

235. Absorption Spectra of Isomeric Aromatic Diazocyanides.

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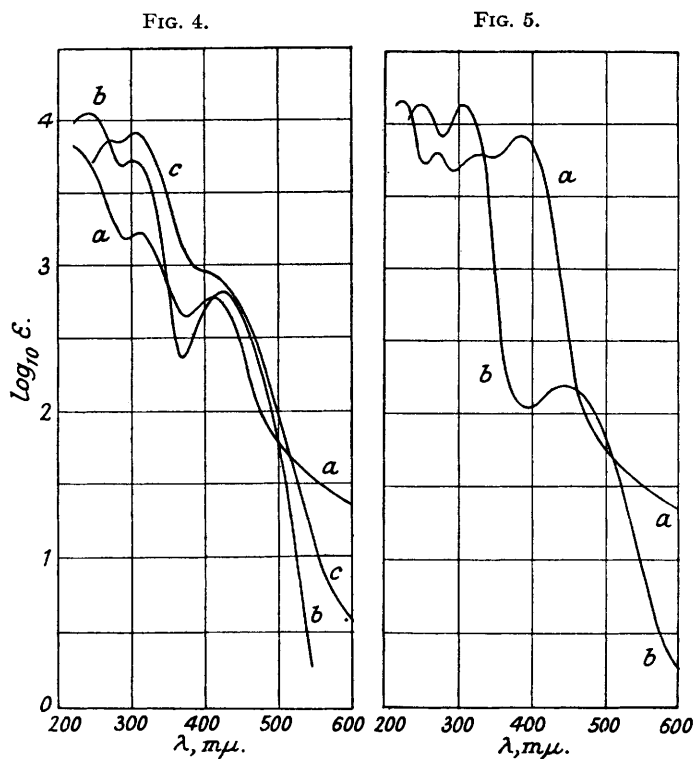
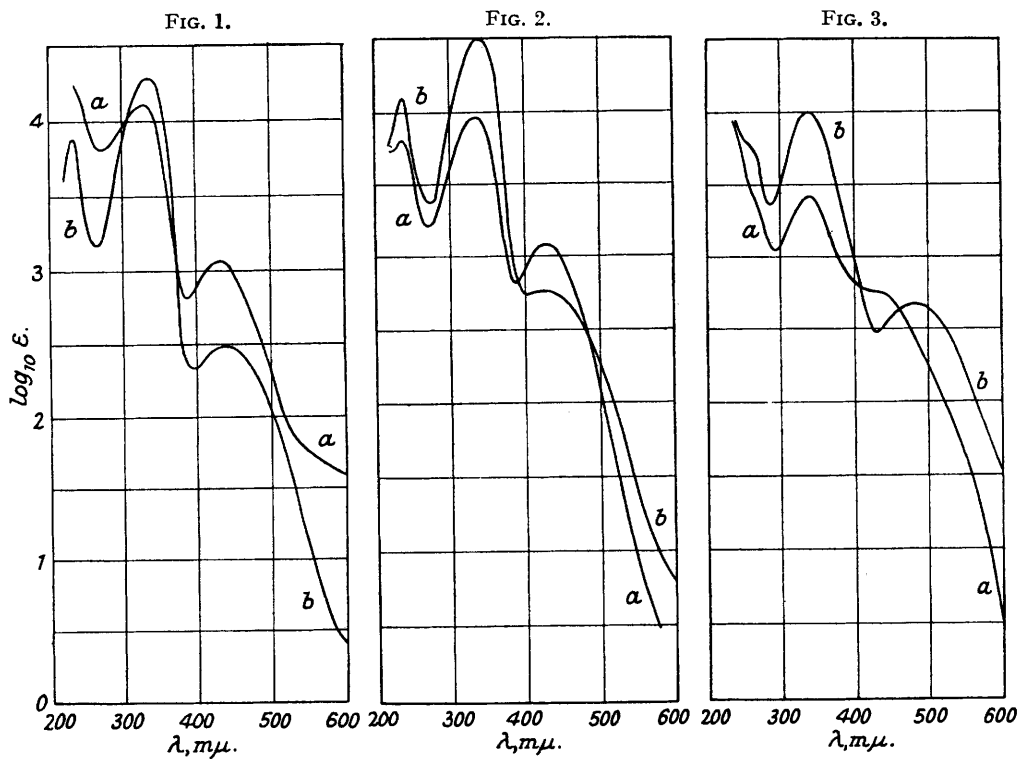
Five pairs of isomeric diazocyanides have been examined in ethereal solution between 220 and 600 $m\mu$. Differences between related forms are not great and lie more in ϵ_{\max} than in λ_{\max} . The data are compatible with the geometrical explanation proposed originally by Hantzsch for these compounds.

IN this paper we describe the ultra-violet spectra of five pairs of isomeric diazocyanides, ethyl ether being the solvent throughout. Although the stable and unstable varieties of two of these structures have been previously examined spectroscopically (Dobbie and Tinkler, *J.*, 1905, **87**, 275; Hantzsch and Lifschitz, *Ber.*, 1912, **42**, 3011), we thought a reinvestigation with modern equipment desirable in view of the opinions expressed during a recent discussion (Hodgson, *Chem. and Ind.*, 1948, 270) on the formulation of a number of $\text{-N}\equiv\text{N-}$ containing molecules.

