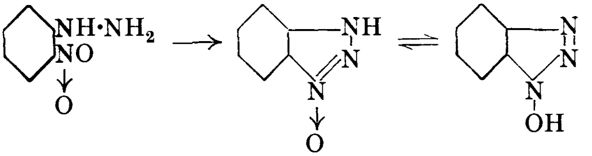
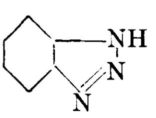
24. *The Absorption Spectra of* 1 : 2 : 3-*Benztriazoles.*

By A. Killen Macbeth and J. R. Price.

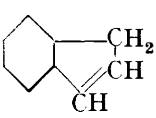
Hydroxy-1 : 2 : 3-benztriazoles are produced by the action of bases on *o*-nitrophenylhydrazines, the yield depending on experimental conditions (Macbeth and Price, J., **1934**, **1637**). Since evidence has been submitted that the nitrophenylhydrazines are not to be formulated as quinonoid compounds (J., **1935**, **1563**), the reaction indicates that the triazoles may be *N*-oxides (I) rather than the tautomeric hydroxy-forms (II). This question has been examined more fully by spectrophotometric methods, and the results of the study of the absorption spectra of a series of 1 : 2 : 3-benztriazoles and their derivatives are now recorded.



(I.) (II.)



(III.)



(IV.)

The analogy between 1 : 2 : 3-benztriazole (III) and indene (IV) might suggest that their spectra should be of similar types, especially since it is known from the comparison of the spectra of benzene and pyridine that the replacement of CH by N in a ring does not greatly affect the positions of the $\lambda_{\text{max.}}$ of the bands. This view is further strengthened by the observation (Morton and de Gouveia, J., **1934**, **916**) that quinoline, *iso*quinoline, and naphthalene show the same three main regions of absorption, but with intensity differences. There is no evidence, however, that electronic excitation in the azo-group will give rise to a band similar to that of the ethenoid system. Indeed, the data available indicate that the electron of the $\text{N}\overset{*}{=}\text{N}$ group gives rise to two bands; for a qualitative examination by Hantzsch and Lifschitz (*Ber.*, **1912**, **45**, **3011**) shows that diazoacetic ester has two maxima of absorption, one of low and the other of high persistence, at *ca.* 370 and 244 mμ respectively. Azomethane, NMe:NMe, which is a better substance for comparison on account of its more definite structure, gives a band at *ca.* 350 mμ and a marked inflexion at *ca.* 245 mμ. The introduction of a benzene ring causes changes in the intensities of the bands and displacement towards longer wave-lengths, benzeneazomethane, NPh:NMe, showing two bands at 400 and 260 mμ approximately (Stobbe and Nowak, *Ber.*, **1914**, **47**, **578**). The latter region expresses the absorption of the benzenoid centre and masks the second maximum of the $\text{N}\overset{*}{=}\text{N}$ group, but the shape of the curve suggests that it may be capable of resolution by the more exact methods of spectrophotometry. Benzeneazoethane gives practically identical absorption, and the line of the curves indicates the existence of a third band, characteristic of $\overset{*}{\text{Ph}}\cdot\text{N}=\text{N}$—, just beyond the region examined. The introduction of a second benzene ring conjugated to the azo-linking causes further displacement of the maxima to 436 mμ ($\log \varepsilon = 2{\cdot}84$) and 318 mμ ($\log \varepsilon = 4{\cdot}37$), together with a significant inflexion at 300 mμ ($\log \varepsilon = 4{\cdot}23$) and a third band due to $\overset{*}{\text{Ph}}\cdot\text{N}=\text{N}$— which is clearly shown at 229 mμ ($\log \varepsilon = 4{\cdot}09$) (Macbeth and Maxwell, J., **1923**, **123**, **370**).

It therefore seems clear that electronic excitation of the $\text{N}\overset{*}{=}\text{N}$ group gives rise to two bands; and in order to deduce the probable absorption of the 1 : 2 : 3-benztriazoles it is further necessary to consider the effect of the third nitrogen atom and of ring closure. Some idea of the first effect may be gained by comparing the spectra of benzeneazomethane and tolueneazodimethylamine, $\text{C}_6\text{H}_4\text{Me}\cdot\text{N:N}\cdot\text{NMe}_2$; and the curves of azobenzene and diazoaminobenzene furnish a second comparison pair. Qualitative records only are available in all the cases apart from azobenzene (Hantzsch and Lifschitz, *loc. cit.*), and too great reliance cannot therefore be placed on the maxima recorded. From the values summarised below, however, it is seen that the introduction of the third nitrogen atom results in the disappearance of the band of longer wave-length associated with the $N\overset{*}{=}N$ system, its position being marked by an inflexion which in the case of tolueneazodimethylamine is of a very minor character indeed. The shape of the qualitative curve again suggests that the band at *ca.* 280 mμ in this compound may be capable of resolution by spectrophotometric methods.

$$\begin{tikzcd}
\text{Azomethane} & & & & 245 & & \mathit{350} \arrow[d] & & & & \\
\text{Benzeneazomethane} & * & & & 260 \arrow[dl] \arrow[dr] & & 400 \arrow[r] \arrow[d] & \text{Tolueneazodimethylamine} & * & 280 & \mathit{370}\,\dagger \\
\text{Azobenzene} & 229 & & \mathit{300} & & 318 & 436 \arrow[r] & \text{Diazoaminobenzene} & * & 345 & \mathit{440}\,\dagger
\end{tikzcd}$$

* Band indicated outside the region of the qualitative curves. † Weak inflexion.

