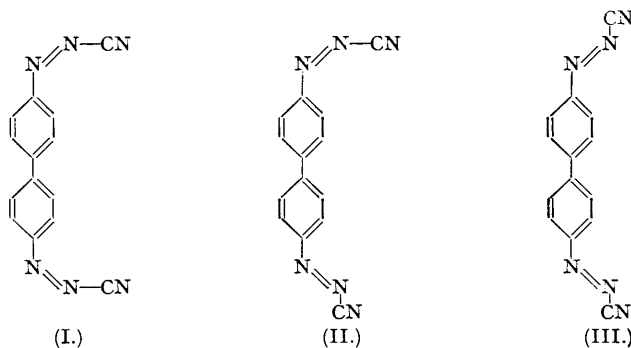


41. *The Isomerisation of Labile Diphenyl-4 : 4'-bisdiazocyanide in Solution.*

By D. D. BROWN, R. J. W. LE FÈVRE, and R. N. WHITEM.

The two *known* isomers of the molecule named in the title are "*cis-cis*-" and "*trans-trans*-" ; a third variety, "*cis-trans*-" should exist but is so far unknown. If the spontaneous formation of the stable from the unstable forms involved simultaneous configurational inversions, the situation would be explicable. However, the process is now found to proceed by a more complex mechanism. Whilst, in benzene solution, it appears to follow first-order kinetics with an activation energy of 26.9 kcal./g.-mol., in the polar solvents *o*-dichlorobenzene, pyridine, and nitrobenzene the reaction is not of the first order. The suggestion is therefore made that the reaction consists of two consecutive first-order inversions, with the "*cis-trans*-" compound as an intermediate. This requires the assumption that, in benzene solution, the rate of one of these inversions is not significant kinetically and that the overall change in this solvent is governed by only one of the two rates.

ON Hantzch's theories of the configuration of the -N=N- group, diphenyl-4:4'-bisdiazocyanide should exist in three isomeric forms, (I), (II), and (III) :



In fact, only two are known (Euler, *Chem. Zentr.*, 1907, i, 1572; Le Fèvre and Vine, *J.*, 1938, 1878; Anderson, Le Fèvre, and Savage, *J.*, 1947, 445). Chemical and physical evidence (Le Fèvre *et al.*) favours the view that the variety with m. p. 97—98° is *cis-cis*- (I) whilst that with m. p. 208—209° is *trans-trans*- (III).

The *cis-trans*-species (II) remains, so far, unknown, notwithstanding the experimental fact

that the spontaneous change of (I) into (III) proceeds quite slowly in the dissolved state (Le Fèvre and Vine, *loc. cit.*). In addition to the work already recorded by Le Fèvre and Northcott (this vol., p. 944) attention has therefore been directed to the kinetics of the production of (III) from (I) in a hope that indications concerning (II) might thereby be revealed.

At the outset there appeared three possibilities. These were: (a) that (I) passes directly into (III) by two simultaneous first-order reactions of equal velocities; (b) as (a) except that the velocities are unequal; and (c) that two consecutive first-order reactions ($I \xrightarrow{k_1} II \xrightarrow{k_2} III$) are involved.

Case (a), if relevant, would explain the absence of isomer (II); it requires that (I) \longrightarrow (III) should appear to be of first order. One would predict that the activation energy needed in such a process is in the region of 46 kcal./g.-mol., *i.e.*, twice that required by each separate azo-inversion.

Case (b) seemed a reasonable contingency. As soon as the isomerisation commences, the environmental (polarisation and polarisability) factors for the second $-N=N-$ cannot be exactly as before. Each azo-group will be under a varying influence, from the other end of the molecule, during the actual act of inversion. Separate molecules, however, would behave similarly and the overall rate (as observed) should still be of the "first order."

Case (c) seemed the most likely mechanism. This would require the reacting molecules to possess, at any one time, only that activation energy necessary for one azo-inversion.* If the quantity $e^{-E/RT}$ represents the probability of a molecule having energy in excess of E then the probability of a molecule having energy in excess of $2E$ will be roughly only $1/e^{40}$ of the first probability. The chance then, that a molecule will react by a consecutive mechanism would appear to be far greater than the chance of both azo-groups being inverted simultaneously.

