391. *The Ultraviolet Absorption Spectra of Nitro-substituted Aromatic Carbonyl Compounds.*

By E. A. Walker and J. R. Young.

The ultraviolet absorption spectra of mononitro-substituted benzaldehydes, acetophenones, and *trans*-chalcones, and of certain dinitrochalcones, are reported. *ortho*-Substituents show steric effects as described by Braude,[1] and mononitrochalcones show electronic substituent effects consistent with the findings of Black and Lutz.[2] There are indications of a specific chromophoric effect from *m*- and *p*-nitrobenzoyl groupings.

o-, *m*-, and *p*-NITRO-BENZALDEHYDE and -acetophenones were obtained in order to prepare the nitro-chalcones which were required for a kinetic study (see following paper). The ultraviolet spectra of all these compounds were measured in ethyl alcohol to establish an analytical method for the kinetic work. A separate treatment of the various correlated features evident in the absorptions was considered desirable.

Benzaldehyde and Acetophenones.—The spectra of these are in Table 1. The values for bands 2 and 3 agree with those reported by Grammaticakis[3] (who did not include the low-wavelength absorption). There was, however, a greater discrepancy than expected in the values for *m*-nitro-benzaldehyde and -acetophenone and these compounds were purified with particular care before the final values were accepted. The accuracy of the values for band 1 is probably lower than of the others owing to the light-scattering defect shown by spectrophotometers at their lower range limit (see Bladon *et al.*[4]). We have checked these maxima on two instruments of different manufacture and find concordant results; from this and other considerations we believe them to be real and not " false."

The weak bands shown by the unsubstituted compounds at 330 mμ were not sought in

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[1] Braude and Sondheimer, *J.*, 1955, 3754.
[2] Black and Lutz, *J. Amer. Chem. Soc.*, 1955, **77**, 5134.
[3] Grammaticakis, *Bull. Soc. chim. France*, 1953, 821, 856.
[4] Bladon, Henbest, and Wood, *J.*, 1952, 2737.

the nitro-derivatives. No significance is attached to the frequent failure of the latter to show band 3 since this may well be overwhelmed by the broad maximum of band 2.

We identify the second bands of Table 1 with Braude's *K*-bands [5] since they correspond with the similarly placed bands both of unsubstituted compounds and of nitrobenzene ($\lambda_{max.}$ 252 mμ; ε 10,000). Bowden and Braude [6] associate such bands with transitions to a dipolar state which involves the substituent. In the nitro-carbonyl compounds either group may serve as the site of the negative charge in the excited state and, therefore, we consider that a competitive interaction between the two substituents occurs. This results in a marked broadening of the band in the disubstituted compounds, a slight bathochromic shift, and a reduction in the intensity of absorption to values which are, in most cases, intermediate between that of the unsubstituted compound and that of nitrobenzene.

TABLE 1. *Ultraviolet light absorption of nitro-benzaldehydes and -acetophenones in constant-boiling ethanol.*

	Band 1		Band 2		Band 3	
Compound	$\lambda_{max.}$ (mμ)	ε	$\lambda_{max.}$ (mμ)	ε	$\lambda_{max.}$ (mμ)	ε
Unsubst. Ph·CHO	—	—	244	12,300	280	1600
o-NO_2	220	8500	252	4700	270	3600
m-NO_2	210	6800	265	11,700	—	—
p-NO_2	211	5800	265	11,400	—	—
Unsubst. Ph·COMe ...	—	—	244	11,800	278	1000
o-NO_2	205	11,000	256	4800	—	—
m-NO_2	227	22,000	~261 (infl.)	~6600	—	—
p-NO_2	218	3500	263	13,800	—	—

For the *o*-nitro-compounds the intensity of band 2 is less than half the average value for the other isomers. On the other hand, there is but little change in the wavelength of the maximum. These are the characteristic features of a type 1 steric effect described by Braude and Sondheimer,[1] and we may regard either of the attached *ortho*-groups as impeding the approach of the second to that planarity with the ring which is required in the polar excited state.