Ramart-Lucas and Amagat (*Bull. Soc. chim.*, 1932, **51**, 965) have shown, from the study of allylbenzene and a series of compounds of the type $Ph{\cdot}[CH_2]_n{\cdot}CH{:}CH_2$, that a double bond which is not conjugated to the benzene ring has no influence on the benzenoid absorption; and it may therefore be inferred that ring closure which does not bring conjugation of this type into play will not materially affect the locations or intensities of the maxima characteristic of electronic excitation of the C=C system of the nucleus. This view is supported by the facts (i) that the spectra of the above compounds resemble those of ethylbenzene, the xylenes, and hydrindene; and (ii) that the styrene series, $CHPh{:}CH{\cdot}[CH_2]_n{\cdot}CH_3$, also examined by Ramart-Lucas and Amagat (*loc. cit.*), give maxima closely related to those of indene (Morton and de Gouveia, J., 1934, 911). In the case of the triazoles, however, ring closure introduces a nitrogen atom as a substituent in the benzene ring, and this effect must not be overlooked. The introduction of the amino-group causes marked displacement of the benzene bands; *e.g.*, in aniline, the 254 mμ maximum of benzene is displaced to 284·5 mμ with increased intensity, and the short-wave band at 190 mμ is brought within the region ordinarily explored and located at 234 mμ. On the other hand, the hydrochlorides and acetyl derivatives of the bases do not show this displacement. Since the triazoles are not markedly basic, the introduction of the nitrogen atom into the nucleus may be more rightly regarded as parallel to the substituent in the acyl derivatives of the bases rather than as analogous to the substitution of the basic amino-group. On this view, the spectra of the triazoles should be similar to that of tolueneazodimethylamine, and we may therefore look for a maximum characteristic of the $\overset{*}{\text{Ph}}{\cdot}N{:}N{\cdot}$ system, together with a band due to the electron of the azo-group influenced by the nucleus, $Ph{\cdot}N\overset{*}{=}N$, and possibly a weak inflexion also due to electronic excitation of the azo-group. The maxima found in the compounds examined are shown in Table I, italicised figures in all tables representing inflexions (see Fig. 1).

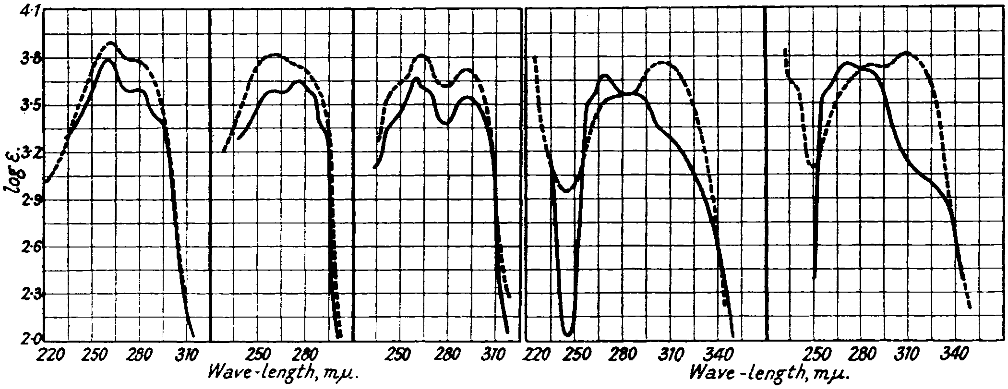
TABLE I.

	$\lambda_{max.}$, mμ.	log ε.	Absorbing centre.*	$\lambda_{max.}$, mμ.	log ε.	Absorbing centre.*
		In alcohol.			In water.	
1 : 2 : 3-Benztriazole	*291*	3·32	b	*275·5*	3·75	b
	282·5	3·58		260·5	3·82	a
	276	3·65				
	259	3·58	a			
1-Methyl-1 : 2 : 3-benztriazole	*291·5*	3·45	b	*277*	3·77	b
	279·5	3·59		261	3·88	a
	258·5	3·79	a			
3 : 6-Dimethyl-1 : 2 : 3-benztriazole	292·5	3·55	b	291	3·73	b
	263	3·61	a	262	3·82	a
	258·5	3·68		*247*	3·65	
	244·5	3·40				

* $a = \overset{*}{\text{Ph}}{\cdot}N{=}N{\cdot}N{\cdot}$; $b = Ph{\cdot}N\overset{*}{=}N{\cdot}N{\cdot}$.

