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Mass Spectrometry of 1-Phenylazo-2-naphthols

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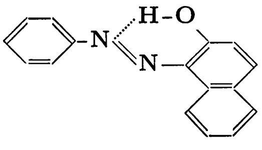
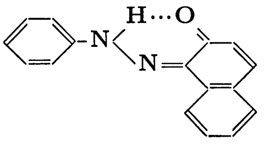
In order to examine the azo-hydrazone tautomerism of substituted 1-phenylazo-2-naphthols and to estimate the effect of substituents on the equilibrium, mono-substituted 1-phenylazo-2-naphthols were synthesized and the spectra were compared with those of the respective acetylated derivatives and β-naphthoquinone-methylphenylhydrazone as references of the azo and hydrazone forms respectively. The spectra of acetylated derivatives show the same pattern as those of the original samples except for the molecular ion and ion at m/e: 43. Moreover, β-naphthoquinone-methylphenylhydrazone displays a different fragmentation process, the cleavage of the N–N bond. In conclusion, the substituted 1-phenylazo-2-naphthols exist in the gaseous state as only the azo form; this is different from the results in the liquid and solid states. The fragmentation processes, in which the reactions of $M^+ \rightarrow (m/e\text{: } 171)^+ \rightarrow (m/e\text{: } 143)^+ \rightarrow (m/e\text{: } 115)^+$ mainly occur, are clarified on the basis of these results. The effect of substituents on the reaction rate of the formation of ions at m/e: 171 from molecular ions is examined. The correlation with the Hammett σ constants is $\rho = 0.078$ for meta substituents, and the plots for para substituents lie under the line, which means that the reaction rate for para substituents is slow. This is explained on the basis of the resonance effect.

Many studies have been carried out in an attempt elucidate the structure of 1-phenylazo-2-naphthols (PAN), which may exist as a true azo form (I) or as a hydrazone form (II).[1)]


(I)


(II)

[1)] H. Zollinger, "Azo and Diazo Chemistry," Interscience, New York (1961), p. 322.

Over thirty years ago, Hendricks and his co-workers[2] and Kuhn[3] discussed how they exist as a resonance hybride or a tautomeric mixture. Later Burawoy and his co-workers, based on the electronic spectra in various solvents, clearly demonstrated that they exist in solution as tautomeric equilibria.[4] Further evidence for the presence of tautomerism in both solid and solution of PAN has been provided by many techniques, such as measurements of the electronic spectra,[5–8] the infrared spectra,[9] the chemical shift of ^{14}N in NMR,[10] the diamagnetic susceptibility,[11] and the fluorescence.[12] Recently Bansho and his co-workers[7] studied these phenomena quantitatively, and concluded that 50—70% of the molecules exist as the hydrazone form whatever the state, a solid in KBr disk or a solution in a polar (ethanol) or non-polar solvent (cyclohexane), by a comparison of the extinctions in the regions of 410—420 mμ and 480—500 mμ. They also pointed out that there is no linear relation between the percentage of the hydrazone form and the Hammett σ constants.

Unfortunately, the tautomeric equilibria of PAN in the gaseous state have not been studied. Recently, it has become apparent that no keto-enol tautomerism takes place after electron bombardment in a mass spectrometer.[13] Thus, we tried to elucidate the tautomeric equilibria in the gaseous state and the effect of substituents by using a mass spectrometer.

Experimental

Measurement of the Mass Spectra. The spectra were obtained by the use of a JMS-01SG double-focusing mass spectrometer (Japan Electron Optics Laboratory Co., Ltd.). Using 75 eV electrons at a regulated emission current of 200 μA, all the experiments were made by the electrical detection method under low resolution conditions, several samples were also examined by the photo-plate detection method under high resolution conitions (*ca.* 20000) in order to confirm the elemental compositions. Samples were introduced through the direct sample inlet system under the condition of an ion-source temperature of 200—210°C and a sample-vaporizing temperature of 50—110°C (selected for each sample). The metastable ion was detected by the accelerating-voltage-scan method.[14] The pattern coefficients were measured at the maximum of the beam current by using a rapid scan to avoid any change in the ion beam.

