85. *The Configurations of the Isomeric Diazocyanides, and Some Measurements of their Rates of Interconversion.*

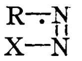
By R. J. W. Le Fèvre and H. Vine.

Measurements of the dipole moments of several pairs of isomeric diazocyanides have provided definite physical evidence for the correctness of the configurations allotted to these compounds by Hantzsch, *viz.*, that the *cis*-isomerides are the less stable and are those primarily produced.* The spontaneous isomerisation which they undergo in benzene solution has been followed by means of the dielectric constant. The *trans*-isomerides are produced at rates obeying the unimolecular law, and in one case measurements at two temperatures have afforded a value of the activation energy. The measured rates of isomerisation of the substituted diazobenzenecyanides examined were in the order

$$\left.\begin{matrix}p\text{-chloro-}\\ p\text{-bromo-}\end{matrix}\right\} > \left.\begin{matrix}p\text{-nitro-}\\ o\text{-bromo-}\end{matrix}\right\} > 2:4:6\text{-tribromo-}$$

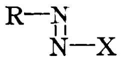
That the majority of aromatic diazo-compounds are electrovalent salts of the type $RN_2^+X^-$ (halides, sulphates, nitrates, etc.) was clearly shown by Hantzsch's work on the conductivity of their solutions. They are water-soluble and generally colourless, and were regarded as salts of the corresponding diazonium hydroxides, $RN_2^+OH^-$. The diazonium sulphites ($RN_2^+SO_3H^-$), cyanides ($RN_2^+CN^-$) and the hydroxides themselves, however, except in very dilute solution or in the presence of acid, pass to a large extent into the covalent diazo-sulphonic acids ($R{\cdot}N{:}N{\cdot}SO_3H$), -cyanides ($R{\cdot}N{:}N{\cdot}CN$), and -hydroxides ($R{\cdot}N{:}N{\cdot}OH$), the normal diazohydroxides and sulphonic acids being capable of isolation only in the form of their metallic derivatives.

In all three cases the covalent diazo-compounds first obtained underwent transformation into more stable isomers, and Hantzsch regarded the two forms as *cis*- and *trans*-isomerides, as (I) and (II). His views on the isomeric diazotates were only generally accepted after a long controversy (1894—1902), in the course of which the discovery of similar isomerism amongst the diazo-sulphonates and -cyanides was of great importance.



$$\begin{matrix}R-N\\ \|\\ X-N\end{matrix}$$

(I.) *cis*-.



$$\begin{matrix}R-N & \\ \| & \\ N & -X\end{matrix}$$

(II.) *trans*-.

The diazonium cyanides could not be isolated except as double salts with silver cyanide, of the general formula $RN_2{\cdot}Ag(CN)_2$, or in one instance, that of the *p*-anisole derivative, which showed the greatest tendency to ionise, as a crystalline salt of the formula

$$CH_3{\cdot}O{\cdot}C_6H_4{\cdot}N_2{\cdot}CN,HCN,2H_2O.$$

The isomeric diazocyanides were both coloured, low-melting solids, readily soluble in organic solvents but sparingly so in water. The labile normal cyanide always had the greater solubility and lower melting point, and in alcoholic solution it coupled much the more rapidly with β-naphthol. The transformation of the normal into the *iso*-diazocyanides proceeded spontaneously in solution in organic solvents at the ordinary temperature, but less rapidly than the transformation of the diazosulphonates; the diazotates generally only changed at an appreciable rate when heated.

Configurations of the Isomerides.—Hantzsch argued by analogy with the isomerism of ethylenic compounds and recognised the less stable forms of the diazotates, cyanides, and sulphonates as *cis* (*syn*) and the more stable forms as *trans* (*anti*). He considered this conclusion to be strongly supported by the fact that the labile cyanides decomposed readily in contact with copper powder, with the liberation of nitrogen and the formation of nitriles, whereas the stable forms did not, it being supposed that this elimination would occur more readily when the groups R and CN were nearer together. The fallacy of reasoning of this

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* A summary of the experimental work of Hantzsch and his collaborators is given in "Die Diazoverbindungen," by Hantzsch and Reddelien, 1921.

type is illustrated by the greater stability of *cis*- than of *trans*-dichloroethylene (Ebert and Büll, *Z. physikal. Chem.*, 1931, *A*, **152**, 451), and by the incorrectness of the oxime configurations derived from a consideration of the Beckmann change and dehydration reactions.