It will be seen that the absorption of the 1 : 2 : 3-triazoles is separable into two regions, *viz.*, 245—263 mμ and 270—291 mμ, the spectra in alcohol being better defined than those in water, in which an envelope of somewhat greater intensity is formed in all cases. Substitution of methyl groups leads to better resolution and clearer definition of the regions, an effect which is paralleled, *e.g.*, in the middle regions of absorption of the alkylnaphthalenes (Morton and de Gouveia, *loc. cit.*) and in the dinitrophenyl- and dinitrotolyl-hydrazines (J., **1935**, 1563). From the comparative study of the qualitative curves of azomethane, benzeneazomethane, etc., discussed above, it seems reasonable to attribute the band of shorter wave-length to the C=C system of the nucleus influenced by N=N. On this view the 254 mμ band of benzene shows but little displacement in the benztriazoles, and the benzene band of shorter wave-length still remains outside the region examined. The existence of such a band is definitely indicated by the shape of the curves of many of the triazole derivatives, notably the hydroxy-triazoles, in which the displacements of the benzene bands are of a higher order. The maxima of the triazoles are therefore not comparable with those of indene, in which both the benzene bands suffer considerable displacement under the influence of the ethenoid grouping. Morton and de Gouveia attribute the maximum at 246 mμ (log ε = 4·0) to the Ph·C$\overset{*}{=}$C— system, and that in the region 270—290 mμ (log ε = 2·2—3·2) to $\overset{*}{\text{Ph}}$·C=C—. The former band appears to be composite, showing in hexane a significant inflexion at 262 mμ (log ε = 3·85); the maxima at 246 and 262 mμ would thus represent respectively the displaced benzene 190 mμ band and the influenced ethenoid absorption. On the other hand, it is only the 254 mμ benzene band, but of increased intensity, which is shown in the spectra of the triazoles in association with that due to the influenced azo-group.

FIG. 1. FIG. 2.



(a) (b) (c) (a) (b)

FIG. 1.—(a) 1-*Methyl*-1 : 2 : 3-*benztriazole*.
(b) 1 : 2 : 3-*Benztriazole*.
(c) 3 : 6-*Dimethyl*-1 : 2 : 3-*benztriazole*.

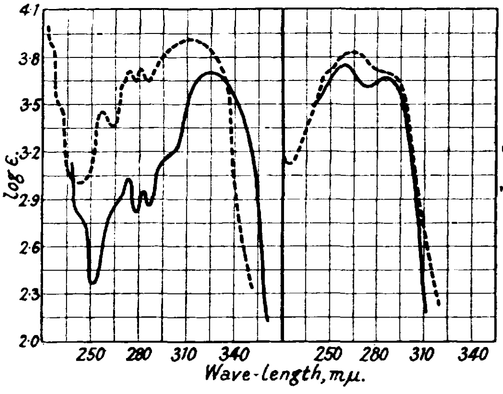
FIG. 2.—(a) 1-*Hydroxy*-1 : 2 : 3-*benztriazole*.
(b) 1-*Hydroxy*-6-*methyl*-1 : 2 : 3-*benztriazole*.

——— *in* EtOH. - - - - - *in* H_2O.

1-*Hydroxy*-1 : 2 : 3-*benztriazole*.—The absorption of this compound differs markedly in alcoholic and in aqueous solution, whereas the spectra of all the nitro-1-hydroxybenztriazoles examined closely resemble one another in both solvents. This suggests that the tautomerism between the forms (I) and (II) manifests itself in alcoholic solutions, but that only one form is stable in aqueous solution and in the case of the nitro-compounds. In this connexion it seems significant that methylation of 6-nitro-1-hydroxy-1 : 2 : 3-benztriazole and its 5-methyl-compound by methyl iodide and sodium ethoxide yields only the corresponding methoxy-derivatives (Brady and Day, J., 1923, **123**, 2258), whereas the 1-hydroxy-compound when methylated under similar conditions yields a mixture of the derivatives of (I) and (II) (Brady and Reynolds, J., 1928, 193). Methylation of 6-nitro-1-hydroxy-5-methyl-1 : 2 : 3-benztriazole with sodium hydroxide and methyl sulphate, however, yields a little of the *N*-oxide derivative as a secondary product (Brady and Day, *loc. cit.*).