To follow a consecutive reaction, involving three molecular species, by the variation of an additive physical property the concentrations of (I), (II), and (III) may be written in terms of A_1 , the initial concentration of (I) and the two constants k_1 and k_2 :

$$\begin{aligned}(C_I)_t &= A_1 e^{-k_1 t} \\ (C_{II})_t &= A_1 k_1 (e^{-k_1 t} - e^{-k_2 t}) / (k_2 - k_1) \\ (C_{III})_t &= A_1 [1 - (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) / (k_2 - k_1)]\end{aligned}$$

The second equation has a maximum value dependent on the ratio $r = k_2/k_1$:

$$(C_{II})_{\max.} = [A_1 r / (1 - r)] [e^{-r \ln r / (r - 1)} - e^{-\ln r (r - 1)}]$$

If the rate displaying property, X , is one which, for each solute separately in dilute solution, conforms to the equation: $X_{SI} = X_S(1 + \alpha w_1)$, where X_S refers to the solvent, X_{SI} refers to the solution of (I), and w_1 is the weight fraction of solute (I), and if the property is additive for a solution containing a mixture of the three solutes, such that:

$$X_{SI,II,III} = X_S(1 + \alpha w_1 + \beta w_2 + \delta w_3)$$

then it is obvious that, in the present problem, a graph of $X_{SI,II,III}$ against time will be, in effect, the sum of three curves: an exponential decay curve, a growth curve, and a curve with an intermediate maximum.

The interpretation of such a graph would be rather limited. If X_{SII} were much greater than X_{SI} and X_{SIII} the curve might show a maximum or points of inflection. The presence of such characteristics would constitute strong evidence for the existence of an intermediate form. In their absence, the fact that the reaction was not of the first or the second order would remain the only evidence for a consecutive mechanism. It is relevant to note here that some consecutive reactions *appear* to be first-order reactions. This occurs when $k_1 \gg k_2$ or *vice versa*, but Walker (*Proc. Roy. Soc. Edinburgh*, 1898, 22, 23), and Mellor ("Chemical Statics and Dynamics," Longmans, 1904, Chapters V and VI) quote numerical examples to show that r needs to be greater than 100 to produce a passable semblance of constancy for k (first order) over all but the early stages of the reaction.

EXPERIMENTAL.

The 4:4'-diphenylbisdiazocyanides were found to be best prepared by the following slight modification of the directions of Anderson, Le Fèvre, and Savage (*loc. cit.*). The benzidine was first purified by several recrystallisations from alcohol, then converted (5 g. in 40 c.c. of EtOH) into the dihydrochloride by adding 10N-HCl (18 c.c.) to its hot solution, and bisdiazotised (NaNO_2 , 3.9 g.; H_2O , 60 c.c.) at 5–10°. The clear resultant liquid was well stirred with chloroform, the whole cooled below –10° (carbon dioxide-alcohol), daylight excluded, and sodium cyanide (3 g. in the minimum amount of water) added. The heavy layer was then quickly separated, washed with water, and run into twice its volume of light petroleum at –30°.

The product, after rapid filtration, was dried, and stored *in vacuo* in the dark. The stable isomeride could be obtained by concentrating the filtrates after they had been kept for several days at room temperature.

Velocity measurements by the dielectric method were made difficult by the relative insolubility of the stable form causing, in most solvents, crystallisation to occur before the reaction had progressed a useful distance. To prevent this, initial concentrations were reduced, but the capacity changes were then so small that their accurate determination required apparatus with a high degree of frequency stability and temperature control. The dielectric-constant method was eventually abandoned in favour of a photometric method. For this latter method the Hilger Spekker-absorptiometer was used, the rate-displaying property being the change in the quantity of light absorbed by the solution from a narrow band of pre-selected wave-lengths. To enable a suitable light range to be chosen for each medium, spectral transmissivities of the two separate forms as solutes were first explored (see later), and of the filters supplied by the makers, those passing the band 5600—6100 Å. used with benzene and those passing 4800—6200 Å. for the other solvents.

In benzene, the maximum concentration that could be used was 0.06%. Crystallisation of the *trans-trans*-compound occurred at higher concentrations. The necessity for using such dilutions limited the accuracy of the measurements. Readings were taken by pouring 30 c.c. at a time from the main reaction flask (painted black to exclude all light) into a 4-cm. cell. The null point was observed at once, under a standard procedure, and with the shutter reset for the pure solvent before each reading. The logarithmic scale of the instrument was first calibrated for known mixtures of *cis-cis*- and *trans-trans*-forms. For benzene solutions, a linear relation was obtained between the scale reading and the concentration of *cis-cis*- in the presence of *trans-trans*-forms. Slight departures from linearity were found to exist in the calibration curves for the other solvents. Now, if at all times during the isomerisation only two molecular species were present, as would be the case in processes (a) and (b), the rate-displaying property chosen above could be used in determining the kinetics of the reaction. This would also apply to process (c) if $\nu > 100$. In the presence of a third molecular species there would be no way of relating scale reading to concentration and any attempt to obtain constant k values from either first- or second-order equations should fail. Such failure to obtain constant k values would be, in itself, evidence for a consecutive mechanism.

