ABSORPTION SPECTRA

of certain classes of

NITROGEN COMPOUNDS.

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TABLE OF CONTENTS.

SYMBOLS.

ε	Molar extinction coefficient $(\varepsilon c l = \log \frac{I_o}{I})$
λ	Wavelengths (in mμ)
$\sim$	Point of inflection in the absorption curve.
f	Group of subsidiary maxima present.

SUMMARY.

Compounds containing the -N=N- group are found to possess three bands in the near ultra-violet region. The longest wavelength band is masked in compounds of the type Ar-N=N-X-Ar (X=NH, S). The second or K band is found to show definite differences for *cis*-*trans* isomers. These differences appear in the diazocyanides and point to *cis*-*trans* isomerism.

Evidence of isomerism is found in compounds of diazocarbonamide type, Ar, N=N.CO. NH_2, but isomers have not been separated. No evidence for isomerism has been found in *p*-nitrobenzene diazothiophenylether or diazoaminobenzene. The former appears to be decomposed by ultra-violet light.

The spectra of quinone diazides have been shown to be in accordance with their quinonoid formulation and that of 1:2:3-benzothiadiazole with a bicyclic structure.

Evidence dealing with the structures of N-nitroso-N-phenyl-glycine and sydnones is presented. The former compound is shown to possess an open chain, uncharged structure.

1. Absorption Characteristics of the -N=N-Group

The near ultra-violet absorption spectra of compounds containing the structure -N=N- includes the following three bands:-

R band - usually at 390 - 480 mμ
K band - " " 320 - 370 mμ
and a third band at 220 - 270 mμ

These may not all be present in the spectrum of one compound of the series, but by their location and intensity, and the effect of substituents on them, they appear to maintain a constant nature throughout the compounds in which they do occur.

In the following pages there is presented a detailed discussion of the nature of these bands as they occur in the compounds containing the -N=N- bond. This has an intrinsic importance and a bearing on the problems of isomerism in the group which are dealt with in Section 2.

(a) The R Band

The name "R" or "Radical" band was given to the long wavelength absorptions in the ultra-violet ~~on~~ or visible region of compounds containing such groups as $C=O$ and -N=N- and of "free radical" type molecules such as triphenylmethyl. It became established largely through the work of Buraway (cf. the papers[1] in which a summary and references to his earlier papers are given). Unfortunately, his ideas are expressed in terms of an "electron isomerism" which tends to obscure the worth of the central parts of his evidence. Bowen[2] has indicated a more adequate treatment. He explains the absorption at *ca*. 300 mμ associated with the C=O group as due to the passage of relatively undisturbed and non-bonding "p" electrons of the oxygen atom to an excited orbital of "π" type. The wavelength of the absorption is much longer than that of ethylene and conjugated C=C molecules of similar complexity, and the changes produced by substitution are different.

Similar behaviour is noted in the long wavelength absorption of molecules containing the -N=N- group. In this case also, Bowen attributes the absorption to the passage to excited π orbitals of non-bonding "p" electrons (from the nitrogen atoms). In support of the assignment, it may be observed that the azoxybenzenes possess one of the absorption bands of the corresponding azobenzene not greatly changed (especially in the *trans* compound where steric efforts will be less important), but the band of longest wavelength is entirely lacking. Comparison of related amines and amine-oxides shows how effective this linkage is in suppressing the auxochromic properties of amine groups (cf Table 1) Thus it would appear that

TABLE 1

	R		K	
	λ	log ε	λ	log ε
cis-Azobenzene[3]	438	3.06	324	4.18
cis-Azoxybenzene[4]			335	3.8-3.9
trans-Azobenzene[3]	445	2.47	319	4.29

	R		K	
trans-Azoxybenzene[4]			320	4.22
Dimethylaniline[5]	300	3.20	244	4.02
ditto - N-oxide[5]			256	2.32
Benzene[6]			256	2.40
NN-Methylethyl-β-naphthylamine[5]	362	3.40	290	3.90
ditto -N-oxide[5]			271	3.52
Naphthalene[6]	314	2.50	275	3.75

the elimination by compound formation of a pair of electrons in a non-bonding state from one of the N atoms has suppressed the R band but not had any great effect on the rest of the spectrum.

Among the properties of R chromophores listed by Burawoy are the following:-

(i) The intensity of absorption is low (ε usually < 2000

(ii) Substitution by NH_2; OR and SR results in a change to shorter wavelengths, but the effect is slight in aromatic compounds.

(iii) Addition of H^+ to the chromophore results in the disappearance of the band in all cases. This type of band does not occur in organic cations.

A band of R type appears in compounds of three of the series considered, namely in the azobenzenes, Ar -N=N-Ar, and the aromatic diazocyanides, Ar-N=N-CN, and the aromatic-diazocarbonamides, Ar-N=N-CO. NH_2, the range of wavelength and intensity values for each series being as shown in Table II

TABLE II

Series	Range of Wavelengths $\lambda\lambda$	Range of Intensities. $\log \varepsilon$
Ar - N=N-Ar$^{(3,7)}$	438-450	2.24 - 3.35
Ar - N=N-CN	388-481	2.75 - 3.92
Ar - N=N-CO NH_2	420 & 434	2.4 & 2.57

The intensities in two of the azobenzenes (*p*-NH_2 & *p*-NMe_2 - compounds) which were originally listed [7] with this band are much higher than those of the others in the group, and at the same time the wavelengths were 20-40 mμ shorter. They have therefore been considered with the K band - a change which appears to agree more with the nature of the substituents. It may be seen that the band occurs over a fairly large range of wavelengths and intensities, particularly in the diazocyanides. The wavelengths are much longer than those of the longest wavelength band in corresponding ethylene compounds (e.g. in trans- stilbene at 295 mμ) and the intensities of absorption are fairly low throughout the compounds. The R band is lacking from the spectra of *p*-nitroazobenzene and *p*-bromobenzene diazocarbonamide. Apparent loss of the band is not unknown in other bands of R type and is probably due to overlapping by the stronger K band.

The progressive change in the R band in azo compounds as substituents change from aliphatic to aromatic type is shown in Table III. It will be seen that the compounds of Table II

TABLE III

	λ	log ε
$CH_3 - N = N - CH_3$ (8)	345	0.60
$C_6H_5 - N = N - CH_3$ (8)	405	1.48
$C_6H_5 - N = N - CH_2 - C_6H_5$ (8)	~400	low
	345	
$C_6H_5 - N = N - C_6H_5$ (3) trans	445	2.47

fall quite readily into the sequence.

No band of R type has been discovered in the other compounds studied except in the quinone diazides where the band appears to be closely related to that in the quinones. In Table III the band appears at longer wavelengths in benzeneazomethane than in benzeneazot~~h~~oluene. This is an unusual observation which may be due to some incidental cause. For compounds of Ar-N=N-X-Ar type (in which X=NH or S), including the bicyclic members, the property (ii) listed above may cause so great a displacement that masking by the K band occurs.

