91. *Magnetic Optical Rotatory Powers and Diamagnetic Susceptibilities of the Isomeric Aromatic Diazocyanides.*

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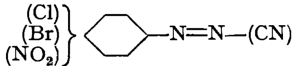
The above properties have been examined, respectively, in solution and in the solid state, for the isomeric pairs of *p*-chloro-, *p*-bromo-, and *p*-nitro-benzenediazocyanides, together with the two known forms of 4 : 4′-diphenylbisdiazocyanide.

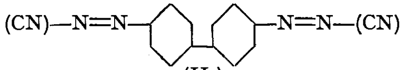
The results agree more closely with expectations based on a geometrical (*cis–trans*-cyanide) relationship (Hantzsch) than with those on a structural (*iso*cyanide–cyanide) relationship (Orton ; Hodgson and Marsden).

RECENTLY (this vol., p. 445) Anderson, Le Fèvre, and Savage discussed the structures of the isomeric aromatic diazocyanides, deciding that they were better represented as pairs of cyanides having a *cis–trans*-relationship, than as *iso*cyanides and cyanides (both *trans*), respectively ; *i.e.*, the "classical" explanation of Hantzsch was preferred to the later one of Orton and of Hodgson and Marsden (see above).

To the evidence previously considered we now add that obtained by an examination of the magnetic optical rotating powers in benzene solution, and the diamagnetic susceptibilities in the solid state, of the eight compounds corresponding to the formulæ (I) and (II).



(I.)



(II.)

At the outset, data, from which we might argue by analogy, showing the direction or degree of difference in these properties likely to be caused by the change of $R-C\equiv N$ into $R-\overset{+}{N}\equiv\overset{-}{C}$, did not appear to be available in the literature. Fortunately, however, methods by which they could be deduced *a priori* had been described. We therefore have used these and compared our experimental observations with the results.

Magnetic Optical Rotatory Powers.—Becquerel (*Compt. rend.*, 1897, **125**, 679) has shown that the magneto-rotatory power, θ, of a substance is connected *inter alia* with its refractive index, *n*. His conclusions can be written (Bhatnagar and Mathur, "Physical Principles and Applications of Magneto Chemistry") in the form

$$\theta = \frac{l\lambda He}{2mc}\cdot\frac{dn}{d\lambda}$$

where *H* is the field, λ the wave-length of the light used, *l* the optical path thickness through the material, **c** the velocity of light, and **e** and **m** the electronic charge and mass respectively.

Accordingly, for a given λ, and otherwise unaltered experimental conditions, the θ values for two isomers will differ if their d*n*/dλ coefficients differ ; further, the relative magnitudes of the θ's will also follow. For the present enquiry, therefore, the refractive indices recorded by von Auwers (*Ber.*, 1927, **60**, 2122) are relevant. In Table I we have listed appropriate data, from which it is clear that d*n*/dλ for an *iso*cyanide is greater than for the corresponding cyanide. At equivalent concentrations, therefore, the magnetic rotations of solutions of the isomeric diazocyanides should display inequalities in the same sense *if* the unstable and stable forms differ only in being *iso*- and normal cyanides.

TABLE I.

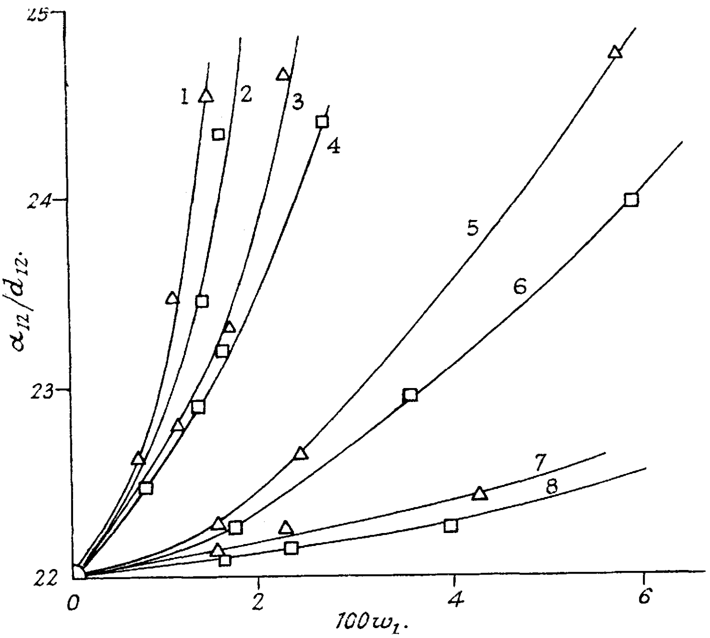
Substance.	*t*.	$n^{t°}_{\alpha}$.	$n^{t°}_{\beta}$.	$n^{t°}_{\gamma}$.	$n^{t°}_{\gamma} - n^{t°}_{\alpha}$.	$n^{t°}_{\beta} - n^{t°}_{\alpha}$.
Me·NC	17·9°	1·34186	—	1·35326	0·01140	—
Et·NC	17·6	1·36124	—	1·37275	0·01151	—
C_6H_5·NC	18·1	1·52240	1·54207	—	—	0·01967
Me·CN	21·9	1·34008	—	1·34943	0·00935	—
Et·CN	21·8	1·36182	—	1·37185	0·01003	—
C_6H_5·CN	25·5 *	1·52035	1·53942	—	—	0·01907