RESULTS.

Roughly, "half-change" times seem to be independent of the initial concentration (cf. Table I). However, despite this, in nitrobenzene (as also in pyridine or *o*-dichlorobenzene) the reaction is unlikely to be truly of the first order, since k , if appropriately evaluated for each observational time interval, is not constant (Table II): On the other hand, in benzene, the values of k , if similarly calculated, do appear almost invariant, and lead to an apparent activation energy for the change of 26.9 kcal./g.-mol. These statements are illustrated in the figure. From these facts we draw the conclusions set out in the last two sentences of the "Summary" to this paper.

TABLE I.

Solvent.	Initial concn.	Temp.	Time for $\frac{1}{2}$ change.
$C_6H_5 \cdot NO_2$	5.4 g./litre	25°	9.5 hr.
"	6.1	"	8.9 "
"	7.8	"	9.0 "
C_6H_6	0.03 wt.-%	35	3.9 "
"	0.03 "	"	3.7 "
"	0.05 "	"	4.0 "
"	0.03 "	25	18 "
"	0.05 "	25	16 "

TABLE II.

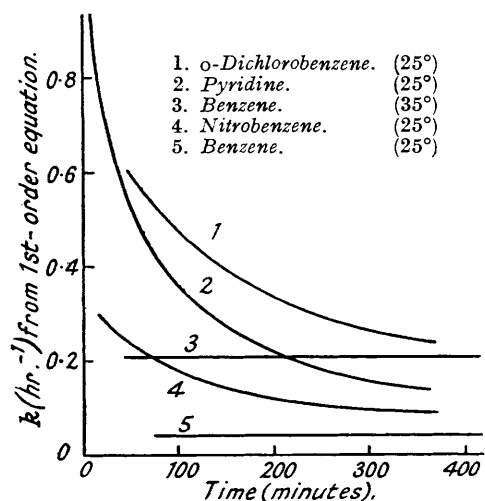
Variation of k with time.

{ k calculated from first order equation; $kt = \ln[a/(a-x)]$.

$C_6H_5 \cdot NO_2$. 25°.		Pyridine. 25°.		<i>o</i> -Dichlorobenzene. 25°.		Benzene. 35°.		Benzene. 25°.	
Time, min.	k .	Time, min.	k .	Time, min.	k .	Time, min.	k .	Time, min.	k .
16	0.300	9	0.94	22	0.49	73	0.22	122	0.041
56	0.224	44	0.55	44	0.60	200	0.19	255	0.051
74	0.208	64	0.46	75	0.53	307	0.22	301	0.048
93	0.180	87	0.39	122	0.43	370	0.21	414	0.048
143	0.151	116	0.33	209	0.33			1267	0.040
171	0.137	189	0.23	309	0.26			2960	0.039
1289	0.057	1340	0.06	1361	0.16				

Visual Absorption Spectra of the Labile and Stable Forms.—For reasons explained by Le Fèvre and Wilson (this vol., p. 1106) when reporting the ultra-violet absorption spectra of isomeric pairs of benzenediazocyanides, we took the opportunity, during the process of filter selection

(see above), to make qualitative comparisons of the absorbing properties of the two bisdiazocyanides of the present work towards visible light.



Equivalent solutions (sometimes prepared directly and sometimes by allowing complete thermal change to occur in the dark) of various concentrations in *cyclohexanone* or *nitrobenzene* were examined in the Hardy recording spectrophotometer. The wave-length range accessible covered only 4000—7000 Å., and since in no cases have the automatic traces traversed an absorption peak they are not reproduced. For each pair of solutions, however, the following facts were consistently and definitely displayed: (a) the point at which 100% absorption ceased was further towards the red end of the spectrum for the stable form; and (b) the general slope of the %-transmittance-wave-length curves was slightly steeper for the unstable form. We are satisfied, therefore, that the type and degree of spectral differences (*i.e.*, of intensity and λ_{\max}), mentioned by Le Fèvre and Wilson (*cf. also* Le Fèvre, Northcott, and Wilson, *Chem. and Ind.*, 1948, 732), occur also for the present cases. It is relevant to recall that in the solid states the

stable variety is maroon-coloured, in contrast to its isomer, which is orange (Anderson, Le Fèvre, and Savage, *J.*, 1947, 451).

Financial assistance from the Commonwealth Science Fund is gratefully acknowledged.

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[Received, July 27th, 1949.]