Turning to band 1 we cannot explain the generally small differential substituent effects. A similar band was observed by Ungnade [7] for the halogenated nitrobenzenes where it showed no steric effects whilst the 250 mμ bands (which also appeared) did. This author regarded the 210 mμ band as derived from the 183 mμ transition of benzene in which the excited state is a dipolar form not involving the substituents as possible charge sites (*i.e.*, the ring alone is polarised). This is also the view taken by Bowden and Braude [6] for other examples of a similar band. Steric effects are also absent from the present bands and we accept Ungnade's explanation.

The outstanding feature of the results for band 1 is the slight bathochromic shift and large increase of intensity shown by *m*-nitroacetophenone. Whilst Ungnade did not record the maxima of his 210 mμ bands, the steepness of his absorption curves at *ca.* 220 mμ suggests that a similar "*meta*-effect" may be present in the halogenonitrobenzenes.

Mononitrochalcones.—On the basis of previous work [2, 8] it may be assumed that the chalcones prepared in the present study are *trans*-isomers. The apparent failure of the second band to appear in most of the nitro-compounds (see Table 2) is characteristic of *trans*-isomers, and is probably due to its being overwhelmed by band 1 or 3 as these show increased intensities relative to the parent molecule. In a similar way the intensity of band 2 in *p'*-nitrochalcones has swamped its first band.

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[5] Braude, *Ann. Reports*, 1945, **42**, 125.

[6] Bowden and Braude, *J.*, 1952, 1068.

[7] Ungnade, *J. Amer. Chem. Soc.*, 1954, **76**, 1601.

[8] Kuhn, Lutz, and Bauer, *ibid.*, 1950, **72**, 5058; Lutz and Jordan, *ibid.*, p. 4090; Black and Lutz, *ibid.*, 1953, **75**, 5990.

The wavelength of band 1 is reasonably constant throughout the three series of compounds (chalcones, aldehydes, and ketones), except for *m*-nitroacetophenone and *m*′-nitrochalcone. Moreover, the intensities observed in the chalcones are free from steric effects and are approximately double the values observed for the single-ring compounds. This consistency leads to the conclusion that the band has the same origin in the three series, *viz.*, it is an *E*-type transition of the benzene nuclei.

TABLE 2. *Ultraviolet light absorption of mononitrochalcones in constant-boiling ethanol.*

Subst. in	Band 1		Band 2		Band 3	
Ph·CH:CH·COPh′	$\lambda_{\text{max.}}$ (mμ)	ε	$\lambda_{\text{max.}}$ (mμ)	ε	$\lambda_{\text{max.}}$ (mμ)	ε
Unsubst.	209	9800	227	9400	309	21,000
o-NO$_2$	210	15,000	—	—	276	19,500
m-NO$_2$	215	13,000	—	—	290	27,000
p-NO$_2$	210	15,000	—	—	315	30,000
o′-NO$_2$	218	15,000	—	—	298	23,000
m′-NO$_2$	237	20,500	—	—	317	21,500
p′-NO$_2$	—	—	268	17,000	321	20,000

The band found with *m*′-nitrochalcones is quite similar to that shown by the *meta*-substituted ketone and we consider that it arises from the same transition in both cases, *i.e.*, in the chalcone it is partial chromophore band. Its position is reminiscent of the bands shown by αβ-unsaturated ketones (*ca.* 230 mμ) discussed by Schubert and Sweeny,[9] and by Mecke and Noack,[10] though its intensity is higher than normal (*ca.* 12,000) for such compounds. Whilst the intensity difference could be reasonably explained, we hesitate to advance firmly this explanation of the anomalous absorption.

