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Abstract

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ON THE STRUCTURE OF ISOMERIC DIAZOCYANIDES

When an aqueous solution of potassium cyanide is added to a solution of a diazonium salt at a temperature below −10°, a labile form of a diazocyanide of composition ArN_2CN precipitates; at room temperature it gradually transforms into a stable compound of the same composition. The existence of diazocyanides in two isomeric forms was first discovered by Hantzsch ([1]). Hantzsch regarded the isomerism of diazocyanides, as well as of diazosulfonates and diazotates, as geometrical, cis-trans isomerism. The erroneousness of his views with respect to diazotates was convincingly demonstrated by the work of Porai-Koshits and coworkers ([2]). The presence of geometrical isomerism in the series of diazocyanides also raises serious doubts. As early as 1903, Orton put forward the hypothesis of the possibility of structural, nitrile-isonitrile, isomerism of diazocyanides ([3]):

$$\underset{\text{labile isomer}}{Ar{-}N{=}N^{+}{=}C^{-}} \qquad \underset{\text{stable isomer}}{Ar{-}N{=}N{-}C{\equiv}N}$$

In 1944, Hodgson and Marsden ([4]) supported this hypothesis, pointing to the great similarity in the chemical behavior of labile diazocyanides and diazoamino compounds (triazenes).

A characteristic property of triazenes is the ease of cleavage of the single N—N bond, which is manifested in the existence of an equilibrium in acidic solutions ([5]):

$$ArN{=}N{-}NR_2 + H^{+} \rightleftarrows ArN_2^{+} + HNR_2,$$

as well as in the ease with which triazenes enter into coupling reactions, and into reaction with bromine ([6]):

$$ArN{-}N{=}NHC_6H_5 \xrightarrow{Br_2} ArN_2Br + H_2NC_6H_2Br_3.$$

Labile diazocyanides have analogous properties. In an acidic medium equilibrium with the diazonium form is established ([7]):

$$ArN_2CN + H^+ \rightleftarrows ArN_2^+ + HCN,$$

they readily couple ([8]), and with $AgNO_3$ they instantly give a precipitate of AgCN ([9]). According to our observations, when labile diazocyanides react with bromine in a solution of carbon tetrachloride, diazonium perbromide immediately begins to precipitate. The stable form of diazocyanides does not couple, does not give a precipitate with $AgNO_3$, and does not react with bromine. Thus there is a sharp difference in chemical behavior, uncharacteristic of geometrical isomers.

Measurements of dipole moments and magnetic susceptibilities of isomeric diazocyanides, carried out by Le Fèvre and co-workers ([10,11]), do not allow a definitive conclusion to be drawn concerning the nature of the isomerism ([12]). In 1947, Le Fèvre and co-workers, as well as Sutherland and Sheppard ([13,14]), seemingly confirmed the geometrical isomerism of diazocyanides predicted by Hantzsch by means of IR spectroscopy. According to their data, the spectra of isomeric diazocyanides in the region of triple bonds are identical: both forms have one absorption band at 2186 cm^{-1}. In the case of geometrical isomerism there should indeed be no large difference in frequencies; for example, the CN group in cis-1-cyano-1-propene absorbs at 2221 cm^{-1}, and in the trans isomer at 2223 cm^{-1} ([15]). Meanwhile, if structural isomerism is present, there should be a difference in frequencies in the region of triple bonds equal to the difference between the absorption frequencies of the CN and NC groups, i.e., approximately 100 cm^{-1} (see Tables 1 and 2).

Table 1

Frequencies and intensities of absorption of the CN group of nitriles RCN (16)

R	ν, cm^{-1}	$A \cdot 10^{-4} \cdot cm^{-2} \times mol^{-1} \cdot l$
CH_3	2251	0,042
C_2H_5	2247	0,048
CCl_3	2253	0,062
C_6H_5	2230	0,084
n-ClC_6H_4	2233	0,048
n-$NO_2C_6H_4$	2238	0,002
n-$CH_3OC_6H_4$	2226	0,37

Table 2

Frequencies and intensities of absorption of the NC groups of isonitriles RNC (17)

R	ν, cm^{-1}	$A \cdot 10^{-4} \cdot cm^{-2} \times mol^{-1} \cdot l$
CH_3 (18)	2166	–
n-C_4H_9	2146	0,16
iso-C_3H_7	2140	0,14
$C_6H_5CH_2$	2146	0,26
C_6H_5	2117	0,31
n-ClC_6H_4	2116	0,34
n-$NO_2C_6H_4$	2116	0,47
n-$CH_3OC_6H_4$	2125	0,17

We studied the IR spectra of three pairs of isomeric diazocyanides and found that the data of Le Fèvre, Saterland, and Sheppard are erroneous (see Table 3). As is evident from the data of Table 1, the difference in frequencies between the isomers reaches 40 cm^{-1}, but remains smaller than the difference in the absorption frequencies of the CN and NC groups. This decrease in the difference is apparently regular and is explained by a lowering of the absorption frequency of the CN group of stable diazocyanides caused by conjugation. In conjugated unsaturated nitriles, the CN group corresponds to a frequency of 2225 ± 7 cm^{-1} (15).