Hodgson says: "When Dobbie and Tinkler and later Hantzsch and Lifschitz recorded the visual spectra of the alleged *cis*- and *trans*-diazocyanides, the *cis*- were found to be identical with the *trans*-graphs. Now Hantzsch never failed to use colour arguments when it suited his purpose, and I was amazed to find that after obtaining the same visual spectra for compounds which are yellow and red, and also having recorded the ready convertibility of *cis*- to *trans*-forms even at -5° , Hantzsch should not immediately have concluded that he had measured one and the same substance on both occasions to account for the identity." A little farther on he adds "I first pointed out that the identity of the Hantzsch spectra indicated identity of compound measured; for even if *cis*- and *trans*-forms really exist they should afford different visual spectra."

Dobbie and Tinkler, and Hantzsch and Lifschitz, of course, published their observations in the older, and rather rough, form of graphs showing oscillation frequency against layer thickness; yet, even so, we submit that these provide no justification for Hodgson's statements. The English authors reported on the isomeric forms of *p*-methoxy- and *p*-chloro-benzenediazocyanides, and the German on the corresponding 2:4:6-tribromo-derivatives. In all cases the spectra were shown as *similar but not identical*. Differences of λ_{\max} are somewhat obscured by the method of presentation, but *differences of intensity are clearly indicated*. Such a situation is to be anticipated for geometrical isomers (Le Fèvre, Northcott, and Wilson, *Chem. and Ind.*, 1948, 732; cf. also Braude, *Ann. Reports*, 1945, **42**, 125).

Present work.—The solutes were prepared by methods already described (Anderson, Le Fèvre, and Savage, *J.*, 1947, 445; Anderson, Bedwell, and Le Fèvre, *ibid.*, p. 457). Ether was selected as the solvent since it had been used by Hantzsch and we desired particularly to check his findings. Solutions were made up immediately before examination. The spectra were recorded over the appropriate range 220—600 $m\mu$ with a Beckman photoelectric spectrophotometer, model DU. They are shown diagram-



matically in Figs. 1—5 and summarised in Table I, values of $\lambda_{\max.}$ being followed in parentheses by those of $\epsilon_{\max.}$ both here and in Table II.

TABLE I.

<i>4-Chlorobenzenediazocyanides.</i>				
Unstable (1a) *	432 (3.07)	330 (4.12)	—	—
Stable (1b)	438 (2.48)	338 (4.29)	—	235 (3.90)
<i>4-Bromobenzenediazocyanides.</i>				
Unstable (2a)	430 (3.08)	335 (3.96)	—	235 (3.80)
Stable (2b)	425 (2.77)	341 (4.50)	—	238 (4.09)
<i>2 : 4 : 6-Tribromobenzenediazocyanides.</i>				
Unstable (3a)	426 (2.76) †	338 (3.42)	262 (3.35) †	—
Stable (3b)	481 (2.67)	341 (4.00)	257 (3.77) †	—
<i>Nitrobenzenediazocyanides.</i>				
<i>o</i> -{ Unstable (4a)	410 (2.75)	310 (3.23)	—	—
Stable (5a)	388 (3.92)	330 (3.79)	270 (3.79)	220 (4.15)
<i>m</i> -{ Unstable (4b)	425 (2.82)	300 (3.71)	—	242 (4.05)
Stable (5b)	443 (2.19)	305 (4.13)	—	248 (4.14)
<i>p</i> -{ Unstable (4c)	405 (2.94) †	306 (3.92)	270 (3.87)	—
Stable	443 (2.38)	308 (4.22)	277 (3.94) †	—

* These references are to the curves.

† Inflexion.

Discussion.—Where the two absorptions common to the six substances listed are concerned, related isomers are seen to differ more in $\epsilon_{\max.}$ than in $\lambda_{\max.}$, the longer-wave absorption being more intense with the unstable forms, and the shorter-wave absorption stronger with the stable forms. The *o*-nitro-compounds are the only exception to this. The situation seems similar to that already known for azobenzene (Table II), and many of its derivatives (Cook, Jones, and

TABLE II.

Solvent.	Configuration.	Absorptions and intensities.	
C_6H_6 *	<i>cis</i> -	430 (3.1)	<i>ca.</i> 300 (3.6)
	<i>trans</i> -	450 (2.7)	330 (4.3)
$CHCl_3$ †	<i>cis</i> -	438 (3.1)	324 (4.2)
	<i>trans</i> -	445 (2.5)	319 (4.3)
$EtOH$ ‡	<i>cis</i> -	430 (3.1)	305 (3.4)
	<i>trans</i> -	450 (2.4)	320 (4.2)

* Le Fèvre and Vine, *J.*, 1938, 431.

† Cook, Jones, and Poly, *ibid.*, 1939, 1315.

‡ Winkel and Siebert, *Ber.*, 1941, 74, 670.

Poly, *loc. cit.*). In each case, too, the nitro-derivatives give the least simple spectra.

As to other analogies, Smakula and Wassermann (*Z. physikal. Chem.*, 1931, *A*, 155, 353) have found the absorption curves in several solvents of *cis*- and *trans*-stilbenes to cross one another (ϵ_{trans} greater than ϵ_{cis} in the 300 $m\mu$ region, and less in the 220 $m\mu$), the actual wave-lengths of maximum absorption being roughly equal for both geometrical isomers. The same characteristics are to be seen in early spectrographic studies of *syn*- and *anti*-oximes (Brady, *J.*, 1914, 105, 2104), confirmed by later work (Brady and Grayson, *J.*, 1933, 1037; Raffouf, *J. Amer. Chem. Soc.*, 1946, 68, 1765).

In conclusion, therefore, it would seem that ultra-violet absorption spectra display no evidence against Hantzsch's configurational explanation of isomerism among the aromatic diazocyanides.

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