

RESEARCHES ON THE AROMATIC AZOCOMPOUNDS

THE OXIDATION OF THE 4-DIMETHYLAMINO-AZOBENZENE

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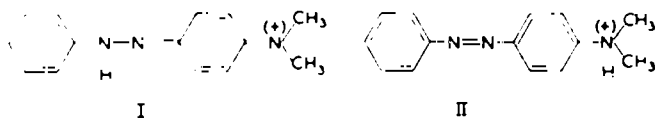
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Abstract—This paper deals with the oxidation of 4-amino-azobenzene. Mono-oxidation leads to the amine oxide, the structure of which is demonstrated. It is concluded that oxygen adds first to the nitrogen atom with the greater electron density, i.e. the nitrogen of the dimethylamino group, and the second oxygen adds to the azo nitrogen remote from the substituted phenyl group.

THE position of the first proton in 4-amino-azobenzene derivatives has been long discussed, mainly because of the difficulty to locate the protonated forms existing in solution. It has been assumed that the deepening colour in weakly acidic solution, and the correlated bathochromic shift in the absorption spectra, is due to the formation of an azonium ion and to the contributing resonance structures.

Rogers *et al.*¹ have studied the primary and secondary ionisation constants of 4'-substituted 4-dimethylamino-azobenzenes. These compounds add a proton in dilute acid and a second in strong acidic solutions. The values of pK, measured spectrophotometrically, provide evidence that the first proton is added to an azo nitrogen atom (form. I) and the second to the dimethylamino nitrogen atom.



Badger *et al.*² have evaluated the primary ionisation constants of 4-amino-azobenzene and of a number of N-substituted derivatives, and assume that ammonium and azonium forms are in equilibrium in solution, the relative intensities of the Q(5000–5400 Å) and K'(3200 Å) bands giving the approximate proportions of the two tautomers present.

Klotz *et al.*³ have determined the acidity constants of a number of related substituted azobenzenes, together with some *p*-dimethylamino-phenylazo-pyridines. The results support a structure of the type (II). In aqueous solution the uptake of protons leads to a benzenoid rather than a quinonoid structure and the relative basicities of the possible competing groups lie in the order: O⁻ > pyridine N > —N(CH₃)₂ > —N—N—.

Miller *et al.*⁴ investigated the absorption spectra of ethanolic and acid-ethanolic solutions of a number of derivatives of 4-amino-azobenzene. Their data are in agreement with the results of Hantzsch⁵ and Badger,² indicating that the first proton can be

¹ M. T. Rogers, T. W. Campbell and R. W. Maatman, *J. Amer. Chem. Soc.* **73**, 5122 (1951).

² G. M. Badger, R. G. Buttery and G. E. Lewis, *J. Chem. Soc.* **1** (1954).

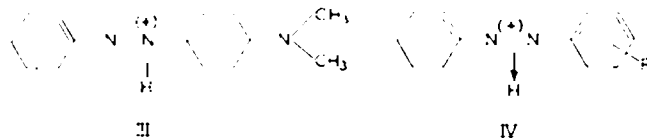
³ I. M. Klotz, H. A. Fiess, J. Y. Chen Ho and M. Melody, *J. Amer. Chem. Soc.* **76**, 5136 (1954).

⁴ G. Cilento, E. G. Miller and J. A. Miller, *J. Amer. Chem. Soc.* **78**, 1718 (1956).

⁵ A. Hantzsch and A. Burawoy, *Ber. Dtsch. Chem. Ges.* **63**, 1760 (1930).

added to either the α -azo-nitrogen or the amino nitrogen to give a mixture of tautomeric forms. The work of Miller was recently confirmed and explained quantitatively by Pullman and Pullman.⁶

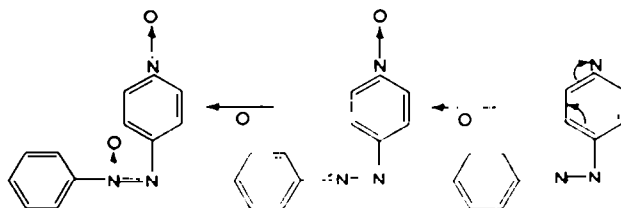
Sawicki⁷ maintained as azonium form the tautomer (III), first suggested by



Sheppard⁸ and rejected by Rogers,¹ whilst Jaffé⁹ suggested a symmetrical structure of the protonated form of the azo group (form IV).