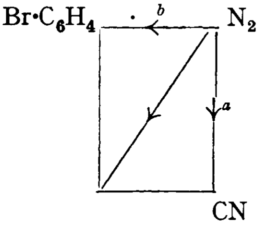
The present work was undertaken because dipole-moment measurements afford a means of determining the configuration of geometrical isomerides independently of arguments from analogy. The results now recorded thus provide the first certain confirmation of the correctness of Hantzsch's allocations. The moments of the substances are given in the following table :

Diazobenzenecyanide derivative.	Dipole moment (D.).*	
	(*cis*-), labile.	(*trans*-), stable.
4-Chloro-	2·93	3·73
4-Bromo-	2·91	3·78
4-Nitro-	2·04	1·47
2-Bromo-	3·79	5·32
2 : 4 : 6-Tribromo-	2·5	4·0

* All moments given subsequently are in Debye units (e.s.u. × 10^{-18}).

These values may be considered in relation to rough vector diagrams of the type given below.

When the measurements on the 4-bromo-derivatives were first reported (*Chem. and Ind.*, 1937, **56**, 680), it was supposed that the moments *a* and *b* associated with the groups N_2—CN and *p*-Br—C_6H_4—N_2 would both be directed *away* from the azo-group, as in (III) and (IV). In these circumstances the greater moment would be that of the *cis*-isomer. However, such a conclusion became doubtful when the moment of *cis*-azobenzene was found to be 3·0 (unpublished work), from which the value of the $C_6H_5 \rightarrow N_2$ link moment could be estimated, by making a reasonable assumption regarding the angle θ (in V).



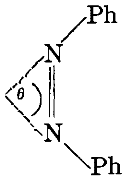
Resultant > a.

(III.)

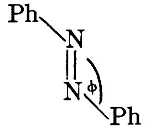
$$\mathrm{Br{\cdot}C_6H_4}\xleftarrow{b}\mathrm{N_2}\xrightarrow{a}\mathrm{CN}$$

Resultant = $a - b$

(IV.)

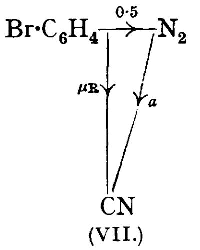


(V.)



(VI.)

The crystal analysis of *trans*-azobenzene (Robertson, Prasad, and Woodward, *Proc. Roy. Soc.*, 1936, *A*, **154**, 187) has not yet been completely performed, but from the isomorphism with *trans*-stilbene it can be concluded that these molecules are similar in that φ is probably *ca.* 130° (VI), and so if (VI) ⟶ (V) merely by rotation about the N = N axis, θ becomes 80°. For such a configuration, since $2\mu\cos\frac{1}{2}\theta = 3{\cdot}0$, the $C_6H_5 \rightarrow N_2$ link moment is *ca.* 2·0. The $C_6H_5 \rightarrow$ Hal. moment being *ca.* 1·5, it now appears that the resultant of the *p*-Hal.–C_6H_4–N_2 group will be *ca.* 0·5, directed *towards* the azo-group. The moment associated with the CN group itself (*ca.* 4·0) will be considerably greater than any opposing $N_2 \leftarrow$CN moment. and the resultant will be directed *away* from the azo-group.



(VII.)

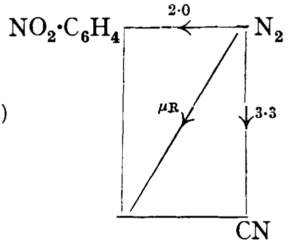
$\mu_R < a$.

$$\mathrm{Br{\cdot}C_6H_4}\xrightarrow{0{\cdot}5}\mathrm{N_2}\xrightarrow{a}\mathrm{CN}$$

(VIII.) $\mu_R \simeq a + 0{\cdot}5$; hence $a \simeq 3{\cdot}3$.

