144. *The Action of Light on Normal and* iso*Diazoates.*

By R. J. W. LE FÈVRE and J. B. SOUSA.

The ultraviolet spectra, in aqueous alkaline solution, of the normal and *iso*diazoates from aniline, *p*-chloroaniline, *p*-bromoaniline, and sulphanilic acid differ notably in that each of the *iso*-forms exhibits an absorption maximum between 270 and 280 mμ with log ε = *ca.* 4·1, while in the same wavelength region, the normal salts all show a very broad inflexion, the centre of which has log ε *ca.* 3. These facts are reconcilable with observations made previously on various substances containing the $-N=N-$ group.

Irradiation of the *iso*diazoates from aniline, *p*-chloroaniline, and sulphanilic acid causes, on spectral evidence, formation of the normal isomers, accompanied by irreversible decomposition. Despite the last effect, signs of reversal on storage in the dark are detectable. The actions of light on the single diazoates from *o*-, *m*-, and *p*-nitroanilines are discussed: illumination does not change their absorption patterns in directions expected by analogy if normal isomers were being generated.

Finally, the ability of many *iso*diazoates to couple with 2-naphthol is emphasised because past literature is often confusing and contradictory on the point.

IRRADIATION as a means of effecting *trans*- to *cis*-isomerisations has been extensively employed in the study of compounds containing the N=N system.[1-5] Le Fèvre and his collaborators have examined in this way a wide range of azo- and diazo-compounds, using both dielectric and spectroscopic methods to identify or follow the changes. In several cases evidence of the production of *cis*-forms has been obtained, and with 2 : 2′-azopyridine the indications [4] have been verified by subsequent isolation of two geometrical isomers.[5]

Only cursory attention has so far been given to the photoisomerisability of diazoates. In 1907 Orton, Coates, and Burdett [6] reported that the normal diazoates are little influenced by light, but Oddo and Indovina [7] have more recently claimed that the same agency converts *iso*diazoates into the normal salts; these topics are the subject of the present paper. Saunders mentions printing processes which almost certainly involve the latter change.[8]

Irradiation superimposes on any existing thermal equilibrium a photochemical one. Half-lives of many *cis*-species are known; they vary from 3·3 minutes for *p*-hydroxyazobenzene to more than 100 hours for azobenzene itself,[2] for which, at ordinary temperatures, the thermal equilibrium mixture contains virtually all *trans*-isomer, though the thermal reaction is slow compared with the photochemical one. Thus Hartley reported [2] that "solutions of the concentration convenient for analysis (*ca.* 3—8 × 10^{-4} mole/l.) have, for a given (total) concentration, photometer readings independent of the initial isomeric

---

[1] Le Fèvre and Vine, *J.*, 1938, 431; Cook, *ibid.*, p. 876; Hartley and Le Fèvre, *J.*, 1939, 531; Cook and Jones, *ibid.*, p. 1309; Stephenson and Waters, *ibid.*, p. 1796; Mechel and Stauffer, *Helv. Chim. Acta*, 1941, **24**, 151; Le Fèvre *et al.*, *Chem. and Ind.*, 1948, 158, 543, 732; Le Fèvre and Wilson, *J.*, 1949, 1106; Le Fèvre and Souter, *ibid.*, p. 1595; Hausser, *Naturwiss.*, 1949, **36**, 313, 314, 315; *idem*, *Z. Naturforschung*, 1950, **5a**, 41, 56; Le Fèvre and Brown, *J.*, 1950, 185; Le Fèvre and Freeman, *J.*, 1950, 3128; 1951, 415; 1952, 2932; Hausser, Jerchel, and Kuhn, *Chem. Ber.*, 1951, **84**, 651; Le Fèvre, Freeman, and Wilson, *J.*, 1951, 1977; Le Fèvre and Liddicot, *ibid.*, p. 2743; Le Fèvre, Freeman, Northcott, and Youhotsky, *J.*, 1952, 3381; Le Fèvre, Freeman, Northcott, and Worth, *ibid.*, p. 3384; Brode, Gould, and Wyman, *J. Amer. Chem. Soc.*, 1952, **74**, 4641; Fischer, Frankel, and Wolovsky, *J. Chem. Phys.*, 1955, **23**, 1367; *J.*, 1955, 3441.

[2] Hartley, *J.*, 1938, 633.