* Data from Landolt–Börnstein "Tabellen".

Fig. 1 has been drawn from the measurements recorded in Table III. It will be seen that for all four cases studied the magnetic rotation of the stable form is *higher* than that of the unstable. The suggestion that the latter series are *iso*cyanides is therefore disfavoured.

Since, however, in general, among authentic geometrical pairs, θ_{trans} is greater than θ_{cis} (*e.g.*, the molecular magneto-optic rotations of ethyl fumarate and maleate are 10·1 and 9·6; Perkin, *J.*, 1896, **69**, 1236), our measurements would be in harmony with the original relationship proposed by Hantzsch, based on geometrical isomerism, in which *all* the forms contain cyanide groups.

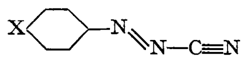
FIG. 1.



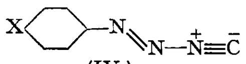
Magneto-optic rotation of the isomeric diazocyanides in benzene solution.

1. trans-p-*Nitrobenzenediazocyanide.*
2. cis-p-*Nitrobenzenediazocyanide.*
3. trans-p-*Chlorobenzenediazocyanide.*
4. cis-p-*Chlorobenzenediazocyanide.*
5. trans-p-*Bromobenzenediazocyanide.*
6. cis-p-*Bromobenzenediazocyanide.*
7. *Stable form of* 4 : 4′-*diphenylbisdiazocyanide.*
8. *Labile form of* 4 : 4′-*diphenylbisdiazocyanide.*

Diamagnetic Susceptibilities.—The "experimental molecular standards" for the two structures (III) and (IV) (X = Cl, Br, or NO_2) have been estimated by the method described



(III.)



(IV.)

by Gray and Cruikshank (*Trans. Faraday Soc.*, 1935, **31**, 1491). This requires a deduction of the "theoretical molecular standards" from figures for the constituent atoms (Pauling, *Proc. Roy. Soc.*, 1927, **114**, 181), account being taken of the residual charges due to the unequal sharing of bond electrons (Sidgwick, "The Covalent Link in Chemistry," Cornell Univ. Press), followed by a correcting subtraction for the depressions of diamagnetism (Gray and Cruikshank, *loc. cit.*) which occur on bond formation. "Experimental molecular standards" result; *i.e.*, Exptl. mol. std. = Theor. mol. std.—Σ Bond depressions. These are the quantities which could be expected from practical measurements, were the actual structures initially assumed truly present. In Table II our experimental observations are compared with the results of calculation.

The results indicate that the stable and the unstable form of each compound are unlikely to be related as cyanide and *iso*cyanide respectively. In every case the unstable form is seen to have only a slightly higher susceptibility than the stable form. This is not incompatible with a *cis–trans*-relationship, Bhatnagar, Mathur, and Nevgi (*Z. Physik*, 1931, **69**, 373) having found *e.g.*, that maleic and fumaric acids have about the same order of difference (maleic acid. $-\chi_M \times 10^6 = 49{\cdot}71$; fumaric acid, $-\chi_M \times 10^6 = 49{\cdot}11$).

TABLE II.

Diazocyanide.	Theor. mol. std. Structure. (III).	Theor. mol. std. Structure. (IV).	Bond depression. Structure. (III).	Bond depression. Structure. (IV).	" Corr. mol. std." (G. and C.). Structure. (III).	" Corr. mol. std." (G. and C.). Structure. (IV).	Expt. mol. diam. (obs.). Unstable form.	Expt. mol. diam. (obs.). Stable form.
Chlorobenzene	125·17	127·14	58·55	65·17	66·62	61·97	65·81	65·02
Bromobenzene	148·07	150·04	59·22	65·84	88·85	84·20	87·46	86·88
Nitrobenzene	136·98	138·95	75·64	82·26	61·34	56·67	59·90	59·22
Diphenylbis	206·96	210·90	118·92	132·16	88·04	78·74	86·89	85·03