Samples. The samples used were 15 PAN (Table 1), 7 PAN acetates (Table 2), and β-naphthoquinonemethylphenylhydrazone (NQH). The PAN were synthesized by the usual coupling reaction between β-naphthol and substituted anilines, were purified three times by recrystallization, and were confirmed by studying the melting point and the mass spectrum. The PAN acetates were synthesized by the usual acetylation of PAN using pyridine and acetic anhydride. They were also purified and confirmed in the same manner. NQH was synthesized by a reaction of β-

Table 1. PAN and their pattern coefficients[a]

Sample No.	Substituents	Melting point °C	Relative Intensities						
			$M^{+\cdot}$	$(M-1)^+$	*m/e* : 171	*m/e* : 143	*m/e* : 115	Ph-X$^+$	Sp$^+$ (*m/e*)[b]
PAN- 1	H	134	82.8	11.1	24.7	100	59.4	42.7	13.3 (51)
2	*o*-NO_2	206	41.8	0.1	27.6	100	47.2	—	21.8 (276)
3	*m*-NO_2	193	65.6	7.2	25.2	100	59.8	—	—
4	*p*-NO_2	246	100	5.4	21.7	99.9	53.2	6.3	—
5	*o*-Cl	166	71.4	5.8	25.3	100	60.2	16.8	14.0 (75)
6	*m*-Cl	159	69.0	6.5	27.2	100	63.7	14.3	14.4 (75)
7	*p*-Cl	161	91.7	9.2	24.6	100	70.6	26.5	18.4 (75)
8	*o*-CH_3	131	86.2	12.3	18.3	100	71.5	70.8	31.2 (65)
9	*m*-CH_3	139	95.7	12.7	27.8	100	46.9	42.1	17.5 (65)
10	*p*-CH_3	134	100	12.7	16.4	70.3	53.4	80.8	33.9 (65)
11	*o*-OCH_3	181	100	1.0	18.8	75.8	39.4	—	16.9 (77)
12	*m*-OCH_3	144	83.8	7.2	25.6	100	38.7	20.5	17.6 (77)
13	*p*-OCH_3	140	100	8.4	9.3	43.7	30.1	50.3	45.4 (77)
14	*p*-$COCH_3$	145	74.7	6.6	20.4	100	42.5	12.4	15.7 (43)
15	3,4-di-CH_3	183	100	9.5	16.2	82.2	39.7	63.1	21.4 (77)

a) The observed values are the mean of quintuples of the measurement.

b) Sp$^+$ means other characteristic ion and the value in parentheses exhibits *m/e* value of the ion.

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[2] S. B. Hendricks, O. R. Wulf, C. E. Hilbert, and U. Liddel, *J. Amer. Chem. Soc.*, **58**, 1991 (1936).

[3] R. Kuhn and F. Bar, *Ann.*, **516**, 143 (1935).

[4] A. Burawoy, A. G. Salem, and A. R. Thompson, *J. Chem. Soc.*, **1952**, 4793.

[5] E. Fisher and Y. F. Frei, *ibid.*, **1959**, 3159.

[6] D. Hadzi, *ibid.*, **1956**, 2143.

[7] I. Saito, Y. Bansho, and A. Katsuta, *Kogyo Kagaku Zasshi*, **70**, 1715 (1967).

[8] C. Dehari, Y. Matsunaga, and K. Tani, This Bulletin, **43**, 3404 (1970).

[9] K. J. Morgan, *J. Chem. Soc.*, **1961**, 2151.

[10] A. H. Berri, P. Hampson, S. W. Longworth, and A. Mathias, *ibid*, (B), **1968**, 1308.

[11] Y. Matsunaga, This Bulletin, **30**, 429 (1957).