(b) The K Band

The "K" or "Conjugation" band is the type characteristic of ethylene absorption and conjugated structures. It arises through activation of a system of coupled π electrons. The characteristics of absorption by K-bands as listed by Burawoy (1) include:-

(i) The intensity of absorption is higher than in R bands (ε usually $>$ 5000)

(ii) There is a displacement of absorption to longer wavelengths, with increasing length of the conjugated system and in the series of terminal atoms, $= NH < = O < = S$.

(iii) There is a displacement of absorption to longer wavelengths on introduction of an NH_2, OH or SH group at the other end of the system, the first group having much greater effect than the second.

(iv) When NH_2, OH or SH is substituted in a side chain, the absorption moves to shorter wavelengths or is almost unaffected.

(v) The band does not disappear in the spectra of organic cations.

Similar bands to those occurring in carbon compounds also appear where nitrogen replaces one or both of the carbon atoms in a double bond of a conjugated system. These bands lie at shorter wavelengths than the R band and may be exemplified by the band at 319-335 mμ in the azo- and azoxybenzenes of Table I. Table IV shows the band in a few members of an ascending series of -N =N - compounds and in some related hydrocarbons. The band occurs at longer wavelengths and lower intensity in these nitrogen compounds (except benzanilide) than in the carbon compounds (but cf (17). This is presumably due to the difference in the orbitals due to

TABLE IV

	λ	log ε		λ	log ε
CH_3-N=N-CH_3 (8)	245	(high)	CH_2= CH_2	185	3.90
C_6H_5-CH=N-CH_3 (6)	247	4.23	C_6H_5-CH=CH_2	244	4.08
C_6H_5-N=C(C_2H_5)$_2$ (6)	250	4.08			
C_6H_5-N=N-CH_3 (8)	258	3.60			
C_6H_5-N=CH-C_6H_5 (6)	263	4.23	C_6H_5-CH=CH-C_6H_5	295	4.43
C_6H_5-N=N-C_6H_5 trans	319	4.29	(trans)		

change from C to N and to the presence of non-bonding electrons on the nitrogen atoms.

In all the compounds studied there are K bands, the position of which is shown in Table V, together with those of some nearly related compounds in which the -N=N- group is replaced by - CH=CH-.

TABLE V

	Wavelengths	Log ε
Ar - N=N-Ar[3,7]	299-410	4.17 -4.49
(C_6H_5-CH=CH-C_6H_5[6] (*cis* & *trans*)	280 & 295	4.13 & 4.43)
Ar - N=N-CN	300-341	3.23 - 4.50
(C_6H_5-CH=CH-CH=CH_2[6]	280	4.45)
Ar - N=N-CO-NH_2	286 & 305	4.03 & 4.54
(C_6H_5-CH=CH-CO-CH_3[8]	285	4.36)
C_6H_5-N=N-NH-C_6H_5	353	3.67
C_6H_5-N=N-S-C_6H_4 (*p*-NO_2)	357	4.47
(14)		
	~ 291	3.32
	~ 282	3.58
	265 *f*	3.80)
	306	3.63
	260 *f*	4.00)

Just as lengthening the conjugation system moves the absorption maximum to longer wavelengths and higher intensities, so any decrease in its length results in changes in the opposite direction. This may be done not only by direct removal of substituents but also by addition of such substituents as will disturb the steric configuration and consequently the conjugation. Examples may be found in the recent studies of steric effects in absorption spectra (9). A further example is provided by the bicyclic compounds of Table V. Another characteristic of these is their tendency to have the absorption of this band resolved, whereas the other compounds have a single maximum.

cis-trans Isomerism should provide a further example of this kind of conjugation breaking. It might be expected that *cis* isomers would show absorption at shorter wavelengths and lower intensities than *trans* isomers. In general, this seems to be the case, although a few exceptions have been noted. In Table VI are shown, for various series of *cis-trans* isomers, the average values of ($\lambda_{cis} - \lambda_{trans} = \Delta\lambda$) and ($\log \varepsilon_{cis} - \log \varepsilon_{trans} = \Delta \log \varepsilon$) in the K band.

TABLE VI

Series	$\Delta\lambda$	$\Delta \log \varepsilon$
Stilbenes (in 4 solvents) (10)	-15	-0.37
Cinnamic acids (in 5 solvents) (10)	-7	-0.34
Sodium cinnamates (10)	-15	-0.24
Furfuraldoximes (11)	-5	+0.01
Ethyl-β-cyanocrotonates (12)	-	-ve

TABLE VI (continued)

Ethylenic -α-nitriles(13)	±	-ve
Azobenzenes(3)	-7	-0.27
Azoxybenzenes (4)	+15	-(0.3-0.4)

The following exceptions to this behaviour have been found:-

(i) Furfuraldoximes have very slightly higher intensity of absorption in the *cis* than in the *trans* forms (*ca* 2% in ε)

(ii) Three ~~ei~~azobenzenes show small positive values for $\Delta\lambda$ and one of these also shows a small positive value for $\Delta\varepsilon$ (*p* -NO_2-).

(iii) Also *o*-methoxyazobenzene and the azoxybenzenes have comparatively large positive values for $\Delta\lambda$ (+34 & +15 mμ) although the former has only a very slightly positive $\Delta\varepsilon$ value and the latter has a normal value for this quantity. (The former of these compounds was not taken into account in the calculation of the azobenzene figures). Some extra steric factor may be operative in these cases.

Thus there exist in the K band definite and fairly regular differences between the spectra of *cis*-*trans* isomers, particularly when averaged over a group. The *cis* isomer having the absorption peak at lower or nearly equal wavelength and intensity. Some early writers (13) did observe that *cis* isomers often had an intensity of absorption about half that of *trans* isomers ($\Delta \log \varepsilon = -0.3$), usually because the K band was the one they observed, its wavelength and intensity being suited to early techniques. But when two or more bands came to be observed, these often changed in opposite directions in the change *trans* to *cis*. The distinctions drawn between the K and R bands and the K and shorter wavelength bands enables the identification of the K band as the one which will reveal conjugation differences such as those of cis and trans isomers.

(c) The Band at 220 - 270 mμ.

In some cases reference has been made to a third band in the region 220-270 mμ in compounds containing the -N=N- group. Cook, Jones & Polya(3) report its presence (but give no figures for its position) in azobenzenes. The aromatic diazocyanides and diazocarbonamides examined have bands in the 220-277 mμ and the 223-243 mμ regions respectively. Probably similar bands occur in others of the compounds at wavelengths below the region accessible with the apparatus used in the particular investigation.