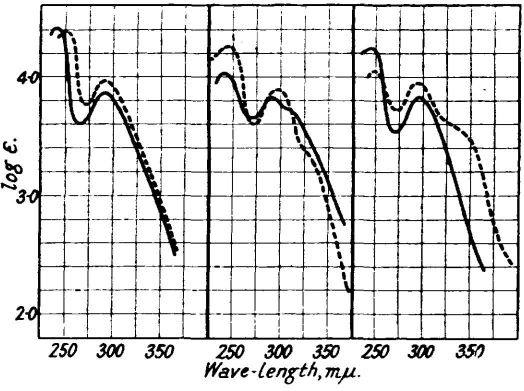
Definite evidence in favour of the existence of the two tautomeric forms (I) and (II) in alcoholic solution is found on examination of the curves of their methyl derivatives and analysis of the absorption of the substance itself in alcoholic solution. The graphs of these substances are shown in Figs. 2 and 3, and the values of the maxima are recorded in Table II. The *O*-ether shows the same regions of absorption in both alcoholic and aqueous solution, but in the latter solvent the intensities are somewhat increased. Similar considerations hold for the *N*-oxide.

FIG. 3.



(a) (b)

FIG. 4.



(a) (b) (c)

FIG. 3.—(a) *3-Methyl-*1 : 2 : *3-benztriazole* 1-*oxide*. —— *in* EtOH. - - - - - *in* H_2O.
(b) 1-*Methoxy*-1 : 2 : 3-*benztriazole*. —— *in* EtOH. - - - - - *in* H_2O–MeOH.

FIG. 4.—(a) ——— 6-*Nitro*-1 : 2 : 3-*benztriazole in* EtOH.
- - - - - 6-*Nitro*-1-*methyl*-1 : 2 : 3-*benztriazole in* EtOH.
(b) ——— 6-*Nitro*-1 : 2 : 3-*benztriazole in aqueous* EtOH.
- - - - - 6-*Nitro*-3-*methyl*-1 : 2 : 3-*benztriazole in aqueous* MeOH.
(c) ——— 6-*Nitro*-3-*methyl*-1 : 2 : 3-*benztriazole in* EtOH.
- - - - - 6-*Nitro*-1-*methyl*-1 : 2 : 3-*benztriazole in aqueous* MeOH.

TABLE II.

1-*Hydroxy*-1 : 2 : 3-*benztriazole*.			
Alcohol.		Water.	
$\lambda_{max.}$, mμ.	log ε.	$\lambda_{max.}$, mμ.	log ε.
305—330	2·88—3·32	305	3·79
287·5	3·58	*278*	3·57
267·5	3·7		
259·5	3·57		
3-*Methyl*-1 : 2 : 3-*benztriazole* 1-*oxide*.			
324·5	3·73	310·5	3·92
298·5	3·17		
281·5	2·96	281	3·72
273	3·04	273	3·71
268	2·9	*268*	3·6
242·5	2·8	257·5	3·45
		228·5	3·5
		223·5	3·88

1-*Hydroxy*-6-*methyl*-1 : 2 : 3-*benztriazole*.			
Alcohol.		Water.	
$\lambda_{max.}$, mμ.	log ε.	$\lambda_{max.}$, mμ.	log ε.
310—330	2·94—3·16	306	3·82
282·5	3·73	284	3·75
271·5	3·77	*234·5*	3·64
258·5	3·6		
1-*Methoxy*-1 : 2 : 3-*benztriazole*.			
284	3·66	*279·5*	3·74
260	3·77	262	3·83
		249	3·72

The maxima shown by the *O*-ether in alcohol are thus (*a*) 284 mμ (log ε = 3·66) and (*b*) 260 mμ (log ε = 3·77). The only maximum shown by the 3-methyl *N*-oxide of sufficient intensity to appear in combination of the two curves is (*c*) 324·5 mμ (log ε = 3·73). The corresponding locations in the hydroxybenztriazole curve are (a_1) 287·5 mμ (log ε = 3·58), (b_1) 267·5 mμ (log ε = 3·70), and (c_1) 324·5 mμ in the inflexion region 310—330 (log ε = 3·02). The difference in log ε values for (*a*) and (a_1), *viz.*, 0·08, gives 83% of (II), whilst that for (*b*) and (b_1) indicates some 85% of (II). On the other hand, (*c*) and (c_1) give a log ε difference of 0·71, corresponding to *ca.* 20% of (I) in solution. The good agreement between the values calculated for the different maxima seems to prove the existence of an equilibrium mixture of the tautomerides in alcoholic solution corresponding to some 80—85% of (II). The absorption of alcoholic solutions of 1-hydroxy-6-methyl-1 : 2 : 3-benztriazole presents the same features as that of the unsubstituted compound, and it therefore appears that in this case also there is an equilibrium mixture of the two forms. Calculation of the percentages is not practicable, as the curves for the corresponding methyl-substituted methoxy-derivative and 1-oxide are not available.