[12] H. Rau and B. Bunsengeo, *Phys. Chem.*, **72**, 637 (1968).

[13] a) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., (1967), p. 158. b) H. Nakata and A. Tatematsu, This Bulletin, **42**, 1678 (1969).

[14] E. Watanabe, T. Aoyama, and M. Shino, *Shitsuryo Bunseki (Mass Spectroscopy)*, **17**, 603 (1969).

Table 2. Acetylated derivatives of PAN and their pattern coefficients[a)]

Sample No.	Substituents	Melting point °C	Relative Intensities							
			$M^{+\cdot}$	$(M-42)^{+\cdot}$	$(M-43)^{+}$	m/e : 171	m/e : 143	m/e : 115	Ph-X^{+}	m/e : 43
PAN-Ac-1	H	115	42.6	100	15.0	30.8	89.1	29.2	40.3	25.2
2	*m*-NO	161	14.7	85.0	9.4	29.8	100	40.2	4.5	35.4
3	*p*-NO_2	190	20.6	100	11.2	23.4	88.2	32.8	6.1	29.4
4	*p*-Cl	132	34.0	100	12.6	27.6	93.0	28.3	23.2	21.4
5	*p*-OCH_3	—[b)]	44.1	100	13.2	11.5	49.4	20.0	64.8	27.2
6	*p*-$COCH_3$	127	36.0	100	12.8	28.2	89.1	26.7	12.3	45.0
7	3,4-di-CH_3	101	53.1	100	15.9	20.3	62.5	24.4	56.4	25.9

a) The observed values are the mean of quintuples of the measurement.

b) This can not be measured because of its tar-like property.

naphthoquinone and methylphenylhydrazinesulfate,[15] and was purified by crystallizing it three times from benzene-ligroin. The sample thus obtained consisted of long, flat, amethyst-colored crystals and melted at 118°C.

Results and Discussion

Mass Spectra of PAN. The characteristic ions observed in the spectra of PAN are $M^{+\cdot}$, $(M-1)^{+}$, $(m/e : 171)^{+}$, $(m/e : 143)^{+}$, $(m/e : 115)^{+}$, a substituted phenyl ion, and a further decomposed ion of the substituted phenyl ion, as is shown in Table 1. The main reaction is $M^{+\cdot} \rightarrow (m/e : 171)^{+} \rightarrow (m/e : 143)^{+} \rightarrow (m/e : 115)^{+}$, which is confirmed by the measurement of the metastable ions. The reaction is similar to that of azobenzenes.[16] It is, however, very dangerous to decide that PAN exist in the gaseous state as the azo form, since there is some possibility that the hydrazone form would react in the same manner.

Recently, some organic compounds which possess keto-enol tautomerism have been studied by means of mass spectrometer.[13,17] As has been mentioned above, no movement of tautomeric equilibria was observed after electron impact. This means that the mass spectra reflect the state of tautomeric equilibria in the gaseous state. Using this phenomenon, Zamir and his co-workers discussed the effect of the inlet temperature on the keto-enol equilibria of the acetylacetone.[18]

It is, at any rate, necessary to determine the state of tautomeric equilibria in order to make the fragmentation process clear.

Azo-hydrazone Tautomerism. It was revealed that the (M-42) ion radical, observed in the mass spectra of acetylated derivatives of compounds which possess keto-enol tautomeric equilibria, corresponds to the enol form of original compounds.[19,20] The acetylated derivatives of PAN were synthesized and measured by means of the mass spectrometer. The spectra obtained were then compared with those of the original PAN (See Figs. 1, 2, and 3). The spectra of PAN and their acetates resemble each other except for a few differences in intensity. That the relative intensities of $(M\text{-}42)^{+\cdot}$ to $(m/e : 171)^{+}$ and/or $(m/e :$