Therefore, as shown in (VII) and (VIII), for *trans-p*-chloro- or -bromo-benzenediazocyanide, $\mu_R \simeq a + 0{\cdot}5$, and for the *cis*-form μ_R will be slightly less than a. Since the moment of the stable form is greater by nearly 1 than that of the labile form, the result is in agreement with Hantzsch's configurations. This conclusion is confirmed by the moments of the *p*-nitro-derivatives, for here the $R \rightarrow NO_2$ moment is *ca.* 4·0, and the resultant of the *p*-$NO_2{\cdot}C_6H_4$—N_2 group is *ca.* 2·0, directed *away* from the azo-group. The moment of the *cis*-form should therefore be greater than that of the *trans*-, as shown in (IX) and (X); experimentally, the labile and the stable form are found to have moments of 2·05 and 1·47 respectively.

(IX.)



$$NO_2{\cdot}C_6H_4 \overset{2\cdot0}{\longleftarrow} N_2 \overset{3\cdot3}{\longrightarrow} CN$$

$$\mu_R \simeq 3{\cdot}3 - 2{\cdot}0.$$

(X.)

The moments of the 2 : 4 : 6-tribromo-derivatives are also in agreement with this scheme, for the moment of the $C_6H_2Br_3$—N_2 group should be very approximately that of C_6H_5—N_2, *i.e.*, *ca.* 2·0, directed *towards* the azo-group, and the *trans*- (stable) form consequently should have a higher moment than its isomer. Since the aromatic nucleus in 2-bromobenzenediazocyanide is not symmetrical, problems of rotation arise, and the moments of this or its derivatives cannot well be predicted.

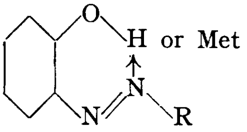
It should be emphasised that the conclusiveness of this argument lies in the reversal of the difference between the moments of the isomers when proceeding from the *p*-halogeno- and 2 : 4 : 6-tribromo-derivatives to the *p*-nitro-derivative.

Previous physical measurements on the diazocyanides have not provided any definite evidence on the point in question. Stewart (J., 1907, **91**, 199) suggested that, of two geometrical isomerides, the more symmetrical showed the greater power of absorbing light, and that this property might be used in the determination of molecular structure. No such generalisation can be applied to the azo- and diazo-compounds, for although in 2 : 4 : 6-tribromobenzenediazocyanide the *trans*- (stable) form has the greater absorption in both the visible and the near ultra-violet region (Hantzsch and Lifschitz, *Ber.*, 1912, **45**, 3011), yet in potassium 2-chlorobenzenediazosulphonate (Hantzsch and Lifschitz, *loc. cit.*), and 4-bromobenzenediazocyanide as well as azobenzene (present work), the stable form absorbs more in the ultra-violet but less in the visible than the labile isomer.

Brühl (*Ber.*, 1896, **29**, 2907) found that normal and *iso*-2 : 4-dibromobenzenediazocyanide had molecular refractions for the Na_D line of 56·59 and 58·64 respectively in benzene solution, which were in accordance with the general observation that the *trans*-isomer of a given pair had the greater molecular refraction. Measurement of the molecular refraction of several pairs of diazocyanides has been incidental to the determination of their dipole moments, and the *trans*- (stable) isomers have the higher value in each case, thus :

Diazobenzenecyanide derivative.	$[R_L]_D$. *cis*-.	*trans*-.	Diazobenzenecyanide derivative.	$[R_L]_D$. *cis*-.	*trans*-.
4-Chloro-	46·1	48·0	2-Bromo-	47·2	51·6
4-Bromo-	49·9	52·3	2 : 4 : 6-Tribromo-	64	68
4-Nitro-	44·7	48·6			