Nitro-derivatives of 1 : 2 : 3-*Benztriazoles.*—The spectra of 6-nitro-1 : 2 : 3-benztriazole and its 1- and 3-methyl derivatives in alcoholic solution are practically identical, absorption occurring as two well-defined bands in the regions characteristic of the alkylbenztriazoles with but little displacement. The two maxima are therefore to be attributed to the absorbing centres already specified in the case of the simple triazoles. When, however, the nitro-triazoles are examined in aqueous solution, a new inflexion is observed at *ca.* 312—330 mμ. In view of the evidence obtained from the nitro-amines (Morton and McGookin, *loc. cit.*) and the nitro- and dinitro-phenylhydrazines (Macbeth and Price, *loc. cit.*), it seems reasonable to attribute this region of absorption to an electron jointly controlled by a nitrogen and an oxygen atom of the nitro-group.

FIG. 5.

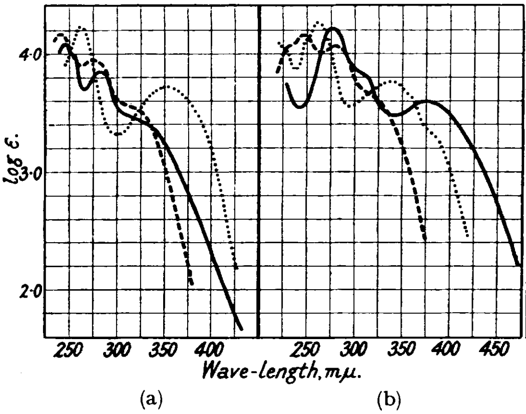


FIG. 6.

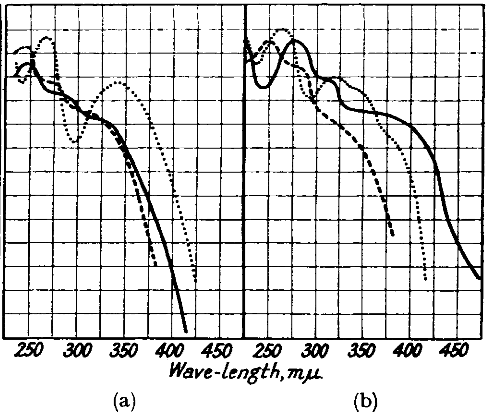


FIG. 5.—(a) ——— 6-*Nitro*-1-*hydroxy*-1 : 2 : 3-*benztriazole in* EtOH.
— — — 6-*Nitro*-1-*methoxy*-1 : 2 : 3-*benztriazole in* EtOH.
- - - - - 6-*Nitro*-3-*methyl*-1 : 2 : 3-*benztriazole* 1-*oxide in* EtOH.
(b) ——— 6-*Nitro*-1-*hydroxy*-1 : 2 : 3-*benztriazole in* H_2O.
— — — 6-*Nitro*-1-*methoxy*-1 : 2 : 3-*benztriazole in aqueous* MeOH (10% MeOH).
- - - - - 6-*Nitro*-3-*methyl*-1 : 2 : 3-*benztriazole* 1-*oxide in* H_2O.

FIG. 6.—(a) ——— 6-*Nitro*-1-*hydroxy*-5-*methyl*-1 : 2 : 3-*benztriazole in* EtOH.
— — — — 6-*Nitro*-1-*methoxy*-5-*methyl*-1 : 2 : 3-*benztriazole in* EtOH.
- - - - - 6-*Nitro*-3 : 5-*dimethyl*-1 : 2 : 3-*benztriazole* 1-*oxide in* EtOH.
(b) ——— 6-*Nitro*-1-*hydroxy*-5-*methyl*-1 : 2 : 3-*benztriazole in* H_2O.
— — — 6-*Nitro*-1-*methoxy*-5-*methyl*-1 : 2 : 3-*benztriazole in aqueous* EtOH (10% EtOH).
- - - - - 6-*Nitro*-3 : 5-*dimethyl*-1 : 2 : 3-*benztriazole* 1-*oxide in* H_2O.

The spectra of 6-nitro-1-hydroxy-1 : 2 : 3-benztriazole and its 5-methyl derivative have also been examined; in alcoholic solution they give curves almost identical with those of the corresponding methoxy-compounds. These compounds also absorb in the two regions characteristic of the centres denoted in Table I, but show in addition the inflexion assigned above to the nitro-group. The absence of any such inflexion in the alcoholic solutions of the nitrotriazoles other than the hydroxy-derivatives and their ethers constitutes a difficulty as yet unexplained.

The curves of the nitro-derivatives of 1 : 2 : 3-benztriazole are shown in Figs. 4, 5, and 6, and the values are set out in Table III; where inflexions occur, the approximate wave-length of the middle region is recorded. For the hydroxytriazoles the solvent was water, but with the other substances it was found necessary on account of solubility to use aqueous alcohol (10% MeOH or EtOH).

TABLE III.