We accept the failure of band 2 to appear in most of the compounds of this series as evidence of a suppression relative to the parent compound, though not necessarily as strongly as the tabulated results suggest owing to the increased breadth of band 3. The results are then comparable with those for the nitro-aldehydes and -ketones where the *K*-band was also depressed and showed the expected steric effects. The anomalous behaviour of *p*′-nitrochalcone is matched by the similar behaviour of *p*-nitroacetophenone, since in both these compounds band 2 is stronger than in other isomers and is even stronger than in its unsubstituted parent compounds. Therefore, in these two cases the *p*-nitro-group assists the transition which cannot be normal carbonyl-ring polarisation such as is involved in the benzoyl chromophore.

The features of band 3 are more constant throughout the *o*′- *m*′- *p*′-series (benzoyl substituted) than through the *o*- *m*- *p*-series (cinnamoyl substituted), giving support to Black and Lutz's conclusion [2] that this is a partial chromophore band of the cinnamoyl group. The *ortho*-compound shows normal steric-hindrance effects which are confirmed by examination of models.

It has been pointed out by Ferguson and Barnes [11] that negative groups in the cinnamoyl ring should tend to depress the polarisation of the cinnamoyl system, leading to changes in band 3 similar to that described for the *o*-nitro-group. It is, therefore surprising to find that *m*-nitro-group has a greater depressing effect (implying greater electron-attraction) than the more favourably placed *p*-nitro-group which even slightly enhances the ease and probability of this transition. This anomaly finds a parallel in the kinetic study of these compounds (see following paper) and is discussed there. The *p*-nitro-group may here be introducing a contribution from the *p*-nitrostyryl chromophore as suggested by Black and Lutz [8] for *cis*-*p*-nitrochalcone.

Dinitrochalcones.—In the absence of definite evidence concerning the configuration of the dinitro-compounds, which were prepared by the method used for the *trans*-mononitro-series, we assume that they also were the *trans*-forms. The striking effect of disubstitution

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[9] Schubert and Sweeny, *J. Amer. Chem. Soc.*, 1955, **77**, 2297.

[10] Mecke and Noack, *Angew. Chem.*, 1956, **68**, 150.

[11] Ferguson and Barnes, *J. Amer. Chem. Soc.*, 1948, **70**, 3907.

is the emergence of band 2 as the strongest band in the spectrum (see Table 3). This is so pronounced that band 3 is frequently swamped, although band 1 is not reported in Table 3 it appears at an almost constant wavelength of 210 mμ with intensities between 15,000 and 20,000.

It is immediately apparent that the nature of band 2 is controlled by the substituent in the benzoyl group. Thus the three compounds containing the *m*′-nitro-group show similar bands; there is no noticeable effect from the other nitro-group as this changes its position in the cinnamoyl ring. Moreover, there is a similarity between these bands and the anomalous band 1 appearing in both *m*-nitroacetophenone and *m*′-nitrochalcone.

TABLE 3. *Ultraviolet light absorption of dinitrochalcones in constant-boiling ethanol.*

Subst. in Ph·CH:CH·COPh′		Band 2 λ		Band 3		Subst. in Ph·CH:CH·COPh′		Band 2		Band 3	
		$\lambda_{max.}$ (mμ)	ε	$\lambda_{max.}$ (mμ)	ε			$\lambda_{max.}$ (mμ)	ε	$\lambda_{max.}$ (mμ)	ε
o	*o*′	255	21,900	—	—	*p*	*m*′	245	16,500	315	22,000
m	*o*′	267	24,500	—	—	*o*	*p*′	265	19,500	—	—
p	*o*′	—	—	307	22,500	*m*	*p*′	272	21,000	305 †	14,000
o	*m*′	245	23,500	300 *	10,000	*p*	*p*′	270	22,500	—	—
m	*m*′	247	16,500	317	28,500						

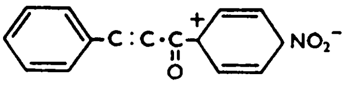
* Weak inflexion. † Strong inflexion.