The problem of the relative basicity of the nitrogen atoms in basic unsymmetrical azocompounds has been approached¹⁰ with particular respect to the heterocyclic unsymmetrical azocompounds, on the basis of some analogies between N-oxidation and N-protonation. The most easily protonated nitrogen, and therefore the nitrogen first protonated in dilute acidic solutions, is the most basic one, with the greater electron density, the lone pair of electrons being easily available, are shared to give a co-ordinate bond with the proton. Similarly, in the N-oxidation, the same pair of electrons on the nitrogen atom will be involved and the extent of availability of the paired electrons will be responsible for the addition of the oxygen atom. On the other hand, the basicity of a nitrogen atom depends on the relative stability of the cation formed by the proton addition; resonance stabilisation is frequently of the same order of importance as electron density in determining their stability. However, the electron density on the nitrogen atoms is a determining factor of the oxygen position and rate control of oxidation. Consequently, sufficient difference among basic nitrogen atoms leads to only one oxidate form, where protonisation often leads to an equilibrium between two forms.

It has been shown, in phenylazo-pyridines and -quinolines, that the mono-oxidation goes toward the nitrogen with highest electron density, to which the first proton adds; thus in the 4-phenylazo-derivatives the first oxygen atom goes to the pyridine nitrogen, to which the first proton adds. In the further oxidation the second



oxygen atom adds to the azo nitrogen farthest from the heterocyclic nucleus (α position), presumably the same azo nitrogen to which the second oxygen adds.

Whereas in the case of the 4-phenylazo-pyridine there is no doubt about the

⁶ A. Pullman and B. Pullman, *C.R. Acad. Sci., Paris* **243**, 1322 (1956).

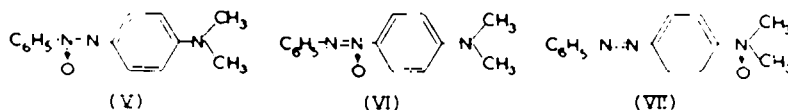
⁷ E. Sawicki, *J. Org. Chem.* **22**, 365 (1957).

⁸ S. E. Sheppard and P. T. Newsome, *J. Amer. Chem. Soc.* **64**, 2937 (1942).

⁹ H. H. Jaffé and R. W. Gardner, *J. Amer. Chem. Soc.* **80**, 319 (1958).

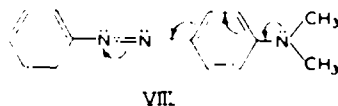
¹⁰ M. Colonna, A. Risaliti and L. Pentimalli, *Gazz. Chim. Ital.* **86**, 1067 (1956).

position of the first proton, and consequently of the first oxygen, the position of the first proton in *p*-dimethylamino-azobenzene is not known for certain from previous work.



On the basis of the above assumptions, in the mono-oxidation of Butter Yellow, the α -azoxy (V) and the amino oxide (VII) are the most probable structures.

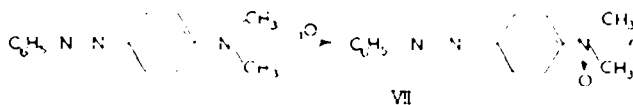
The structure (VI) seems unlikely, on the basis of Rogers' considerations, supported afterward by Badger *et al.*,² who rule out the form (III) protonated on the azo nitrogen closest to the substituted phenyl group. While in the unsubstituted azobenzene the two nitrogens are equivalent, the presence of the dimethylamino grouping in *para* position, with its $-I$ and $-M$ effect, gives rise to an electronic conjugation producing an



increase of the negative charge on the nitrogen farthest from the amino group.

Both the azoxy compounds (V) and (VI) are reported in literature.¹¹ The single structure of the two tautomer isomers has been established by Anderson¹¹ on the basis of their properties, as stability and absorption curves (Fig. 1).