Basic data for the constituent groups :

Group.	Theor. mol. std.	Bond depression.	" Exptl. mol. std."
$C{-}Cl$	31·23	0·08, calc. from CH_3Cl by Gray and Cruikshank's method	31·15
$C{-}Br$	54·11	0·75, calc. from CH_3Br by Gray and Cruikshank's method	53·36
$N{-}N$	16·56	2·13, by analogy, from $C{-}C$, $N{-}H$, $C{-}H$	14·43
$N{=}N$	16·56	12·85, by analogy, from $C{=}O$, $N{=}O$, $C{=}C$	4·71
$C{-}NO_2$	43·02	16·20	26·82
C_6H_4	61·81	37·62	24·19
$C{-}N{=}N{-}C{\equiv}N$ ...	32·15	21·91	10·24
$C{-}N{=}N{-}\overset{+}{N}{\equiv}\overset{-}{C}$ ...	34·10	27·17	6·93

Method of calculation (*e.g.*, for C_6H_4) :

$$\begin{array}{lll} \text{C} & \left.\begin{array}{l} 6 \times 0{\cdot}04 \times 14{\cdot}69 \\ 6 \times 0{\cdot}96 \times 8{\cdot}60 \end{array}\right\} & 53{\cdot}08 \\ \text{H} & \left.\begin{array}{l} 4 \times 0{\cdot}04 \times 0 \\ 4 \times 0{\cdot}96 \times 2{\cdot}273 \end{array}\right\} & 8{\cdot}73 \\ & \therefore \text{ Theor. mol. std. } (C_6H_4) & \underline{\overline{61{\cdot}81}} \end{array}$$

$$\begin{array}{lr} \text{Bond depressions } 3C{=}C \ldots & 28{\cdot}5 \\ 3C{-}C \ldots & 5{\cdot}94 \\ 6C{-}H \ldots & 3{\cdot}18 \\ \therefore \text{ Bond depressions } (C_6H_4) \ldots & \overline{37{\cdot}62} \\ \therefore \text{ `` Expt. mol. std.'' } \ldots & \underline{\overline{24{\cdot}19}} \end{array}$$

EXPERIMENTAL.

Measurement of Magneto-optic Rotations.—The apparatus was based on that used by Roger and Watson (*Proc. Roy. Soc.*, 1895, *A*, **58**, 234; *Phil. Trans.*, 1895, **186**, 654) and Bhatnagar, Mathur, and Jain (*Ind. J. Physics*, 1930, **4**, 503), in which the field was produced within a solenoid. The latter was wound on a brass former, and the ends of the polarimeter tube were fitted with aluminium friction-tight rings which slid easily inside, thus providing a centring device. A brass pin projecting from the inner wall ensured that the tube could always be replaced in the region of uniform field towards the centre of the solenoid (Fig. 2). The coil was supported by square end-plates standing in grooves along which it could be slid laterally to allow withdrawal of the polarimeter tube.

The field inside the solenoid, ascertained by means of a search coil, was found to be reproducibly fixed at 3880 gauss by always adjusting the current in *A* to read 15 amps. All measurements were conducted in benzene solution at 25°.

The results are shown in Table III. w_1 is the weight fraction of the solute in each solution, and d_{12} and a_{12} are respectively the density and rotation.

TABLE III.

$100\,w_1$.	$(d_{12})^{25°}_{4°}$.	a_{12}.	a_{12}/d_{12}.
0	0·87255	19·2	22·01
cis-p-*Nitrobenzenediazocyanide.*			
0·7820	0·87641	19·7	22·48
1·437	0·87834	20·6	23·46
1·603	0·87879	21·4	24·35
trans-p-*Nitrobenzenediazocyanide.*			
0·7710	0·87516	19·8	22·62
1·1470	0·87734	20·6	23·48
1·5260	0·87855	21·6	24·59
cis-p-*Chlorobenzenediazocyanide.*			
1·385	0·87770	20·1	22·9
1·821	0·87895	20·4	23·2
2·555	0·88099	21·5	24·4
trans-p-*Chlorobenzenediazocyanide.*			
1·154	0·87704	20·0	22·80
1·734	0·87876	20·5	23·33
2·338	0·88047	21·7	24·65

