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Abstract

Full Text

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CORRELATION OF THE FREQUENCIES AND INTENSITIES OF IR ABSORPTION BANDS FOR DIAZONIUM SALTS X—$C_6H_4N_2Cl$ WITH SUBSTITUENT CONSTANTS

Recently, works have appeared in which the authors relate the frequencies and intensities of IR absorption bands of functional groups X with the substituent constants Y ([1,2]) in systems of the type X—A—Y.

We carried out a correlation of the IR frequencies and intensities of the absorption bands of the diazonium group in diazonium salts with the values of the Hammett constants of p- and m-substituents in the benzene ring, in order to establish the relative position of the diazonium group among other electron-acceptor groups. Some investigators have already attempted to relate $\nu_{N\equiv N}$ in diazonium compounds to the Hammett σ values of substituents Y in the benzene ring ([3,4]), using $\nu_{N\equiv N}$ obtained from measurements of the IR spectra of solid compounds, but the authors did not find a clear regularity.

In dilute solutions $\nu_{N\equiv N}$ characterizes the diazocation solvated by the solvent; the frequency $\nu_{N\equiv N}$ in a given solvent is determined mainly by the nature of the substituent in the phenyl ring (Table 1). On the basis of these data we constructed a plot of the dependence of ν—σ for the values of $\nu_{N\equiv N}$ obtained in solutions of dimethylformamide, acetone, methanol, and ethyl acetate, and obtained clearly expressed linear dependences. The best rectilinearity is observed for acetone solutions; the greatest scatter of points is obtained in the case of solutions in dimethylformamide, which is probably explained by an additional interaction of the diazonium cations with the solvent. Figure 1 shows the plot of the dependence $\nu_{N\equiv N}$—σ for acetone solutions. In constructing the plot we used for the substituents the usual Hammett constants σ ([5]), with the exception of the constant values for such strong electron-donor groups as p-OH and p-OCH_3. For the latter, values of σ^+ ([5]) were taken, characterizing the additional polar conjugation of the oxygen atom with the diazonium group.

Table 1

Values of $\nu_{N\equiv N}$ (cm^{-1}) of diazonium cations in different solvents X—$C_6H_4N_2$

Substituent	Dimethylformamide	Methanol	Acetone	Ethyl acetate
o-OH	2256	2244	2258	–
m-OH	2292	2284	2287	2293
p-OH	2253	2242	2255	2251
o-CH_3O	2274	2266	2266	2266
m-CH_3O	2295	2287	2288	2288
p-CH_3O	2255	2251	2258	2255
o-CH_3	2275	2273	2274	2271
m-CH_3	2293	2280	2285	2284
p-CH_3	2276	2272	2279	2276
H	2298	2290	2292	2294
o-Cl	2293	2284	2285	2286
m-Cl	2308	2300	2298	2298
p-Cl	2298	2289	2291	2293
p-Br	2298	2289	2292	2293
o-$COOC_2H_5$	2301	2293	2293	–
p-$COOC_2H_5$	2309	2297	2299	–
o-NO_2	2299	2299	2300	–
m-NO_2	2315	2306	2309	2307
p-NO_2	2314	2309	2309	2311

The interaction of the para substituent with the diazonium group is manifested even more strongly in the *p*-dimethylaminophenyldiazonium cation: $\nu_{N\equiv N}$ for this cation has a value of ~ 2165 cm^{-1} ([4]), and even the use in this case of σ^+, characterizing the dimethylamino group (-1.7), does not place the point on the obtained straight-line dependence $\nu_{N\equiv N}$—σ.

The found dependence of $\nu_{N\equiv N}$ on substituent constants reflects certain differences in the structure of the diazonium compounds studied. In the case of substituents Y possessing electron-acceptor or weak donor properties, the diazocation exists in form (I), and in this

$$Y - \langle \text{benzene ring} \rangle - N^+ \equiv N \qquad (I)$$

$$Y^{+\delta} - \langle \text{benzene ring} \rangle - N^+ \equiv N \qquad (II)$$

$$^{+}Y - \langle \text{benzene ring} \rangle = N^{+\delta} \equiv N^{-\delta} \qquad (III)$$

case one may use the ordinary values of Hammett' s σ; in the case of substituents having definitely expressed donor properties, the structure of the aryldiazo cation may be represented by form (II), and finally, in the case of very

Fig. 1. Dependence of $\nu_{N\equiv N}$ on the substituent constant for substituted aryldiazonium compounds.