Mono-oxidation of 4-dimethylamino-azobenzene leads almost exclusively to the



N-oxide on the amino nitrogen (VII), the structure of which has been unequivocally demonstrated.

This result is not surprising and it is in agreement with the acidity constant values reported by Klotz *et al.*³ From the conjugation scheme (VIII) it would seem that the presence of the dimethylamino group should result in a higher basicity for the α -azoxy nitrogen with respect to the amino nitrogen. Actually, because of the reciprocal effect between the two substituents, $-N(CH_3)_2$ and $-N=N-$, the azo group does become more basic than it is in the unsubstituted azobenzene, while the dimethylamino group becomes less basic with regard to the unsubstituted dimethylaniline; the relative basicity will be still higher for the dimethylamino group which will be thereby oxidised, and protonated, first.

TABLE I. ACIDITY CONSTANTS, pK_a , AT 25 C

Azobenzene ³		2.48
Dimethylaniline ¹²	6.2-5.5	
<i>p</i> -Dimethylamino-azobenzene ³	3.5	4.37

¹¹ W. Anderson, *J. Chem. Soc.* 1722 (1952).

¹² C. K. Ingold, *Structure and Mechanism in Organic Chemistry* p. 746. Cornell University Press, New York (1953); the higher value has been reported by W. C. Davies and H. W. Addis, *J. Chem. Soc.* 1622 (1937), the lower value by G. Thompson, *J. Chem. Soc.* 1112 (1946).

The observed value of the second acidity constant for the 4-dimethylamino-azobenzene referring to the azogroup, is lower than that of the unsubstituted azobenzene, due to the $-I$ effect of the protonated amino group.

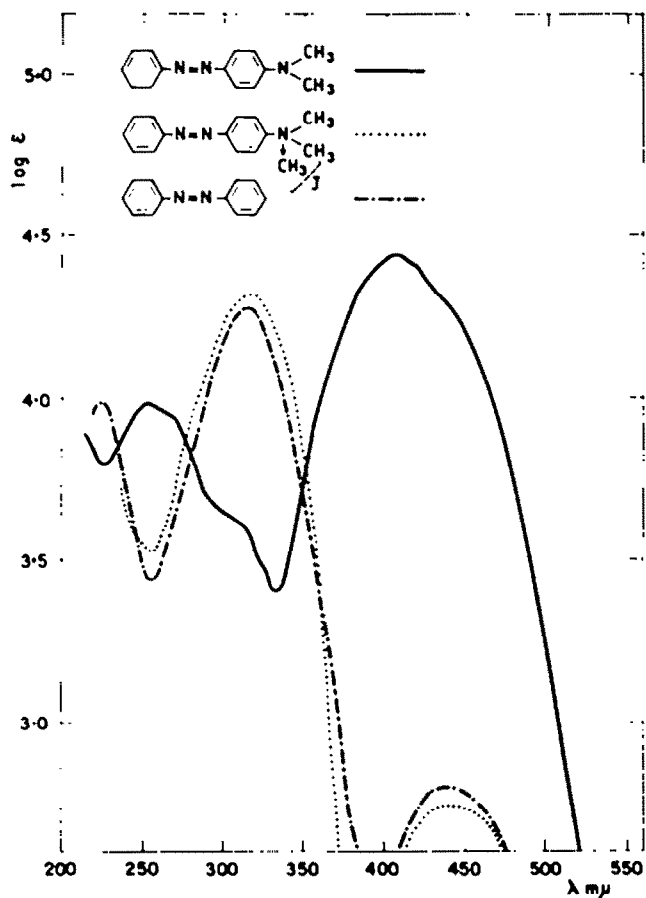


FIG. 1.

Evidence for the structure assigned to the amino-oxide azo (VII) is provided by the following facts:

(a) Analytical data correspond to the formula $C_{14}H_{15}N_3O$, with one more oxygen atom than the *p*-dimethylamino-azobenzene;

(b) The intense orange colour is favourable to the azo structure, the azoxy compounds being markedly less coloured;

(c) The compound is different from the α - and β -azoxy compounds described by Anderson,¹¹ as to colour, crystal form, solubility and absorption spectrum;

(d) The features of the absorption curve are in agreement with the assigned structure. The values of λ_{max} and related absorption intensities of *p*-dimethylamino-azobenzene and related oxidation derivatives are collected in Table 2.