A band at about 270 mμ often occurs in compounds where the group $-C_6H_4-NO_2$ is present, e.g. in the nitrobenzene-diazocyanides. Burawoy(1) finds in the compound $-C_{10}H_7-N=N-C_6H_5$ a new band at 269 mμ (log ε 4.08) which he relates to the naphthalene absorptions at 272 and 275 mμ. Such so-called "partial chromophores" have been used as an explanation in a number of instances. For the present groups of compounds, this band appears to involve the differences between members of a series rather than their common features. Consequently the bands will not receive more than mention in the subsequent treatment of the spectra.

(d) *Summary*:

The spectra of the azobenzenes, aromatic diazocyanides and aromatic diazocarbonamides include recognisable R bands, at long wavelengths and fairly low intensity.

All the compounds containing the -N=N- bond which have been studied contain K bands, more intense than the R bands and at shorter wavelengths. These bands are shifted to longer wavelengths than those in corresponding compounds containing carbon-carbon double bonds only. In compounds in which conjugation through a -C=C- or -N=N- band is decreased by the presence of a *cis* grouping (whether in a suitable ring structure or in a *cis*-*trans* pair) the band is shifted to shorter wavelengths and/or lower intensities.

In addition there are bands of shorter wavelength in a number of the compounds which may, in some cases at least, be due to absorption arising chiefly from aromatic rings and their substituents other than the -N=N- bond.

(Since this chapter was written, two important papers by Braude *et al* (16,17) have become available. These give a very excellent treatment of the basic facts of sections (b and c). The present conclusions are not at variance with those of these papers.)

2. cis-trans Isomerism in - N = N- Compounds:

Evidence relating to the occurrence of isomerism of cis-trans type in several compounds containing the -N=N- bond has been found in spectral investigations and is presented here. The series dealt with are (a) azobenzenes, (b) aromatic diazocyanides, (c) aromatic diazocarbonamides, (d) an aromatic diazothioether, and (e) diazoaminobenzene.

(a) Azobenzenes.

The spectra of these compounds display both R and K bands. Cook, Jones and Pólya(3) state that the cis compounds show a slight shift in the R band which is usually more intense than in the trans compounds. The shifts in the K band have been discussed above (Table VI). They are similar to the changes observed in other cis-trans isomers.

For comparison with other compounds treated in this chapter, some figures taken from Cook, Jones and Polya's paper are listed in Table VII. They refer to chloroform solutions, with

TABLE VII

		Azobenzene.		
cis	438	3.06	324	4.18
trans	445	2.47	319	4.29
		4- Chloroazobenzene.		
cis.	445	2.94	332	4.07
trans	445	2.81	327	4.33
		4- Bromoazobenzene		
cis	445	3.05	324	4.04

TABLE VII (continued)

trans	445	2.88	330	4.36
4-Nitroazobenzene.				
cis	-		330	4.22
trans	-		327.5	4.20

the exception of 4 - nitroazobenzene, in which case the solvent is "petroleum". In this case, no R band absorption is shown in the table although the graphs of Pongratz *et al* (7) have an inflection at about the expected position. Incidentally the Table includes three of the exceptions mentioned in the notes to Table V1 to expected behaviour in *cis* -*trans* isomers.

An X-ray examination of the azobenzenes (26) reveals that the *cis* isomer has the benzene ring rotated out of the plane containing the two nitrogen atoms by 56° and the C_{Ar}-N distance as 1.46A, compared with 1.41A in the *trans* compound and a normal single bond distance of 1.47A. There is thus slight contribution of resonance forms involving C_{Ar}= N and the shift in the K band of the spectrum accompanies a very considerable decrease in the extent of conjugation.

(b) The Aromatic Diazocyanides.

The isomerism occurring in these compounds was originally attributed to *cis* - *trans* relationships (Euler & Hantzsch, (18) 1901), but, because of the difference in reactivity of the isomers, Orton (19) suggested that nitrile - isonitrile isomerism was present. This latter suggestion was generally considered less probable. It was again proposed, in 1944, by Hodgson and Marsden (20) as explaining the previous data and some new observations then reported.

Evidence from dipole moments and refractivity,(21) infrared spectra(22) magnetic rotatory power and magnetic susceptibility(23) has been presented and this supports Hantzsch's formulation.

In reports of lectures by Hodgson(24) it was claimed that Hantzsch had misinterpreted the early spectral studies in the group (Dobbie & Tinkler(25); Hantzsch & Lifschitz(26)) and that these had actually "indicated identity of compound measured." Although the studies were early ones and the results are only semi-quantitative, the conclusion seemed false and a re-investigation was undertaken, primarily to check the distinctness of the spectra of isomeric pairs.

The results are shown in Table VIII and Figs.I-V, and refer to solutions in diethyl ether.

TABLE VIII

	A		B		C		D	
	4-Chlorobenzenediazocyanides.							
* 1(a) Unstable	432	3.07	330	4.12	-		-	
1(b) Stable	438	2.48	338	4.29	-		235	3.90
	4-Bromobenzenediazocyanides.							
2(a) Unstable	430	3.08	335	3.96	-		235	3.80
2(b) Stable	425	2.77	341	4.50	-		238	4.09
	2:4:6 -Tribromobenzenediazocyanides							
3(a) Unstable	~426	2.76	338	3.42	~262	3.35	-	
3(b) Stable	481	2.67	341	4.00	~257	3.77	-	

TABLE VIII (continued)

Nitrobenzenediazocyanides

			A		B		C		D	
4(a)	o-	(Unstable	410	2.75	310	3.23	-		-	
5(a)		(Stable	388	3.92	330	3.79	270	3.79	220	4.15
4(b)	m-	(Unstable	425	2.82	300	3.71	-		242	4.05
5(b)		(Stable	443	2.19	305	4.13	-		248	4.14
4(c)	p	(Unstable	~405	2.94	306	3.92	270	3.87	-	
5(c)		(stable	443	2.38	308	4.22	~277	3.94	-	

* The numbers refer to the graphs.

TABLE IX

Diazocyanides	Δ λ	Δ log ε
4 - chloro -	-8	-0.17
4 - Bromo -	-6	-0.54
2:4:6 -Tribromo -	-3	-0.58
o-Nitro -	-20	-0.56
m - Nitro -	-5	-0.42
p - Nitro -	-2	-0.30.

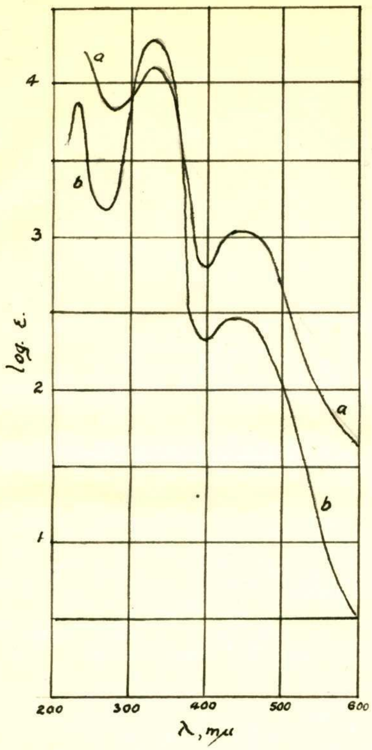


Fig. I.