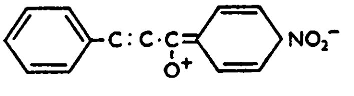
An identical comparison may be made with the spectra of the *p*′-dinitro-compounds and band 2 of *p*′-nitrochalcone. We conclude from this consistency that the same transition is involved in both the mono- and the di-nitro-series. It should be noted that we have traced anomalies, first noticed in *m*- and *p*-nitroacetophenone, through all compounds containing these nitro-carbonyl systems. The band increases in intensity and decreases in wavelength from the ketone, through the chalcone, to the dinitrochalcone; *i.e.*, as the other group attached to carbonyl-carbon becomes more electronegative. We cannot, therefore, consider that the transition involved is a normal polarisation of the benzoyl group, which would otherwise fit the results. It seems more likely that a normal polarisation of the nitro-group might be involved.

Band 3 is regarded as arising from the cinnamoyl group transition which gives rise to band 3, of the same wavelength, in the mononitro-compounds. Thus the three instances where it appears (*po*′, *mm*′, and *pm*′) contain the *m*- or *p*-nitrocinnamoyl group, being those which showed enhanced values for band 3 in the mononitrochalcones. The intensities of the present bands are lower than the corresponding bands of the *m*- and *p*-nitrochalcones; this is attributed to the general depression of polarisability of carbonyl groups by the second nitro-group.

It is noteworthy that the appearance of band 3 is accompanied by a decrease in the intensity of band 2. Thus structures which favour the transition involved in band 3 are more resistant to the transition involved in band 2. This supports our conclusion that band 2 may involve transition to an excited state of the structure (I) or (II).

(I)





(II)

EXPERIMENTAL

The chalcones were prepared by the standard method of shaking equimolar quantities of the appropriate aldehyde and ketone in methanol *ca.* 0·2 molar in sodium hydroxide. After ice-cooling and filtration the solid product was washed with methanol before repeated recrystallisation.

Chalcone	Solvent	M. p.	Chalcone	Solvent	M. p.	Chalcone	Solvent	M. p.
Unsubtd....	EtOH	57·5°	*p'*-NO_2	EtOH	147—148°	*mm'*-$(NO_2)_2$	Ac_2O	206—208°
o-NO_2	„	119*	*oo'*-$(NO_2)_2$...	„	133—134	*pm'*-$(NO_2)_2$	„	205
m-NO_2......	„	141	*mo'*-$(NO_2)_2$	„	124—125	*op'*-$(NO_2)_2$...	Benzene	121—122
p-NO_2	„	162—163	*po'*-$(NO_2)_2$	„	178—179	*mp'*-$(NO_2)_2$	AcOH	197—199
o'-NO_2......	„	125—126	*om'*-$(NO_2)_2$	AcOH	160—161	*pp'*-$(NO_2)_2$...	„	129 †
m'-NO_2 ...	„	130·5						

* Air-drying at 100° increased the m. p. to *ca.* 125° with accompanying darkening.
† Commencement of melting indefinite.

The aldehydes and ketones were purchased, except *o*-nitroacetophenone which was prepared by the method in *Organic Syntheses.*[12]

Absorption Spectra.—The spectra were determined upon freshly prepared solutions in constant-boiling ethanol, at dilutions giving optical densities of *ca.* 0·6 at the maxima. The solubilities of the substituted chalcones in constant-boiling alcohol are very small at room temperature and prolonged shaking was necessary to obtain standard solutions. In certain difficult cases solutions *ca.* 0·0003M were prepared directly in 250 ml. of solvent. The *mm'*- and *pp'*-dinitrochalcones resisted even this treatment and the samples had first to be dissolved in dioxan, the initial solution being diluted with constant-boiling ethanol so that the spectrum was actually measured in 1% dioxan–alcohol with a similar control. The controls examined against alcohol showed no absorption.

Measurements were made with both a Unicam SP500 and a Hilger Uvispek spectrophotometer with concordant results.

WEST HAM COLLEGE OF TECHNOLOGY, LONDON, E.15.

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[12] *Org. Synth.*, 1950, **30**, 70.