Derivatives of 1 : 2 : 3-*Benztriazole.*

	Absorbing	6-Nitro-.		6-Nitro-1-methyl-.		6-Nitro-3-methyl-.	
Solvent.	centre.*	$\lambda_{max.}$, mμ.	log ε.	$\lambda_{max.}$, mμ.	log ε.	$\lambda_{max.}$, mμ.	log ε.
Alcohol	*b*	290	3·86	290·5	3·98	295	3·82
	a	240·5	4·22	250	4·21	244·5	4·26
Water	NO_2	*ca. 312*	3·7	*ca. 327*	3·63	*ca. 328*	3·37
	b	292·5	3·83	294	3·95	297	3·9
	a	241	4·05	250·5	4·05	247	4·26

		1-Methoxy-.		6-Nitro-1-methoxy-.		6-Nitro-1-hydroxy-.	
Alcohol	NO_2	—	—	*ca. 315*	3·57	*ca. 315*	3·48
	b	284	3·66	273	3·96	281	3·88
	a	260	3·77	241·5	4·16	*254* 247	4·01 4·12
Water	NO_2	—	—	*ca. 315*	3·65	375	3·59
	b	*279·5*	3·74	280	4·09	*ca. 306*	3·84
	a	262 *249*	3·83 3·72	244 *232*	4·17 4·09	274·5	4·2

		6-Nitro-1-methoxy-5-methyl-.		6-Nitro-1-hydroxy-5-methyl-.	
Alcohol	NO_2	*ca. 312*	3·5	*ca. 320*	3·45
	b	*ca. 272*	3·75	*ca. 278*	3·66
	a	245	4·05	249	3·92
Water	NO_2	*ca. 320*	3·42	*ca. 375*	3·48
	b	*ca. 274*	3·89	*ca. 312*	3·75
	a	249	4·08	274·5	4·11

* See Table I.

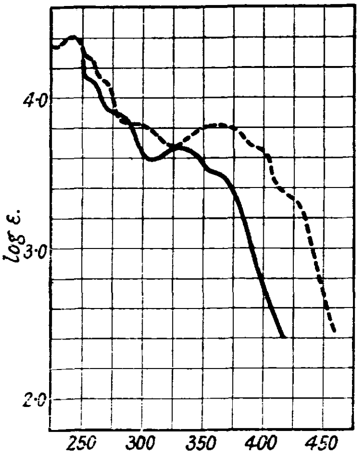
1 : 2 : 3-*Benztriazole* 1-*Oxides.*—Three substances of this type, *viz.*, 3-methyl-, 6-nitro-3-methyl-, and 6-nitro-3 : 5-dimethyl-1 : 2 : 3-benztriazole 1-oxides, were examined in both aqueous and alcoholic solution. The maxima for them are recorded below and the curves are shown in Figs. 3, 5, and 6. Since these compounds differ from the benztriazoles in having a co-ordinately linked oxygen atom attached to one of the nitrogen atoms of the N=N group, some modification of the absorption characteristic of the latter is to be expected, just as a difference is observed in the case of the azo- and azoxy-compounds. Comparison of the absorption spectra of a series of azoxybenzene derivatives with that of azobenzene shows that the change from —N=N— to $\underset{\underset{\textstyle O}{\downarrow}}{\text{—N=N—}}$ results in a displacement of the main band (318 mμ) to longer wave-lengths, this displacement being increased by the presence of nitro-groups (Szegö, *Ber.*, 1928, **61**, 2087; 1929, **62**, 736). The diagram below illustrates the analogous behaviour of the triazole oxides, which supports the interpretation put forward concerning the location of the chromophores responsible for the absorption of the 1 : 2 : 3-benztriazoles.

$$\begin{tikzcd}
\text{Azobenzene} \atop \text{318 m}\mu \arrow[r] \arrow[dr] & \text{Azoxybenzene} \atop \text{322 m}\mu \arrow[r] & p\text{-Nitroazoxybenzene} \atop ca.\ \text{340 m}\mu \\
& p\text{-Nitroazobenzene} \atop \text{333 m}\mu \arrow[ur] &
\end{tikzcd}$$

$$\begin{tikzcd}
\text{1-Methyl-1 : 2 : 3-benztriazole} \atop \text{280 m}\mu \arrow[r] \arrow[dr] & \text{3-Methyl-1 : 2 : 3-benztriazole 1-oxide} \atop \text{324 m}\mu \arrow[r] & \text{6-Nitro-3-methyl-1 : 2 : 3-benztriazole 1-oxide} \atop \text{349 m}\mu \\
& \text{6-Nitro-1-methyl-1 : 2 : 3-benztriazole} \atop \text{290 m}\mu \arrow[ur] &
\end{tikzcd}$$

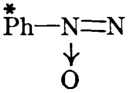
The spectra of the nitro-compounds in alcoholic solution are comparatively simple, showing two well-defined maxima at *ca.* 263—265 and 340—349 mμ. As in the case of the simple 1 : 2 : 3-benztriazoles, the former is attributed to the aromatic C═C system, and the latter to the azoxy-group. In aqueous solution the two main maxima are still observed with some displacement of the second maximum towards shorter wave-lengths, and a new inflexion appears at *ca.* 379 mμ, which, by analogy with the nitro-triazoles, may be attributed to the nitro-group.