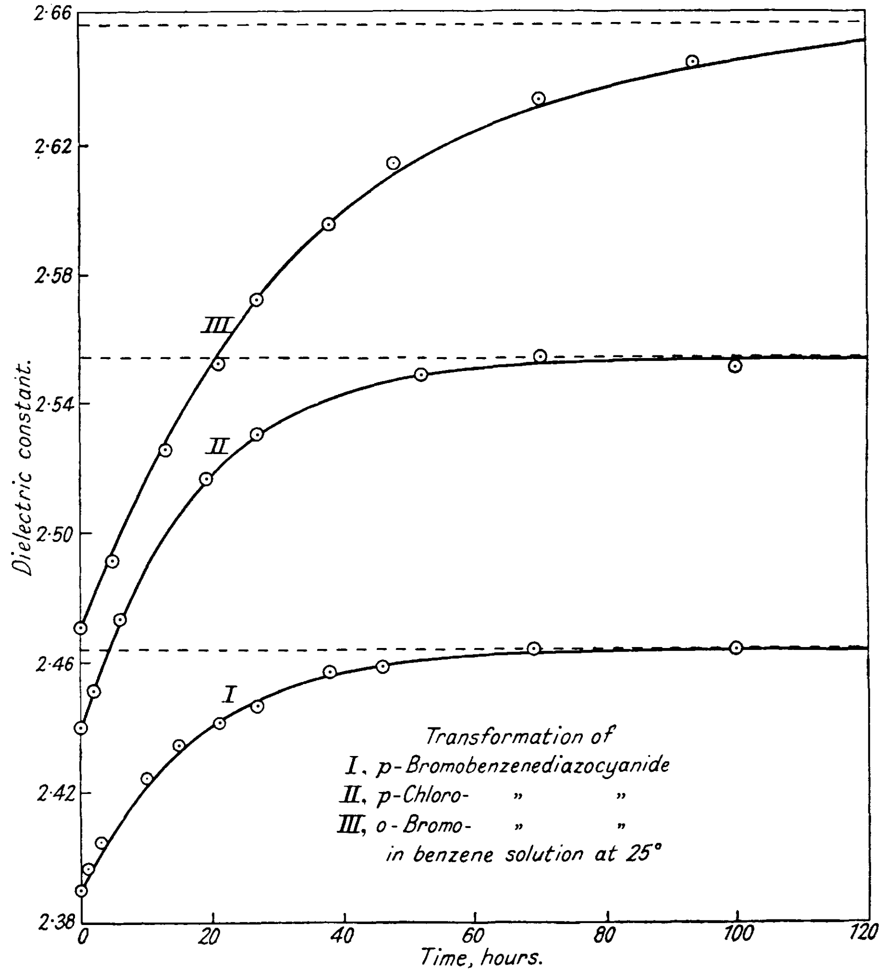
It seems probable that among azo-compounds the *trans*- form is always the more stable, for in addition to the results now recorded, Bergmann, Engel, and Sándor (*Ber.*, 1930, **63**, 2572) have reported a zero moment for azobenzene. This, in view of the fact that no tendency to pass into a more stable form had been observed, was evidence for the greater stability of the *trans*-configuration of the azo-group in this molecule. Such a view is in harmony with the formulation of the *o*-hydroxyazo-mordant dyes as chelated compounds in which the azo-group *must* have



a *trans*-structure (Pfeiffer, *J. pr. Chem.*, 1930, **126**, 108; Sidgwick, "The Electronic Theory of Valency," p. 234), and also with the recent discovery of a second, less stable, form of azobenzene, produced by the action of light (Hartley, *Nature*, 1937, **140**, 281) and shown by its moment to be the *cis*-isomer.

Rates of Isomerisation.—The transformation of the *cis*- into the *trans*-diazocyanides in pure benzene solution has been followed by dielectric-constant measurements. The solutions were kept in brown glass bottles, although ordinary daylight does not have much effect at the concentrations used (1—5%). The change goes to completion, following the unimolecular law, and Fig. 1 shows the transformation of the *p*-chloro-, *p*-bromo-, and *o*-bromo-diazocyanides at 25°. The broken lines show the final values obtained. The curves have been calculated from the equation $dx/dt = k(a - x)$, the best values of k being chosen. The transformation of *p*-nitrobenzenediazocyanide is shown in Fig. 2, but in this case the change in dielectric constant is smaller and the experimental error is therefore increased. Fig. 3 shows the transformation of *p*-bromobenzenediazocyanide at 57·5°, at which temperature a rough measurement of the rate of change of 2 : 4 : 6-tribromobenzenediazocyanide (which does not invert at an appreciable rate at 25°) has also been made. The velocity constants are summarised on p. 435 :

FIG. 1.



