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Substituent Effects on the Mass Spectra of *ortho*-Hydroxyaromatic Aldehyde *para*-Substituted Benzylidenehydrazones1)

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The difference between the mass spectra of Ar–CH=N–N=CH–Ar derivatives and those of Ar(OH)–CH=N–N=CH–Ar(OH) derivatives was pointed out.

Mass spectra of 24 kinds of *ortho*-hydroxyaromatic aldehyde *para*-substituted benzylidenehydrazones (Ar(OH)–CH=N–N=CH–Ar'–R) were determined. These compounds were shown to have several kinds of characteristic fragment ions; $[\mathrm{Ar(OH)–CH=N}]^+$ (g ion), $[\mathrm{N=CH–Ar'–R}]^+$ (g' ion), $[\mathrm{Ar(OH)–CH=N+H}]^{+\cdot}$, $[\mathrm{Ar(OH)–CH=N-H}]^{+\cdot}$, $[\mathrm{N=CH–Ar'–R+H}]^{+\cdot}$, $[\mathrm{N=CH–Ar'–R+2H}]^+$ and $[\mathrm{M–OH}]^+$ (b ion). The relative ion intensities of g, g' and b ions were found to be strongly dependent on the substituent constant. And all of the values of $\log[\mathrm{g}^+]/[{}^d\mathrm{M}^{+\cdot}]$, $\log[\mathrm{g}'^+]/[{}^d\mathrm{M}^{+\cdot}]$, and $\log[\mathrm{b}^+]/[{}^d\mathrm{M}^{+\cdot}]$ were shown to correlate linearly with σ^+. The substituent effect on the value of either $\log[\mathrm{g}'^+]/[\mathrm{g}^+]$ or $\log[\mathrm{b}^+]/[\mathrm{g}^+]$ was found to be the reflection of the substituent effect on the difference of ionization potentials of either g· and g'· radicals or g· and b· radicals, respectively.

Aromatic aldehyde azines having the symmetrical structure do not show any distinct substituent effects in their physicochemical properties, such as ultraviolet spectra,3) infrared spectra4) and mass spectral fragmentations.5) However, it is expected that aromatic aldehyde azines having the asymmetrical structure will show fairly distinct substituent effects. This paper deals with the results of investigation of the substituent effects on the mass spectral fragmentations of 24 aromatic aldehyde azines having the asymmetrical structure (VIII—XXXI). And a few comments on the mass spectra of 7 aromatic aldehyde azines having the symmetrical structure (I—VII) are also given.

Experimental

Materials——Syntheses of 18 aromatic aldehyde azines having the asymmetrical structure were already reported.6) Eight compounds were newly synthesized by the same method as that described in the previous paper.6) Appearances, melting points and the results of elemental analyses of these new compounds are shown in Table I with those of a new aromatic aldehyde azine having the symmetrical structure (V).

Mass spectra were measured on a JMS-01SG mass spectrometer at 75 eV electron energy, 200 μA trap current and 6.2—6.4 kV accelerating potential. The source temperature was between 105—210°. The samples were introduced by the all-glass direct inlet system. The temperature of the sample chamber was between 50—150°.

Molecular orbital calculations were carried out on a FACOM 230—60 computer at the Computation Center of the Kyushu University. The INDO calculations were performed according to the literature.7)

Compounds employed in this study were as follows:

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1) This paper forms Part VIII of "The Application of Molecular Orbital Method." Part VII: K. Ogawa, Y. Ono, and Y. Ueda, *Yakugaku Zasshi*, **96**, 44 (1976). A part of this work was presented at the 22nd Annual Meeting of the Japan Society for Analytical Chemistry, Fukuoka, November, 1973.

2) Location: *Maedashi, Higashi-ku, Fukuoka, 812, Japan.*

3) L.N. Ferguson and T.C. Goodwin, *J. Am. Chem. Soc.*, **71**, 633 (1949).

4) L.D. Frederickson, Jr., *Anal. Chem.*, **36**, 1349 (1964).

5) R.G. Cooks and S.W. Tam, *Org. Mass Spectrom.*, **1**, 583 (1968); B. Zeeh and R. Beutler, *ibid.*, **1**, 791 (1968); O. Tsuge, M. Tashiro, and K. Hokama, *Nippon Kagaku Zasshi*, **90**, 572 (1969).

6) K. Ogawa, Y. Ono, and Y. Ueda, *Yakugaku Zasshi*, **96**, 44 (1976).

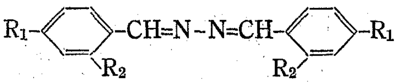
7) J.A. Pople, D.L. Beveridge, and P.A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967); J.A. Pople, D.L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill Inc., New York, N. Y., 1970.

