The Infrared Spectra of *p*-Substituted Benzenediazonium Cations

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(Received August 8, 1967)

The infrared spectra of some aromatic diazonium cations have already been measured by several authors and the change of the diazonium group stretching frequency by the introduction of a substituent into the aromatic nucleus was discussed with reference to the change of N–N bond order.[1,2] However, any other vibration than the diazonium stretching one has never been studied.

In the present report, the infrared spectra of twenty kinds of *p*-substituted benzenediazonium cation were measured in the form of solid chloromercurate to study the aryl carbon - nitrogen bond (Ar–N) stretching vibration in relation to the electronic effect of a *p*-substituent.

In an aromatic diazonium cation, the aryl carbon-nitrogen bond stretching vibration appeared in the frequency region 1300—1400 cm^{-1}, and the above assignment was made with reference to that of nitrobenzenes[3] and phenyl isocyanides[4].

The wave numbers of the characteristic absorption band of diazonium cation, $\nu_{N\equiv N}$ and ν_{Ar-N} were listed in Table 1.

From the data of Table 1, it was shown that an electron-donating *p*-substituent increases the wave number of ν_{Ar-N} and decreases that of $\nu_{N\equiv N}$.

An electron-attracting *p*-substituent, on the other hand, seems to be rather less effective upon the above two absorption bands.

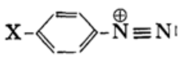
By plotting the wave numbers of ν_{Ar-N} and $\nu_{N\equiv N}$ against Hammett's σ_p value for the substituent in Figs. 1 and 2, it can be clarified that there is almost a linear correlation between them, and that the straight line was distorted as represented by the dotted line above the region of plus σ_p value.

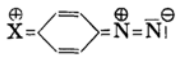
Table 1. IR spectra of *p*-substituted benzenediazonium salts

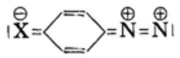
No.	*p*-Substituent	Hammett σ_p*	dp (°C)	ν_{Ar-N} (cm^{-1})	$\nu_{N\equiv N}$ (cm^{-1})
1	NO_2	+0.78	98	1316	2280
2	CN	+0.63	97—98	1309	2270
3	$COCH_3$	+0.52	95—96	1312	2275
4	$COOC_2H_5$	+0.45	106	1320	2270
5	COOH	+0.27	109	1320	2275
6	I	+0.28	120	1310	2260
7	Cl	+0.23	120—121	1314	2265
8	Br	+0.23	117—118	1314	2250
9	CHO	+0.22	108—110	1319	2275
10	C_6H_5	+0.01	109	1325	2250
11	H	0.00	—**	1314	2260
12	C_2H_5	−0.15	87—89	1332	2250
13	CH_3	−0.17	107—108	1324	2255
14	OC_2H_5	−0.25	119	1340	2230
15	OCH_3	−0.27	120	1342	2235
16	OH	−0.46	155—156	1385	2235
17	NH_2	−0.66	157—159	1365	2165
18	$N(CH_3)_2$	−0.83	146—148	1394	2155
19	$NHCOCH_3$		137—138	1340	2245
20	NHC_6H_5		114—115	1328	2240

* H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).
** This double salt does not show sharp decomposition temperature. 100—130°C of dp is reported in the literature; O. A. Reutov and Yu. G. Bundel, *Chem. Abstr.*, **48**, 623 (1954).

The high frequency shift of the aryl carbon-nitrogen bond stretching vibration by the substitution of an electron-donating group can be explained in the same way as described in the case of the diazonium group stretching band,[5,6] that is, the substitution of an electron-donating group at the para position of the benzene ring increases the contribution of the polarized structure (II) to the ground state (I), namely it decreases the N≡N bond order and at the same time increases the aryl carbon - nitrogen (Ar–N) bond order.


(I)


(II)


(III)

The break in the linear correlation by the substitution of a strong electron-attracting group, on the other hand, may be partly interpreted by taking the polarized structure (III) into consideration.