Diazobenzenecyanide derivative.	$k_{25°}$, hr.$^{-1}$.	$k_{57·5°}$, hr.$^{-1}$.
4-Chloro-	0·058	—
4-Bromo-	0·058	2·08
4-Nitro-	0·026	—

Diazobenzenecyanide derivative.	$k_{25°}$, hr.$^{-1}$.	$k_{57·5°}$, hr.$^{-1}$.
2-Bromo-	0·028	—
2 : 4 : 6-Tribromo-	—	0·11

Within the limits of experimental error, identical values have been found for the *p*-bromo-compound at 25° and 55° by Dr. G. S. Hartley, using a photometric method in which solutions of much greater dilution than ours are used. From the dielectric-constant measurements at two temperatures on the *p*-bromo-derivative, since $\log_e k_2/k_1 = E(T_2—T_1)/\boldsymbol{R}$, the energy of activation is 21·6 kg.-cals. (Hartley finds 22·0 kg.-cals.). The transformation of *cis*- into *trans*-azobenzene has a similar activation energy (23·0 kg.-cals., Hartley), and it is therefore probable that the transformation in this case and in the diazocyanides occurs by the same mechanism.

FIG. 2.

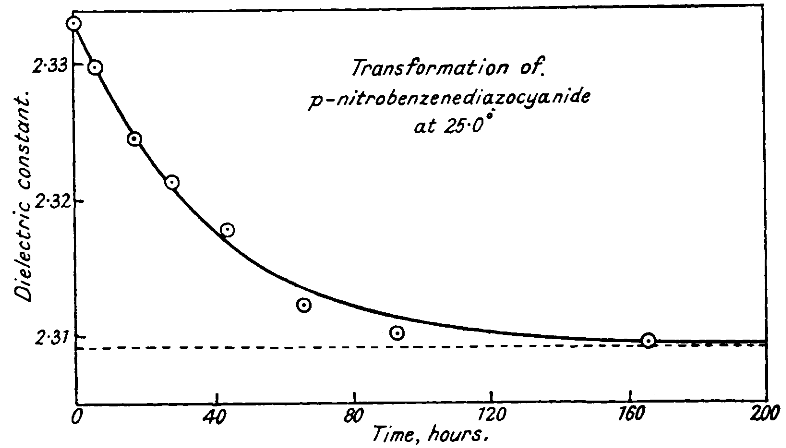
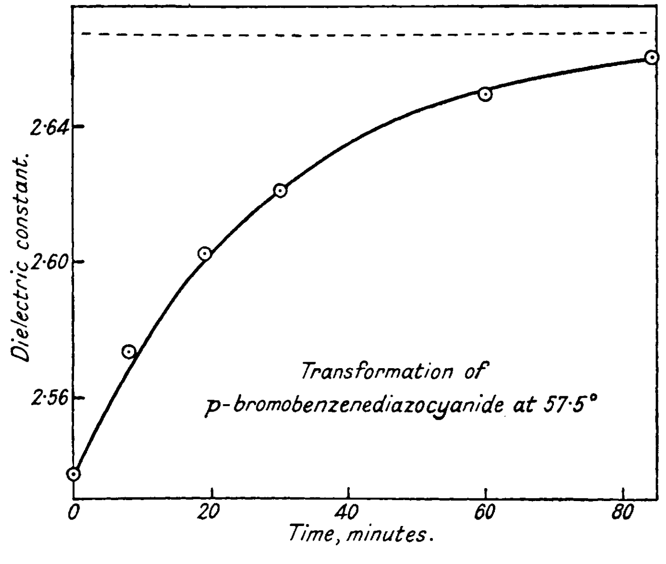


FIG. 3.



The effect of substituents in the benzene ring is of interest. Hantzsch and Danziger (*Ber.*, 1897, **30**, 2529) concluded that, in general, halogen atoms in the para- and more especially the ortho-positions reduced the readiness of transformation and increased the stability of the *cis*-diazocyanides, whilst alkyl or methoxy-groups had the opposite effect. They made purely qualitative observations of the behaviour of the *cis*-cyanides in the solid state or when dissolved in alcohol and reprecipitated with water. Those substances which have been investigated in the present work were tabulated by them as follows:

Derivative.		
4-Nitro-	Unstable	Very easily isomerisable
4-Chloro-	More stable	Easily isomerisable
4-Bromo-	Stable	Fairly easily isomerisable
2-Bromo-	Very stable	Difficultly isomerisable
2 : 4 : 6-Tribromo-	Very stable	Difficultly isomerisable

We have found, however, that the rates of change of the *p*-chloro- and the *p*-bromo-cyanide in benzene solution at the same temperature are equal, whereas that of the *p*-nitro-cyanide is less. The transformation of the *o*-bromo- is half as fast as that of the *p*-bromo-cyanide, and that of the 2 : 4 : 6-tribromo-derivative is reduced to one-twentieth. The influence of substituents in the *p*-position is in the same order as their permanent electron-attracting effect.