[3] Le Fèvre and Northcott, *J.*, 1949, 333; 1952, 4082; 1953, 867.

[4] Le Fèvre and Worth, *J.*, 1951, 1814.

[5] Campbell, Henderson, and Taylor, *J.*, 1953, 1281.

[6] Orton, Coates, and Burdett, *J.*, 1907, **91**, 35.

[7] Oddo and Indovina, *Gazzetta*, 1935, **65**, 1099.

[8] Saunders, "The Aromatic Diazo-Compounds and their Technical Applications," 2nd Edn., Arnold, London, 1949, p. 136.

composition, if they have been exposed to bright daylight (not necessarily sunlight) for a few minutes." While the thermal will scarcely affect the photochemical equilibrium in a case such as azobenzene, this will obviously not be so when the rate of the thermal reaction approaches that of the photochemical.

The foregoing provides a convenient classification of our results. In one group we have the normal and *iso*diazoates from aniline, *p*-chloroaniline, and sulphanilic acid, and in the other those from *o*-, *m*-, and *p*-nitroanilines. Rapid spectral recording, which was essential for compounds of the second group, was made possible by the use of the Cary recording ultraviolet spectrophotometer of the N.S.W. University of Technology (we thank Mr. R. L. Werner for access and assistance).

EXPERIMENTAL

Normal Diazoates.—A 15% solution of the diazonium chloride (10 c.c.) was dropped with stirring into potassium hydroxide (150 g.) in water (60 g.) at −5°. The temperature was then allowed to rise to 0° and the mixture centrifuged in pre-cooled tubes. The undissolved inorganic material sank and the organic salt formed a layer on top of the concentrated alkaline solution. This was then skimmed off the surface, dried rapidly on a tile, dissolved in absolute alcohol at −5°, and precipitated with anhydrous ether. This method proved more convenient and yielded a purer product than Bamberger's,[9] which required the temperature of the mixture to rise to 15—20° in order to dissolve the hydroxide (in our hands this never dissolved completely and the crude product always contained alkali, which was not easy to eliminate). The preparation of *p*-sulphobenzene-*n*-diazoate di-sodium salt has already been described by us.[10]

iso*Diazoates from Aniline,* p-*Chloroaniline, and Sulphanilic Acid.*—These, prepared by Schraube and Schmidt's method,[11] were obtained crystalline by dissolving them in alcohol at 40—50°, filtering, and precipitating with ether.

Sodium p-*Nitrobenzenediazoate.*—A 10% solution of *p*-nitrobenzenediazonium chloride, prepared from *p*-nitroaniline (5·4 g.), was poured rapidly into 18% aqueous sodium hydroxide (160 c.c.) at 50—60° with vigorous stirring. The golden-yellow plates of the sodium salt which separated on cooling were recrystallised from alcohol and dried *in vacuo.*

Sodium o-*Nitrobenzenediazoate.*—A 15% solution of *o*-nitrobenzenediazonium chloride, prepared from *o*-nitroaniline (3 g.), was poured gradually into 66% aqueous sodium hydroxide (25 c.c.) at 0°. The crude product, reprecipitated from alcohol in crystalline form by ether, was dried *in vacuo.*

Sodium m-*Nitrobenzenediazoate.*—A 15% solution of *m*-nitrobenzenediazonium chloride, from *m*-nitroaniline (5 g.), was dropped with stirring into a mixture of sodium hydroxide (90 g.) and water (50 c.c.) at −5°. The temperature was allowed to rise to 5° and the crude product collected, shaken with 95% alcohol at 0°, filtered, and washed with ice-cold alcohol and ether. It was dried *in vacuo.*

Spectra.—Unless otherwise stated, these were observed on 10^{-4}M-solutions in 0·15N-sodium hydroxide. The solutes were dissolved immediately (<5 min.) before use. No changes in the spectra were observed by making a re-run, after which the solutions were found still to couple with 2-naphthol.

The Beer–Lambert law was checked on the Cary instrument for the normal diazoates, and for the more stable *iso*diazoates with a Beckman spectrophotometer. The solutions used for the photochemical experiments were of the same concentration as those used for the spectroscopic examination

Irradiation.—Solutions were irradiated in a 10 c.c. quartz cell for the times stated. Three sources of light were used: (*a*) sunlight, (*b*) a General Electric A.H.3 mercury-vapour lamp, and (*c*) the hydrogen lamp source of the Cary instrument.

