193. *The Absorption Spectra of the Nitrotoluidines and Related Substances.*

By R. A. Morton and A. McGookin.

In considering the spectral absorption curves for the ten isomeric nitrotoluidines several methods of approach are possible. (i) Starting from benzene, the curves for toluene, aniline, and nitrobenzene may first be considered, then those for the *o*-, *m*-, and *p*-nitrotoluenes, -toluidines, and -nitroanilines, followed by those of the nitrotoluidines in alcohol, in water, and in hydrochloric acid. (ii) The ten nitrotoluidines all exhibit well-defined absorption bands and some of the maxima are common to several isomerides. Although the wave-length of maximum absorption may be the same for two isomerides, the intensity of absorption may be different. Such variations may be considered in relation to the problem of *o*-, *m*-, and *p*-isomerism. (iii) In several of the isomerides, three separate broad absorption bands are shown, and any simple relationship, in the sense of constant or recurring frequency differences, obtaining between the wave-length maxima should be apparent. The conditions are specially favourable for such a test, since most of the maxima can be measured independently and with some accuracy on more than one compound. Moreover, the different bands are so well separated on the wave-length scale that the displacement of maxima due to overlapping absorption bands is likely to be as small as can be expected for complicated absorption spectra shown by substances in solution.

Benzene.—In the vapour state benzene exhibits a typical banded spectrum which is capable of a high degree of resolution, the frequencies corresponding with $\nu = 38{,}600 + 922n - 80p$, where $n = -1, 0, +1, +2, \ldots$, and $p = 0, 1, 2, 3, \ldots$; whilst the vapour fluorescence spectrum is reproduced by the same equation when $n = +1, 0, -1,$

— 2, — 3, . . . We may therefore accept $\nu = 38{,}600$ cm.$^{-1}$ (259·1 mμ) as being very close to the electronic frequency for benzene.

Allsopp (*Proc. Roy. Soc.*, 1934, **143**, *A*, 618) has shown that *cyclo*hexene exhibits a maximum at 185 mμ, log ε 3·7, and a step-out at 230—280 mμ of extremely low intensity, both regions of selective absorption being ascribed to the double bond. The curve for 1 : 3-*cyclo*hexadiene shows maxima at 185 mμ, log ε 4·75, and two new maxima at 256 and 268 mμ, log ε 4·0 and 3·8 respectively; the absorption at *ca.* 260 mμ is about 2×10^4 times more intense than in *cyclo*hexene. From the dispersion data, a maximum at about 110 mμ is inferred alike for *cyclo*-hexane, -hexene, and -hexadiene.

For benzene dissolved in alcohol or hexane, the maximum occurs at 254·3 mμ, the ε value of 320 being relatively low, but a second more intense band appears in the region near 190 mμ, whilst the dispersion requires a maximum well into the Schumann region. From the work of Allsopp it is clear that the latter is unrelated to the unsaturation of the molecule. Restricting attention, therefore, to the double bond, we have to account for two transitions in benzene, *viz.*, those associated with the chromophore C:C (190 mμ or 150,000 cals./g.-mol.) and with conjugated double bonds (259 mμ or 110,000 cals./g.-mol.), the difference being about 40,000 cals./g.-mol. Substitution of a methyl group to give toluene slightly displaces the observed maximum, but the extinction coefficient of 300 at 261·7—264·7 mμ is practically unaltered. Naturally, the introduction of a methyl group confers on the molecule the possibility of new vibrational frequencies, but there seems no reason to doubt that the same electronic change and virtually the same electronic energy levels are concerned in the spectral absorption of toluene as of benzene. This is also true of ethylbenzene (cf. Ramart-Lucas and Amagat, *Bull. Soc. chim.*, 1932, **51**, 965) with its maximum near 260 mμ, log ε 2·6. It may therefore be concluded that the absorption band near 260 mμ is due to a valency electron in a C:$C_{\text{arom.}}$ linkage, and is characterised by a relatively low $\varepsilon_{\text{max.}}$ of the order 300.

Nitrobenzene.—The absorption spectrum in solution shows a well-defined maximum at 257 mμ, but the extinction coefficient is now 10,000. The wave-length is sufficiently close to that of the benzene absorption at 254 mμ to justify the hypothesis that it corresponds with the same type of electronic transition, *i.e.*, that the C:C group is still the site of the act of absorption represented by the maximum. Nitrobenzene also exhibits two quite distinct inflexions in the absorption curve, *viz.*, those at 275—300 mμ (log ε *ca.* 3·2) and 320—365 mμ (log ε *ca.* 2·3). It will be necessary to investigate whether these inflexions represent partially masked bands due either to the nitro-group or to additional electronic energy levels associated with the C:C group.