It is probable that the thermal transformation takes place only very slowly in the solid but more rapidly in the fused state. Therefore in those cases where the production of small amounts of *trans*- can depress the m. p. of the *cis*-form below room temperature, the initially slow isomerisation could proceed more rapidly in the melt. Since both *cis-p*-chloro- and -*p*-nitro-benzenediazocyanides have lower m. p.'s (28—30°) than that of *cis-p*-bromobenzenediazocyanide (42—43°), this suggestion may account for Hantzsch and Danziger's observation that the former underwent transformation more readily than the latter. We noticed that a sample of *cis-p*-chlorobenzenediazocyanide left in a desiccator at *ca.* 23° for a few hours became partly liquid, and then resolidified on mixing. On the other hand, a pure dry sample of the *p*-bromo-derivative could be kept unchanged at 0° for two months.

However, transformation can occur under the action of light in both the solid and the dissolved state. For instance, Ciusa (*Atti R. Accad. Lincei*, 1906, **15**, II, 137) observed that isomerisation of *cis*-2 : 4 : 6-tribromobenzenediazocyanide was brought about in benzene solution by sunlight, and Hartley has shown the effect to be reversible in both azo-compounds and diazocyanides. We found that solid *cis*-tribromobenzenediazocyanide, when exposed to the spectrum of a mercury-vapour lamp, also became reddened on the surface by the chief mercury lines between wave-lengths 3000 to 4500 A.

EXPERIMENTAL.

Preparation of Materials.—*p*-Chloro-, *o*- and *p*-bromo-, and *p*-nitro-benzenedizaocyanides were prepared by the following modification of the recorded procedures (Hantzsch and Schultze, *Ber.*, 1895, **28**, 666; Hantzsch and Danziger, *loc. cit.*). The appropriate base (0·1 g.-mol.) was dissolved in concentrated hydrochloric acid (45 c.c., 0·45 g.-mol.) and water (45 c.c.) and treated with sodium nitrite (0·1 g.-mol.). The diazotised solution was filtered and cooled to —10° in solid carbon dioxide–alcohol, 50 c.c. of absolute alcohol being added in order to prevent the mixture freezing. Potassium cyanide (*ca.* 13 g., 0·2 g.-mol.) in 25 c.c. of water was added slowly, the mixture being well stirred. The final mixture thus remained acid to litmus. The orange-coloured precipitate was filtered off, washed with ice-cold water, and spread on a porous plate. It was then dissolved in light petroleum with a little ether, dried over anhydrous sodium sulphate, and well cooled in solid carbon dioxide–alcohol. The pure labile diazocyanides were thus obtained as small orange-coloured needles or plates, which were readily dried on a porous tile.

The stable diazocyanides were obtained by evaporation of the solutions used in the measurement of the dipole moments and the velocity of transformation of the labile isomers, and were recrystallised in a similar manner from ether and light petroleum by cooling strongly. They were very similar in appearance to their isomers, but somewhat redder. They crystallised in needles, and slow evaporation of *trans-p*-chlorobenzenediazocyanide solution produced crystals up to 4 cm. in length.

2 : 4 : 6-Tribromoaniline, being a very weak base, could not be treated in the above manner. The pure diazonium sulphate was obtained by the addition of amyl nitrite to the amine dissolved

TABLE I.