All of the azocompounds show an absorption band (R band) at about 440 $m\mu$, with

TABLE 2. MAXIMA WAVELENGTH ($m\mu$) AND CORRESPONDING INTENSITIES ($\log \epsilon$) IN THE ABSORPTION SPECTRA OF AZO- AND AZOXY-BENZENES IN ETHANOL

Azobenzene	318 (4.32)	440 (2.73)
Azoxy-benzene trans	322 (4.19)	—
<i>p</i> -Dimethylamino-azobenzene		410 (4.44)
<i>p</i> -Dimethylamino-azobenzene (methiodide) ¹³	319 (4.23)	443 (2.73)
α -Azoxy (V)	410 (4.55)	—
β -Azoxy (VI)	394 (4.49)	—
Amino-oxide-azo (VII)	318 (4.28)	435 (2.78)
Amino-oxide- α -azoxy (X)	321 (4.18)	—

low intensity ($\log \epsilon$ about 2.73), regarded as characteristic for the azo group (Fig. 2); this band is undoubtedly also present in the spectrum of the *p*-dimethylamino-azobenzene but it is hidden by the broad band in the same region, with λ_{\max} at 410

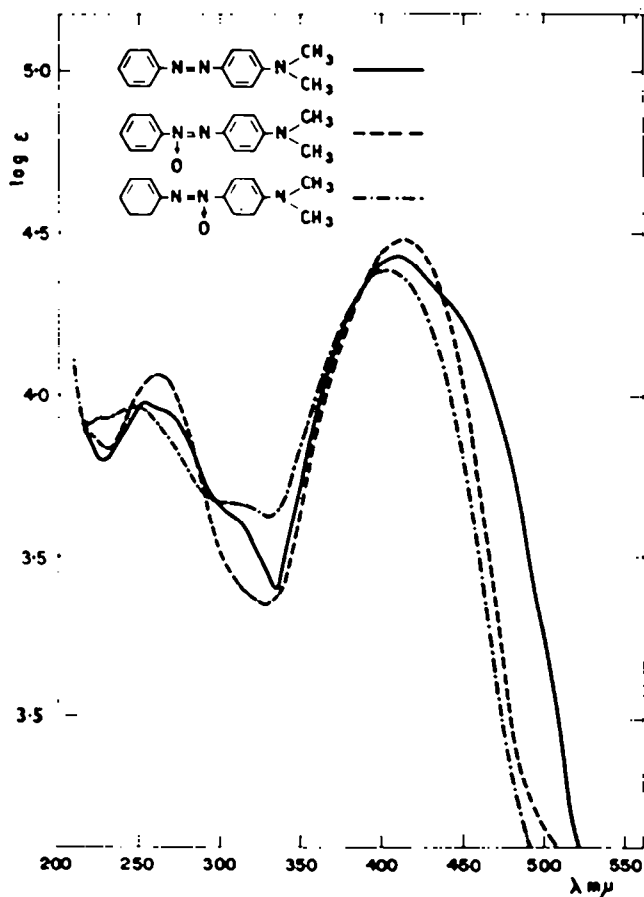


FIG. 2.

¹³ A. Pongratz, G. Markgraf and E. Mayer-Pitsch, *Ber. Dtsch. Chem. Ges.* 71, 1293 (1938).

