367. *The Absorption Spectra of Nitrophenylhydrazines.*

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FROM a qualitative examination of the absorption spectra of a series of phenylhydrazines, Baly and Tuck (J., 1906, **89**, 982) concluded that *p*-nitrophenylhydrazine in neutral solution existed in the quinonoid form. Their deduction was based on the fact that the absorption curve of this compound differed considerably from those of the other hydrazines examined, but was practically identical with that of *p*-nitroaniline, which had previously been assumed to be quinonoid on account of the coincidence of its absorption maximum with that characteristic of *p*-benzoquinones (Baly, Edwards, and Stewart, *ibid.*, p. 515). The relatively complex nature of the reaction of *o*-nitrophenylhydrazines with bases (Macbeth and Price, J., 1934, 1637) led us to examine their absorption spectra for evidence of a tautomerism which might account for such behaviour. However, since the work was undertaken, Morton and McGookin (J., 1934, 901) have discussed the spectra of nitrotoluidines and related substances; and as the spectra of the nitrophenylhydrazines fall into line with the cases there recorded, it does not appear to be valid to ascribe a quinonoid structure to any of the compounds on the evidence of their absorption curves.

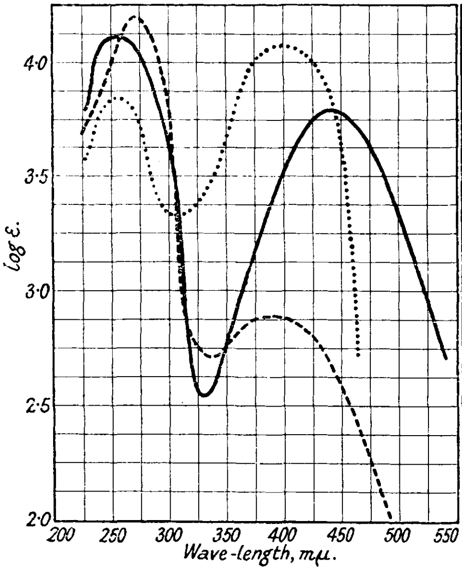
In the absorption spectrum of nitrobenzene two inflexions appear (275—300 mμ, log ε *ca.* 3·2; and 320—365 mμ, log ε *ca.* 2·3) in addition to the band of shorter wavelength characteristic of electronic excitation of the C=C system of the nucleus. The question thus arises whether these inflexions represent bands indicative of additional electronic energy levels associated with the nucleus, or are due to electronic excitation in the nitro-group.

The same question arises with the nitroanilines and nitrotoluidines, the spectra of which show, in addition to the bands characteristic of the nucleus, well-defined maxima, the positions and intensities of which are readily traced to the relative positions of the nitro- and amino-groups (Morton and McGookin, *loc. cit.*). The locations and intensities of these additional maxima in alcoholic solution are set out below, and it is apparent that the $\lambda_{max.}$ region for the *o*-compounds differs markedly from that common to the *m*- and *p*-derivatives; but the latter may be differentiated by intensity differences, the ε values of the $\lambda_{max.}$ of the *p*-compounds being some ten times greater than those of the *m*-derivatives.

	$\lambda_{max.}$, mμ.	log ϵ.
o-Nitrotoluidines	407—417	3·5 —3·85
m-Nitrotoluidines	352—375	3·07—3·24
p-Nitrotoluidines	373—379	4·12—4·24

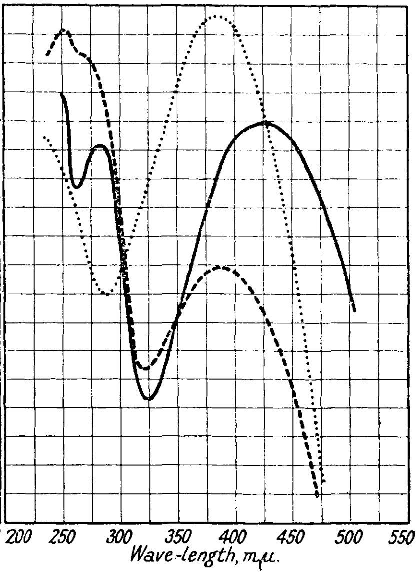
Since these characteristic maxima do not appear in the simple nitro- or amino-compounds, it was concluded that they were due to an electron of the nuclear C═C system jointly influenced by the amino- and nitro-groups, or alternatively " to an electron controlled by a nitrogen atom and influenced by unsaturation within the same molecule." No solution of the question of the origin of such maxima was presented, but the spectra of the nitrophenylhydrazines now provide definite evidence that the bands are due to an electron of the nitro-group influenced by the amino- or hydrazino-group. The maxima in these spectra (Figs. 1 and 2) are recorded in Table I, together with Morton and McGookin's

FIG. 1.