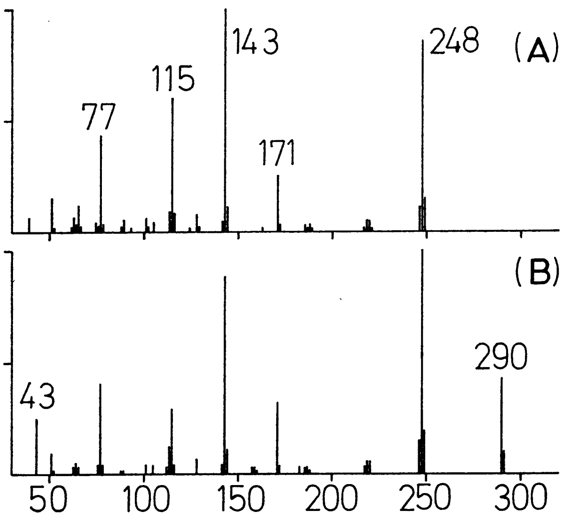

Fig. 1. Mass spectra of 1-phenylazo-2-naphthol (A) and 1-phenylazo-2-naphthol acetate (B).

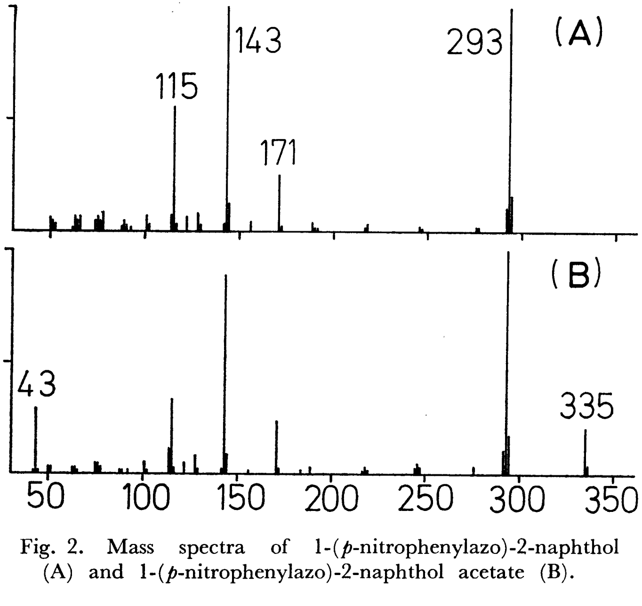

Fig. 2. Mass spectra of 1-(*p*-nitrophenylazo)-2-naphthol (A) and 1-(*p*-nitrophenylazo)-2-naphthol acetate (B).

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15) W. MacPherson, *Amer. Chem. J.*, **22**, 364 (1899).

16) J. H. Bowie and G. E. Lewis, *J. Chem. Soc.*, *B*, Part 1, **1967** 621.

17) J. K. McLeod, J. B. Thompson, and C. Djerassi, *Tetrahedron*, **23**, 2095 (1967).

18) L. Zamir, B. S. Jensen, and E. Larsen, *Org. Mass Spectrom.*, **2**, 49 (1969).

19) K. Heyns and D. Muller, *Tetrahedron Lett.*, **1966**, 6061.

20) D. G. B. Boocock and E. S. Waight, *J. Chem. Soc.*, *B*, **1968** 258.