Aniline.—Alcoholic solutions of aniline differ markedly from those of benzene in respect of absorption spectra. A new maximum appears at 234 mμ with considerable intensity (ε 11,500) but there is also a second band at 284·5 mμ of lower intensity (ε 1,750). It seems evident that the introduction of an amino-group has radically altered the energy levels of the molecule. Inasmuch as the absorption spectrum of benzylamine resembles that of ethylbenzene, and, moreover, amides exhibit little that is characteristic in their absorption spectra, the new maxima can hardly be ascribed to electrons connecting nitrogen and hydrogen atoms. It is not so easy to dispose of the idea that electrons under the joint control of carbon and nitrogen atoms are responsible, in view of the similarity in extinction coefficients between the 257 mμ band of nitrobenzene and the 234 mμ band of aniline, but as benzonitrile shows a band at 225 mμ (log ε 4·1) and a second maximum near 280 mμ (log ε 2·85), the simplest view to adopt provisionally is to assume that the C:C chromophore is responsible in all these cases for all the bands. The fact that benzoic acid shows a maximum at 227 mμ (log ε 4·15), and that in the toluic acids similar results are obtained, does not lessen the plausibility of this, the simplest, assumption.

	$\lambda_{\text{max.}}$, mμ.	$\varepsilon_{\text{max.}}$	$\lambda_{\text{max.}}$, mμ.	$\varepsilon_{\text{max.}}$
o-Toluic acid	275	2,200	229	12,200
m- ,, ,, ...	278·8	1,600	231	13,500
p- ,, ,, ...	(no clear maximum)		236	15,300

Disubstituted Products.—(*a*) The nitrotoluenes do not differ greatly from nitrobenzene:

	$\lambda_{max.}$, mμ.	$\epsilon_{max.}$		$\lambda_{max.}$, mμ.	$\epsilon_{max.}$
Nitrobenzene	257	10,000	*m*-Nitrotoluene	263·7	12,000
o-Nitrotoluene	257	6,500	*p*- ,, ...	272·2	11,500

and it may be provisionally assumed that, in the main, the same electronic levels occur in these as in nitrobenzene. The vibrational frequencies may, however, be expected to vary somewhat, thus accounting, perhaps, for the relatively small but real wave-length displacements. Evidence in support of this view may be obtained from the data on the chloronitrobenzenes (see Fig. 1):

FIG. 1.

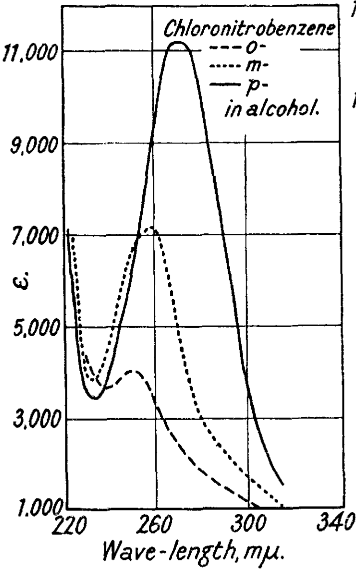
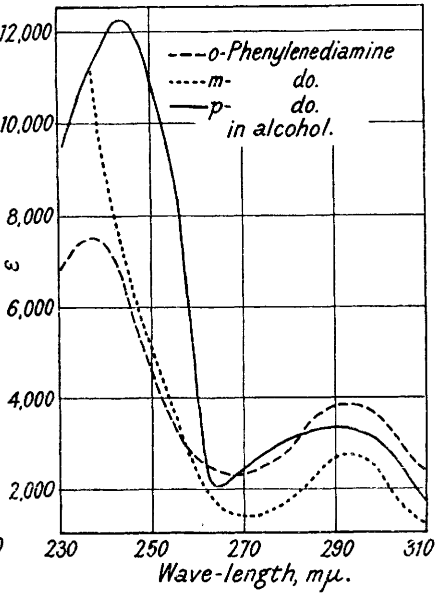


FIG. 2.



	$\lambda_{max.}$, mμ.	$\epsilon_{max.}$
o-Chloronitrobenzene	250·7	4,000
m- ,, ...	256·5	7,150
p- ,, ...	270·1	11,300

(*b*) The toluidines closely resemble aniline:

	$\lambda_{max.}$, mμ.	$\epsilon_{max.}$
o-Toluidine	284·3, 233·1	2,130, 11,500
m- ,, ...	287·2, 236·9	1,950, 11,500
p- ,, ...	290·5, 235·7	2,000, 10,300

and, indeed, the chloroanilines, aminophenols (Fig. 16), and the phenylenediamines (see Fig. 2) are closely similar, but in the acetotoluidides (Fig. 17) the 280—290 mμ maximum is absent.

(*c*) The nitroanilines differ entirely from the preceding compounds (see Figs. 3, 4, 5):

	$\lambda_{max.}$, mμ.	$\epsilon_{max.}$
o-Nitroaniline	403·6, 275·2	5,400, 5,100
m- ,, ...	375·0, 233·0	1,580, 18,000
p- ,, ...	374·0	15,350

It is evident that new chromophores have come into existence, and it is necessary to investigate their nature. The effective electrons may still belong in some cases to the C⁚C group, the strength of binding being modified so as to permit new transitions. On the other hand, the new electronic frequencies may be due to the nitro- or the amino-groups auxochromically influenced by the remainder of the molecule. Further light is thrown on these alternatives by consideration of the data on the three nitrodimethylanilines (see p. 909), but it is first necessary to discuss the nitrotoluidines (Figs. 6—15).

FIG. 3.