In aqueous alcohol (20% EtOH).

FIG. 2.



In alcohol.

———— o-*Nitrophenylhydrazine.*
•- - - - - - - m- ,,
.... p- ,,

TABLE I.

Solvent.	Ortho. $\lambda_{max.}$, mμ.	Ortho. log ϵ.	Meta. $\lambda_{max.}$, mμ.	Meta. log ϵ.	Para. $\lambda_{max.}$, mμ.	Para. log ϵ.
			Nitrophenylhydrazines.			
Aqueous alcohol	438·5	3·8	387·5	2·89	398·5	4·08
(20% EtOH)	254	4·14	271	4·2	256·5	3·86
Alcohol	429	3·78	387·5	3·12	382	4·21
	281·5	3·64	*ca.* 270	4·03		*
			252·5	4·14		
			Nitroanilines.			
Alcohol	403·6	3·73	375	3·2	374	4·18
	275·2	3·71	233	4·26		
			Nitrodimethylanilines.			
Water	441	3·29	385	2·99	422	4·34
	242	4·24	247	4·21	232·5	3·96
Alcohol	416	3·47	400·3	3·13	386·5	4·33
	245·5	4·33	246	4·36	*ca.* 200	4·23

* The curve of the *p*-compound indicates the existence of a band just outside the region of examination.

values for the nitro-anilines and -dimethylanilines (*loc. cit.*). Italicised numbers in the tables represent minor inflexions in the curves.

The values of the $\lambda_{max.}$ of the band of shorter wave-length common to all the curves of the nitrophenylhydrazines in aqueous-alcoholic solution are nearly the same; and it seems reasonable to attribute this absorption, as in nitrobenzene, the nitrotoluenes, benzonitrile, etc., to the electronic transition of the C=C system of the nucleus, the small differences being due to vibrational effects. The other $\lambda_{max.}$ recorded for *o*-nitrophenylhydrazine differs markedly in location from the corresponding bands shown by the *m*- and the *p*-compound. This is true for both alcoholic and aqueous-alcoholic solutions of the nitrophenylhydrazines, and is in agreement with the spectra of the nitroanilines in alcohol and of the nitrotoluidines in either alcohol or water. Further, similar differences in the intensities of these bands of the *m*- and *p*-compounds are observed in all cases; *e.g.*, the ratio of ε for *p*- to *m*-compounds is approx. 10 for the nitroanilines in alcohol; 12 for the nitrophenylhydrazines in alcohol, and 16 in aqueous alcohol; and 16 for the nitrodimethylanilines in alcohol, and approx. 21 in water.

It might be suggested that the difference in the $\lambda_{max.}$ values should be interpreted as evidence of structural differences more profound than position isomerism, indicating, *e.g.*, a benzenoid–quinonoid change. Such a view is untenable, for it would imply similarity in structure between the *m*- and *p*-compounds, since the positions of the maxima in these compounds are relatively close; and *m*-quinones do not exist. Further, such a contention cannot be maintained in view of the close analogy presented by the spectra of the nitrodimethylanilines.

The results, moreover, can be accounted for on the assumption that the long-wave absorption is due to electronic excitation in the nitro-group influenced by the nuclear amino- or hydrazino-group. Hantzsch and Voigt (*Ber.*, 1912, **45**, 85), in the qualitative examination of the absorption spectra of a series of simple aliphatic nitro-compounds, showed that the true nitro-group (as distinct from the *aci*-form) is capable of weak selective absorption in the region λ *ca.* 270—280 mμ. Regions of rapid extension ("kicks") are also found in the qualitative curves of other nitro-compounds such as dibromodinitromethane, phenylbromodinitromethane, chloro- and bromo-nitroform, and nitroform itself in sulphuric acid (Graham and Macbeth, J., 1922, **121**, 1109), the inflexions in these compounds being within the limits λ *ca.* 250—290 mμ.

The view that the maxima of longer wave-lengths in the nitroamines and nitrophenylhydrazines are due to an electron controlled by the nitrogen atom of the nitro-group is supported by the spectra of 2 : 4-dinitrophenylhydrazine, 4 : 6-dinitro-*m*-tolylhydrazine, and 2 : 4-dinitroaniline. The curves for these compounds are shown in Figs. 3—5, and the values are recorded in Table II.