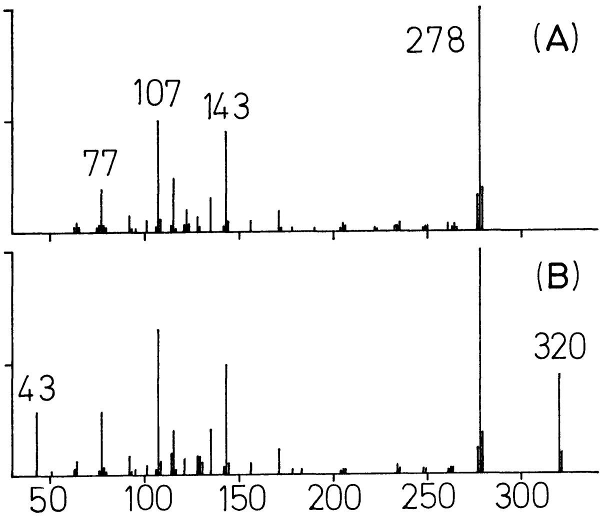


Fig. 3. Mass spectra of 1-(*p*-methoxyphenylazo)-2-naphthol (A) and 1-(*p*-methoxyphenylazo)-2-naphthol acetate (B).

$143)^+$ in the spectra of acetylated derivatives are somewhat larger than those of M^+ to $(m/e:171)^+$ and/or $(m/e:143)^+$ in the spectra of original ones, can be reasonably explained by the energy loss at a de-ketene reaction. Actually, the spectra of PAN electron-bombarded at 50 eV are more similar even in intensity to those of acetylated derivatives electron-bombarded at 75 eV. An examination of the metastable ions generated in the first field-free region showed that the fragmentation processes were all same except for $(M\text{-}43)^+$. Also, the metastable ions generated in the second field-free region were found to be equal in shape and in relative abundance to the precursor ions; this means that the structure of the precursor ions in the spectra of both PAN and their acetates are the same.[21] These facts also support the theory that PAN exist in the gaseous state as the azo form, but they are insufficient to clarify the tautomeric equilibria, because the fragmentation processes of the hydrazone form remain undissolved. As it is impossible to measure the mass spectrum of PAN in the hydrazone form, we synthesized *β*-naphthoquinone-methylphenylhydrazone (NQH) as a model compound for the hydrazone form and measured its mass spectrum, which is shown in Fig. 4. The fragmentation process, as determined by the measurements of the precise mass and the metastable ions, is shown in Scheme 1. The main reaction can be understood as a cleavage of $M^{+\cdot}$ to $(m/e:106)^+$, which corresponds to an ion designated as $(X\text{-}Ph\text{-}NH)^+$ in the spectra of PAN. The reaction of $M^{+\cdot}\rightarrow(m/e:247)^+\rightarrow(m/e:219)^+$ in the spectrum of NQH corresponds to that of $M^{+\cdot}\rightarrow(M-1)^+\rightarrow(M-1-28)^+$ in the spectra of PAN. These observations do not always support the existence of the hydrazone form in PAN, because there is some possibility that the azo form reacts in the same manner. That $(M\text{-}CH_3)^+$ is observed, while $(M\text{-}Ph)^+$ is not, means that the hydrazone form of PAN will produce $(M-1)^+$ rather than $(M\text{-}Ph)^+$. This also supports the theory that PAN exists as the azo form. The ion radical at *m/e* : 157 in the spectrum of NQH would be produced by the cleavage of the N–N bond with hydrogen transfer from CH_3, so the reaction does not give any information about the tautomerism of PAN. The fact that the $(X\text{-}Ph\text{-}NH)^+$ ion, which should come from the hydrazone form, is not observed supports the idea that PAN exist in the gaseous state as the azo form. In the spectrum o f PAN-13 (p-OCH_3), an ion at *m/e* : 122 corresponding to $(X\text{-}Ph\text{-}NH)^+$ was observed as a 9% intensity of the base peak. This fact indicates some coexistence of the hydrazone form.