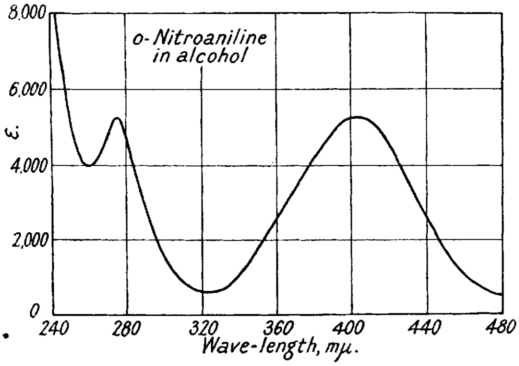


FIG. 4.

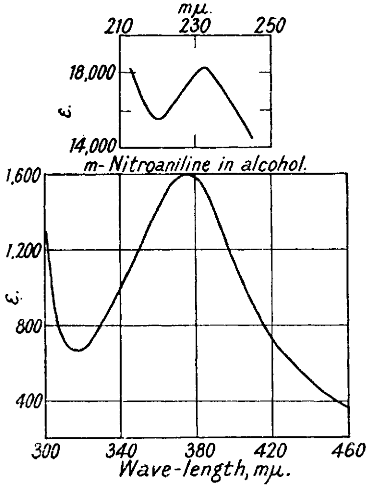
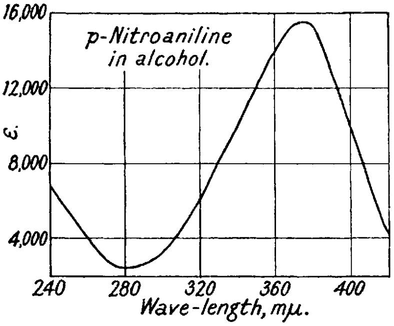


FIG. 5.



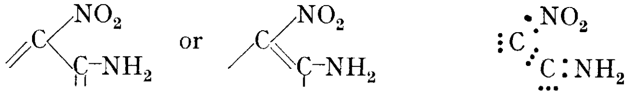
These are readily classified as regards absorption spectra into three classes, those with the amino- and the nitro-group *o*-, *m*-, and *p*- to each other (see Table I). It will be seen that in alcoholic solution, as regards both location and intensity of bands, the determining

TABLE I.

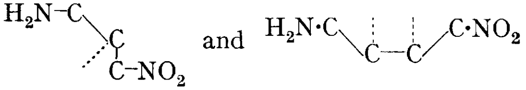
	CH_3.	NO_2.	NH_2.	$\lambda_{max.}$, mμ.	log ε.	$\lambda_{max.}$, mμ.	log ε.	$\lambda_{max.}$, mμ.	log ε.
o	—	2	1	403·6	3·73	275·2	3·71	—	—
	1	3	2	408·2	3·62	283·5	3·65	230	4·17
	1	2	3	404	3·50	282·5	3·53	236	4·19
	1	4	3	405	3·85	286	3·93	231	4·33
	1	3	4	417·5	3·76	280	3·80	230	4·32
	—	—	1	—	—	284·3	3·24	234	4·06
m	—	3	1	375	3·20	—	—	233	4·26
	1	5	3	375	3·07	287	3·59	235	4·18
	1	4	2	373	3·24	288·5	3·69	253 231	4·08 4·08
	1	6	2	352·5	3·14	inflexion	3·3—3·5	235	4·20
	1	2	4	373·5	3·15	—	—	235	4·23
p	—	4	1	374	4·19	—	—	—	—
	1	2	5	373·5	4·12	—	—	233	3·87
	1	5	2	379	4·24	—	—	230	3·8