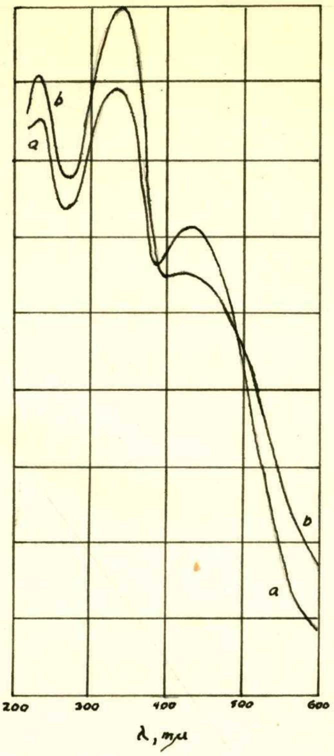


Fig. II.

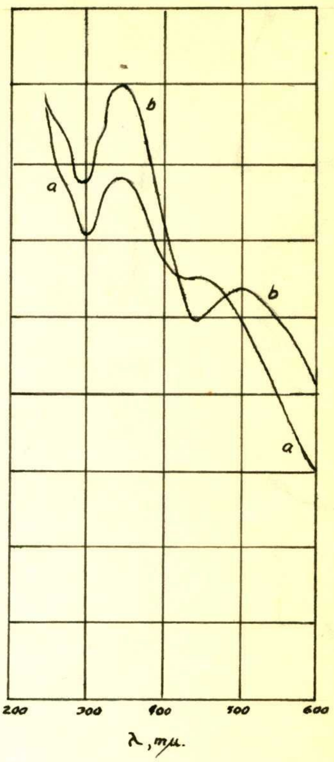
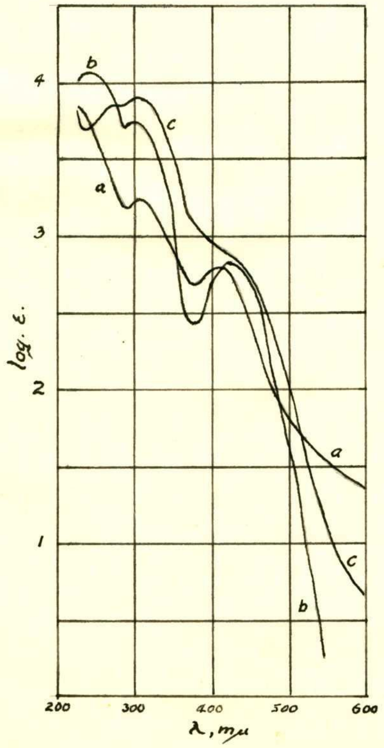


Fig. III.



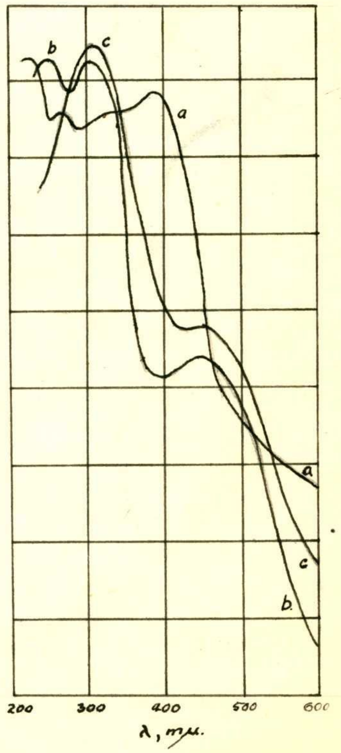


Fig. IV

Fig. V

In the terms of the previous discussion, the band I is to be regarded as an R band and Band II as a K band. The R band is more intense in the unstable forms than in the stable, with the exception of the o- nitrobenzenediazocyanides. This situation is similar to that found in the azobenzenes.

The K band also falls at similar wavelengths to those in the azobenzenes. As Table IX shows, the isomers have the same order of values for (λ unstable - λ stable = $\Delta\lambda$) and (log ε unstable - log ε stable = Δ log ε) as those previously listed for cis - trans isomers (Table VI) in the K Band.

The only nitrile - isonitrile pair for which absorption data is available is the pair benzonitrile - benzoisonitrile. These have absorptions(6,27) at 270 mμ (log ε 2.81) and 275 (log ε 3.00) respectively. If these correspond to the K bands, as they may be expected to do, they would give values for $\Delta\lambda$ and Δ log ε of +5 and +0.19 - of opposite sign to those actually found. It is very unlikely that the insertion of an extra ethylene bond (cinnamonitrile and -isonitrile) would reverse the relative extents of conjugation in these structural isomers, especially since extra steric effects are unlikely to appear. Also, it has been shown that the absorption of corresponding -N=N- and -CH=CH- compounds in this band is similar, except for an auxochromic effect in the former. The $\Delta\lambda$, Δlog ε values to be expected for the structural isomers of Hodgson's proposal should therefore be similar to those found for C_6H_5 CN and C_6H_5 NC.

The appearance of shorter wavelength maxima is found in this series also. Examples of the bands at ca .270mμ mentioned in 1(c) are found in the stable o - nitro + the p - nitrobenzenediazo -cyanides, while the 262 & 257 mμ bands of 2:4:6 - tribromobenzenediazo -cyanide may be due to displacement of the lower wavelength bands in the 4- bromo-compound through the further substitution.

The spectra are quite distinct and show differences in contour and absorption maxima very much greater than experimental errors. No support is given to Hodgson's contention regarding the spectra, which are more closely related to those of undoubted cis-trans isomers than to those of nitrile-isonitrile isomers.

(C) The Aromatic Diazocarbonamides.

Three compounds of this series, namely benzene-, *p*-bromobenzene, and *p*-nitrobenzenediazocarbonamide, have been examined for evidences of isomerism. The absorption maxima in ethyl alcohol solution are shown in Table X and the graphs in Fig VI.