$m\mu$. With the azoxy-compounds, where the $N=N$ group is replaced by the azoxy group, such a band does not appear and it is doubtless absent also for the α - and β - Butter Yellow azoxy derivatives, wherein the corresponding region is covered by the broad conjugation band of the dimethylamino grouping. Evidence

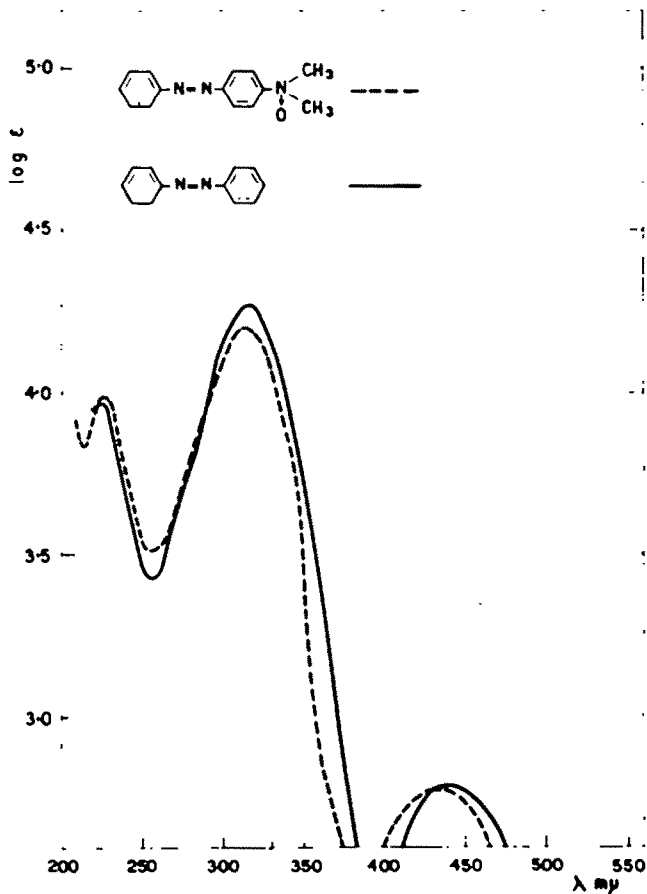


FIG. 3.

for this is provided by the spectra of the azoxybenzene and of the *p*-dimethylaminoazoxybenzenes amino-oxides (IX) and (X), showing no absorption beyond 400 $m\mu$ (Fig. 4).

The peak at 435 $m\mu$ with a low intensity value, $\log \epsilon$ 2.78, for the oxidation compound with suggested structure (VII), indicates clearly the occurrence of the $-N=N$ group.

The amino oxide structure is also supported by the disappearance of the broad intense absorption band at λ_{max} about 410 $m\mu$, associated with the conjugation of the substituent. This is shown by the comparison of the values collected in Table 3: the spectrum of the amino-oxide azo is practically identical to that of the methiodide and therefore identical to that of the unsubstituted azobenzene (Figs. 1 and 3).

TABLE 3. λ_{\max} (m μ) AND INTENSITIES (log ϵ) OF ABSORPTION SPECTRA IN ETHANOL.

Azobenzene	229 (4.11)	318 (4.32)	440 (2.73)
<i>p</i> -Dimethylamino- (methiodide)	...	319 (4.32)	443 (2.73)
<i>p</i> -Dimethylamino amino oxide	229 (4.05)	318 (4.28)	435 (2.78)

The conclusion that the first oxygen, in *p*-dimethylamino-azobenzene, goes to the amino nitrogen is consistent with the results reported by Klotz *et al.*, who attribute to the amino group the primary ionisation constant. The question of the absorption

