77. The Configurations of α- and β-Naphthalenediazocyanides and Other Unsubstituted Hydrocarbondiazocyanides.

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The dipole moments of the four known forms corresponding to the formula $C_{10}H_7 \cdot N:N \cdot CN$ are explicable if the substances are *cis-* or *trans-* α- or -β-naphthalenediazocyanides. The phenyl and *p*-tolyl analogues, which are homogeneous oils at ordinary temperatures, have properties which indicate that the *trans*-configurations largely predominate. Photochemical and thermal transformations of the six substances now studied are parallel to those previously recorded for substituted benzenediazocyanides and the azobenzenes.

In earlier work (Le Fèvre and Vine, *J.*, 1938, 431, 1878; Anderson, Le Fèvre, and Savage, *J.*, 1947, 445; Anderson, Bedwell, and Le Fèvre, *ibid.*, p. 457) studies were made of various halogeno- and nitro-derivatives of benzenediazocyanide. The measurements now to be recorded deal with *unsubstituted* hydrocarbondiazocyanides—a class for which dipole-moment data are wholly lacking.

On Hantzsch's hypothesis (for summary see " Die Diazo-verbindungen ", 1921) that isomeric diazocyanides are configurationally related as *cis-trans*-cyanides it is easy to see *a priori* that the moments of the *trans*-forms (I) should exceed those of the *cis*-forms (II). The dotted

(I.)   (II.)

arrows indicate the component vectors found to lead to consistent analyses of Le Fèvre and Vine's results (*loc. cit.*). Hence at the outset we anticipated moment differences of 2—3 D. units.

The choice of materials for study is limited by the fact that only a few unsubstituted diazocyanides have been *separated* into two forms. The simpler monocyclic members, *e.g.*, the phenyl and the *p*-tolyl member, exist as oils at ordinary temperatures and—by analogy with molten *cis*-azobenzene (Hartley, *J.*, 1938, 633)—one should expect thermal change to proceed rapidly, giving in each case the more stable isomer. The moments and other properties now observed for these preparations are compatible with their having mainly *trans*-configurations. In the action of light they resemble *trans*-azobenzene and other pure stable diazocyanides.

All four isomeric varieties of the α- and β-naphthalene diazocyanides are solids (Danziger and Hantzsch, *Ber.*, 1897, **30**, 2545). Their moments are :

	α-Naphthalene.	β-Naphthalene.
Stable diazocyanide	5·6	6·9
Unstable diazocyanide	3·2	4·0

These data support the allocation of *cis*-configurations to the unstable, and *trans*- to the stable, forms.

It has further been found that, in the absence of light, each unstable variety in benzene solution passes spontaneously into the stable isomer. The reactions can easily be followed by changes in E and seem to be kinetically of the first order. From the velocity constants at 25° and 45°, the energy of activation, $E = \log_e(k_2/k_1)\mathbf{R}T_1T_2/(T_2 - T_1)$, of the two inversions appears to be approximately the same, *viz.*, 23 kcals./g.-mol. :

Naphthalene-diazocyanide.	T, °K.	Half-change period, hrs.	k (hr.$^{-1}$).	E (kcals./g.-mol.).
α-	$\begin{cases} 298 \\ 318 \end{cases}$	3·1 0·26	$\left. \begin{matrix} 0·224 \\ 2·568 \end{matrix} \right\}$	22·9
β-	$\begin{cases} 298 \\ 318 \end{cases}$	4·3 0·36	$\left. \begin{matrix} 0·165 \\ 1·926 \end{matrix} \right\}$	23·1

This value is closer to the average reported for the analogous transformations of *cis*- into *trans*-azobenzene and its derivatives (*i.e.*, 23 kcals./g.-mol., Hartley, *loc. cit.*) than for the *p*-halogenobenzenediazocyanides (*p*-chloro-, 21·4; *p*-bromo-, 21·6, kcals./g.-mol.; Le Fèvre and Northcott, unpublished; Le Fèvre and Vine, *loc. cit.*).

In daylight the above thermal change is affected by a photochemical one. In the experimental part we record observations which demonstrate the photo-formation of *cis*- from *trans*-isomers and their reversion to the more stable forms in the dark.

The parallelism between these diazocyanides and those studied previously (*loc. cit.*), as well as with the two azobenzenes (Hartley and Le Fèvre, *J.*, 1939, 531), seems thus quite clear. Where the same type of experimental observation has been made, the appropriate arguments of Anderson, Le Fèvre, and Savage (*loc. cit.*) are applicable; *e.g.*, in particular, not only the dipole moments but also the densities and molecular refractions are consistent with Hantzsch's configurations. Were these hydrocarbondiazocyanides related as (both *trans*) cyanides and *iso*cyanides (Hodgson and Marsden, *J.*, 1944, 395), known analogies suggest that the moments should be nearly equal, while the molecular refractions should differ in the *opposite* manner to that now found. For a summary of our case for the (Hantzsch) configurational theory, see Calderbank, Le Fèvre, Northcott, and Wilson (*Chem. and Ind.*, 1948, **67**, 158, 543, 732, 782).