TABLE II.

	Aqueous alcohol (20% EtOH).		Alcohol.	
	$\lambda_{max.}$, mμ.	log ε.	$\lambda_{max.}$, mμ.	log ε.
2 : 4-Dinitrophenylhydrazine	*403*	4·04	*392*	3·92
	366	4·22	352	4·16
	263	4·05	262	4·0
4 : 6-Dinitro-*m*-tolylhydrazine	*410*	3·75	*395*	3·8
	365	3·98	350	4·06
	281	3·90	*279·5*	3·95
	267·5	3·97	269	4·02
			261	3·97
2 : 4-Dinitroaniline			*379*	3·9
			337	4·2
			258·5	3·89

If all the bands in the nitroamines and the nitrophenylhydrazines were due to electronic excitation of the C=C of the nucleus jointly influenced by the nitro- and amino-groups, the introduction of a further nitro-group would express itself merely by the change in position of the bands, or at most in the development of a new band as a consequence of increased complexity of the chromophore (compare carotene and other long conjugated ethylenic compounds). On the other hand, if it is postulated that the long-wave maxima are due to an electron of the nitro-group influenced by the amino- or the hydrazino-group, it may reasonably be expected that in the dinitro-compounds the bands due to each of the influenced nitro-groups will persist and be capable of detection unless their locations

FIG. 3.

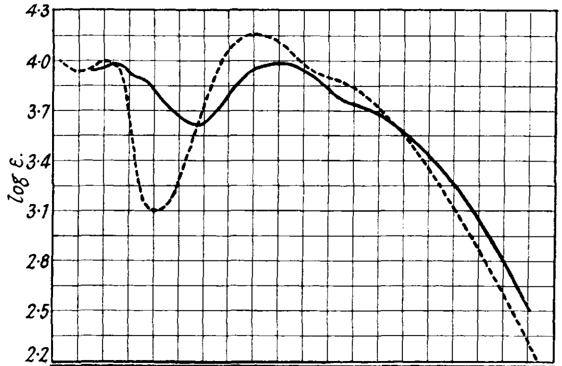


FIG. 4.

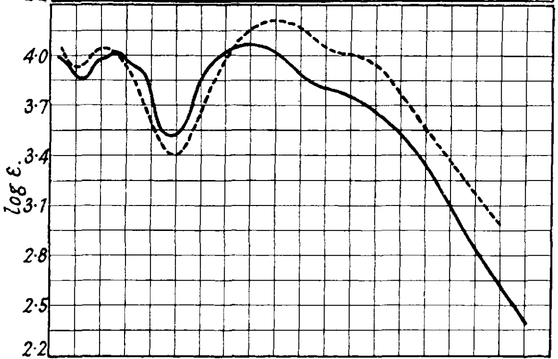


FIG. 5.

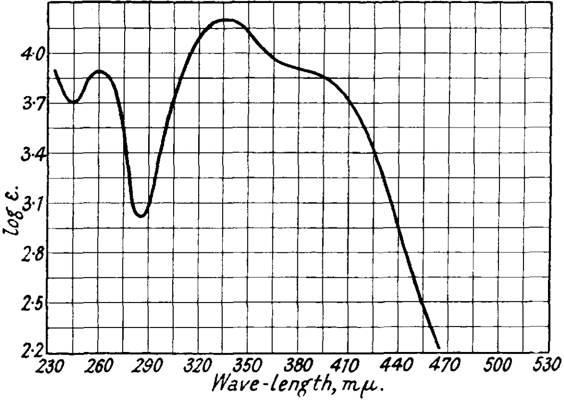


FIG. 3.

——— 4 : 6-*Dinitro*-m-*tolylhydrazine in aqueous alcohol* (20% EtOH).
- - - - - 2 : 4-*Dinitrophenylhydrazine in alcohol.*

FIG. 4.

——— 4 : 6-*Dinitro*-m-*tolylhydrazine in alcohol.*
- - - - - 2 : 4-*Dinitrophenylhydrazine in aqueous alcohol* (20% EtOH).

FIG. 5.