RESULTS AND DISCUSSION

Spectra of Normal and iso*Diazoates.*—When normal diazoates are dissolved in water the extent of hydrolysis depends on the dilution, as indicated by Hantzsch's conductivity

---

[9] Bamberger, *Ber.*, 1894, **27**, 679; 1896, **29**, 446.

[10] Le Fèvre and Sousa, *J.*, 1955, 3154.

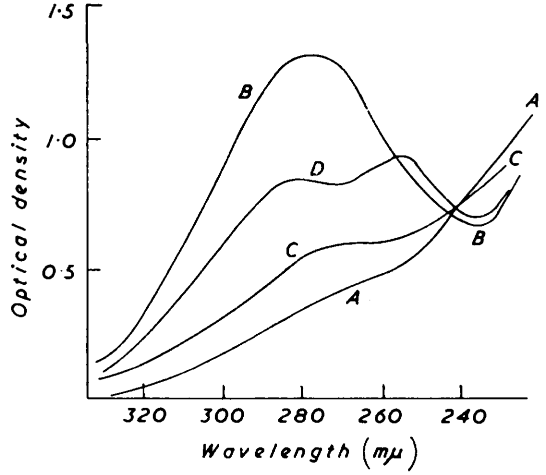
[11] Schraube and Schmidt, *Ber.*, 1894, **27**, 514.

measurements.[12] It is generally considered that the hydrolysis produces the diazonium ion (revealed by the rapid coupling of aqueous solutions of normal diazoates with dilute alkaline 2-naphthol) :

$$\text{Ph-N=N-}\bar{\text{O}} + \text{H}_2\text{O} \rightleftharpoons \text{Ph-}\overset{+}{\text{N}}\text{≡N} + 2\text{OH}^-$$

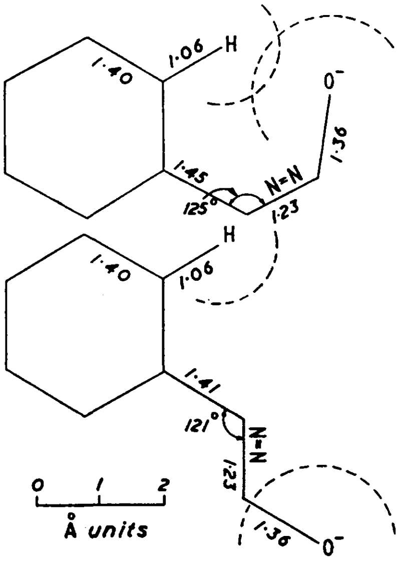
For the disodium salt of *p*-sulphobenzene-*n*-diazoate at 10^{-4}M, hydrolysis to the diazonium ion is virtually complete. This can be observed spectroscopically, the diazoate having a spectrum with a maximum of 268 mμ and an optical density identical with that of a solution of diazobenzene-*p*-sulphonic acid of the same concentration. The normal diazoate from sulphanilic acid was selected because it is the purest and most stable at present available. For similar solutions but of increasing alkalinity the band due to the diazonium ion gradually diminishes until in 0·15N-sodium hydroxide it ceases to be visible above the general absorption, the solute thereafter obeying the Beer–Lambert law at higher concentrations. The spectrum at this stage appears as the descending curve shown in Fig. 1, *A*, indicating a maximum in the Schumann region beyond the limits of the spectrophotometer. Such a spectrum is characteristic of the normal diazoates from aniline and *p*-chloro- and -bromo-anilines and is in general agreement with the earlier measurements by Hantzsch and Lifschitz,[13] Dobbie and Tinkler,[14] and Cambi and Szego.[15]

FIG. 1. *Spectra of the disodium salts of* p-*sulphobenzene diazoates in* 0·15N-*sodium hydroxide solution.*



A, the normal salt; *B*, the *iso*-salt; *C*, the *iso*-salt after irradiation; *D*, the solution used for *C* after storage in the dark for 2 days.

FIG. 2. *Plane projections of* cis- *and* trans-*diazoate anions.*



(Interatomic distances and valency angles from Robertson, *J.*, 1939, 232, and Pauling, " The Nature of the Chemical Bond," 2nd Edn., 1945, Cornell Univ. Press.) Wirkungsradien are from Stuart, *Z. phys. Chem.*, 1935, **27**, *B*, 350; the oxygen–hydrogen overlap shown is probably minimal since Pauling (*op. cit.*) gives the radius of O⁻ as 1·32 Å while Stuart's wirkungsradius of 1·22 Å has been used in the drawing.