Since an increase in the contribution of the structure (III) to the ground state (I) increases the aryl carbon - nitrogen (Ar–N) bond order and

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1) M. Aroney, R. J. W. Le Févre and R. L. Werner, *J. Chem. Soc.*, **1955**, 276.
2) K. B. Whetsel, G. F. Hawkins and F. E. Johnson, *J. Am. Chem. Soc.*, **78**, 3360 (1956).
3) R. D. Kross and V. A. Fassel, *ibid.*, **78**, 4225 (1956).
4) I. Ugi and R. Meyr, *Chem. Ber.*, **93**, 239 (1960).
5) K. B. Whetsel, G. F. Hawkins and F. E. Johnson, *J. Am. Chem. Soc.*, **78**, 3360 (1956).
6) M. Sukigara and S. Kikuchi, This Bulletin, **40**, 1077 (1967).
7) A. N. Nesmejanow, *Ber.*, **62**, 1010 (1929).

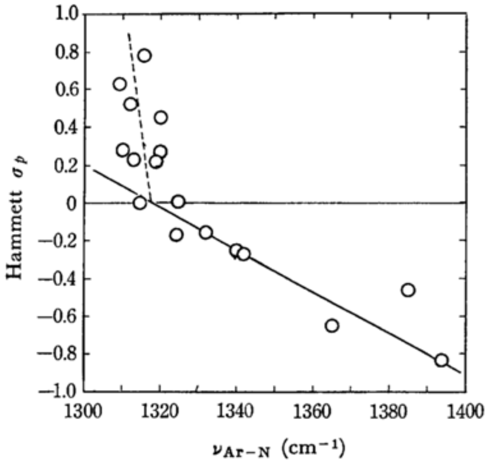

Fig. 1. Plot of aryl carbon-nitrogen bond stretching frequency *vs.* Hammett's σ_p constant for the corresponding *p*-substituent.

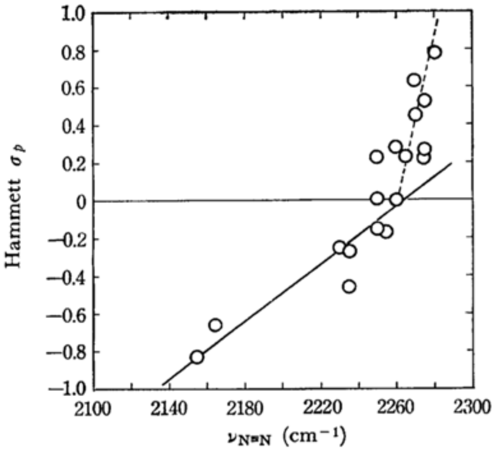

Fig. 2. Plot of diazonium group stretching frequency *vs.* Hammett's σ_p constant for the corresponding *p*-substituent.

at the same time, decreases the N≡N bond order, the substitution of a strong electron-attracting group shifts the aryl carbon-nitrogen (Ar-N) stretching vibration to the higher frequency side and at the same time, shifts that of the diazonium group to the lower frequency side. However, the above contribution of the structure (III) by the substitution of a strong electron-attracting group is less important than that of structure (II), because there is an unstable, doubly positive charged N=N bonding in the former structure.

The net effect of a strong electron-attracting group upon the characteristic infrared absorption bands of diazonium cation seems to be small and then the absorption band of ν_{Ar-N} and $\nu_{N\equiv N}$ of the diazonium salts having a strong electron-attracting group at para position of benzene nucleus appears in the narrow frequency regions 1310—1320 cm^{-1}, and 2260—2280 cm^{-1}, respectively.

Experimental

Preparation of Diazonium Double Salts. The preparation of the mercuric chloride double salt of *p*-substituted benzenediazonium chlorides was carried out following the method of Nesmejanow[7]; The diazotization of an arylamine was done by a usual method with the corresponding amount of moles of sodium nitrite in 20% hydrochloric acid solution at 0—5°C.

The diazotized solution was filtered and then poured into a solution of one and a half times as much as the corresponding amount of moles of mercuric chloride in 20—30 m*l* of cooled concentrated hydrochloric acid. The mixture was stirred at 0—5°C for ten minutes or so.

After precipitation of the double salt, the crystal was collected on a glass-filter, washed with cooled water, ethanol and ether, in that order, and dried in a vacuum desiccator. The yield of dried double salt was 10—60%.

Infrared Spectra of Diazonium Double Salts. The infrared spectra of the double salts were measured by using a JASCO DS-301 infrared spectrophotometer in a KBr disk. The wave numbers of $\nu_{N\equiv N}$ and ν_{Ar-N} are listed in Table 1.

The authors wish to express their deep gratitude to Miss Michiko Hayama of Tokyo College of Pharmacy for her infrared measurement.