442. *The Probable Existence of Geometrically Isomeric Diazocarboxyamides.*

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The dipole moment of the one known form of benzenediazocarboxyamide is 3·9 D., a value which is consistent with a *trans*-configuration about the azo-group. After exposure to sunlight, solutions in benzene show signs of a slight increase of solute polarity; parallel experiments with ethanol solutions give spectrophotometric indications similar to those previously observed with diazocyanides and various other N : N-containing molecules. The fact that geometrical isomers of the structure, $R{\cdot}N{:}N{\cdot}CO{\cdot}NH_2$, have not so far been actually isolated cannot therefore be taken as contrary to the views of Hantzsch.

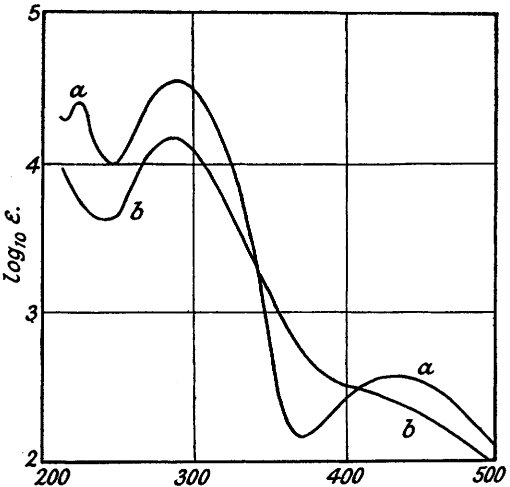
DURING the relevant researches of Hantzsch, beginning about half a century ago (see Saunders, " The Aromatic Diazo-Compounds and Their Technical Applications," 2nd edn., Arnold and Co., London, 1948, Chap. XI, for references) isomers of types generalisable as R–N:N–X were successfully isolated only when X was O–Metal (diazoates), CN (diazocyanides), or $SO_2{\cdot}O$–Metal (diazosulphonates). All other diazo-derivatives seemed to occur as single forms, a fact which, while not opposed, was unhelpful to Hantzsch's stereochemical ideas concerning the –N:N– group. The discovery of a second and more polar variety of azobenzene (Hartley, *J.*, 1938, 633; Hartley and Le Fèvre, *J.*, 1939, 531) and of a similar multiplicity of other azoaryl compounds (Cook and Jones, *J.*, 1939, 1309) has therefore been a particularly important step in the modern development of the subject (cf. Hodgson, *J.*, 1948, 1097; Le Fèvre and Souter, *J.*, 1949, 1595), while recently Le Fèvre and Worth (*J.*, 1951, 1814) have reported indications that 2 : 2′-azopyridine exists as more than one form. Accordingly a re-examination is now in hand of certain cases, notably diazocarboxyamides, diazoamino-compounds, diazo-ethers, and diazo-sulphones, where Hantzsch found no isomerism.

This paper records experiments showing that aryldiazocarboxyamides undergo changes by the action of light which parallel in essential respects those previously described for a number of diazocyanides and diazosulphonates, for azobenzene, and for 2 : 2′-azopyridine (cf. Calderbank, Le Fèvre, and Northcott, *Chem. and Ind.*, 1948, 158; Le Fèvre, Northcott, and Wilson, *ibid.*, p. 732; Freeman and Le Fèvre, *J.*, 1950, 415; Le Fèvre and Worth, *loc. cit.*).

Three diazocarboxyamides, $\mathrm{R{\cdot}N{:}N{\cdot}CO{\cdot}NH_2}$, have been prepared with R = Ph, p-$\mathrm{Br{\cdot}C_6H_4}$, and p-$\mathrm{NO_2{\cdot}C_6H_4}$. All were sparingly soluble in non-polar solvents, the first-named being least so. By using concentrations up to saturation (which seemed to be about 0·45% at 25°) in benzene, we have estimated the dipole moment of $\mathrm{C_6H_5{\cdot}N{:}N{\cdot}CO{\cdot}NH_2}$ as 3·9 D., when measurements were made in the absence of daylight. One hour's exposure to the sun caused slight increases in the solute polarity. Interpretation of these results might have been assisted by corresponding data for the p-$\mathrm{Br{\cdot}C_6H_4}$-compound but unfortunately the maximum w_1 achieved at 30° was less than 0·08%.