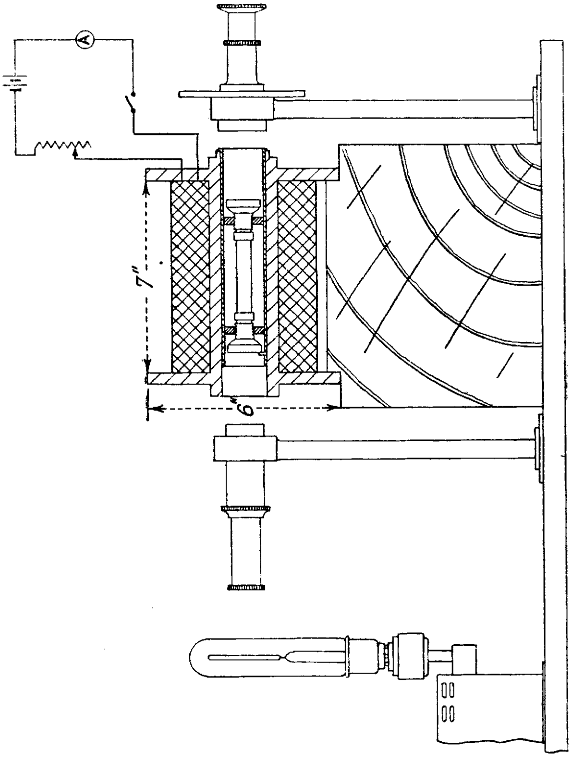
$100\,w_1$.	$(d_{12})^{25°}_{4°}$.	a_{12}.	a_{12}/d_{12}.
cis-p-*Bromobenzenediazocyanide.*			
1·735	0·88136	19·6	22·24
3·601	0·88878	20·4	22·95
5·898	0·89699	21·5	23·96
trans-p-*Bromobenzenediazocyanide.*			
1·597	0·88021	19·6	22·27
2·466	0·88346	20·0	22·63
5·847	0·89754	22·2	24·74
Unstable p-*diphenyldiazocyanide.*			
1·606	0·87804	19·4	22·08
2·304	0·88043	19·5	22·12
4·003	0·88604	19·7	22·24
Stable p-*diphenyldiazocyanide.*			
1·581	0·87839	19·4	22·09
2·264	0·88081	19·6	22·25
4·299	0·88831	19·9	22·41

Measurement of Magnetic Susceptibility.—The modified Gouy method of measurement was employed (*Compt. rend.*, 1889, **109**, 935; Trew and Watkins, *Trans. Faraday Soc.*, 1933, **30**, 1310; Angus and Hill, *ibid.*, 1943, **39**, 185), a field of 10,000 gauss being used and a pole gap of 2·0 cm. with a current of 12 amps. at 220 volts D.C. Sensible heating of the coils did not occur during the course of experiments. In order to prevent damage by the initial surge of current when contact was made or broken, the circuit included a voltage limiting resistance and a d. p. contactor, which were on a switchboard remote from the Gouy balance. The d. p. contactor was operated by a pole-switch on the balance table.

The field was measured by means of a Grassot fluxmeter and search coil, but the balance constant was determined by measurements on a column of pure acetone.

All measurements were made at 20°. The molar susceptibilities were calculated from the expressions $\chi_M = M \times \chi_S$ and $10^6 \chi_S = (\alpha F + 0\cdot0294V)/W$, where χ_M and χ_S are the molar and specific susceptibilities, M is the molecular weight of the substance, α the balance constant, F the pull on the substance due to the magnetic field, V the volume of the column of the substance (equal to the volume of acetone used in calibration), and W the weight of the substance employed.

FIG. 2.



The susceptibility of acetone was taken to be $\chi_{\text{acetone}} = -0\cdot5866 \times 10^{-6}$ (French and Trew, *Trans. Faraday Soc.*, 1945, **41**, 442).

The results are shown in Table II.

Preparation of Diazocyanides.—By the following modification of the directions of Le Fèvre and Vine (*J.*, 1938, 431, 1878) greatly improved specimens of unstable forms are obtained: The amine (0·1 mol.) in concentrated hydrochloric acid (45 c.c.) and water (45 c.c.) is diazotised (sodium nitrite, 6·9 g.; water, 50 c.c.). The filtered solution, plus alcohol (50 c.c.), is cooled to −25° (EtOH–CO_2), and stirred almost to an emulsion with light petroleum (b. p. 40—60°; 200 c.c.) under careful exclusion of light. Potassium cyanide (13 g.) in water (50 c.c.) is then added dropwise. Stirring is continued while the mixture warms to 0°. The hydrocarbon layer is separated, dried (Na_2SO_4), and cooled in the dark to −30°. Rapid filtration (dry air), followed by storage at 0° in an opaque vacuum desiccator, then provides, without further purification, materials with m. p.s as high as ever previously recorded (yields *ca.* 0·025 mol.). From the mother-liquor, stable forms are obtained by concentration at the b. p., followed by cooling, etc.

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