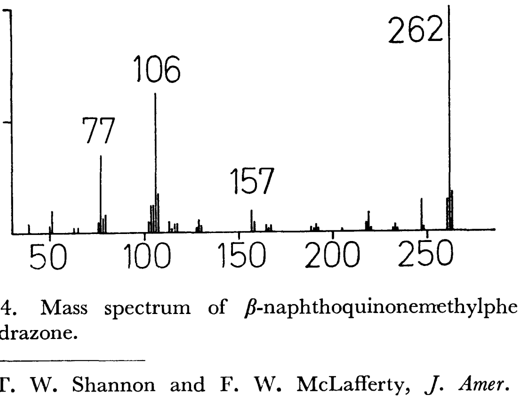
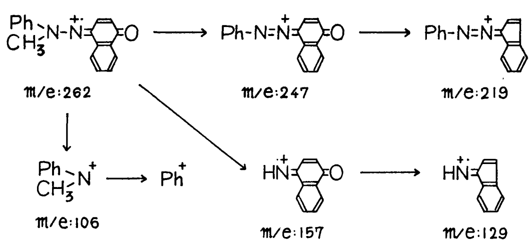


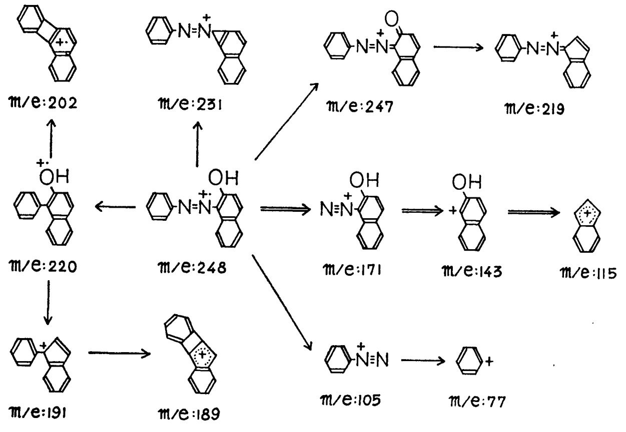
Fig. 4. Mass spectrum of *β*-naphthoquinonemethylphenylhydrazone.



Scheme 1

It can be concluded, for the foregoing reasons, that PAN exist in the gaseous state at the measured temperature as the azo form, except for the para methoxy derivative, in which a little hydrazone form coexists.

Fragmentation Process of PAN. The fragmentation process of PAN-1 is determined on the basis of the azo form by measurements of the precise mass and the metastable ions (see Scheme 2). The other PAN



Scheme 2

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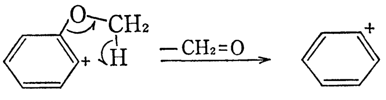
[21] T. W. Shannon and F. W. McLafferty, *J. Amer. Chem. Soc.*, **88**, 5021 (1966).

are explained by the same process. The scission of both sides of the azo group is a main reaction which resembles that of azobenzenes.[16] The cleavage of $M^{+\cdot}$ to $(m/e : 171)^+$ is more liable to occur than that to $(m/e : 105)^+$, for the naphthol ring is a stronger electron donor than the phenyl ring.[22] The $(Ph\text{–}X)^+$ ion becomes stronger with an increase in the electron-donating power of the substituents (see Table 1).

The common ions with intensities of less than several percent are $(M-1)^+$, $(M-17)^+$, $(M-28)^{+\cdot}$, $(M-29)^+$, $(m/e : 218)^{+\cdot}$, and $(m/e : 189)^+$. The $(M-28)^{+\cdot}$ contains reaction products of the elimination of a nitrogen molecule and a carbonyl group.

When a substituent is attached to the ortho position, characteristic reactions have been observed by the mass spectrometer; this has been called the "ortho effect".[23] In the spectra of PAN, the ortho nitro group shows typical effect compared with the meta and para positions-i.e., the very weak $(M-1)^+$, strong $(M-17)^+$, and strong $(M-47)^+$ corresponding to $(M\text{–}OH\text{–}NO)^+$. As for the methoxy group, the ortho derivative shows the weak $(M\text{-}1)^+$, strong $(M\text{-}15)^+$, strong $(M\text{-}31)^+$, weak $(m/e : 107)^+$, and strong $(m/e : 77)^+$ relative to the meta and para derivatives. The last two cases can be explained in terms of the low-energy barrier of a reaction as follows:



m/e : 107 m/e : 77

In the case of chloro and methyl groups, the typical ortho effect was not observed.