TABLE X

	A		B		C	
1. Benzenediazocarbonamide	434	2.57	286	4.54	223	4.39
2. *p*-Bromobenzenediazocarbonamide	(not observed)		305	4.03	228	3.81
3. *p*-Nitrobenzenediazocarbonamide	~420	2.4	283	4.16		

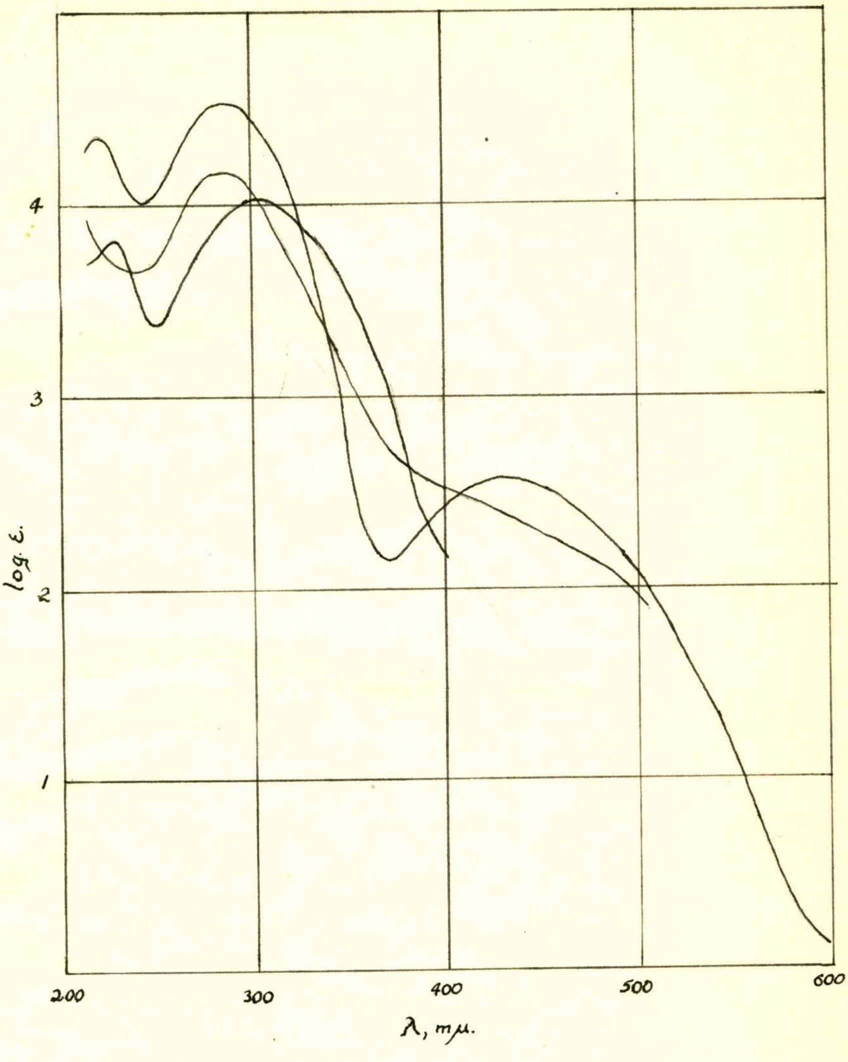
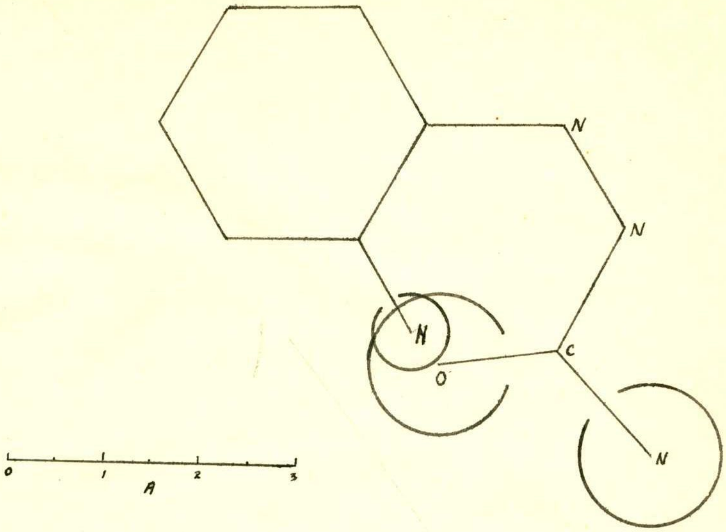


Fig. VI.



cis Benzenediazocarbonamide

flattened into one plane - dimensions as in _cis_-azobenzene(28) and (29,51).

Fig. VII.

The solutions (ca 0.5×10^{-4}M) used for examination of the spectra were irradiated for varying periods with a mercury vapour lamp and their absorption at one of the maxima observed with a Beckman spectrophotometer after irradiation. An initial change was seen followed by reversion in the course of 20-120 mins. to the value before irradiation. Examples of the values of $\Delta \log \varepsilon$ observed in this way are given in Table XI. It will be seen that the values of $\Delta \log \varepsilon$

TABLE XI

	Irradiation	λ	$\Delta \log \varepsilon$
Benzenediazocarbonamide	240 mins	286	+0.04
		220	+0.03
p -Bromobenzenediazocarbonamide	4 "	305	-0.12
p -Nitrobenzenediazocarbonamide	0.5 "	400	+0.05

for the two *p* substituted compounds are of the same sign as those for the corresponding maxima of the diazocyanides, but that the figure at the absorption band of the parent compound is of opposite sign to that expected. (The unsubstituted azobenzenes show an opposite sign for the $\Delta \lambda$ value but a normal one for $\Delta \log \varepsilon$).

Examination of the spectrum of benzenediazocarbonamide after irradiation and reversion revealed no differences from that of the original solution. Decomposition of the solute has therefore not interfered. Indeed, this compound is remarkably stable, resisting treatment with boiling water for some minutes, or long periods of exposure to sunlight.

Irradiation of saturated alcoholic solutions of benzene - and *p*-bromobenzenediazocarbonamides for periods of four hours and precipitation with water or crystallisation at -30°C gave samples of unchanged melting point. There was thus no successful separation of isomeric forms.

Molecular diagrams (Fig.VII) indicate considerable steric hindrance in the *cis* form, and that this is unlikely to be planar, but the hindrance is not greater than that indicated for *cis* azobenzene.

Accordingly alcoholic solutions of benzenediazocarbonamide of three strengths were examined for evidence of failure of Beer's Law, which would be expected to follow any association in the compounds. Table XII records the values found for the extinction coefficients of such solutions at varying wavelengths. There is no evidence of association, as the figures show only an irregular variation. The separation of isomers of this group is still considered possible.

TABLE XII

Concentration (M)	ε 434mμ	ε 500mμ	ε 520mμ	ε 540mμ
0.0130	-	105	52.7	21.7
0.00260	369	108	52.5	21.1
0.00066	371	108	52.1	20.7

(d) *p*-Nitrobenzenediazothiophenylether.

The above compound, the most stable simple member of the known diazothioethers, Ar-N=N-S-R', was prepared and its spectrum in hexane recorded. It shows maxima at 351 and 273 mμ (log ε 4.47 and 4.39 respectively). A solution of the compound of spectroscopic strength was irradiated and the extinction coefficient at the longest wavelength maximum observed after each exposure period. There was continuing decrease in ε, and no sign of reversibility. This compound appears to be decomposed by ultraviolet light and not isomerised.

(e) Diazoaminobenzene.