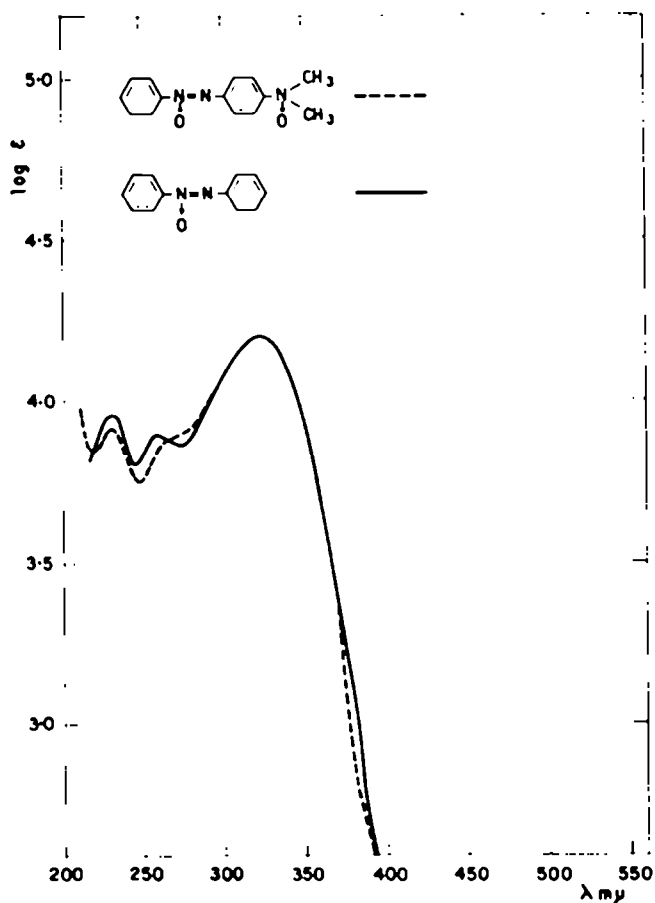
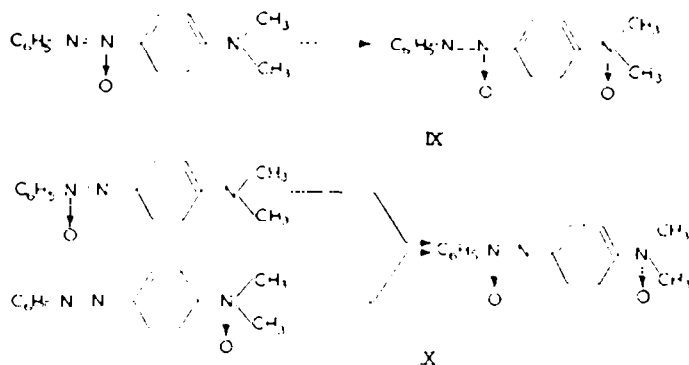


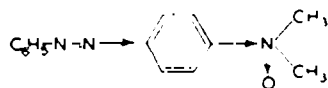
FIG. 4.

spectra of amino-azobenzenes in weakly acidic solution, however, is not readily resolved. It has been seen, from the resonance structure (VIII), that the effect of conjugation between the amino group and the azo group is to increase the basicity of the latter at the expense of the basicity of the former. The deep red colour and the strong spectroscopic absorption of the acidic solutions can be explained by the existence of two tautomeric forms, ammonium and azonium, present in equilibrium, as maintained by cited authors.

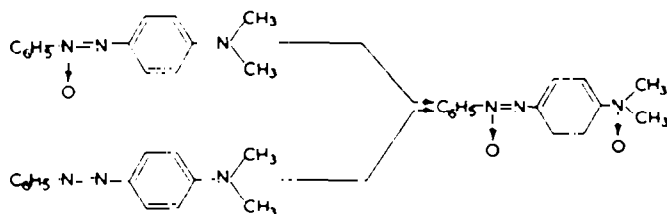
Another feature apparently inconsistent with results is the structure assigned by Angeli¹⁴ to the bis-oxidation product of *p*-dimethylamino-azobenzene. By oxidation of Butter Yellow by excess peracetic acid an amino-oxide azoxy is obtained to which Angeli assigned the structure (IX). Among the possible mono-oxidation products, an amino-oxide β -azoxy can be obtained only through the β -azoxy (VI), which by oxidation can give only the corresponding amino oxide (IX). As the mono-oxidation



furnishes the N-oxide at the amino group, (VII), that is the primary oxidation step, even in the bis-oxidation, and through it, by further oxidation, one can obtain only the amino oxide α -azoxy (X). Indeed, of the two azo nitrogen atoms in the azo amino oxide (VII), the β nitrogen becomes positively charged, owing to the I effect of the substituent, and will have less tendency to bind the oxygen atom, which takes up the free electron pair on the α nitrogen atom.