EXPERIMENTAL.

Preparation of Materials.—Benzenediazocyanide. Aniline (3·8 g.), dissolved in dilute hydrochloric acid (30 c.c., 1 : 1), was diazotised (sodium nitrite, 2·8 g. in the minimum of water) at 0°, alcohol (10 c.c.) then added, followed by ether (7 c.c.) and light petroleum (8 c.c.), and the whole cooled to −10°. The mixture was stirred to a coarse emulsion while sodium cyanide (2·5 g. in the minimum of water) was run in dropwise. The upper layer (pale yellow) was then separated as rapidly as possible, dried (Na$_2$SO$_4$), and evaporated in a vacuum. The diazocyanide (1·1 g.) remained as a yellow oil which darkened on exposure to sunlight and, if not preserved in a desiccator, decomposed in a few days to a black tar.

p-Toluenediazocyanide. This was prepared similarly from *p*-toluidine (2·2 g.), diluted hydrochloric acid (20 c.c.), sodium nitrite (1·4 g.), alcohol (10 c.c.), ether (15 c.c.), and sodium cyanide (1·2 g.). The diazocyanide (0·5 g.) was also a yellow oil, but deeper in colour than the parent substance.

α- and β-Naphthalenediazocyanides. These were similarly obtained by immediate extraction : The base (5 g.) was dissolved in alcohol (35 c.c.) and water (28 c.c.), and concentrated hydrochloric acid (10 c.c.) added, followed by sodium nitrite (3 g.) at 10°. The filtered diazo-solution, plus sodium acetate (0·25 g.) and chloroform (25 c.c.), was treated slowly and under vigorous shaking with sodium cyanide (4 g., in water, 10 c.c.). The heavy layers, after separation and drying (Na$_2$SO$_4$) gave the labile diazocyanides, as deep orange needles, on cooling to *ca.* −30° in solid carbon dioxide–alcohol. The specimens were dried in a vacuum desiccator (CaCl$_2$). The stable forms were obtained by heating a chloroform solution of the appropriate labile isomeride to 40—50° for 15 minutes and then recrystallising from the same solvent by cooling strongly.

The m. p.s observed were as follows, those recorded by Danziger and Hantzsch (*loc. cit.*) being added in parentheses :

cis-α-Naphthalenediazocyanide	57° (57—58°)	*cis*-β-Naphthalenediazocyanide	52° (51—52°)
trans-α-Naphthalenediazocyanide	117·5° (116°)	*trans*-β-Naphthalenediazocyanide	132·5° (131°)

During each of the six preparations above, from the addition of aqueous cyanide onwards, all operations were conducted in the absence of light.

Apparatus and Technique.—Various quartz oscillator circuits, all essentially of the types previously described (*J.*, 1948, 1949), have been used. One of these, constructed for the observations at 45°, where only readings of capacity change with time were required, had a variable radio-condenser (0·0005 μ F.) and a small micrometer condenser (2—8 μμF. range, copied from Groves, *J.*, 1938, 1144), mounted and connected in parallel under the chassis. The desired readings were conveniently taken on the protruding micrometer head. During the course of the work, glass cells (see Le Fèvre, " Dipole Moments ", Methuen, 1935, p. 32) were replaced by concentric brass tubular condensers, and liquid paraffin, dyed a deep red (with Waxoline Red E.P.S.), adopted as a thermostat liquid instead of water.

The brass tubes were mounted in a glass envelope after the manner illustrated by Higasi (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1934, **24**, 57) except that we deliberately made the length/diameter ratio larger (*ca.* 10 : 1). These alterations have proved especially advantageous during prolonged "rate" determinations, which were formerly liable to spoliation by the slow deterioration of the silver layers. In other respects we have followed routine practice (Le Fèvre, *op. cit.*, p. 35; *J.*, 1937, 1805).