FIG. 7.



5-*Nitro*-3-*hydroxy*-*αβ*-*naphtha*-1 : 2 : 3-*triazole.* —— *in* EtOH. - - - *in* H_2O.

The absorption of 3-methyl-1 : 2 : 3-benztriazole 1-oxide is more complex. In addition to the main band at 324·5 mμ, which shows displacement towards shorter wave-lengths on change of solvent from alcohol to water, as with the nitro-triazoles oxides, the absorption curves show a group of maxima in the region 260—280 mμ which may be attributed to the chromophore

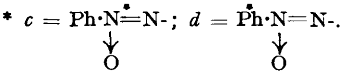


$\overset{*}{\mathrm{Ph}}\text{—}\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{N}}{=}\mathrm{N}$

. The resolution in this region is more marked than with the nitro-compounds, and although increased intensity is observed on change of solvent from alcohol to water, even in the latter solvent the log ε values are much less than those found for the nitro-derivatives. The shape of the curves in both solvents gives a clear indication of another more intense maximum outside the region of examination, which probably represents the second band of benzene which has been recorded at 190 mμ.

1 : 2 : 3-*Benztriazole* 1-*Oxides.*

		3-Methyl-.		6-Nitro-3-methyl-.		6-Nitro-3 : 5-dimethyl-.	
Solvent.	Absorbing centre.*	$\lambda_{max.}$, mμ.	log ε.	$\lambda_{max.}$, mμ.	log ε.	$\lambda_{max.}$, mμ.	log ε.
Alcohol	*c*	324·5	3·73	349	3·75	341·5	3·76
		298·5	3·17				
	d	281·5	2·96				
		273	3·04				
		268	2·90	263	4·24	265·5	4·15
		242·5	2·80				
Water	NO_2	—	—	*379*	3·34	*379*	3·28
	c	310·5	3·92	*357*	3·67	*339*	3·71
				338	3·78	318·5	3·80
	d	281	3·72				
		273	3·71				
		268	3·60	262	4·27	263	4·20
		257·5	3·45	*252*	4·17	*247·5*	4·04
		228·5	3·50				
		223·5	3·88				



$* \; c = \mathrm{Ph{\cdot}}\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{N}}\overset{*}{=}\mathrm{N}\text{-}; \; d = \overset{*}{\mathrm{Ph}}\mathrm{{\cdot}}\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{N}}{=}\mathrm{N}\text{-}.$

Displacements.—The displacements on change of solvent of the maxima of some of the triazoles and their derivatives are set out below, from which it will be seen that the Δ $cm.^{-1}$ values for the nitro-hydroxy-derivatives are markedly greater than in the case of any other compound examined. This also holds for a nitro-hydroxy-naphthatriazole which was prepared and examined (Fig. 7), and is apparently connected with the ionisation of these substances in aqueous solution. The values of the simple hydroxy-derivatives of triazoles are not discussed in this connexion on account of the tautomerism already described.

Displacements : Alcohol ⟶ Water.

1 : 2 : 3-Benztriazoles.	$\lambda_{max.}$, mμ.	cm.$^{-1}$.	⟶ $\lambda_{max.}$, mμ.	cm.$^{-1}$.	Δ cm.$^{-1}$.
6-Nitro-	290	34,500	292·5	34,200	− 300
	240·5	41,600	241	41,500	− 100
6-Nitro-1-methyl-	290·5	34,400	294	34,000	− 200
	250	40,000	250·5	39,900	− 100
6-Nitro-3-methyl-	295	33,900	297	33,700	− 200
	244·5	40,900	247	40,500	− 400
1-Methoxy-	284	35,200	279·5	35,800	+ 600
	260	38,450	262	38,200	− 250
6-Nitro-1-methoxy-	273	36,600	280	35,700	− 900
	241·5	41,400	244	41,000	− 400
6-Nitro-1-methoxy-5-methyl-	312	32,050	320	31,250	− 800
	272	36,750	276	36,250	− 500
	245	40,800	249	40,200	− 600
6-Nitro-1-hydroxy-	*ca.* 315	31,750	*ca.* 375	26,650	− 5100
	281	35,600	306	32,700	− 2900
	247	40,500	274·5	36,400	− 4100
6-Nitro-1-hydroxy-5-methyl-	*ca.* 320	31,250	*ca.* 375	26,650	− 4600
	278	36,000	312	32,050	− 3950
	249	40,200	274·5	36,400	− 3800
5-Nitro-3-hydroxy-αβ-naphtha-	360	27,800	398·5	25,100	− 2700
	333	30,000	363·5	27,500	− 2500
	274	36,500	294	34,000	− 2500
	255	39,200	269	37,200	− 2000

EXPERIMENTAL.