Effects of Substituents on the Rate of Reaction from $M^{+\cdot}$ *to Ion at* m/e : 171. Bursey and his co-workers[24–26] have examined the kinetic approach to the reaction of acetophenones and benzophenones in a mass spectrometer. They have stated that electron-impact fragmentations may be related to ground-states processes, since the relative abundances of acetyl (*m/e* : 43) and benzoyl (*m/e* : 105) cations in various spectra are quantitatively related to the Hammett σ constants. Bowie and his co-worker observed the same correlations for the $(Ph\text{–}N\text{=}N)^+$ ion in the monosubstituted azobenzenes ($\rho=1.05$).[16] In our experiments, the effect of substituents on the reaction from M^+ to $(m/e : 171)^+$ were examined. The results obtained are shown in Fig. 5, where Z and Z_0 indicate the relative intensities of $(m/e : 171)^+$ to $M^{+\cdot}$ in the spectra of PAN and PAN-1 respectively. The same treatment of the reaction from $(M\text{-}42)^{+\cdot}$ to $(m/e : 171)^+$ was done upon the acetylated derivatives; the $\log(Z/Z_0)$ thus obtained was consistent with that of the original samples within the range of experimental error. In Fig. 5 the meta substituents correlate with each other by means of Hammett σ constants, but some deviations are observed with regard to the para substituents. Such poor correlations have so far been observed.[27] In order to solve this problem, Johnstone and his co-worker have proposed a concept of the participation of excited-state reactions, where good Hammett correlations are found for para but not meta substituents.[28] In our case, however, the results may indicate that the reaction proceeds through a ground state rather than through an excited state, since good Hammett correlations are found for meta but not para substituents. Moreover, the correlations are improved by an application of the Yukawa-Tsuno equation[29] except for the para nitro derivative, as is shown in Fig. 6; the vafues obtained are $\sigma=0.08$ and $r=11$ (r is a parameter of the relative strength of the resonance effect.). The small ρ-value, which is very different from that of azobenzenes, is probably dependent on a relaxation effect of the hydrogen bond.

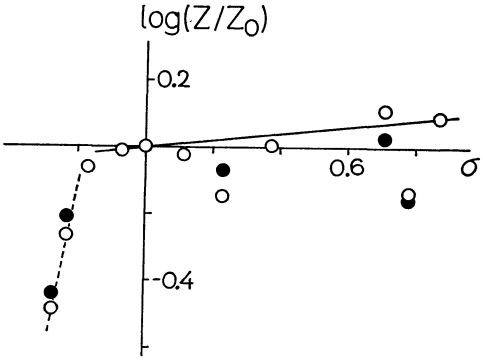


Fig. 5. Correlation of the intensities of ion at *m/e*: 171 with Hammett σ.

○: PAN, ●: PAN acetates

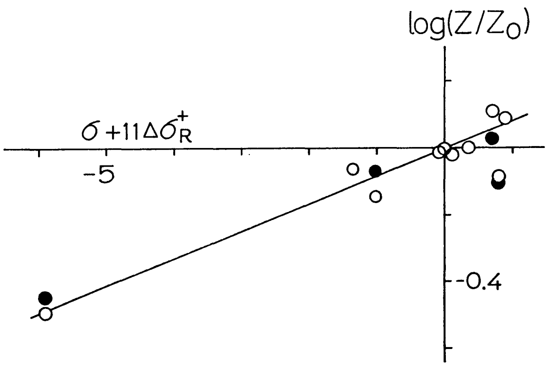


Fig. 6. Improved correlation of the intensities of ion at *m/e*: 171 with Hammett σ by using Yukawa-Tsuno equation.

○: PAN, ●: PAN acetates

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24) M. M. Bursey and F. W. McLafferty, *J. Amer. Chem. Soc.*, **88**, 529 (1966).

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