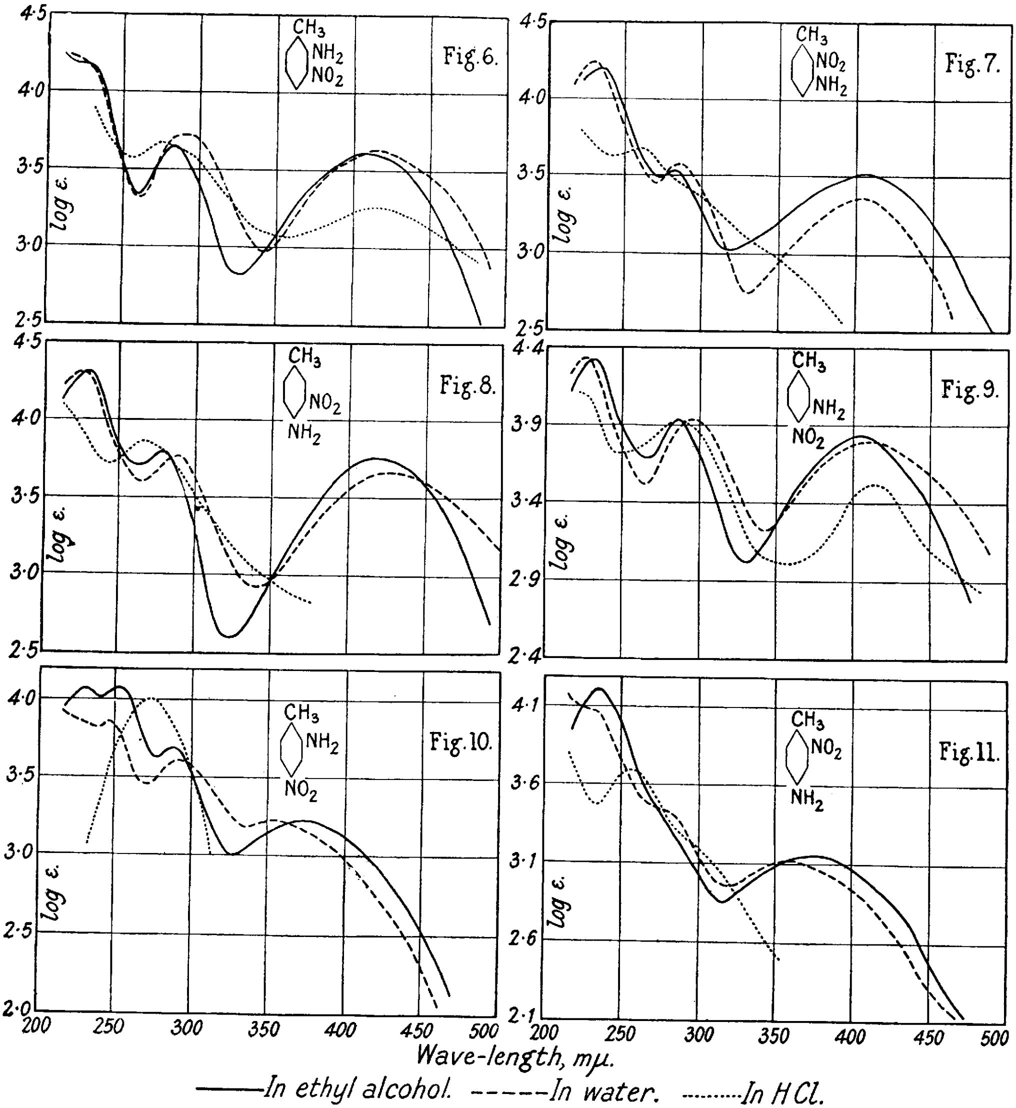
factor in the nitrotoluidines is the relative position of these two groups. The chromophoric groups responsible for the 400—420 and 350—375 mμ bands must be

(*a*)



(*b*)

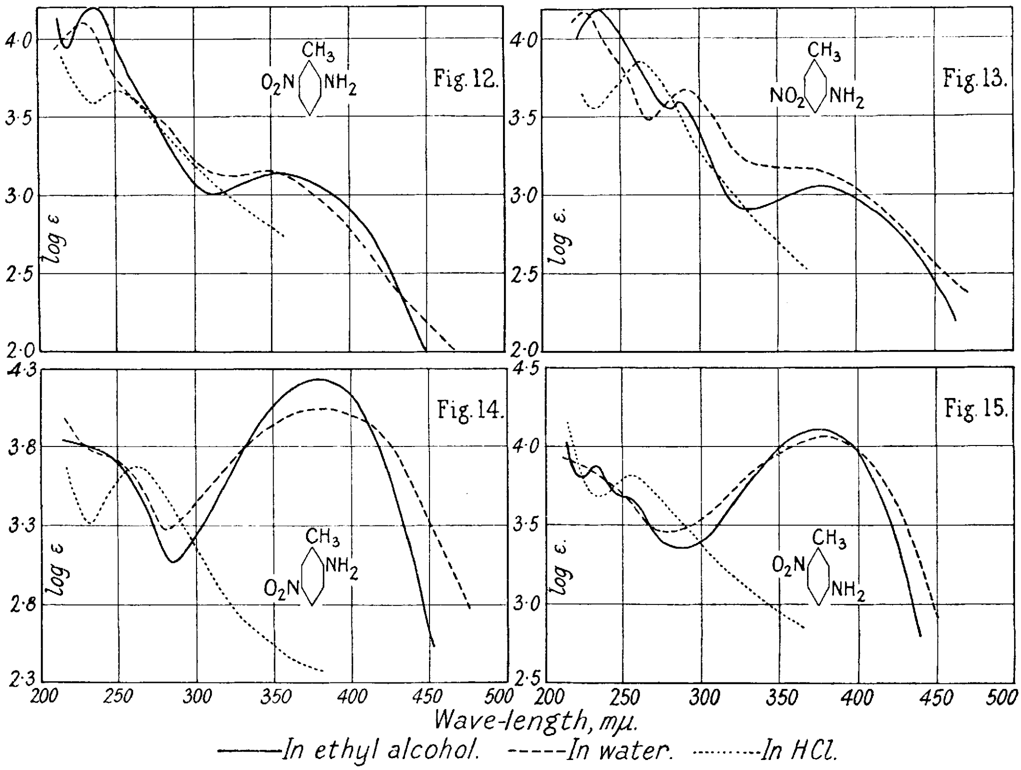




The absorption spectra of the nitrotoluidines in 10% hydrochloric acid have also been measured and a clear correlation with the *o*-, *m*-, and *p*-nitrotoluenes at once emerges. As may be seen from Table II (in which the positions of the substituents are denoted by numerals; $CH_3 = 1$), with the exception of two isomerides (denoted by an asterisk), these bases resemble the corresponding nitrotoluenes very closely. It is difficult to see why the acid should not inhibit the visible colour in the two exceptional cases: the effect may perhaps be interpreted as a sign of steric hindrance.