Figure 1: Fig. 1. Dependence of $\nu_{N\equiv N}$ on the substituent constant for substituted aryldiazonium compounds.

strong electron-donor substituents of the type R_2N, the aryldiazo cation apparently has structure (III). Such a dependence of the structure of diazonium compounds on the electronic properties of the substituent is in good agreement with the data from the UV spectra of these compounds. According to Anderson et al. ([6]), the UV spectra of diazoimines having a quinoid structure are close to the spectra of the salts of *p*-dimethylaminophenyldiazonium, i.e., they have the structure

Fig. 1. Dependence of $\nu_{N\equiv N}$ on the substituent constant for substituted aryldiazonium compounds (for *p*-OH and *p*-OCH_3, the values σ^+ were taken; for *p*-C_2H_5OOC, the value $\sigma = 0.52$ was used). The lower curve gives data for ortho-substituted aryldiazonium compounds; the upper curve gives data for para- and meta-substituted aryldiazonium compounds.

Table 2

Intensities of IR absorption bands of the
$\overset{+}{N} \equiv N$ bond
for diazo cations having different substituents in the phenyl ring

Compound	$\nu_{N\equiv N}$, cm^{-1}	$\Delta\nu^H_{1/2}$	$\Delta\nu_{1/2}$	ε_{max}	$A \cdot 10^{-4}$, $l \cdot cm^{-2} \cdot mol^{-1}$	$\lg A$
p-$CH_3OC_6H_4N_2Cl$	2251	27.5	27.2	395	3.85	4.5855
p-$CH_3C_6H_4N_2Cl$	2272	26.5	26.2	235	2.05	4.3118
p-$ClC_6H_4N_2Cl$	2289	20.2	20	222	1.59	4.2014
$C_6H_5N_2Cl$	2290	21.3	21	169	1.27	4.1028
m-$ClC_6H_4N_2Cl$	2300	22.3	22	143	1.13	4.0531
p-$NO_2C_6H_4N_2Cl$	2309	19.7	19.5	101	0.71	3.8513
m-$NO_2C_6H_4N_2Cl$	2306	19.7	19.5	89	0.62	3.7924

represented by form (III). The UV spectra measured by us for *p*-benzoquinonediazide and for the cations of *p*-hydroxy- and *p*-methoxyphenyldiazonium differ from

Fig. 2

Figure 2: Fig. 2

one another ([7]), which does not allow the structure (III) to be accepted for the methoxy- and hydroxyphenyldiazonium cations; apparently, structure (II) is characteristic of these compounds.

The frequencies of the valence vibrations of the triple bond for diazonium cations with substituents in the *o*-position relative to the diazo group depend linearly on the constant σ^*, proposed by Taft for *o*-substituents ([5]).

For seven substituted diazocations we measured the intensity of the absorption band of the triple bond $\nu_{N\equiv N}$ (Table 2). The data obtained satisfy a linear dependence $\lg A_{N\equiv N} - \sigma^+$ (Fig. 2). In accordance with the electron-acceptor properties of the diazonium group, ρ for the straight line $\lg A - \sigma^+$ has a negative value. It is noteworthy that, both for the dependence $\nu_{N\equiv N} - \sigma$ and for the dependence $\lg A_{N\equiv N} - \sigma^+$, the point corresponding to the unsubstituted compound does not lie on the straight line.

Fig. 2

The regular influence of the substituent on the properties of the diazocation is manifested not only in the IR spectra, but is also reflected in certain reactions ([8,9]). Table 3 gives comparative data on the magnitude and variation of absorption-band intensities for various electron-acceptor groups. The integral intensities of the diazonium group are substantially higher than those of the nitrile group and are close in magnitude to the intensities of the carbonyl and nitro groups. In contrast to the carbonyl group, the absorption intensity of the diazonium group changes quite strongly under the influence of the substituent in the benzene ring. The value $\rho^{\oplus}$ found by us for the diazonium group $-\overset{+}{N} \equiv N$ is -0.42. Consequently, the "sensitivity" of the $-N \equiv N$-group to the character of the substituent is considerably greater than that of the carbonyl group and is close to that of the $C \equiv N$-group.

Experimental Part

Intensity measurements were carried out on an IKS-14 spectrophotometer with a LiF prism for methanolic solutions of diazonium chlorides at concentrations from 0.3 to 0.07 mole/liter in a cell of constant thickness $d = 0.1$ mm.

The shape of the absorption band $\nu_{N\equiv N}$ corresponds to a Lorentz curve

$$\ln\left(\frac{I_0}{I}\right)_\nu = \frac{a}{[(\nu-\nu_0)^2 + b^2]}.$$

The spectral slit width of the monochromator was $\Delta S = 2.6$ cm^{-1}.