w_1.	$\epsilon^{25°}_{1200}$.	$d^{25°}_{4°}$.	$\alpha\epsilon_2$.	β.	$n^{25°}_{D}$.	r_{12}.	$[R_L]_D$.
0	2·2725	0·87378	—	—	1·49725	0·33503	—
p-*Chlorobenzenediazocyanide.*							
Labile form (*cis*-).							
0·01629	2·3708	0·87839	6·03	0·324	1·49866	0·33408	45·8
0·03023	2·4531	0·88234	5·97	0·324	1·50003	0·33335	46·2
0·03865	2·5005	0·88478	5·90	0·326	1·50076	0·33285	46·1
Stable form (*trans*-).							
0·00592	2·3285	0·87537	9·46	0·308	1·49794	0·33482	49·5
0·00692	2·3386	0·87571	9·55	0·319	1·49798	0·33471	47·8
0·01098	2·3771	0·87690	9·53	0·325	1·49848	0·33453	47·8
0·01154	2·3824	0·87703	9·52	0·322	1·49854	0·33453	48·3
p-*Bromobenzenediazocyanide.*							
Labile form (*cis*-).							
0·00746	2·3084	0·87675	4·81	0·456	1·49795	0·33430	49·8
0·00879	2·3138	0·87729	4·70	0·457	1·49811	0·33418	50·0
0·01220	2·3301	0·87867	4·72	0·459	1·49844	0·33384	49·9
Stable form (*trans*-).							
0·00595	2·3186	0·87605	7·75	0·437	1·49788	0·33452	52·4
0·00766	2·3329	0·87678	7·88	0·448	1·49810	0·33437	52·3
0·01058	2·3548	0·87790	7·78	0·446	1·49840	0·33411	52·1
p-*Nitrobenzenediazocyanide.*							
Labile form (*cis*-).							
0·01667	2·3218	0·87920	2·96	0·372	1·49855	0·33371	45·0
0·01960	2·3286	0·88010	2·86	0·369	1·49866	0·33343	44·6
0·02037	2·3275	0·88032	2·70	0·367	1·49868	0·33335	44·4
0·02060	2·3329	0·88042	2·93	0·369	—	—	—
Stable form (*trans*-).							
0·00880	2·2872	0·87654	1·67	0·359	1·49824	0·33454	49·2
0·01031	2·2895	0·87699	1·65	0·356	1·49834	0·33443	48·8
0·01240	2·2934	0·87771	1·68	0·363	1·49850	0·33424	47·8
o-*Bromobenzenediazocyanide.*							
Labile form (*cis*-).							
0·01417	2·3814	0·87997	7·69	0·500	1·49864	0·33346	47·0
0·02509	2·4710	0·88447	7·91	0·488	1·49956	0·33229	47·5
Stable form (*trans*-).							
0·00665	2·3730	0·87642	15·11	0·454	1·49803	0·33447	52·7
0·01186	2·4532	0·87853	15·23	0·458	1·49846	0·33391	50·6
2 : 4 : 6-*Tribromobenzenediazocyanide.*							
Labile form (*cis*.-)							
0·00642	2·2861	0·87726	2·12	0·620	1·49781	0·33402	65·5
0·00874	2·2904	0·87852	2·05	0·620	1·49790	0·33359	62·5
Stable form (*trans*-).							
0·00729	2·3085	0·87769	4·94	0·614	1·49793	0·33393	67·7

TABLE II.

Diazobenzenecyanide derivative.	M. p.	*M*.	$\alpha\epsilon_2$.	β.	P_∞.	$[R_L]_D$.	μ.
cis-*p*-Chloro-	29°	165·5	5·97	0·325	224	46·1	2·93
trans-*p*-Chloro-	105	165·5	9·52	0·322	335	48·0	3·73
cis-*p*-Bromo-	42—43	210	4·71	0·457	225	49·9	2·91
trans-*p*-Bromo-	132	210	7·80	0·444	348	52·3	3·78
cis-*p*-Nitro-	29—30	176	2·92	0·369	134	44·7	2·04
trans-*p*-Nitro-	86	176	1·67	0·359	94	48·6	1·47
cis-*o*-Bromo-	52—53	210	7·80	0·494	344	47·2	3·79
trans-*o*-Bromo-	109	210	15·17	0·456	638	51·6	5·32
cis-2 : 4 : 6-Tribromo-	59—60	368	2·09	0·620	192	64	2·5
trans-2 : 4 : 6-Tribromo-	149	368	4·94	0·614	390	68	4·0

in acetic acid (Hantzsch, *Ber.*, 1901, **34**, 3339) and precipitation with ether. It was dissolved in aqueous alcohol and treated with an equimolecular quantity of potassium cyanide solution (Hantzsch and Danziger, *loc. cit.*; Ciusa, *loc. cit.*) The pale yellow *cis*-diazocyanide was formed slowly, but it was filtered off and washed as soon as possible on account of the tendency of a diazocyanide to combine with hydrogen cyanide, with the formation of a diazoimidocyanide (Gabriel, *Ber.*, 1879, **12**, 1637; Hantzsch and Schultze, *loc. cit.*). Recrystallisation in the previous manner from light petroleum gave small, pale yellow plates of the *cis*-diazocyanide, which was found to isomerise spontaneously at 57·5° in benzene solution, then becoming intensely red.