TABLE II.

NO_2.	NH_2.	$\lambda_{max.}$.	log $\epsilon_{max.}$.	NO_2.	NH_2.	$\lambda_{max.}$.	log $\epsilon_{max.}$.	NO_2.	NH_2.	$\lambda_{max.}$.	log $\epsilon_{max.}$.
2	—	257	3·81	3	—	263·7	4·08	4	—	272·2	4·06
6	2	252·5	3·66	*3	2	416	3·25	4	2	273·5	4·0
2	3	258·5	3·67			276	3·67	*4	3	416	3·52
2	5	256	3·82	5	2	263	3·67			286	3·93
2	4	256	3·7	5	3	263	3·84			225	4·1
			inflex	3	4	266	3·86				
		290	3·25								



The interpretation which involves fewest assumptions regards the amino- and the nitro-group as being purely auxochromic. On this view, all the absorption bands represent different states of electronic excitation of the aromatic C⁚C group; *i.e.*, we may regard the 230—235 and 275—285 mμ bands which recur so regularly in the alcoholic solutions of the nitrotoluidines as being precisely analogous to those shown by aniline, whilst the 375 and 405 mμ bands must be due either to a C⁚C electron influenced by both these groups, since neither is effective in this sense alone, or to an electron controlled by a nitrogen atom and influenced by unsaturation within the same molecule.

That the classification of the absorption spectra of nitrotoluidines is reasonably correct may be inferred from the following data on more complicated molecules.

CH_3.	NO_2.	NH_2.	
1	4 : 5	2	Alcoholic solution: $\lambda_{max.}$, 375·2, $\epsilon_{max.}$ 12,000 (log ε 4·08); inflexion 235—255, $\epsilon_{max.}$ 9000—10,000. Aqueous solution: $\lambda_{max.}$ 391·5, $\epsilon_{max.}$ 7000; inflexion 245, $\epsilon_{max.}$ 7000 (compare *m*- and *p*-nitroanilines).
1 : 3	5	4	$\lambda_{max.}$ 425, 286; inflexion 230—250.
1 : 3	6	4	$\lambda_{max.}$ 370, 286, 230—250.
1 : 2	4 : 6	3	$\lambda_{max.}$ 320, 274.
1 : 2	3 : 5	4	Clear maximum near 416 mμ, as would be expected from *o*-nitroaniline.

TABLE III.

Nitrotoluidines. Band displacements (alcohol ⟶ water).

NO_2.	NH_2.	λ.	cm.$^{-1}$.	λ.	cm.$^{-1}$.	Δcm.$^{-1}$.	NO_2.	NH_2.	λ.	cm.$^{-1}$.	λ.	cm.$^{-1}$.	Δcm.$^{-1}$.
3	2	408·2	(24,500) to	416	(24,040)	− 460	4	3	236·0	42,370 to	229	43,670	+ 300
		283·5	(35,280)	292·5	34,190	−1090			405	24,690	410	24,390	− 300
		230		230		nil			286	34,970	296	33,780	−1190
4	2	373	26,810	353	28,330	+1520			231	43,290	228	43,860	+ 570
		288·5	34,660	292	34,250	− 410	5	3	375	26,670	368	27,170	+ 500
		253	39,530	246	40,650	+1120			287	34,840	292	34,250	− 590
		230·6		230					235	42,550	228	43,860	−1310
5	2	379		380		negl.	2	5	373·5	26,770	378	26,460	− 310
		230		230					250				
6	2	353·5	28,290	345	28,990	+ 700			233		230		small
		235·0	42,550	230	43,480	+ 930	3	4	417·5	23,950	428	23,360	− 590
2	3	404·0		403·5					280	35,710	288	34,720	− 990
		282·5		285		v. small			230	43,480	227	44,050	+ 570
							2	4	373·5	26,770	355	28,170	+1400
									235·0	42,550	230	43,480	+ 930

FIG. 16.

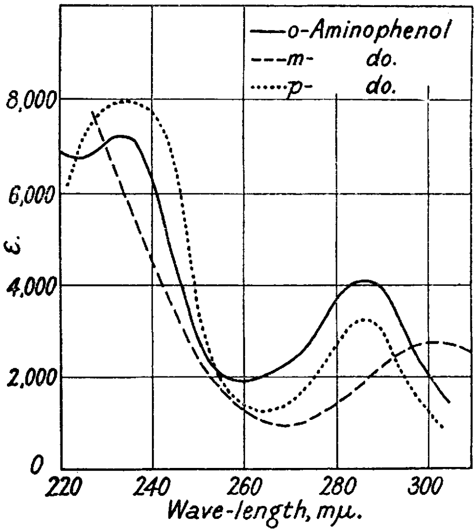
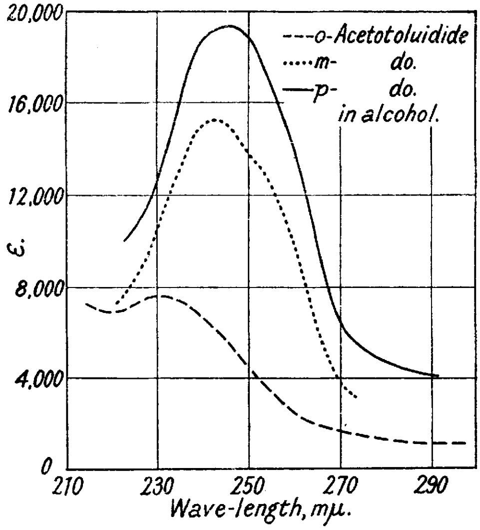