The spectrum of a sample of diazoaminobenzene, purified by the method of Dwyer (30) was recorded, since a quantitative measurememt seems not to have been published. In alcoholic solution there are maxima at 353 (3.67);288 (3.23) and 235 (3.64)

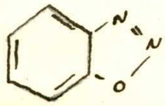
A molecular weight study has been made by Hunter (31) This indicates association in concentrated solutions. Consequently, it was felt that the isomerism which has not been found in the solid state might appear in the behaviour of the dilute solutions convenient in spectral examination. No reversible changes in intensity of absorption after irradiation were observed. If they occur they may be (a) too rapid for measurement by the present technique (time lapse at least 20 secs.)

(b) Too slight for detection.

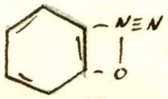
This question seems worthy of treatment with apparatus capable of more rapid measurements.

3. *Quinone diazides.*

A study of compounds of the above type was included in the studies of compounds containing the azo grouping because of the possibility that they contained a bicyclic structure. The formulation of the compounds has been under discussion for many years. Since they are preparable from *o*- and *p*-aminophenols, but not from *m*-aminophenols, many of the earlier investigators favoured structures with *ortho*-or *para*-rings, e.g. I(32,33) or II(34) although Wolff (35) proposed quinonoid representations, e.g. III or IV, largely from colour arguments. These avoid the steriochemical difficulties of a 1:4 bridge, allow for the observed similarity of properties and reactions of the 1:2 and 1:4 series, and are in closer agreement with the observed ultraviolet spectra.



I



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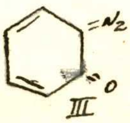
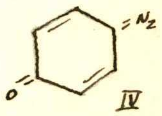


III



IV

The first spectral study was made by Hantzsch and Lifschitz(26) who compared the spectra of *p*-benzoquinonediazide with those of diazoacetic ester and *p*-benzoquinone. They concluded that this compound has a quinonoid structure. More recently, Anderson & Roedel (35) have examined a number of quinonediazides and compared their spectra with those of corresponding quinones. They find a general similarity to quinones and difference from the nitrogen and sulphur analogues of the ortho- compounds, the thiadiazoles and triazoles. These latter have very much more stability than the quinone diazides and have been formulated usually with a bicyclic structure.

The spectra of certain members of the series which had been prepared by Mr.Anderson for dipole moment measurements were examined and the results are compared with relevant quantitative data for other members and other series in the Tables XIII,– XV.

TABLE XIII

Diazides.

		A		B		C	
p- Benzoquinonediazide	E(35)	~448	1.80	342	4.47	287	3.37
						279	3.51
						269	3.53
1:4-Naphthaquinonediazide	E(35)	~477	1.81	371	4.55	312	3.83
				354	4.38	291	4.00
						282	4.00
						242	3.73
3:5-Dibromo-1:2-benzoquinone diazide -				~419	3.55	285	3.97
	H			408	3.59	~275	3.92
				~349	3.31	226	4.14

TABLE XIII (continued)

		A		B		C	
4-Nitro-1:2-benzoquinonediazide	A	-		396	3.79	258	4.07
				325	4.03	238	4.00
1:2 -Naphthaquinone-1-diazide	E(35)	~455	2.1	404	3.65	285	4.21
				388	3.78	~278	4.13
				370	3.72	250	4.29
				335	3.43		
				322	3.42		
1:2-Naphthaquinone - 2-diazide	E(35)	~475	2.0	~413	3.82	305	3.80
				397	4.00	293	3.80
				~389	3.95	261	4.57
				~372	3.82		
				317	3.70		
4-Nitro-1:2-naphthaquinone-1-diazide				~400	3.49	284	3.90
	H	-		395	3.51	247	4.16
				332	3.35	225	4.26
Azibenzil	E(35)	434	2.04	319	3.73	264	4.29

Solvents are indicated by A=alcohol, E= ether, H= *n* hexane in this and other tables.

TABLE XIV

Related quinones and benzil.

		A		B		C	
p- Benzoquinone	H(37,38)	478	1.08	-		280	2.57
		457	1.29			242	4.34
		434	1.30				
	E(38)	472	1.10	-		278	2.85
		455	1.28			242	4.36
		443	1.18				
		429	1.30				
		~417	1.13				
		412	1.20				
	A(38)	435	1.28	-		296	2.63
						242	4.25
1:2-Naphthaquinone	E(35)	538	1.55	389	3.55	252	4.52
		503	1.54	331	3.54	248	4.50
1:4-Naphthaquinone	E(35)	424	1.65	331	3.50	Below 250	
		403	1.67				
Benzil	E(35)	386	1.83	~335	2.22	~273	4.1
		368	1.81			259	4.36

TABLE XV

Thiadiazoles & triazoles.

Benzo - 1 thia - 2:3 - diazole H	-	306	3.63	264	3.92
				254	4.02
				225	4.23
Naphtho (1':2'-5:4)-1:2:3-thiadiazole	-	353	3.35	~282	3.93

TABLE XV(continued)

	E(35)			338	3.37	255	4.76
Benzo- 1:2:3-triazole	A(15)	-		~291	3.32	~282.5	3.58
						276	3.65
						259	3.58
Naphtho (1':2'-5':4)-1:2:3-triazole		~ca.350	1.70	342	3.81	283	4.06
	E(35)			~316	3.42	272	4.07
				312	3.68	251	4.57
				305	3.35	247	4.60
				298	3.37		

Measurements made on various products obtained in attempted preparations of the unsubstituted 1:2-benzoquinonediazide are not included in Table XIII as they are qualitative only. Absorptions were noted as follows:-

Ethereal extract from alkaline solution	422	300	272	256	242
" " " acid solution	416	308	272	~255	-
Alcoholic solution of solid after partial dehydration to constant weight............	403	-	-	263	-

A certain similarity with the results of Table XIII is apparent. Fukushima and Horie(40) have similarly reported semiquantitative spectra for the diazotisation products of o-,m- and p-aminophenols, and 1- amino -2- naphthol - 4 - sulphonic acid, Their figures for maximum absorption are:-

Product from o- aminophenol	392	~345	263	
" " p- aminophenol	~358	338	238	~212
" " aminonaphthol sulphonic acid	393	327	286	~247

They remark on the difference between the data quoted and those from m- aminophenol (compare the non-occurrence of 1! 3- diazophenols)

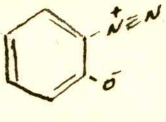
The parallelism between the absorption of related molecules containing the $>C=O$ and $>C=N_2$ groups is evident from comparison of Tables XIII, XIV. It was first claimed clearly by Wolf(39) for ethyldiazoacetate and certain Ketones although Hantzsch & Lifschitz(26) had previously used it.

The results of Table XIII differ from those for the related o-and p- methoxydiazonium sulphates reported by Wohl(41) :-

o-Methoxybenzenediazonium sulphate 353(3.65); 263(4.05).

p-Methoxybenzenediazonium sulphate 326(4.10);311(4.50);~291 (4.10); ~270(3.55);254 (3.05)

This is relevant to the conclusion of Hodgson and Marsden(42) that the compounds should be regarded as resonance hybrids to which structures III and V (or the corresponding para structures) contribute the spectra



indicate that there is not extensive contribution from the form V since this should absorb substantially as do these diazonium salts.