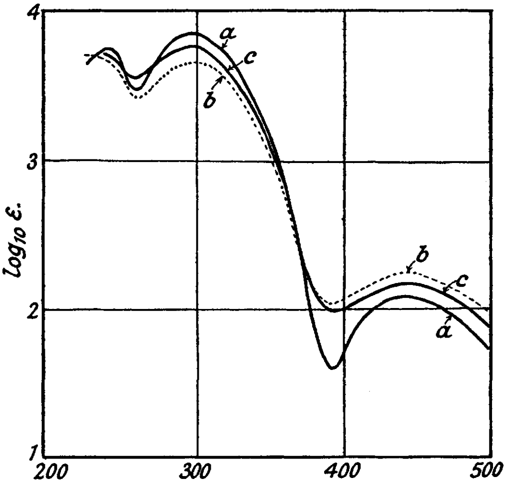
Two comments seem justifiable : (*a*) In a *trans*-configuration of $\mathrm{R{\cdot}N{:}N{\cdot}CO{\cdot}NH_2}$ the two $\mathrm{C \longrightarrow N}$ moments associated with the azo-group should approximately cancel, leaving a molecular resultant of the order of that for benzamide; such is in fact the case, the two recorded values for the last-named substance being μ = 3·6 (Devoto, *Gazzetta*, 1933, **63**, 129) and 3·8 (Davis, Bridge, and Svirbely, *J. Amer. Chem. Soc.*, 1943, **65**, 857). (*b*) For a *cis*-configuration of $\mathrm{R{\cdot}N{:}N{\cdot}CO{\cdot}NH_2}$ there can be no certainty concerning the direction of action of the component vector due to the $\mathrm{CO{\cdot}NH_2}$; it will most probably not lie along the $\mathrm{N_2}$–amide link, and could easily be roughly at right angles to a " *cis*-azo "-component of *ca.* 3 D. (*i.e.*, $\mu_{cis\text{-azobenzene}}$). The molecular resultant to be expected would then be obviously about 5 D.

FIG. 1.



(*a*) $\mathrm{Ph{\cdot}N_2{\cdot}CO{\cdot}NH_2}$. (*b*) p-$\mathrm{NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}CO{\cdot}NH_2}$.

FIG. 2.



p-$\mathrm{Br{\cdot}C_6H_4{\cdot}N_2{\cdot}CO{\cdot}NH_2}$: (*a*) *before irradiation* ; (*b*) *after irradiation* ; (*c*) *solution from* (*b*) *after 24 hours in the dark.*

Clearer evidence of the type sought has been obtained with dilute (0·5 × 10^{-4} M.) solutions of the three diazocarbonamides in 96% ethyl alcohol. When made up and kept in the dark these gave absorption spectra as in Figs. 1 and 2 (curve *a*). It was found that the light source in the Beckman spectrophotometer used had no influence on the results, but exposure of the filled cells to the unfiltered radiation from a mercury-discharge lamp caused changes in the intensities of absorption at the absorption peaks. These changes became gradually reversed when irradiated solutions were kept in the dark although ultimately their initial absorption features were only partly reproduced. Fig. 2 (curve *c*) illustrates the degree of this recovery. As a check on the experimental technique, samples from a bulk solution of benzenediazocarboxyamide stored in an opaque flask were examined at intervals during four days and gave transmission readings which varied by only small amounts, such as could be attributed to slight solvent loss during cell filling and emptying, etc., which were much less than the alterations following illumination by the mercury lamp.

It will be noted that the general forms of the curves in Fig. 1 resemble those of the related diazocyanides (cf. Le Fèvre and Wilson, *J.*, 1949, 1106), so that, by analogy, the modifications of intensity by irradiation now observed are in the directions to be expected if, by the action of light, a fraction of the *trans*-molecules are (reversibly) transformed into their *cis*-isomers.

These details are summarised in Tables I and II. Hantzsch and Lifschitz (*Ber.*, 1912, **45**, 3011) recorded a spectrum of benzenediazocarboxyamide between the "Schwingungzahlen" 2600 and 4300. One absorption maximum is shown at about 282 mμ., with indications that others exist in the regions outside the limits 235—400 mμ.; in general outline therefore these earlier results appear to resemble ours.

TABLE I.

Spectra of diazocyanides and diazocarboxyamides.

	Diazocyanides (stable forms).		Diazocarboxyamides.	
Aryl group.	$\lambda_{\max.}$ (mμ.).	$\log_{10} \varepsilon_{\max.}$.	$\lambda_{\max.}$ (mμ.).	$\log_{10} \varepsilon_{\max.}$.
Ph	—	—	434	2·57
	—	—	286	4·54
	—	—	223	4·39
p-$\mathrm{Br{\cdot}C_6H_4}$	425	2·77	440	2·09
	341	4·50	300	3·87
	238	4·09	245	3·77
p-$\mathrm{NO_2{\cdot}C_6H_4}$	443	2·38	420	2·4 *
	308	4·22	283	4·16
	277	3·94 *		

* Point of inflexion.

Irradiation of saturated alcoholic solutions of benzenediazocarboxyamide or of its *p*-bromo-derivative for 4 hours produced no evident decomposition or visible colour change. Recovery of the solute either by cooling to −30° or by precipitation with water gave samples, melting at 115° and 177°, which were apparently identical with our initial preparations. Such homogeneity in the solid state could be caused by association, between the amide groupings, on the pattern of formulæ (I*a* and *b*) shown by Chaplin and Hunter (*J.*, 1937, 1116) since clearly steric requirements would best be satisfied when all the $-\mathrm{N{:}N}-$ units have the *trans*-configuration.

TABLE II.