6-Nitro-1-hydroxy-5-methyl-1 : 2 : 3-benztriazole was obtained in excellent yield by refluxing 4 : 6-dinitro-*m*-tolylhydrazine on a water-bath with alcoholic ammonia until the solution became quite clear (*ca.* 5 hours); it was precipitated by addition of dilute hydrochloric acid after removal of the alcohol, and several crystallisations from dilute alcohol afforded pale yellow prisms, m. p. 196—197° (Brady and Day, *loc. cit.*, give 194°).

1-*Hydroxy*-6-*methyl*-1 : 2 : 3-*benztriazole*.—*p*-Chlorotoluene (100 g.) nitrated with nitric acid (*d* 1·42; 120 g.) and concentrated sulphuric acid (170 g.) gives a mixture of 2- and 3-nitro-4-chlorotoluene. The fraction, b. p. 255—260°, is rich in 3-nitro-4-chlorotoluene; this (5 g.) was refluxed for 20 hours with excess of an aqueous-alcoholic solution of hydrazine hydrate, the unchanged material removed with ether, and the solution acidified with hydrochloric acid. The required *compound* was precipitated, and crystallised from dilute alcohol as colourless needles, m. p. 178—179° (Found : N, 28·3. $C_7H_7ON_3$ requires N, 28·2%).

5-*Nitro*-3-*hydroxy*-αβ-*naphtha*-1 : 2 : 3-*triazole*.—2 : 4-Dinitrochloronaphthalene (25 g.; Ullmann and Bruck, *Ber.*, 1908, **41**, 3932) was heated on a water-bath for 6 hours with alcohol (180 c.c.) and 50% hydrazine hydrate (20 c.c.), and the mixture filtered hot. The residue was extracted with boiling water, and on cooling the hydrazine salt of 2 : 4-dinitro-α-naphthol separated. This was removed, and acidification of the solution with dilute hydrochloric acid afforded the triazole as a flocculent precipitate which, after several crystallisations from alcohol, detonated at 236° (Muller and Weisbrod, *J. pr. Chem.*, 1925, **111**, 307, give 215°). Other triazoles used in the work were prepared by standard methods. 6-Nitro-3 : 5-dimethyl-1 : 2 : 3-benztriazole 1-oxide, recrystallised successively from water (twice), methyl alcohol, and benzene, had m. p. 268—269° (Brady and Day, *loc. cit.*, give m. p. 265°); 6-nitro-1-methoxy-1 : 2 : 3-benztriazole, m. p. 130°; 6-nitro-1-hydroxy-1 : 2 : 3-benztriazole detonates at 206°; 6-nitro-1-methoxy-5-methyl-1 : 2 : 3-benztriazole, m. p. 134—135° (Brady and Day, *loc. cit.*); 6-nitro-1-methyl-1 : 2 : 3-benztriazole, colourless needles, m. p. 188° (Brady and Reynolds, J., 1930, 2672, reported pale yellow needles, m. p. 187°); 6-nitro-3-methyl-1 : 2 : 3-benztriazole, m. p. 197—198°, and its 1-oxide, m. p. 163° (Brady and Reynolds, J., 1931, 1277); 1-methoxy-1 : 2 : 3-benztriazole, m. p. 88—89°; 3 : 6-dimethyl-1 : 2 : 3-benztriazole, m. p. 49°; 3-methyl-1 : 2 : 3-benztriazole 1-oxide, m. p. 144—145° (Brady and Reynolds, J., 1928, 198); 1 : 2 : 3-benztriazole, m. p. 97—98° (Ladenburg, *Ber.*, 1876, **9**, 222); 1-methyl-1 : 2 : 3-benztriazole, m. p. 64—65° (Reissert, *Ber.*, 1914, **47**, 676); 6-nitro-1 : 2 : 3-benztriazole, m. p. 211° (Zincke, *Annalen*, 1900, **311**, 290).

SUMMARY.

(1) 1 : 2 : 3-Benztriazole and its derivatives absorb in two main regions, the shorter-wave region being attributed to an electron in the C=C system of the benzene nucleus,

and the other being assigned to the N=N of the triazole ring. The introduction of alkyl substituents into the nucleus results in improved separation of the two regions.

(2) For the nitro-compounds no absorption characteristic of this group is observed unless (*a*) an aqueous solvent is used, or (*b*) a methoxyl or hydroxyl group is present in the triazole ring.

(3) 1-Hydroxy-1 : 2 : 3-benztriazole exists in alcoholic solution as an equilibrium mixture of the two tautomeric forms, some 20% of the 1-oxide being present. Similar behaviour is also observed in the case of 1-hydroxy-6-methyl-1 : 2 : 3-benztriazole. The nitro-hydroxy-triazoles exist as the stable hydroxy-form in both alcoholic and aqueous solution.

(4) Marked displacements of the maxima are found on change of solvent from alcohol to water in the case of the nitro-hydroxytriazoles, a behaviour which is probably connected with the ionisation of the compounds in the latter medium.

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