FIG. 17.



The Nitrotoluidines in Aqueous Solution.—Comparison of the absorption spectra of alcoholic and aqueous solutions of the nitrotoluidines shows that the same absorption bands occur in both solvents; although the curves are very similar in shape, the exact locations of the maxima differ appreciably, the bands being displaced either not at all or in either direction, as shown in Table III. It will be noticed that Δcm.$^{-1}$ varies from + 1520 to — 1190, a range of frequencies typical of the intramolecular vibrational frequencies appearing in the Raman effect. The following are some of the Raman frequencies for relevant compounds (intensities in parentheses):

Benzene: 605(3), 849(1), 991(10), 1178(3), 1584(3), etc.

Aniline: 385(3), 530(3), 615(3), 762(2), 813(56), 993(10), 1028(5), 1153(3), 1270(4), 1600(10), 3046(4), 3360(3), 3423(2).

Toluene: 217(4), 520(2), 622(2), 786(4), 1002(4), 1029(1), 1154(1), 1209(3), 1604(6), 2929(1), 3054(6).

Nitrobenzene: 620(2), 805(26), 1007(4), 1030(1), 1187(2), 1597(2), 2252(3), 2913(2), 3057(4).

Nitrotoluenes (strong lines), *o*: 546(4), 571(4), 791(5), 1047(5), 1197(4), 1138(10), 1178(5); *m*: 506(4), 793(6), 1000(6), 1095(5), 1334(2), 1580(6); *p*: 636(3), 860(4), 1105(6), 1334(20), 1586(6).

Toluidines (strong lines), *o*: 748(5), 1040(4), 1273(4); *m*: 742(5), 998(5), 1285(3), 1605(3); *p*: 850(2), 998(2), 1269(2), 1625(2).

Allowance being made for experimental error, the Δcm.$^{-1}$ values from absorption spectra for the nitrotoluidines are 520, 1025, and 1410. Good agreement with particular Raman lines cannot be expected, but the data tend to justify the assumption that the solvent displacements are due to changes in vibrational sub-levels, with electronic levels unchanged in alcohol and water. This assumption is consistent with the absence of any regularities in the sense that the observed displacements may be positive or negative even in the same compound.

The maxima for the nitrotoluenes and toluidines may be considered in this connexion:

	Nitrotoluenes.				Toluidines.		
	$\lambda_{max.}$, mμ.	cm.$^{-1}$.	Δcm.$^{-1}$.		$\lambda_{max.}$, mμ.	cm.$^{-1}$.	Δcm.$^{-1}$.
o	257	38,910	990	*o*	284·3	35,170	350
m	263·7	37,920	1190	*m*	287·2	34,820	400
p	272·2	36,730		*p*	290·5	34,420	

It would seem that a given electronic transition is common to a given set of *o*-, *m*-, and *p*-isomerides, but the wave-lengths of the observed maxima indicate a displacement as a result of quantised changes in interatomic vibrations.

This suggestion implies that the observed wave-length of maximum absorption need not necessarily, or even usually, indicate with any great exactness the magnitude of the quantum necessary for the electronic transition. Even an approximate diagram of electronic levels in polyatomic organic substances like these would, however, be very useful.

On the basis of the best methods of interpretation now current, there is no reason to predict that the absorption spectrum of toluene should be displaced as compared with that of benzene. The methyl group is itself quite transparent, and in aliphatic compounds its introduction effects no corresponding displacement. The highest absorption for toluene, diphenylmethane, and triphenylmethane ("Handbuch der Physik," Vol. 21, p. 129) is reached at 262 mμ (cm.$^{-1}$ 38,150) as against 254·3 mμ (39,520) in benzene. The sub-maxima occur at the same wave-lengths in all these compounds, and the difference, 39,520 − 38,150 = 1370 cm.$^{-1}$, is of the right order for a vibrational frequency. The fact that the value 1370 cm.$^{-1}$ does not agree exactly with the recorded Raman frequencies need not necessarily invalidate the argument, because the vibrational sub-levels of the ultra-violet band are vibrations of the excited molecule, whereas the observed Raman frequencies are recorded on unexcited molecules.

Hence, in benzene, toluene, and di- and tri-phenylmethane, the act of absorption has exactly the same electronic mechanism, the wave-length displacement being due to slightly different vibrational effects.