Tables XIII and XV suggest separate structure for the quinonediazides and the ortho nitrogen or sulphur compounds for which similar structures could be written. The relation of the spectra of compounds of related structures in which an oxygen atom is successively replaced by sulphur or nitrogen appears to involve change in intensity of absorption rather than wavelength (cf. Table XVI) By analogy, then, if the quinonediazides

TABLE XVI

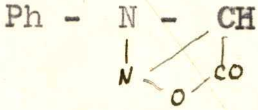
Oxygen Compounds		Sulphur Compounds		Nitrogen Compounds	
Et-O-Et(6)	~190 (3.00)	Et-S-Et(6)	195 (3.15)	Et-NH-Et(6)	195(3.45)
Ph-O-H(6)	275f (2.30)	Ph-S-H(6)	269f (2.86)	Ph-NH_2(6)	280f(2.30
Furan(6,43)	250 (0.00)	Thiophene(6,43,44)	~268(-0.25)	Pyrrole(6,43)	240 (2.48
	~200 (4.00)		~241(3.22)		210 (4.18
			234 (3.64)		
			215 (2.1)		
Oxazole(45)	230 (1.48)	Thiazole(6)	240 (3.60)	Glyoxaline(6)	250 (1.78

were structurally related to the thiadiazoles, they should not be expected to absorb at wavelengths much greater than 350 mμ. In fact, they do also, since compounds containing the $>C=S$ group often absorb in the visible region,(6) the spectra of thiadiazoles indicates absence of this group.

Thus the spectra favour a quinonoid structure for this group of oxygen compounds and bicyclic structures for the sulphur and nitrogen analogues. These structures have been confirmed by the dipole moment measurements.(36)

4. Sydnones:

In 1935, Earl and Mackney(46) reported the formation of a colourless crystalline substance by the action of acetic anhydride on N-nitroso-N-phenylglycine. Analysis and molecular weight determinations indicated that its formation involved loss of the elements of water from a molecule of nitrosophenylglycine, and for its structure they tentatively suggested.



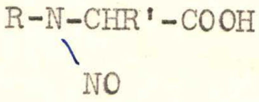
as being analogous to the product of the reaction of nitroso compounds and ketenes. Earle & Eade(47) have reported the discovery of a number of other similar compounds formed under similar conditions from other N-nitroso-N-monosubstituted glycines. For this new class of compound the name "sydnone" was suggested. The compound ~~form~~ from N- nitrosophenylglycine was named as "N-phenylsydnone" and its bromination product (in which the hydrogen atom of the sydnone structure is replaced) as "C- bromo-N-phenyl-sydnone."

The improbable nature of the proposed fused ring structure was recognised by Baker and Ollis(48) and Earl.(49) Evidence from optical activity studies,(50) dipole moments(5152) and chemical reactivity(53) has been presented, and this gives evidence that the sydnones have a mesomeric heterocyclic nucleus of unusual nature, in which all the contributing forms are zwitterionic (with one possible exception- an N-nitroso/amino ketene form(51,54)

Conclusions about two aspects of the chemistry of the "sydnones" have been drawn from studies of the absorption spectra of some sydnones and of N-nitroso-N-phenylglycine.

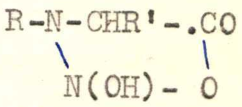
(a) Structure of N-nitroso-N-phenylglycine.

Earl, Leake and Le Fèvre (51) noted the possibility that N-nitroso- mono substituted glycines could possess any of several structures of which were I and II and "zwitterions". From the dipole moment evidence they



$$\mathrm{R-\underset{\diagdown NO}{N}-CHR'-COOH}$$

I



$$\begin{array}{l}\mathrm{R-N-CHR'-.CO}\\ \quad\ \diagdown \qquad\qquad\ \ \mid \\ \quad\ \ \mathrm{N(OH)-\ O}\end{array}$$

II

presented, the zwitterionic structures were contra-indicated, but a decision between I and II could not be made.

The spectrum of N-nitrosa-N-phenylglycine was accordingly compared with that of its benzyl ester, which, it was thought, would be unlikely to exist in the form II. Also, in this case, ($R=C_6H_5$; $R'=H$) I should show absorption very similar to that of N-nitrosoethylaniline, whereas II would be expected to show absorption similar to that of phenylhydrazines (55). These latter have no band analogous to that at 366 mμ in N-nitrosoethylaniline. The results are listed in Table XVII and graphed in Fig. VIII.

TABLE XVII

	λ	log ε	λ	log ε
1. N-nitroso - N-phenylglycine	~366	2.28	272	3.83
2. ditto, benzyl ester.	(Not observed)		275	3.83
3. N-nitroso - N-ethylaniline.	~366	2.34	272	3.89

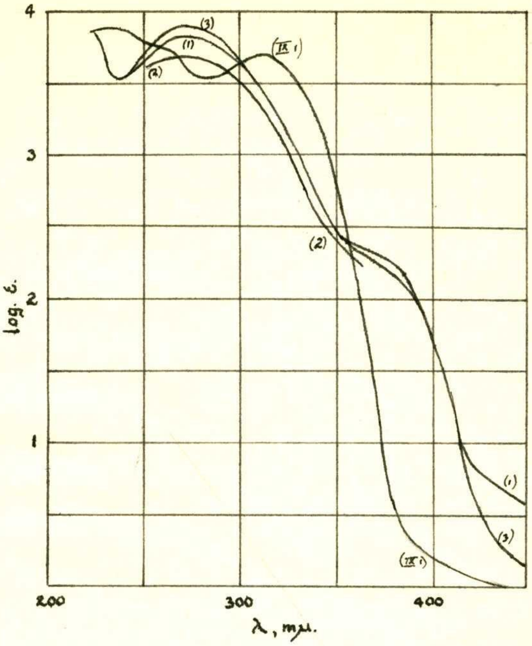


Fig. VIII

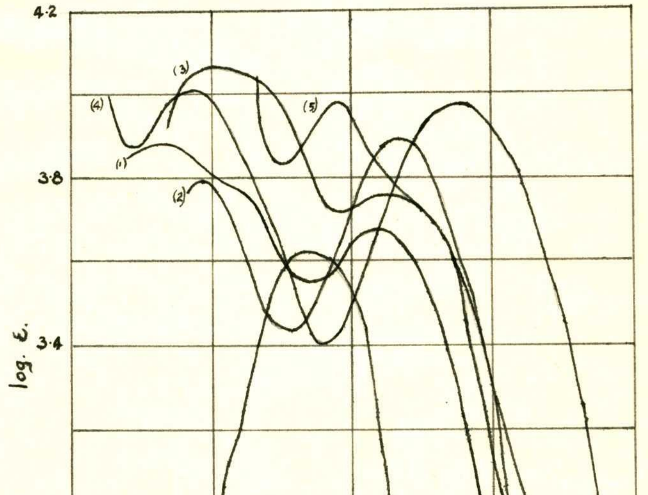


Fig. IX

The curves for the three substances are very similar in contour throughout the range of measurement. The second compound was examined only with a Hilger medium spectrograph and sector photometer and the examination is less accurate than for the others, the spectra of which were confirmed with the Beckman DU spectrophotometer. The 3 mμ deviation from the other results may be within the experimental error. The structure I is thus preferred to II.