2 : 4-*Dinitroaniline in alcohol.*

are very close. Examination of the curves of 2 : 4-dinitrophenylhydrazine (A) and 4 : 6-dinitro-*m*-tolylhydrazine (B) shows that both the ortho- and the para-nitrohydrazino effects do persist in alcoholic and aqueous-alcoholic solutions, the former being characterised by the inflexions at 392 mμ (alcohol), 403 mμ (aqueous), and 395 mμ (alcohol), 410 mμ (aqueous); and the latter by the bands at 352 mμ (alcohol), 366 mμ (aqueous), and 350 mμ (alcohol), 365 mμ (aqueous) in the compounds A and B respectively.

The positions of the maxima do not coincide exactly with those of the simple *o*- and *p*-nitrophenylhydrazines themselves, but this is to be expected as being the effect of introducing an additional nitro-group into the nucleus. The displacement of the bands is approximately 2200 cm.$^{-1}$, and by applying this value to the nitroanilines the band positions in 2 : 4-dinitroaniline may be deduced. The good agreement between the values so calculated and the experimental results illustrates the analogous effect of the introduction of the nitro-group in that case also.

	mμ.	cm.$^{-1}$.
o-Nitrophenylhydrazine	429	23,300
p-Nitrophenylhydrazine	382	26,200
2 : 4-Dinitrophenylhydrazine	392	25,500
	352	28,400
Displacement of the *o*-band		25,500 − 23,300 = 2200
Displacement of the *p*-band		28,400 − 26,200 = 2200
o-Nitroaniline..................................	403·6	24,800
p-Nitroaniline	374	26,700
Whence, 2 : 4-dinitroaniline		27,000 and 28,900
Calc.	or 370 and 346	
Found	379 and 337	

Although the curves of the nitrophenylhydrazines in alcoholic and in aqueous solution are similar in character, the positions of the maxima are appreciably altered (Table III). The displacements are in either direction, as found for nitroamines (Morton and McGookin, *loc. cit.*), and although a strict comparison cannot be made, aqueous-alcoholic solutions having been used instead of water for the hydrazines owing to solubilities, yet the Δ cm.$^{-1}$ values were, with two exceptions, generally of the same order as those recorded by the previous workers.

TABLE III.

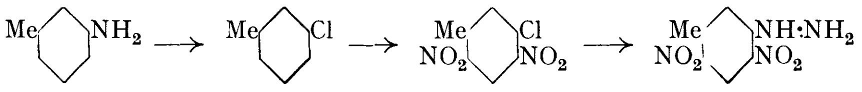
Band displacements [*alcohol* ⟶ *aqueous alcohol* (20% EtOH)].

Nitrophenylhydrazines.

	λ, mμ.	cm.$^{-1}$.	Δ cm.$^{-1}$.	λ, mμ.	cm.$^{-1}$.	Δ cm.$^{-1}$.
o-	429 → 438·5	23,300 → 22,800	−500	281·5 → 254	35,500 → 39,400	+3900
m-	387·5 → 387·5	25,800 → 25,800	—	252·5 → 271	39,600 → 36,900	−2700
p-	382 → 398·5	26,200 → 25,100	−1100			
2 : 4-Dinitro- ...	392 → 403	25,500 → 24,800	−700	352 → 366	28,400 → 27,300	−1100
				262 → 263	38,200 → 38,000	−200
4 : 6-Dinitro-*m*-tolyl-	395 → 410	25,300 → 24,400	−900	350 → 365	28,600 → 27,400	−1200
				279·5 → 281	35,800 → 35,600	−200
				269 → 267·5	37,200 → 37,400	+200

2 : 4-Dinitroaniline was prepared by heating 2 : 4-dinitrochlorobenzene with excess (2—3 mols.) of urea at 200—210°. Excess urea was extracted with water on cooling, and the dinitroaniline extracted with acetone and repeatedly recrystallised from aqueous acetone; m. p. 179° (cf. Benda, *Ber.*, 1912, **45**, 56).

Giua's synthesis of 4 : 6-dinitro-*m*-tolylhydrazine from hydrazine and 2 : 4 : 5-trinitrotoluene (*Gazzetta*, 1919, **49**, ii, 166) affords no definite proof of the position of the substituents, so the compound was synthesised by the following steps :



The hydrazine precipitated on the addition of 50% hydrazine hydrate to a warm alcoholic solution of 5-chloro-2 : 4-dinitrotoluene was twice crystallised from alcohol and obtained as orange-yellow needles, m. p. 194—195°. It is thus identical with Giua's compound.

The other materials used were prepared by standard methods and rigorously purified.

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