The absorption spectra of the nitrotoluidines and related substances may now be considered from the point of view of two well-known theories. According to Henri, the different $\lambda_{max.}$ values for the isomerides should correspond with frequencies which are integral multiples of infra-red frequencies of maximum absorption. This theory has been adequately examined by Ramart-Lucas (*Bull. Soc. chim.*, 1932, **51**, 289). The infra-red absorption spectra of the nitrotoluidines are not known, but in any case there is little reason on modern ideas of band spectra to expect integral multiple relationships between infra-red and ultra-violet bands, *i.e.*, between characteristic vibrational and electronic frequencies.

If, on the other hand, Baly's theory of molecular phases were valid, the frequencies of maximum absorption in the case of the nitrotoluidines should be integral multiples of a common frequency. Careful analysis of the figures shows that the essential hypothesis can neither be proved nor disproved. In its original form the phase hypothesis seems—on account largely of its elasticity—to be unserviceable except as a qualitative interpretation of different states of molecular activation.

Dr. J. R. Edisbury has kindly examined the nitrodimethylanilines and his results are summarised in Table IV. It is noteworthy that the middle band of the nitrotoluidines disappears or is masked in the dimethylamino-isomerides. The auxochromic effect of the dimethylamino-group appears to be very similar to that of the amino-group, but the

TABLE IV.

Solvent.	Ortho. $\lambda_{max.}$, mμ.	Ortho. log ϵ.	Meta. $\lambda_{max.}$, mμ.	Meta. log ϵ.	Para. $\lambda_{max.}$, mμ.	Para. log ϵ.
			Nitrodimethylanilines.			
Alcohol	416	3·47	400·3	3·13	386·5	4·33
	245·5	4·33	246	4·36	*ca.* 200	4·23
Water	441	3·29	385	2·99	422	4·34
	242	4·24	247	4·21	232·5	3·96
Aq. HCl (5 eq. HCl)	439	2·78	378	2·90	422	4·30
	248	3·95	247	4·18	*ca.* 231	4·0
,, (500 eq. HCl)	—	—	—	—	—	—
	261·7	3·86	—	—	—	—
,, (5000 eq. HCl)	—	—	—	—	—	—
	262	3·86	251	4·0	*ca.* 240	3·90
			Nitroanilines.			
Alcohol	403·6	3·73	375	3·20	374	4·18
	275·2	3·71	233	4·26	—	—

quantity of hydrochloric acid necessary before the nitroaniline type of absorption is replaced by the nitrobenzene type is very large. As in the nitroanilines, the relative position of the nitro- and the dimethylamino-group determines very largely the locations of the maxima. Just as in *m*-nitroaniline the 375 mμ maximum has only one-tenth of the intensity of the same band in *p*-nitroaniline, so the 400 mμ band of *m*-nitrodimethylaniline is about 1/16 of the intensity of the 386·5 mμ band of *p*-nitrodimethylaniline. The data show clearly the apparently arbitrary way in which the $\lambda_{max.}$ values can vary from solvent to solvent; *e.g.*, replacement of alcohol by water results in displacements in opposite senses for *m*- and *p*-nitrodimethylaniline: 400·3 ⟶ 385, 386·5 ⟶ 422 mμ. The basicity of *p*-nitrodimethylaniline is very small, but the visible absorption is greater than for the *o*- and the *m*-isomeride. Hence the long-wave maxima are probably due to undissociated molecules. The hydrochlorides are transparent to visible radiation.

EXPERIMENTAL.

The ten isomeric nitrotoluidines used in this investigation were prepared by the usual methods, improvements being sometimes introduced in order to increase the yields. The compounds were carefully purified by repeated crystallisation alternately from alcohol and dry benzene until of constant m. p. In the following table, the m. p.'s are compared with those recorded in the literature.

Compound.			M. p.			Compound.			M. p.		
				Literature.						Literature.	
CH_3.	NO_2.	NH_2.	Obs.	Highest.	Lowest.	CH_3.	NO_2.	NH_2.	Obs.	Highest.	Lowest.
1	3	2	97°	97°	94—94·5°	1	4	3	110°	112°	109°
1	4	2	107	109	104—105	1	5	3	98	98—98·4	95
1	5	2	129	131	127	1	6	3	134	138—140	133
1	6	2	92	92	90—91	1	2	4	78	78·5	77
1	2	3	108	108	106	1	3	4	117	117—118	110

The experimental details given below are typical.

2-*Nitroaceto*-p-*toluidide*.—The acetylation of the nitroamines was carried out preferably by shaking the finely powdered solid (100 g.) with water (600 c.c.), adding freshly distilled acetic anhydride (100 g.), and again shaking vigorously; the mixture was ice-cooled, and the acetyl derivative filtered off and crystallised from water. If this method was not successful, 100 g. of base were dissolved in pure acetic anhydride (130 g.) and concentrated sulphuric acid (0·5 g.) added; heat was developed, and acetylation was usually instantaneous, but 10 minutes' boiling under reflux was carried out to ensure completion of reaction. The mixture was poured into water (800 c.c.), with rapid stirring, cooled with ice, and the acetyl derivative filtered off and washed free from acid. 2-Nitroaceto-*p*-toluidide forms colourless flakes, m. p. 145°.