To explain this the *p*-dimethylamino-azoxy compounds described by Anderson have been prepared. Additional evidence that the structures assigned to the azoxy isomers are correct was obtained by the action of bromine. The β isomer undergoes smooth bromination while the α isomer under the same conditions does not react. By oxidation of the α isomer with peracetic acid a product was obtained which was



identical with the amino oxide azoxy prepared from Butter Yellow by oxidation with an excess of peracetic acid.

By oxidation of the β azoxy (VI) a bis-N-oxide was obtained, having properties different from those of the bis-oxidation product of Butter Yellow. The assigned

¹⁴ A. Angeli, *Rend. Accad. Lincei* **24**, 1190 (1915); *Gazz. Chim. Ital.* **46**, 94 (1916).

structure of amino oxide β azoxy (IX) is therefore correct. The absorption spectra (Fig. 5) are very similar for the two bis-N-oxides, owing to the analogous structures and the lack of different conjugation forms.

Hence, in 4-dimethylamino-azobenzene the nitrogen atom with higher electron density is the amino nitrogen and for the bis-oxidation compound the structure of α -azoxy amino oxide is correct.

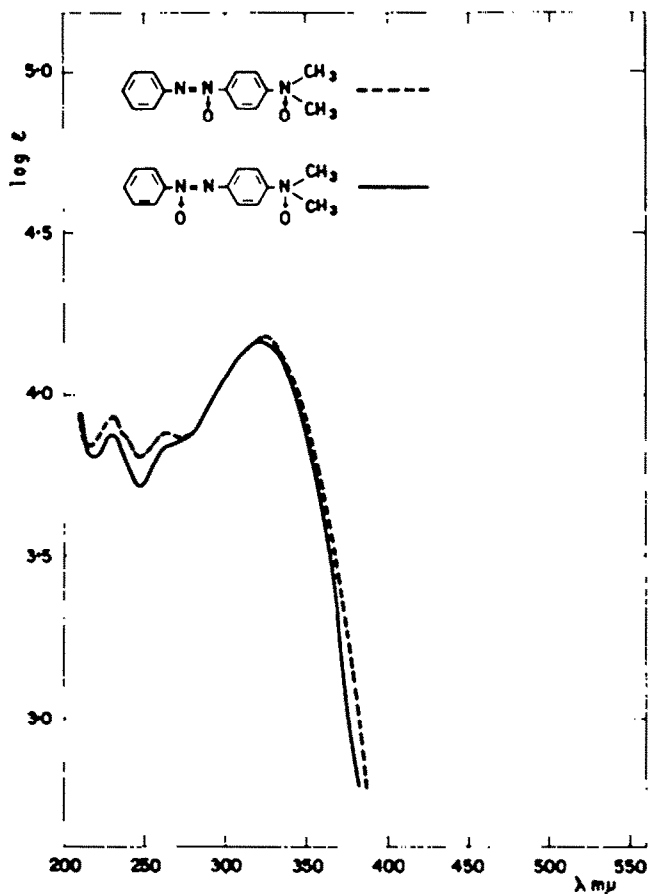


FIG. 5.

EXPERIMENTAL

p-Dimethylamino-azobenzene amino-oxide (VII)

To a cold solution of *p*-dimethylamino-azobenzene (10 g, 1 mole) in chloroform (15 ml) a cold solution of perbenzoic acid (6.12 g, 1 mole) was added dropwise. After standing overnight the peracid had disappeared, the solvent was evaporated and the residue stirred for 1 hr with sodium carbonate solution (200 ml) filtered and washed with water. The orange yellow crystals were air dried, washed with ether and dried over P_2O_5 *in vacuo*: yield, m.p. 123–125°, 11 g. Long orange prisms (dioxane), dried for 24 hr *in vacuo* over P_2O_5 , yield 9.8 g. m.p. 126–127°. (Found: N, 17.36; Calc. for $C_{14}H_{15}N_3O$: N, 17.42%).