---

[12] Hantzsch and Davidson, *Ber.*, 1898, **31**, 1612; Hantzsch and Engler, *Ber.*, 1900, **33**, 2147; Hantzsch, *Ber.*, 1896, **29**, 743.

[13] Hantzsch and Lifschitz, *Ber.*, 1912, **45**, 3011.

[14] Dobbie and Tinkler, *J.*, 1905, **87**, 273.

[15] Cambi and Szego, *Ber.*, 1928, **61**, 2087.

The *iso*diazoates corresponding to the above substances each exhibited a single band of maximum absorption between 270 and 280 mμ (ε *ca.* 14,000). $\lambda_{\max.}$ for the *iso*diazoates from aniline, *p*-chloroaniline, and sulphanilic acid in 0·15N-sodium hydroxide occur at 273, 277, 279 mμ respectively. Fig. 1, *B*, shows the spectrum of the last of these; it is, in appearance, typical of the other two.

Relations between the Spectra of Normal and iso-*Forms.*—It is important to compare the spectra of normal and *iso*diazoates with those of other *cis–trans* isomers containing the azo-group. Among the simpler azobenzenes,[16, 17] diazocyanides,[18] diazosulphonates,[19] etc., there is usually little displacement of the *K*-band on passing from the *trans*- to the *cis*-form, the main characteristic being a diminution of $\varepsilon_{\max.}$. The last effect becomes much enhanced, and shifts of $\lambda_{\max.}$ clearly seen, when conjugation in the *trans*-structure is likely to be considerable. A few examples are listed in Table 1.

TABLE 1. *Wavelength and intensity differences for the* K-*band in isomeric azo-compounds.*

	$\lambda_{trans} - \lambda_{cis}$ (mμ)	$\varepsilon_{trans} - \varepsilon_{cis}$	Ref.
o-$Cl\cdot C_6H_4\cdot N{:}N\cdot SO_2\cdot ONa$	− 8	*ca.* 900	19
$C_6H_5\cdot N{:}N\cdot C_6H_5$	− 5	4,500	16
p-$C_6H_4Cl\cdot N{:}N\cdot CN$	+ 8	*ca.* 7,400	18
p-$Me\cdot C_6H_4\cdot N{:}N\cdot C_6H_5$	+ 1	9,000	16
p-$NH_2\cdot C_6H_4\cdot N{:}N\cdot C_6H_5$	+45	16,600	17
p-$Me_2N\cdot C_6H_4\cdot N{:}N\cdot C_6H_5$	+48	16,300	17
p-$Me_2N\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot OH$-*p*	+73	19,600	17
p-$Me_2N\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot C_6H_5$-*p*	+51	23,400	17

Such changes are explicable if, for steric reasons, the molecular planarity requisite for resonance cannot be attained in the *cis*-variety as fully as it can in the *trans*. Braude *et al.*[20] state the basic principles thus : " If the steric interference resulting in non-planarity is relatively small, then the characteristic transition of the chromophore might be restricted to vibrational states in which appropriate bonds are sufficiently extended to allow of a large degree of co-planarity. Solution spectra . . . will then show little change in wavelength location, but the intensity of absorption will be restricted to a smaller number of vibrational states. . . . If, however, steric interference is large and resonance interaction takes place despite non-planarity, the energy content of the contributing resonance forms will be increased and the energy level of the excited state will therefore be raised relatively to that of the ground state; *i.e.*, the characteristic band itself will be displaced towards shorter wavelengths."

The spectra of *syn*- and *anti*-diazocyanides [18] and of labile and stable diazosulphonates [19] can be accounted for on these lines, since models show the *cis*-forms to be incapable of planarity.[19]

TABLE 2. *Intensity differences between* iso- *and normal diazoates at* ca. 280 mμ.

	$\lambda_{\max.}$ (*iso*) (mμ)	$\varepsilon_{iso} - \varepsilon_{normal}$
$C_6H_5\cdot N{:}N\cdot ONa$	273 *	approx. 7,000
p-$Cl\cdot C_6H_4\cdot N{:}N\cdot ONa$	277 *	,, 12,000
p-$Br\cdot C_6H_4\cdot N{:}N\cdot ONa$	284 *	,, 7,000
p-$(SO_2\cdot ONa)C_6H_4\cdot N{:}N\cdot ONa$	279	,, 15,000

* The curves presented by Cambi and Szego [15] indicate maxima for the three salts respectively which closely correspond with these data.