2 : 3- *and* 2 : 5-*Dinitroaceto*-p-*toluidides*.—The foregoing compound (20 g.), powdered and sieved, was added, 0·2 g. at a time (90 mins.), to pure fuming nitric acid (300 c.c.) (mechanical

stirring), the temperature being kept below 0°. After a further hour's stirring at 0°, the mixture was poured into ice-water (2 l.), the solid filtered rapidly upon a Buchner funnel of large area, quickly washed free from all traces of acid, and dried; yield 94%.

2 : 3- *and* 2 : 5-*Dinitro*-p-*toluidines*.—The finely powdered nitration product (20 g.) was dissolved in concentrated sulphuric acid (150 c.c.), and an equal volume of water slowly added; the mixture was cooled, poured into ice-water (1·5 l.), and kept for 2 hours in the ice-chest. The solid was filtered off, washed with ice-water, and dried; yield 99%. This mixture of dinitrotoluidines was fractionally crystallised from aqueous acetone, 98% of the mixture being completely separated into its constituents. 2 : 3-Dinitro-*p*-toluidine, large yellow prisms, m. p. 124°, was the more soluble isomeride (acetyl derivative, m. p. 175°); the 2 : 5-compound, dark red needles, m. p. 189°, formed approximately one-third of the total yield of isomerides (acetyl derivative, m. p. 124°).

2 : 3-*Dinitrotoluene*.—2 : 3-Dinitro-*p*-toluidine (34 g.) was dissolved in absolute alcohol (100 c.c.) and heated under reflux on a water-bath after concentrated sulphuric acid (12 g.) had been gradually added. Finely powdered, dry sodium nitrite (23 g.) was added through the condenser in small portions; when all evolution of gas had ceased, the flask was cooled, and the alcohol evaporated in a desiccator. To the slightly tarry residue nitric acid (50 c.c.; *d* 1·42) was added, and the liquid refluxed until brown fumes ceased to be evolved. The solution was cooled, diluted with water (200 c.c.), and extracted with ether. After removal of the ether, the dinitrotoluene was crystallised from alcohol; m. p. 60°; yield 80%. Other methods of diazotisation failed to improve the yield.

2-*Nitro*-m-*toluidine*.—Burton and Kenner's method (J., 1921, **119**, 1047) gave a 79% yield of orange crystals, m. p. 108°; acetyl derivative, m. p. 126°.

3 : 5-*Dinitroaceto*-p-*toluidide*.—Aceto-*p*-toluidide (20 g.) was nitrated as previously described; yield 59%; m. p. 195°.

3 : 5-*Dinitro*-p-*toluidine*.—Hydrolysis was effected as with the other isomerides; yield 99·2%. The highly purified compound consisted of golden spangles, m. p. 169°, the ordinarily purified solid being brownish.

3 : 5-*Dinitrotoluene*.—The diazotisation was conducted as previously described, but the product was steam-distilled; yield 77%; m. p. 93°. The theoretical yield mentioned by Cohen and McCandlish (J., 1905, **87**, 1257) could not be attained.

5-*Nitro*-m-*toluidine*.—Very prolonged boiling of 3 : 5-dinitrotoluene with alcoholic ammonium sulphide gave an 85% yield of the base, which crystallised from hot water in fine red needles, m. p. 98°; acetyl derivative, m. p. 186°. Other reducing agents did not increase the yield.

CONCLUSIONS.

1. The electronic mechanism of absorption in benzene, toluene, diphenylmethane, etc., is essentially the same, any small differences in spectra being due to vibrational effects ($\lambda_{max.}$ *ca.* 260 mμ).
2. The main absorption band in nitrobenzene, the nitrotoluenes, and the chloronitrobenzenes is due to the same electronic transition.
3. New electronic levels emerge when amino- or carboxyl groups are introduced into the benzene ring; quanta corresponding with *ca.* 230 and 280 mμ recur in the toluic acids, in aniline, and in the toluidines.
4. The nitroanilines show new levels at 375 and 405 mμ approx.
5. The determining factor in the absorption of the nitrotoluidines is the relative position of the nitro- and the amino-group; for instance, those isomerides with these groups in the *o*-position give spectra resembling that of *o*-nitroaniline, etc. The 375 mμ maximum is about 10 times as intense in *p*- as in *m*-nitroaniline. This ratio also applies to the nitrotoluidines, in which the amino- and the nitro-group are in *p*- and *m*-positions respectively with regard to one another.
6. The spectra of the nitrotoluidines in acid solution resemble those of nitrotoluenes, the relative position of the methyl- and the nitro-group now exercising the determinative rôle.
7. Comparison of the absorption spectra of the nitrotoluidines in alcoholic and in aqueous solution shows that the maxima vary irregularly, although the general shape of the curves is always the same in the two solvents. The broad bands shown in solution

are considerably influenced by vibrational effects, and the actual wave-lengths of maximum absorption afford only very approximate estimates of the electronic levels. The displacements due to change of solvent appear to correspond with vibrational sub-levels.

8. Theories involving possible integral multiple relationships between $\lambda_{max.}$ values are not supported.

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