p. 45/3 mm; $n^{22.5}$ 1.5722
m-Hydroxy-	m.p. 108 (106)	m.p. 104
p-Hydroxy-	m.p. 115-116	m.p. 117
m-Iodo-	m.p. 57	m.p. 57
p-Iodo-	m.p. 77-78	m.p. 76
o-Methoxy-	m.p. 36; n^{20} 1.5600	b.p. 71/2 mm; n^{21} 1.5604
m-Methoxy-	b.p. 230; n^{20} 1.5530	b.p. 62/1 mm; n^{25} 1.5511
p-Methoxy-	b.p. 248; $n^{12.7}$ 1.5764	b.p. 83/2 mm; n^{22} 1.5717
o-Nitro-	m.p. 43-44	m.p. 42
m-Nitro-	m.p. 58	m.p. 57
p-Nitro-	m.p. 106	m.p. 106
o-Carboxy-	m.p. 97	m.p. 97.2
p-Carboxy-	m.p. 248-250 (256)	m.p. ca.250

Most of the compounds used were obtained commercially. Those which were prepared by the author, or which needed special purification, are given below.

m-Aminobenzaldehyde

Obtained in polymer form. Depolymerised by refluxing 6 g. of polymer for 30 minutes with 200 ml. of $3\bar{N}$ dilute hydrochloric acid, under nitrogen. The monomer was then precipitated with saturated aqueous sodium hydroxide solution, the pH being kept below 7. The mixture was then cooled rapidly, and the m-aminobenzaldehyde extracted with ether. As the compound polymerised immediately on removal of the solvent, the ether extract was diluted with cyclohexane to about 2% ether. The spectrum was then determined, and the solution evaporated to dryness and the residue weighed, to determine the concentration of the solution. Owing to the immiscibility of ether and cyclohexane, the C-band could not be determined. Yield ca. 30%.

p-Aminobenzaldehyde

A similar procedure to that described above was followed for p-aminobenzaldehyde.

Yield ca. 30%.

m-Iodobenzaldehyde

This was prepared from m-aminobenzaldehyde polymer by the standard diazotisation and Sandmeyer method (for example, 24a). Iodine was added as potassium iodide, and the product separated by steam distillation. The distillate was extracted with ether, evaporated to dryness, and recrystallised from ethanol to give pale yellow crystals. Yield ca. 70%. Sublimed to give white crystals.

p-Iodobenzaldehyde

A similar procedure to that described for m-iodobenzaldehyde was used for the para-isomer, which was recrystallised from ethanol to give pale yellow crystals. Yield ca. 70%.

Solvents

Solvents were used as received, with the exception of dioxane, which was purified according to the method given by Vogel (24 b). One litre of dioxane, 14 ml. concentrated hydrochloric acid and 100 ml. of water were refluxed for 12 hours, nitrogen being bubbled slowly through the solution to remove the acetaldehyde formed. The solution was then cooled, and shaken with potassium hydroxide pellets until some pellets would not dissolve. The aqueous layer was then removed, and the dioxane allowed to stand over potassium hydroxide pellets for 24 hours. It was then refluxed over sodium for about 12 hours, or until the sodium became bright. The dioxane was then distilled from sodium. Only that dioxane, which had an optical density of 0.5 or less in a 1 cm. cell against air, was used in determining spectra.

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