The isomeric diazoates so far studied exhibit two patterns of absorption : the *iso*-compounds all show strong *K*-bands between 270 and 290 mμ while the normal forms display a broad shoulder or inflexion, more or less centred below the peak of the *iso*-salt, which

---

[16] Cook, Jones, and Polya, *J.*, **1939**, 1315.
[17] Brode, Gould, and Wyman, *J. Amer. Chem. Soc.*, 1952, **74**, 4641.
[18] Le Fèvre and Wilson, *J.*, **1949**, 1106.
[19] Freeman and Le Fèvre, *J.*, **1951**, 415.
[20] Braude, Jones, Koch, Richardson, Sondheimer, and Toogood *J.*, **1949**, 1890.

(between 230 and 310 mμ) never has $\varepsilon < 1000$. One may reasonably infer that a submerged *K*-band is present although its precise location obviously cannot be fixed. On this basis the facts may be represented as in Table 2.

Although unfortunately figures for $\lambda_{iso} - \lambda_{\text{normal}}$ cannot be given, and the estimates of $\varepsilon_{iso} - \varepsilon_{\text{normal}}$ have to be rough, the data of Tables 1 and 2 permit the view that the ultraviolet spectra of diazoates are analogous to those of other $^{-}$N:N^{-} containing isomers and are affected by structural factors in similar ways.

The extent of steric hindrance in *syn*-benzenediazoate and its absence in the *anti*-isomer is revealed in the scale planar projections shown in Fig. 2. Prevention of planarity may have greater effects in the diazoates, where there exists an opportunity for direct conjugation of a full uncompensated charge with the benzeneazo-system, than in the diazocyanides and the diazosulphonates, where such a situation does not normally occur. The degrees of contrast between diazoate pairs will therefore depend on the amount of conjugation achieved in the *syn*-isomer, steric hindrance in this form tending to restrict resonance between the benzene ring and diazo-oxy-group.

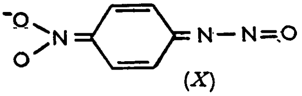
In conclusion, therefore, it is claimed that the details of these spectra are not out of harmony with Hantzsch's allocation of a *syn*-structure to the normal salts and an *anti*-structure to the *iso*-salts.

The Photoisomerisation of Diazoates.—The differences between the ultraviolet spectra of normal and *iso*diazoates made the spectroscopic method convenient for examining changes on irradiation. Solutions of the three *iso*diazoates were illuminated in quartz cells in 0·15N- and 0·2N-sodium hydroxide solutions. The maxima due to the *iso*diazoates diminished rapidly and the spectra began to assume the forms characteristic of normal diazoates. The development of normal isomers in the irradiated solutions was checked by observing increased rapidity of coupling with 2-naphthol solution; quantitative results were obtained on 10^{-4}M-solutions of the *iso*diazoates in the more weakly alkaline of the above media.

The *iso*diazoates from aniline and *p*-chloroaniline behaved differently from that from sulphanilic acid, in that the latter appeared to come to equilibrium on illumination. Each of the first two, if illuminated for two or three minutes by the mercury-vapour or the hydrogen lamp showed a diminished absorption maximum. On being kept in the dark a very slight increase in the absorption maximum was noticeable, consistent with some reconversion into the *iso*diazoate. On irradiation for ten minutes complete decomposition appeared to take place since no recovery was observed during 2 days in the dark. The change appeared to be continuous and at no time was an equilibrium detectable. The decomposition product was possibly phenolic.

With the *iso*diazoate from sulphanilic acid (Fig. 1, *B*), on the other hand, radiation from a mercury lamp for 4 minutes caused the rapid change from Fig. 1, *B* to Fig. 1, *C*. The appearance of *C* is reconcilable with the presence of a mixture of normal and *iso*-diazoates, in which the normal form predominates. The shape of the absorption curve for the irradiated solution altered only slightly after exposure for another 5 minutes, suggesting that an equilibrium, disturbed by slow decomposition, had been reached. During 2 days in the dark, partial reconversion into the *iso*diazoate was noticeable (Fig. 1, *D*). The evidence, therefore, suggests that photoisomerisation takes place on irradiation.