Dielectric-polarisation Data.—These are tabulated below together with indications of the conditions under which they were obtained. The symbols used denote the following quantities : w weight fraction, ϵ dielectric constant ($\lambda = 300$ m.), d_4^{r} density, and p specific polarisation. Subscripts 1 and 2 refer to solute and solvent, respectively. $_\infty P_T$ indicates the total polarisation of a solute at infinite dilution. The extrapolation is made by calculation, assuming that the densities and dielectric constants of a series of solutions have rectilinear dependence on the concentration, *i.e.*, $d_{12} = d_2(1 + \beta w_1)$ and $\epsilon_{12} = \epsilon_2 (1 + aw_1)$. The approximate constancy of the quantities $a\epsilon_2$ and βd_2 justifies this treatment in the present instances. The specific polarisations at infinite dilution are obtained as $p_2(1 - \beta) + Ca\epsilon_2$, where $p_2 = (\epsilon_2 - 1)/(\epsilon_2 + 2)d_2$ and $C = 3/d_2(\epsilon_2 + 2)^2$; $_\infty P_T$ is given by $M_1 \times (p_1)_{w_1} = 0$. Benzene is used as solvent throughout. The values of C and p_2 are :

Temp.	25°.	27°.	30°.
C	0·1881	0·1890	0·1901
p_2	0·3409	0·3413	0·3416

Benzenediazocyanide.

$100w_1$.	$\epsilon^{25°}$.	$d_4^{25°}$.	$a\epsilon_2$.	β.	$100w_1$.	$\epsilon^{25°}$.	$d_4^{25°}$.	$a\epsilon_2$.	β.
0	2·2725	0·87378	—	—	—	—	—	—	—

(A) Freshly prepared specimens dissolved soon after isolation, under ordinary laboratory daylight :

0·5859	2·3976	0·87507	21·35	0·252	1·1829	2·5251	0·87643	21·35	0·256

(B) Above solutions exposed to sunlight in clear glass flasks for about 0·5 hour and immediately remeasured :

0·5859	2·3682	—	16·33	—	1·1829	2·4733	—	17·00	(0·26)

(C) Solutions from (B) then stored in the dark in amber glass bottles and remeasured after 4 hours with the greatest possible exclusion of light :

0·5859	2·3974	—	21·31	—	1·1829	2·5250	—	21·43	(0·26)

p-*Toluenediazocyanide.*

The same sequence of experiments was followed as above (bath temp. 25°).

(A)
0·7859	2·3700	0·87580	12·4	0·294	0·9107	2·3745	0·87621	11·2	0·305
0·9076	2·4113	0·87613	15·3	0·297					

(B)
0·7859	2·3574	—	10·8	—	0·9107	2·3705	—	10·8	(0·3)
0·9076	2·3619	—	9·9	—					

(C) After 10 hours in the dark :

0·7859	2·3928	—	15·3	—	0·9107	2·4114	—	15·25	(0·3)
0·9076	2·4113	—	15·3	—					

α-*Naphthalenediazocyanides.*

(A) Solutions of the pure labile form made up in brown glass bottles and handled with the maximum exclusion of light (bath temp. 27°).

$100w_1$.	$\epsilon^{27°}$.	$d_4^{27°}$.	$a\epsilon_2$.	β.	$100w_1$.	$\epsilon^{27°}$.	$d_4^{27°}$.	$a\epsilon_2$.	β.
0	2·2685	0·87130	—	—	0·7386	2·3187	—	6·80	—
0·4893	2·3015	0·87258	6·74	0·301	0·7912	2·3222	0·87338	6·78	0·302
0·5062	2·3029	0·87267	6·80	0·310					

(B) As in (A) but with the stable form :

0·4928	2·3638	0·87254	19·34	0·289	0·8027	2·4242	0·87331	19·40	0·287
0·6892	2·4015	0·87301	19·30	0·285	1·0252	2·4668	0·87386	19·34	0·285

(C) As in (B) but at 30° :

0	2·2628	0·86848	—	—	1·1630	2·4873	0·87139	19·3	0·289
0·6507	2·3897	0·87007	19·5	0·288					

(D) Solutions of $100w_1 = 0·8027$ and $1·0252$ from series (B), above, were remeasured after exposure to sunlight in clear glass flasks for 0·5 hour, and then again after being stored in the dark for two days :

$100w_1$.	$\epsilon_{initial}$.	$a\epsilon_2$.	$\epsilon_{exposed}$.	$a\epsilon_2$.	ϵ_{final}.	$a\epsilon_2$.
0·8027	2·4242	19·4	2·3907	15·2	2·4232	19·3
1·0252	2·4668	19·3	2·4179	14·6	2·4658	19·2

β-Naphthalenediazocyanides.

(A) As for the α-compound (A), except that bath temperature was 25° :

$100w_1$.	$\epsilon^{25°}$.	$d_{4°}^{25°}$.	$\alpha\epsilon_2$.	β.	$100w_1$.	$\epsilon^{25°}$.	$d_{4°}^{25°}$.	$\alpha\epsilon_2$.	β.
0	0·2725	0·87378	—	—	0·2148	2·2946	0·87448	10·29	0·373
0·1116	2·2843	0·87417	10·60	0·400	0·3853	2·3240	0·87506	—·	0·380
0·1947	2·2930	0·87446	10·52	0·400					

(B) As for the α-compound (B), but at 25° :

0·2490	2·3447	0·87454	29·0	0·349	0·4821	2·4129	0·87529	29·8	0·358
0·2635	2·3583	0·87459	29·0	0·358	0·4855	2·4162	0·87526	29·6	0·348
0·3795	2·3859	0·87495	29·9	0·352	0·7569	2·5013	0·87616	—	0·360

Molecular Refractions of the Isomeric Naphthalenediazocyanides.—These were determined in chlorobenzene solutions at concentrations of 1—2%, with an Abbé refractometer (temp., 25°).