Table 3

Frequencies and intensities of absorption in the triple-bond region of isomeric diazocyanides $XC_6H_4N_2CN$ in CCl_4 solution

X		ν, cm^{-1}	$A \cdot 10^{-4} cm^{-2} \cdot mol^{-1} \cdot l$
n-CH_3O	labile	2150	0,11
n-CH_3O	stable	2190	0,47
n-Br	labile	2154	0,026
n-Br	stable	2192	0,17
n-NO_2	labile	2162	0,037
n-NO_2	stable	2193	0,064

A further lowering of the frequency in stable diazocyanides to 2190 cm^{-1} is explained by interaction of the CC N bond with the free electron pair of nitrogen:

$$Ar-\ddot{N}=N-C\equiv N$$

An analogous phenomenon occurs in the spectra of N-cyanoketimines,

$$R_2C=N-C\equiv N,$$

in which the CN group absorbs at 2175 cm^{-1} (19, 20). It should be noted that the presence of such strong conjugation apparently promotes equalization of the chain

$$-N=\overset{+}{N}-C=N^-$$

(linearity) and makes the possibility of geometrical isomerism unlikely. The strong conjugation of the CN group of stable diazocyanides is also indicated by absorption intensities higher than those of aromatic nitriles (cf. Table 1). In the case of structural isomerism, the absorption frequencies of labile diazocyanides in the triple-bond region should be close to the absorption frequencies of the NC group. Indeed, they are at the level of aliphatic isonitriles (see Tables 2 and 3). This becomes understandable if one recalls that the triazene chain is not inclined to conjugation with the aromatic ring (for example,

$$R_2N-N=N-C_6H_4X$$

) and all triazenes are light-yellow powders (21). In labile diazocyanides a similar possibility,

$$: C=N-N=N-C_6H_4X,$$

probably is likewise not realized. This is evidenced by the coloration, lighter than that of stable diazocyanides, and by lower intensities.

From the standpoint of ideas of geometrical isomerism, the sharp decrease in the frequencies and intensities of absorption of the labile diazocyanides in comparison with the stable ones is completely incomprehensible. Both the chemical and spectral data point to nitrile–isonitrile isomerism in the series of diazocyanides. We believe that ideas of geometrical isomerism of diazocyanides should be abandoned as unfounded.

The labile diazocyanides studied by us, $XC_6H_4N_2NC$ ($X = NO_2, Br, CH_3O$), are arranged in the following order of stability: n-NO_2 > n-Br > n-CH_3O. Labile n-nitrophenyldiazocyanide slowly (over several weeks) isomerizes in the solid state in a closed vessel, more rapidly in air (several days) and in carbon tetrachloride solution, being converted into the stable isomer. The isomerization proceeds especially rapidly in pyridine (30 min). Both Hantzsch and Le Fèvre give m.p. 30° for labile n-nitrophenyldiazocyanide. We found that, if the isolation of the substance during its synthesis is carried out sufficiently rapidly, labile n-nitrophenyldiazocyanide with m.p. 49–51° can be obtained. On storage of this substance in air the melting point falls to 30°, and then begins to rise. The melting point of the rearranged stable cyanide (86°) agrees with the literature data (1).

Labile *n*-bromophenyldiazocyanide in the solid state rearranges slowly, but much more rapidly in carbon tetrachloride solution. If the spectrum of a 1–2 *M* solution of labile *n*-bromophenyldiazocyanide in carbon tetrachloride is recorded in the region 2100-2200 cm^{-1} several times at intervals of 30-40 min, it may be observed that the intensity of the band at 2154 cm^{-1} decreases, while an absorption band of the stable form appears at 2192 cm^{-1}, the intensity of which increases with time. The rearrangement occurs still more rapidly in labile *n*-methoxyphenyldiazocyanide, which very quickly isomerizes completely both in the solid state (about one day) and in solution.