The m. p.'s of the various materials, included in Table II, were in substantial agreement with those recorded by Hantzsch and his collaborators, but were slightly higher in some cases.

The absorption spectra of the isomeric *p*-bromobenzenediazocyanides in benzene solution, shown in Fig. 4, were obtained with a Hilger quartz spectrograph E.2 and a Spekker photometer.

FIG. 4.

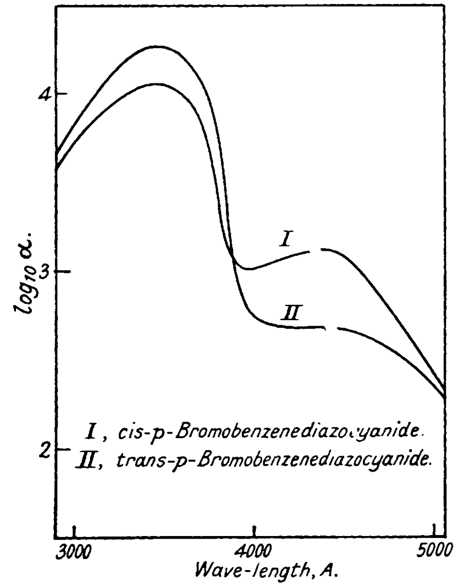
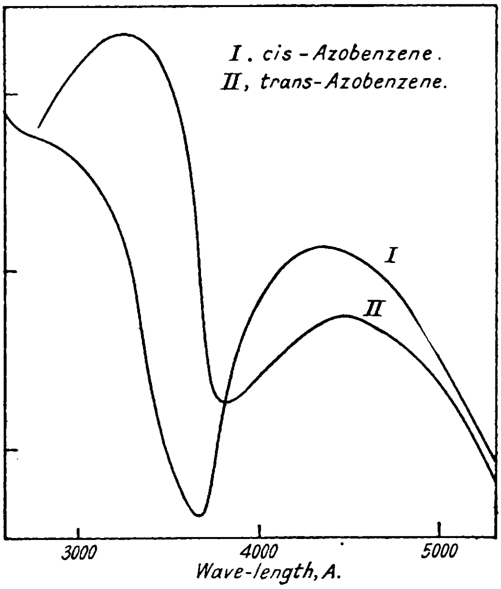


FIG. 5.



They are very similar in form, but differ in the intensity of the absorption bands. The extinction coefficient, α, is defined by $\log_{10} I_0/I = \alpha cl$, where c is the concentration in g.-mols./l. and l is in cm. The spectra of the two forms of azobenzene (Fig. 5), specimens of which were kindly provided by Dr. G. S. Hartley, were obtained in the same way. In *cis*-azobenzene the ultra-violet absorption band is considerably shifted towards a higher frequency, but an analogous effect has been observed in other cases of geometrical isomerism; the isomeric diazotates provide an example (Dobbie and Tinkler, J., 1905, **87**, 276; Hantzsch and Lifschitz, *loc. cit.*; Cambi and Szegö, *Ber.*, 1928, **61**, 2081).

Dielectric-polarisation Measurements.—The required observations are recorded in Table I under the usual headings: w_1 the weight fraction, $d_{4^\circ}^{25^\circ}$ the density, $\epsilon_{1200}^{25^\circ}$ the dielectric constant, $n_D^{25^\circ}$ the refractive index, and r_{12} the specific refraction. The results have been calculated from the equation (Le Fèvre and Vine, J., 1937, 1809) $P_\infty = Mp_\infty = M[p_2(1-\beta) + C\alpha\epsilon_2]$, the mean values of $\alpha\epsilon_2$ and β involved being tabulated in cols. 4 and 5 of Table II.

The following constants were employed: $p_2 = 0{\cdot}3409$, $C = 0{\cdot}1881$.

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