α - and β -p-dimethylamino-azoxybenzenes (V and VI)

The isomeric *p*-dimethylamino-azoxybenzenes were prepared by condensation of phenylhydroxylamine with nitroso-dimethylaniline.¹¹

The β isomer (VI), m.p. 122° (1 g) in chloroform (20 ml) was added to a solution of bromine (1 ml) in chloroform (7 ml); after 4 hr in the refrigerator crystals separated. These were filtered, stirred with sodium carbonate solution, washed with water and dried. Orange yellow plates (ethanol), of brominated azoxy compound, were obtained. (Found: N, 13.20; Calc. for C₁₄H₁₄BrN₃O : 13.12%).

The α isomer (V), under the same conditions, was recovered unchanged.

p-Dimethylamino- α -azoxy-benzene amino oxide (X)

(a) *bis-Oxidation of the Butter Yellow*. To a fine suspension of *p*-dimethylamino-azobenzene (10 g) in glacial acetic acid (75 ml), 36% hydrogen peroxide (50 ml) was added and the mixture heated at 40° for 48 hr until the purple colour became orange-yellow. To the cooled solution, diluted with an equal volume of water, a great excess (ca. 400 ml) of dilute (1 : 10) H₂SO₄ was added, by cooling in ice. The sulphate of the azoxy-amino-oxide separated as bright orange leaves. After 6 hr in ice the sulphate was filtered, suspended in little water and stirred for 30 min with sodium carbonate solution (200 ml). The crude compound, yellow leaves, (10 g) gave pale yellow prisms (dioxane), m.p. 125–126°, after 3 days over P₂O₅ *in vacuo*. (Found: N, 16.30. Calc. for C₁₄H₁₅N₃O₂ : N, 16.33%).

(b) *Oxidation of the p-dimethylamino- α -azoxy-benzene (V)*. To a deep green solution of α -azoxy compound (0.3 g) in glacial acetic acid (10 ml) 36% hydrogen peroxide (1 ml) was added, and heated at 40° for 24 hr. A citron yellow solution resulted which was neutralised with sodium hydroxide and extracted with chloroform. The solvent was evaporated and the residue, washed with benzene and dried *in vacuo* over P₂O₅, melted at 118–123°. The crude compound was poured onto an alumina column in dioxane. The upper broad yellow band gave a yellow product, m.p. 125–126° (dried over P₂O₅ *in vacuo*), identical with the above *p*-dimethylamino- α -azoxybenzene amino oxide, as shown by mixed m.p. and the u.v. spectra. (Found: N, 16.40. Calc. for C₁₄H₁₅N₃O₂ : N, 16.33%).

(c) *Oxidation of the p-dimethylamino-azobenzene amino oxide (VII)*. To a suspension of the azocompound amino oxide (2 g) in glacial acetic acid (20 ml), 36% hydrogen peroxide (2 ml) were added and the mixture heated at 40° for 48 hr. The resulting yellow solution was neutralised with sodium hydroxide and extracted with chloroform. The solvent was evaporated to give a yellow residue which was recrystallised from dioxane in pale yellow prisms, m.p. 126–127° (dried for 3 days over P₂O₅ *in vacuo*), identical with the above α -azoxy-amino-oxide compound. (Found: N, 16.51; Calc. for C₁₄H₁₅N₃O₂ : N, 16.33%).

p-Dimethylamino- β -azoxybenzene amino oxide (IX). Oxidation of the β -azoxy isomer (VI).

To a solution of *p*-dimethylamino- β -azoxybenzene (2 g) in glacial acetic acid (20 ml), 36% hydrogen peroxide (2 ml), were added and the mixture heated at 40° for 24 hr. The resulting orange solution was neutralised with sodium hydroxide and extracted with chloroform. The solvent was evaporated to give brown crystals which were washed with little benzene and recrystallised from dioxane in yellow needles,

m.p. 117-118°, of *p*-dimethylamino- β -azoxy-benzene amino oxide, not identical with the isomer α -azoxy amino oxide, as shown by the physical aspect and m.p. (Found: N, 16.44. Calc. for $C_{14}H_{15}N_3O_2$: N, 16.33%).

Ultra-violet-visible absorption spectra

The absorption spectra were determined in 95% ethanol with a Beckman Model DU Quartz spectrophotometer.

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