Effects of irradiation on $\log_{10}\varepsilon$ *at stated wave-lengths.*

	Diazocyanides.		Diazocarboxyamides.		
Aryl group.	$\lambda_{\max.}$ (mμ.).	$\log_{10} \varepsilon_{syn.}$ minus $\log_{10} \varepsilon_{anti.}$.	Irradiation period (hrs.).	λ (mμ.).	Change in $\log_{10}$ ε.
Ph	—	—	4	287·5	+0·04
	—	—	4	220	+0·03
p-$\mathrm{Br{\cdot}C_6H_4}$	341	−0·6	2·4	300	−0·12
	425	+0·3	2·4	440	+0·07

Our experience with benzenediazocarboxyamide appears to differ from that of Hantzsch and Schultze (*Ber.*, 1895, **28**, 2073), who abandoned the examination of this substance because of its instability. Their specimens were obtained from the oily benzenediazocyanide, which we have previously found (*J.*, 1949, 333) to be hard to purify and difficult to keep. For the present work we have obtained our material *via* the oxidation of 1-phenylsemicarbazide—a route which leads to highly crystalline products.

EXPERIMENTAL.

Solutes.—Benzenediazocarboxyamide was obtained from phenylsemicarbazide (Thiele, *Ber.*, 1895, **28**, 2599); it formed red needles, m. p. 114°, from benzene. In connection with possible hydrogen-bond formation it is noteworthy that from water this material can separate as a hydrate, m. p. 84° (Thiele, *loc. cit.*). The *p*-bromo- and *p*-nitro-benzenediazocarboxyamides were easily produced by refluxing the corresponding diazocyanides with water (Hantzsch and Schultze, *Ber.*, 1895, **28**, 666, and *loc. cit.*); recrystallised from alcohol they had m. p. 177° and 183° respectively. We confirm that as solutions in alcohol these substances do not couple with alcoholic or alkaline β-naphthol either before or after irradiation by ultra-violet light (cf. Hantzsch and Schultze, *loc. cit.*; Hodgson and Marsden, *J.*, 1944, 395).

Dipole Moments and Related Observations.—The apparatus, symbols and methods used are those described in *J.*, 1949, 333. Solutions could not be prepared with the cold solvent. The solutes were accordingly weighed into tared brown bottles, benzene was added, the mixtures were boiled until dissolution was complete, and the final weighings (bottle and solution) were made on cooling. Table III presents our measurements on benzenediazocarboxyamide and its *p*-bromo-derivative. Owing to the low solubility and consequent unavoidable experimental errors, the moment quoted for the second solute cannot be regarded as more than an estimate of order of magnitude.

TABLE III.

Benzenediazocarboxyamide in benzene at 25°.

$10^6 w_1$.	ε_{12}.	d_{12}.	$\alpha\varepsilon_2$.	βd_2.
0	2·2725	0·87378	—	—
2040	2·2955	0·87425	11·3	$0{\cdot}23_0$
2708	2·3043	0·87419	11·7	$0{\cdot}15_1$
3016	2·3054	0·87423	10·9	$0{\cdot}14_9$
3157	2·3083	0·87461	11·3	$0{\cdot}26_3$
4215	2·3170	0·87451	10·6	$0{\cdot}17_3$
		Mean	11·2	$0{\cdot}19_3$

Whence, with $[R_L]_D$ calc. = 48·7 c.c., and M_1 = 149·15, we find ${}_TP$ = 353·9 c.c., ${}_OP$ = 305·2 c.c., and μ = 3·86 D.

p-*Bromobenzenediazocarboxyamide in benzene at* 30°.

$10^6 w_1$.	ε_{12}.	d_{12}.	$\alpha\varepsilon_2$.	βd_2.
0	2·2628	0·86718	—	—
376	2·2660	0·86746	8·5	$0{\cdot}75_5$
401	—	0·86746	—	$0{\cdot}60_5$
455	2·2670	0·86742	9·2	0·53
465	2·2663	—	7·5	—
720	—	0·86761	—	0·60
732	—	0·86748	—	0·41
		Mean	8·4	0·58

Whence, with $[R_L]_D$ calc. = 59·4 c.c., and M_1 = 228·1, we find ${}_TP$ = 390 c.c., ${}_OP$ = 331 c.c., and μ = about 4 D.

The changes in dielectric constant (all measured at 25°) produced by illumination (sunlight) of benzene solutions of benzenediazocarboxyamide are shown by their $\alpha\epsilon_2$ values in Table IV, where line (i) gives $\alpha\epsilon_2$ for each original solution, and lines (ii) and (iii) the same property first after one hour in sunlight and then after 24 hours in darkness.

TABLE IV.

$10^6 w_1$	2040	2708	3016	3157	4125
$\alpha\varepsilon_2$ (i)	11·3	11·7	10·9	11·3	10·6
$\alpha\varepsilon_2$ (ii)	12·7	12·8	11·8	12·4	11·2
$\alpha\varepsilon_2$ (iii)	11·2	12·1	17·1 *	13·4 *	— *

* These solutions were cloudy when measured for the third time, showing that crystallisation had commenced.

The results for the first and second solutions were not inconsistent with a reversible photochemical change. With all five solutions there seemed to be an increase in the polarity of the solute. The two cases not marred by crystallisation show that we have not wrongly drawn this conclusion from an irreversible concentration change caused by evaporation of this solvent.

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