The Nitrobenzene Diazoates.—The diazoates from *o*-, *m*-, and *p*-nitroanilines exist in only the *iso*-form, according to the literature. The isolation of a single variety of the product from *p*-nitroaniline at room temperature is understandable if its anion is a mesomeride to which quinonoid structures (such as *X*) contribute significantly. A similar view may be taken of the *o*-nitro-derivative, subject to the added complications introduced by steric hindrance. Obviously the same explanation cannot be applied to the *m*-nitro-derivative. Attempts have therefore been made to prepare a second form in each case, but without success. However, indications of the



(*X*)

differing stabilities of the *ortho*- and *para*-derivatives on the one hand and of the *meta*-derivative on the other have been obtained: the *ortho*- and *para*-compounds could be prepared in solutions of lower alkaline concentration and at higher temperatures, and hence are both relatively stable; the *meta*-derivative, however, was only satisfactorily isolable at temperatures below 0° and in highly concentrated alkaline solutions. When this *meta*-derivative was subjected to the conditions used to transform normal into *iso*-salts (*i.e.*, heating in strong alkali) it lost nitrogen and gave a diazo-resin (which had no strong ultraviolet absorption). The *meta*-derivative therefore has a lower stability than that expected for *iso*-salts, but like these salts it couples slowly with alkaline 2-naphthol. The *o*- and the *p*-nitrobenzenediazoate also couple slowly, but are otherwise quite different in stability from their *meta*-isomer.

The spectra of the nitrobenzenediazoates are illustrated in Fig. 3. Fig. 3, *A* refers to sodium *p*-nitrobenzenediazoate in 0·15N sodium hydroxide. The position of the long-wave *K*-band at 330 mμ ($\varepsilon_{\text{max.}}$ 15,000) in this compound, contrasted with 260 mμ for nitrobenzene in alcohol, or 273 mμ for benzene*iso*diazoate in alkali, provides evidence for conjugation in the *p*-nitrobenzenediazoate. This supports the suggestion that in this compound conjugation has lowered the N=N bond order and thus diminished the barrier to " free " rotation. In the *ortho*-substance, however, steric hindrance is noticeable (Fig. 3, *B*). The *K*-band appears at about 255 mμ, and the intensity is diminished. Fig. 3, *C*, records the effect of irradiation by a hydrogen lamp on the solution used for *B*.

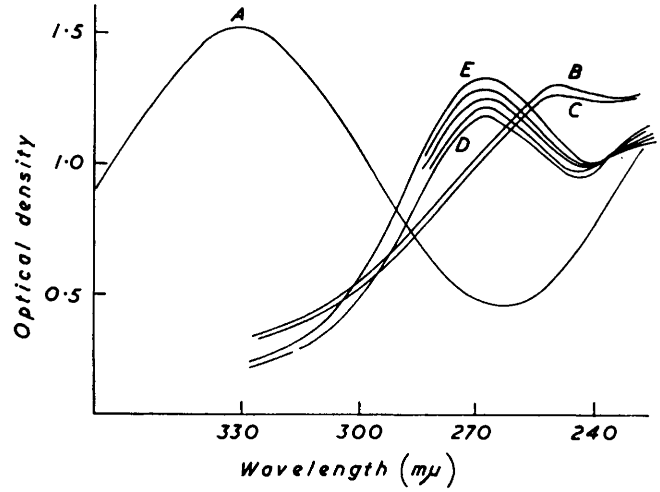


FIG. 3. *Sodium* o-, m-, *and* p-*nitrobenzenediazoates.*

(The curves between *D* and *E* show the progressive effects of irradiation.)

The sodium *meta*-diazoate gave the curve *D*. This has a maximum at 268 mμ, which is close to the *K*-band of nitrobenzene. (The spectra of the *ortho*- and the *meta*-derivative were measured in 2 cm. cells, all other measurements being made in 1 cm. cells.)