The results also provide a confirmation of the conclusion from dipole moment evidence. Zwitterionic forms of nitrosophenylglycine would be special cases of the ammonium compounds. These absorb at wavelengths considerably shorter than those in the corresponding amines. Differences of 60 mμ between anthranilic acid and its hydrochloride or 30 mμ between <u>o</u>- toluidine and its hydrochloride(56) may be taken as typical. For further examples, c.f. (57). The similar differences between amines and amine oxides (5) or nitroso and nitrobenzene(6) provide examples from other groups. These shifts are much greater than that observed between nitrosophenylglycine and its ester, and moreover, the free acid has been observed to absorb at the same wavelengths as the corresponding N-nitrosoamine. It may be concluded that N-nitroso- N-phenylglycine has the structure, I.

(b) <u>The Sydnones:</u>

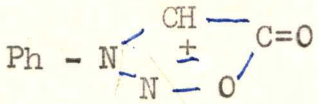
The spectra of six sydnones in ethyl alcoholic solution have been examined. The results (Table XVIII and Fig.IX) indicate that the sydnones have two absorption bands, one at ca. 290-340 mμ and the other at 245-295 mμ . Results in good general agreement with those here presented have been found by Strauss(58) (N-phenylsydnone) and Baker, Ollis and Poole(53) (N-*cyclo* hexyl-, N-benzyl-, N-phenyl- and NC-diphenyl-sydnones.)

TABLE XVIII

Sydnone	λ	log ε	λ	log ε
1. N-Phenyl-	310	3.69	~252 233	3.81 3.89
2. N-Phenyl-C-bromo-	320	3.88	245	3.80
3. N-*p*-Bromophenyl-	315	3.74	255	4.06
4. NC-Diphenyl-	340	3.97	245	4.01
5. N-β-Naphthyl-	~315	3.8	295	3.98
6. N- Benzyl -	290	3.61	~260	3.1

The band at 290-340 mμ is to be attributed to the "sydnone" grouping since it occurs in benzyl- (and *cyclo* hexyl-(51)) sydnone, where conjugation with another chromophoric group is not possible. This band may be seen to move to longer wavelengths and higher intensities, when the compounds are substituted at either nitrogen or carbon by a chromophoric group or when an N- *p* -bromophenyl group is substituted for the N- phenyl- group. There is thus some conjugation throughout the compounds.

The change in this "sydnone" band in the change from N- alkyl to N- aryl substituent is only 20 mμ and the change in log ε small (0.08). Also, in bromine substituted compounds, the C- bromo- compound (2) absorbs at higher wavelength and intensity than the p- bromo phenyl compound (3). These results are to be expected if, as indicated especially by dipole moment investigations, the compound have a heterocyclic ring of the type which Baker, Ollis and Poole (53) have termed "meso~~c~~-ionic" and in which the fully substituted nitrogen carries an excess positive change. This structure has been represented (53) by the formula



The band at 245-295 mµ seems to arise chiefly through the presence of aromatic C or N substituents as it is almost absent from benzylsydnone (the inflection in which is presumably benzene absorption, somewhat raised in intensity) and shifts to longer wavelengths in β-naphthylsydnone much (6)
as the absorption of naphthalene is shifted from that of benzene.

The variations in the longer wavelength band are not greater than those found in other series, e.g. acridine and its amino-and hydroxy-derivatives (59), 1:2:3- benzotriazoles (15), various p -benzoquinones (60) or 3- and 5-pyrazolones (61). The presence of a common structural arrangement in the group is thus confirmed

EXPERIMENTAL

(a) Solutes

(i) Diazocyanides.

The samples of the 4- chloro-, 4-bromo-, and 2:4:6- tribromo- diazocyanides were samples prepared by Miss Northcott. The others were prepared according to methods previously published.(21,22,23) Solution of the unstable forms were made as soon as possible after their preparation and examined immediately. In the case of 4-chlorobenzene diazocyanide, the least stable of those examined for which data is available for the rate of isomerisation (Le Fèvre & Northcott),(21) this would indicate some 5-8% contamination with the stable isomer at the conclusion of measurements, (2-3 hours) in benzene solution. Actually, ether was used as the solvent and somewhat increased contamination may occur, but it will not be so great as to mask the absorption of the unstable form. The contamination in the case of more stable compounds (e.g. the 2:4:6-tribromo- body) will be quite negligible.

(ii) Diazocarbonamides.

The samples of benzenediazocarbonamide were prepared by the methods of Thiele(62) and Darapsky.(63) The compound was found to be much more stable than is suggested by Hantzsch and Schultze,(64) who abandon its examination because it is somewhat unstable. Their sample was prepared directly from benzene diazocyanide and experience with the other isomers suggests that impurity in this latter would greatly affect the quality of the product.

4- Bromobenzenediazocarbonamide and 4-nitrobenzenediazocarbonamide were prepared by methods given in Bielstein's "Handbuch," XVI.

(iii) Diazoaminobenzene:

The samples of diazoaminobenzene were prepared by the method of Hartman and Dickey(65) on a much smaller scale, and purified (from traces of diazoaminoazobenzene) by absorption of the contaminant on cadmium hydroxide.(30)

(iv) 4-Nitrobenzenediazothiophenylether:

Samples of the compound were prepared according to the methods of Hantzsch & Freese,(66) Recrystallisation from 96% alcohol gave well-crystallised specimens at the published melting point (96-97°C)

(v) Quinonediazides and sydnones:

The samples of the quinonediazides were prepared by Mr.Anderson and those of the sydnones were specimens prepared for dipole moment measurements by Earl, Leake & Le Fèvre.(51) N-Nitroso-N-ethylaniline was prepared from purified ethylaniline and redistilled under 10 mm. pressure immediately before use.(67)

(b) Spectra

The spectra of some of the nitrosophenylglycines and sydnones were originally examined with a Hilger medium spectrograph and rotating sector photometer. Later they were checked with a Beckman DU. photoelectric spectrophotometer, with the exception of N-nitroso-N-phenylglycine benzyl ester. The other compounds were examined only with the Beckman instrument

(c) Irradiation:

The irradiation mentioned in sections 2(b), (c) and (d) was carried out by placing the solutions in the cells and cell holder of the Beckman instrument at a distance of 10 cms. from a mercury vapour lamp and illuminating through the polished surfaces of the cells. They were then replaced in the spectrophotometer and readings taken.

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