$100w_1$.	$d_{4°}^{25}$.	$n_D^{25°}$.	r_{12} (c.c.).	$[R_L]_D$ (c.c.).	$100w_1$.	$d_{4°}^{25°}$.	$n_D^{25°}$.	r_{12} (c.c.).	$[R_L]_D$ (c.c.).
0	1·1015	1·5252	0·36203	—	—	—	—	—	—

α-Naphthalenediazocyanide (*stable form*)					α-Naphthalenediazocyanide (*labile form*)				
1·7512	1·1081	1·5294	0·36193	64·5	1·8789	1·1091	1·5290	0·36166	62·0

β-Naphthalenediazocyanide (*stable form*)					β-Naphthalenediazocyanide (*labile form*)				
2·0694	1·1107	1·5312	0·36195	64·9	1·9481	1·11075	1·5310	0·36173	62·8

The molecular refractions for the benzene- and toluene-diazocyanides have been calculated from previous determinations on p-bromobenzenediazocyanide (52·8 c.c.; Le Fèvre and Vine, *loc. cit.*) by deducting 8·9 c.c. for Br and adding 1·1 or 5·7 for H or CH_3, respectively.

Apparent Dipole Moments from Above Data.—These are given in the last column of the following table.

Diazocyanide.	Ref. to tables.	Mean $\alpha\epsilon_2$.	Mean β.	M.	$_\infty P_T$.	$[R_L]_D$.	μ, D.
Benzene-	A	21·35	0·254	131·1	560	45	5·0
,, ...	B	16·7	(0·26) *	,,	445	,,	4·4
,, ...	C	21·37	(0·26) *	,,	560	,,	5·0
p-Toluene-	A	*ca.* 13	0·299	145·1	389	50	4·05
,, ...	B	10·5	(0·3) *	,,	321	,,	3·6
,, ...	C	15·3	(0·3) *	,,	452	,,	4·4
α-Naphthalene-	A	6·78	0·304	181·1	275	62·0	3·2
,, ...	B	19·35	0·287	,,	706	64·5	5·6
,, ...	C	19·4	0·288	,,	712	64·5	5·6
β-Naphthalene-	A	10·47	0·388	,,	394	62·8	4·0
,, ...	B	29·46	0·354	,,	1043	65·0	6·9

* Maximum estimates.

Discussion.—The significant points demonstrated by the above figures are that, when dissolved in benzene : (*a*) benzenediazocyanide is probably a single form with a *trans*-configuration, since its observed moment (5·0 D.) falls to 4·4 D. on sunlight illumination, but is restored after a few hours when this is terminated; (*b*) p-toluenediazocyanide as prepared contains some *cis*-isomer, since its moment (4·05 D.) falls to 3·6 D. in daylight, and rises again to 4·4 D. on standing in the dark (4·4 D. is presumably the moment of the *trans*-form); (*c*) the moments of the pairs of α- (3·2 and 5·6 D.) and β- (4·0 and 6·9 D.) naphthalenediazocyanides differ by 2—3 D., as expected, the higher value in each case belonging to the *trans*-isomer; and (*d*) *trans*-α-naphthalenediazocyanide by irradiation (sunlight) acquires an apparent moment of 4·9 D., corresponding to a *cis*-content of approximately 35% (evaluated by applying a mixture law to μ_{cis}^2 and μ_{trans}^2), which reverts to 5·6 D. (100% *trans*) in the absence of light. The opposing effects of the photochemical (*trans* ⟶ *cis*) and the dark thermal (*cis* ⟶ *trans*) reactions are thus qualitatively demonstrated. For comparison it may be noted that benzene solutions of p-bromobenzenediazocyanide and azobenzene have been found to contain 20% and 22% respectively of the *cis*-forms at equilibrium in sunlight (Le Fèvre and Vine; Hartley; *locc. cit.*; Hartley and Le Fèvre, *J.*, 1939, 531). Section (A) of p-toluenediazocyanide suggests that the undiluted cyanide undergoes photo-inversion more readily than its benzene analogue, since the order in which the three solutions are made up seems to determine the magnitude of $\alpha\epsilon_2$, those

prepared first from a given batch having the highest values and *vice versa*. After irradiation, etc., these differences disappear (sections B and C).