Irradiation of Sodium o- *and* p-*Nitrobenzenediazoates.*—As has been previously indicated, if the thermal *cis*→*trans* change is fast, the nature of the equilibrium produced by irradiation may be affected. The content of the *cis*-form in the total equilibrium mixture will tend to be lower in proportion to the rapidity of the thermal reaction. In addition, on cessation of illumination—provided no decomposition occurs—the reconversion into the original (dark) state might be rapid, thus making it seem that on recording the spectrum before and after illumination no change has occurred. When a solution of sodium *p*-nitrobenzenediazoate in 0·15N-sodium hydroxide (Fig. 3, *A*) is irradiated with light from a mercury-vapour lamp for 7 minutes, only a slight difference, within the bounds of instrumental error, is observable. (It is here relevant to recall that solutions of azobenzenes and of other *iso*diazoates previously mentioned are markedly affected by, or come to an equilibrium within, seven minutes of irradiation.) Continued irradiation gives rise to a slow irreversible decomposition.

The *o*-nitro-derivative before the mercury lamp behaved practically the same as did the *p*-nitrodiazoate except that the rate of permanent decomposition seemed slightly greater. Fig. 3, *B* and *C*, relate to solutions before and after 5 minutes' irradiation.

Sodium m-*Nitrobenzenediazoate.*—The *m*-nitro- behaves very differently from the *ortho-* or *para*-derivative on irradiation (Fig. 3, *D* and *E*). At 10^{-4}M in 0·15N-sodium hydroxide a spectrum represented by the lowest curve (*D*) was obtained. Irradiation (hydrogen lamp) produced a symmetrical increase in the band already present. This certainly indicated the photochemical production of a compound already existing in the unirradiated solution. The inorganic contaminants likely, alkali and smaller traces of sodium chloride, cannot account for the absorption at 268 mμ or for the photochemical behaviour. An organic impurity could be nitrobenzene ($\lambda_{max.}$ 260 mμ in alcohol), arising from deamination; the presence of this, however, seemed improbable since the intensity of absorption observed would require a high percentage, not easily escaping notice, of nitrobenzene in the *m*-nitrobenzenediazoate before purification. Moreover the compound which gave rise to the 268 mμ maximum appeared to decompose on standing in the dark.

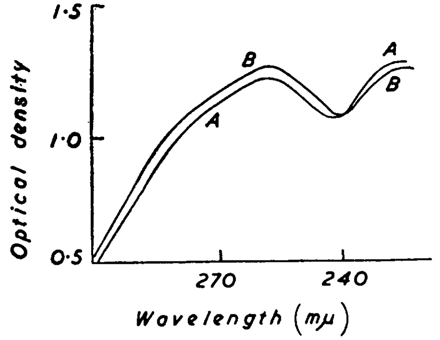


FIG. 4. *Effect of storage in the dark for 2 days on an unirradiated (A) and an irradiated (B) solution of sodium* m-*nitrobenzenediazoate.*

Fig. 4 reproduces spectra of an unirradiated solution (*A*) and of one irradiated for six minutes (*B*) after both had been stored in the dark for 2 days. They also suggest that some decomposition had occurred causing a shift of the main band to 257 mμ, and indicate that the compound giving rise to the 268 mμ maximum changes, since the optical densities of the irradiated solution (first curve above *D*, Fig. 3) and the unirradiated solution (Fig. 3, *D*) at 268 mμ drop from 1·25 to 1·18 and 1·15 to 1·11 respectively (Fig. 4). No such decomposition can be expected with nitrobenzene. The conclusion is, therefore, that nitrobenzene is not detectable in the original solution, nor is it photochemically produced on irradiation.

A possible contaminant in the unirradiated solution, and one which *could* be produced photochemically, is *m*-nitrophenol. 10^{-4}M-*m*-Nitrophenol in 0·15N-sodium hydroxide showed three bands, at 227 mμ ($\varepsilon_{max.}$ 13,570), 253 mμ ($\varepsilon_{max.}$ 10,000), and 293 mμ ($\varepsilon_{max.}$ 4000). The single band at 268 mμ in the unirradiated or freshly irradiated *m*-nitrobenzenediazoate cannot therefore be due to *m*-nitrophenol.

Yet both these solutions do display evidence of decomposition to *m*-nitrophenol after several days in the dark. There is a shift of the main band from 268 mμ in Fig. 3, *D*, to 257 mμ in Fig. 4; this is close to the 253 mμ band of the *m*-nitrophenoxide ion. Further, signs of the 293 mμ band at *ca.* 280 mμ are visible. The presence of the 227 mμ band of the *m*-nitrophenoxide ion is also detectable.