The integral intensity was determined from the formula

$$A = 2.303 \cdot \varepsilon \cdot \Delta\nu_{1/2} \cdot K \text{ cm}^{-2} \cdot \text{mole}^{-1} \cdot \text{l}.$$

The values of the coefficient K were taken from the tables of A. V. Iogansen ([14]), calculated as functions of $\lg(T_0/T)_{\max}$ and $S/\Delta\nu_{1/2}$. At a ratio $S/\Delta\nu_{1/2} = 0.1$, the coefficient K took values from 1.568 to 1.570, depending on the optical density at the absorption maximum. The half-width of the absorption band $\Delta\nu_{1/2}$ was determined by means of the same tables ([14]) from the relation

$$\Delta\nu^{\text{H}}_{1/2}/\Delta\nu_{1/2} = 1.011 \quad (\text{for } \Delta S/\Delta\nu_{1/2} = 0.1),$$

where $\Delta\nu^{\text{H}}_{1/2}$ is the observed width of the absorption band at half the optical density.

The straight lines in Figs. 1 and 2 were constructed by the method of least squares. Diazonium chlorides were synthesized by the Knoevenagel method and were repeatedly reprecipitated from methanol with ether and acetone. The purity of the substances studied was checked by determination of diazo nitrogen. The deviation of the determined amount of diazo nitrogen from that calculated theoretically did not exceed—

Table 3

Dependence of the integral absorption intensity ($A \cdot 10^{-4}\,\text{l mol}^{-1}\,\text{cm}^{-2}$) of the electrophilic groups on the character of the para- or meta-substituent in benzene ring $X - \text{C}_6\text{H}_4 - Y$

X	$>C=O$, acetophenones in CCl_4	$>C=O$, acetophenones in $CHCl_3$	$>C=O$, benzaldehydes in CCl_4	$>C=O$, ethyl benzoates in CCl_4	$>C=O$, ethyl benzoates in $CHCl_3$	$-C\equiv N$, in CCl_4	$-C\equiv N$, in $CHCl_3$	$-C\equiv N$, in KBr plate	$-NO_2$, sym., in CCl_4	$-NO_2$, sym., in $CHCl_3$	$-NO_2$, asym., in KBr plate	$-NO_2$, asym., in KBr plate	$-N^+\equiv N$, in CH_3OH
n-$(CH_3)_2N$	2.14[12]				0.92[18]	1.75[12]	1.08[15]	6.7[12]	5.6[12]	8.45	0.84	3.85	
n-OCH_3			3.35[11]	3.85[11]	0.54[1]; 0.57[13]; 0.37[3]; 0.28[1]	0.76[1]	0.63[15]			2.22	1.64		

X	$>C=O$, acetophenones in CCl_4	$>C=O$, acetophenones in $CHCl_3$	$>C=O$, benzaldehydes in CCl_4	$>C=O$, ethyl benzoates in CCl_4	$>C=O$, ethyl benzoates in $CHCl_3$	$-C\equiv N$, in CCl_4	$-C\equiv N$, in $CHCl_3$	$-C\equiv N$, in KBr plate	$-NO_2$, sym., in CCl_4	$-NO_2$, asym., in $CHCl_3$	$-NO_2$, sym., in KBr plate	$-NO_2$, asym., in KBr plate	$-N^+\equiv N$, in CH_3OH
n-CH_3	2.44[10]	2.06[11]				0.26[12]; 0.26[13]; 0.20[1]	0.48[1]; 0.55[3]		4.19[3]	2.18[10]			2.05
n-Cl	2.25[10]	2.12[11]	2.08[11]			0.22[2]; 0.04[13]	0.36[1]; 0.31[3]; 0.35[1]	0.28[15]			1.22	1.64	1.59
H	2.20[10]; 1.90[10]		2.12[11]	3.23[11]	3.71[11]	0.20[1]	0.32[3]						**1.27**
m-Cl	2.02[10]; 1.93[10]	1.70[11]	1.95[11]	3.01[11]; 2.77[11]	3.63[11]; 3.45[11]		0.97[13]; 0.13[3]	0.14[15]; 0.15[15]			1.27[15]; 1.4	1.84	1.13
m-Br													0.62
m-NO_2													0.71
n-NO_2													−0.42
ρ^+	−0.05	−0.08[11]	0.067[2]	0.055[2]		−0.461[2]	−0.397						

The yield was 0.2-0.4%. Each compound was synthesized no fewer than four times, and the intensity measurements for each sample were carried out 3-4 times at different concentrations.

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