Le Fèvre et al. studied the IR spectra of isomeric diazocyanides using *n*-nitro and bromo derivatives as examples. They did not detect any difference in the spectra, apparently because they did not have labile *n*-nitrophenyldiazocyanide in pure form, and did not see the frequencies of the bromo derivatives owing to their low intensity.

Experimental Part

Isomeric *n*-nitrophenyldiazocyanides. To 10 ml of water cooled to 0°, with stirring, a warm solution of 0.015 g-mole of *n*-nitroaniline in a mixture of 4 ml of conc. hydrochloric acid and 10 ml of water is added. The suspension formed is cooled to 10° and 0.017 g-mole of solid sodium nitrite is added at once. After 15 min, 10 ml of methanol is added to the reaction mixture with cooling, it is cooled to −15°, and at this temperature a solution of 0.03 g-mole of potassium cyanide in 4 ml of water is added dropwise. The light-orange precipitate is rapidly filtered off, washed with a small amount of cold water, dissolved in 50 ml of carbon tetrachloride without attempting complete dissolution, filtered through a folded filter, separating the undissolved portion and water, a little petroleum ether is added to the mother liquor, and it is cooled to $-10 \div -20°$. Light-orange needles precipitate, m.p. 49-51°.

Found, %:	N 31.83
$C_7H_4O_2N_4$. Calculated, %:	N 31.81

On storage in air, the melting point after one day falls to 30°, then begins to rise and after three days reaches 80°. After crystallization from petroleum ether—bright-red needles, m.p. 86° (1). If it is necessary to isomerize labile *n*-nitrophenyldiazocyanide rapidly, it is dissolved in pyridine; after 30 min the pyridine is distilled off in vacuo, and the residue is crystallized from petroleum ether.

Interaction of labile *p*-nitrophenyldiazocyanide with bromine. To a solution of 0.005 g-mole of labile *p*-nitrophenyldiazocyanide in 30 ml of carbon tetrachloride is added a solution of 0.011 g-mole of bromine in 15 ml of carbon tetrachloride. After several minutes a precipitate begins to form. After one day, 0.0043 g-mole of diazonium perbromide, *p*-$NO_2C_6H_4N_2Br_3$, is filtered off. Its

decomposition temperature is 76°; in the IR spectrum there is an absorption band at 2300 cm^{-1}, characteristic of the diazonium group.

$C_6H_4O_2N_3Br_3$.	Found, %:	Br 60.84
	Calculated, %:	Br 61.52

Stable *p*-nitrophenyldiazocyanide does not give an analogous reaction.

Isomeric *p*-bromobenzenediazocyanides. A mixture of 0.02 g-mole of *p*-bromoaniline, 7 ml of conc. hydrochloric acid, and 20 ml of water is diazotized at 0° with a solution of 0.021 g-mole of sodium nitrite in 8 ml of water. To the reaction mass are added 10 ml of methanol; it is cooled to −12°, and, with stirring, a solution of 0.06 g-mole of potassium cyanide in 10 ml of water is poured in. The yellow precipitate is rapidly filtered off, washed with a small amount of cold water, dissolved at room temperature in 100 ml of petroleum ether, filtered through a folded filter, and cooled. A finely crystalline yellow precipitate forms, m.p. 48°/22. On standing in a solution of carbon tetrachloride, the labile form passes into the stable one, m.p. 132°/22 (from petroleum ether).

Isomeric *p*-methoxyphenyldiazocyanides. A mixture of 0.01 g-mole of *p*-anisidine, 3 ml of conc. hydrochloric acid, and 1 ml of water is diazotized at 0° with a solution of 0.012 g-mole of sodium nitrite in 3 ml of water. To the reaction mixture are added 5 ml of methanol; it is cooled to −12°, and, with stirring, a solution of 0.03 g-mole of potassium cyanide in 4 ml of water is poured in. The orange precipitate is rapidly filtered off, washed with a small amount of cold water, dissolved in petroleum ether, filtered, and cooled. Orange needles precipitate, m.p. 48-50°/8. After one day the melting point rises to 120°. After crystallization from carbon tetrachloride, m.p. 120-121°/8.

IR spectra were recorded on an IKS-14 spectrophotometer with a LiF prism. For measuring intensities, 0.04-1 *M* solutions in carbon tetrachloride were prepared. The cuvette thickness was 0.041 cm.

It has been established that isomeric diazocyanides have a difference in absorption frequencies in the region of triple bonds of the IR spectrum reaching 40 cm^{-1}, as well as a substantial difference in intensities. Both the spectral data and the chemical properties of the isomeric diazocyanides speak in favor of structural, nitrile-isonitrile, isomerism of diazocyanides.

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Note: Figure translations are in progress. See original paper for figures.