The observations appear to be consistent with the following statements: (*a*) The *m*-nitrobenzenediazoate specimens actually examined were mixtures of at least two compounds, one of which is photochemically producible from the other. (*b*) In view of the absence of any other bands in the spectrum, and assuming the *anti*-isomer to have a long-wave *K*-band not far removed from that of the *syn*-isomer, the two compounds may possibly be related as *syn*- and *anti*-forms. (*c*) Although photoisomerisation usually results in a preponderance of the *cis*- or the *syn*-form, the reverse may sometimes be true. In this instance the content of *iso*diazoate seems, with increasing exposure, to become higher, in conformity with a progressive approach to equilibrium. (Ciusa[21] reported the formation of *anti*-2 : 4 : 6-tribromobenzenediazocyanide from the *syn*-form on irradiation.) (*d*) The two constituents both decompose, *m*-nitrophenol is formed from possibly one or both forms, and the form presumed to be *syn* decomposes—and decomposes faster—to *m*-nitrophenol than that presumed to be *anti* (cf. the inversion of the curves below 237 mμ in Fig. 4).

In conclusion, it is submitted that the photochemical properties of the *o*- and *p*-nitrobenzenediazoates are not necessarily out of keeping with the views of Hantzsch, and that, further, the spectrographic behaviour of the *m*-derivative may yet be reconcilable with the same theory.

Coupling by iso*Diazoates.*—As a side issue, the ability of *iso*diazoates to couple has been checked. The matter is important since literature and text-books in general give the impression that they undergo this reaction either with great difficulty or not at all.

Subsequent to our experiments we found that Cain[22] had pointed out that "The presence of alkali has a great effect on the combining power of the two isomers : Schraube and Schmidt had a large excess of alkali present when they noticed that the stable form did not combine, but when less is used it does combine although much more slowly than the labile form." Hodgson and Marsden[23] considered that there is an abrupt prevention of coupling in solution at pH 8 in the case of *iso*diazoates.

An experimental study of the coupling of five *iso*diazoates has revealed that they couple slowly in the absence of light. Even at pH 9·5—the highest at which the reaction was attempted—reaction was appreciable. That coupling was not due to impurities was shown by the fact that carefully purified sodium *p*-nitrobenzene*iso*diazoate coupled quantitatively in the dark and at room temperature with an excess of 2-naphthol solution buffered at pH 9·15. The rate of coupling decreased continuously with increase of pH of the coupling solution, and rise of temperature tended to accelerate the rate of coupling.

The *iso*diazoates from aniline, *p*-chloroaniline, *p*-bromoaniline, sulphanilic acid, and *p*-nitroaniline were added to buffered solutions containing 2-naphthol in excess. The buffers were made with "AnalaR" sodium borate and sodium carbonate, 2-naphthol or its sodium salt being added as required. The pH of the solutions were approximately 8·5, 9·2, and 9·5 and were constant during the coupling reactions.

Attempts to determine the order, and to compare the rates, of coupling of sodium *p*-nitrobenzenediazoate and the (sodium) *iso*diazoate from sulphanilic acid in alkaline 2-naphthol at pH 9·2, were abandoned when it was found that the *p*-nitro-azo-dye began to precipitate. The coupling of the second *iso*diazoate was followed colorimetrically; half the total colour was developed in 14 hr. at ordinary temperatures.

In aqueous solution, hydrolysis of an *iso*diazoate will produce some *iso*diazohydroxide which, in turn, presumably generates diazonium ions, since these are accepted as the coupling species. In an *iso*diazohydroxide resonance, relatively unhindered by steric effects, will confer a partial double-bond character on the N–O bond and so the slower rate of coupling of *iso*- compared with that of the normal diazoates is in harmony with theory. Certain other reactions shown by *iso*diazoates in dilute alkaline solution indicate the presence of the diazonium ion, *e.g.*, the alleged *iso*diazoate of tribromoaniline, which

---

[21] Ciusa, *Atti R. Accad. Lincei*, 1906, **15**, *II*, 137.

[22] Cain, *Ber.*, 1913, **46**, 101.

[23] Hodgson and Marsden, *J.*, 1945, 207.

actually exists in the strongly alkaline solution used for its formation, appears as a quinone diazide on dilution; this reaction is known [24] to proceed through the diazonium ion.

One of us (J. B. S.) thanks the Research Committee of the University of Sydney for a Studentship.

UNIVERSITY OF SYDNEY, N.S.W., AUSTRALIA. [*Received, July 25th,* 1956.]

---

[24] Ingold, " Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, New York, 1953, p. 803.