TABLE I

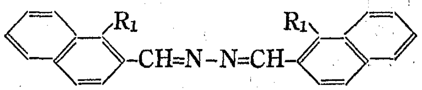
Compd. No.	Appearance	mp[a] (°C)	Analysis (%) Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
V	orange needles	254	77.63	4.74	8.23	77.68	4.80	8.18
XII	yellow needles	>300	67.16	4.48	10.45	66.87	4.59	10.23
XIV	yellow needles	160—161	62.45	4.09	15.61	62.52	4.21	15.53
XVIII	orange needles	102	78.83	5.11	10.22	78.58	5.12	9.91
XXII	orange needles	185	67.71	4.08	13.17	67.64	4.14	13.08
XXIX	yellow needles	268 (decomp.)	71.70	4.40	8.81	71.40	4.57	8.71
XXXI	yellow needles	182 (decomp.)	67.71	4.08	13.17	68.08	4.16	13.11

[a] uncorrected

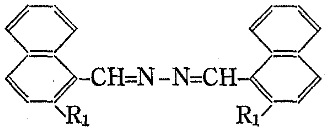
aromatic aldehyde azines having the symmetrical structure



I: $R_1=H$; $R_2=H$
II: $R_1=H$; $R_2=OH$
III: $R_1=OH$; $R_2=H$

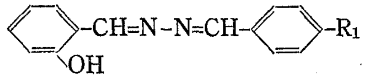


IV: $R_1=H$
V: $R_1=OH$



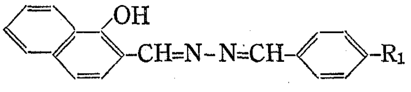
VI: $R_1=H$
VII: $R_1=OH$

salicylaldehyde *para*-substituted benzylidene hydrazones (S-series)



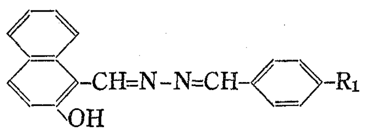
VIII: $R_1=N(CH_3)_2$
IX: $R_1=CH_3$
X: $R_1=Cl$
XI: $R_1=Br$
XII: $R_1=COOH$
XIII: $R_1=CN$
XIV: $R_1=NO_2$

1-hydroxynaphthalene-2-carbaldehyde *para*-substituted benzylidene hydrazones (α-series)



XV: $R_1=N(CH_3)_2$
XVI: $R_1=OCH_3$
XVII: $R_1=CH_3$
XVIII: $R_1=H$
XIX: $R_1=Cl$
XX: $R_1=Br$
XXI: $R_1=CN$
XXII: $R_1=NO_2$

2-hydroxynaphthalene-1-carbaldehyde *para*-substituted benzylidene hydrazones (β-series)



XXIII: $R_1=N(CH_3)_2$
XXIV: $R_1=OCH_3$
XXV: $R_1=CH_3$
XXVI: $R_1=H$
XXVII: $R_1=Cl$
XXVIII: $R_1=Br$
XXIX: $R_1=COOR$
XXX: $R_1=CN$
XXXI: $R_1=NO_2$

Results and Discussion

At first a brief discussion is made on the results of measurements of compounds having the symmetrical structure. It was reported that fragment ions $[M-1]^+$, $[M-27]^{+\cdot}$, $[M-28]^+$ and $[M-\text{aromatic ring}]^+$ are rather abundant and characteristic in the mass spectra of aromatic aldehyde azines.[5] Our results shown in Table II indicate that these four ions were abundant only in the mass spectra of four compounds which do not have the *ortho*-hydroxy structure (I, III, IV and VI), and they were neither abundant in the mass spectra of II nor present in the mass spectra of V and VII having the *ortho*-hydroxy structure. The fragment ion, $[M/2+2H]^+$, was observed in the mass spectra of II, V and VII. The fragment ion, $[M/2+H]^{+\cdot}$, was much more abundant in the mass spectra of II, V and VII than in the mass spectra of I, III, IV and VI. From these results it can be concluded that the four ions, $[M-1]^+$, $[M-27]^{+\cdot}$, $[M\text{–}28]^+$ and $[M\text{–aromatic ring}]^+$, are no more characteristic in the mass spectra of aromatic aldehyde azines having the *ortho*-hydroxy structure, and that the fragment ion, $[M/2+2H]^+$, may be useful to differentiate the compounds having the *ortho*-hydroxy structure from other kinds of aromatic aldehyde azines.

TABLE II. The Results of Mass Spectral Measurements of Symmetrical Aromatic Aldehyde Azines

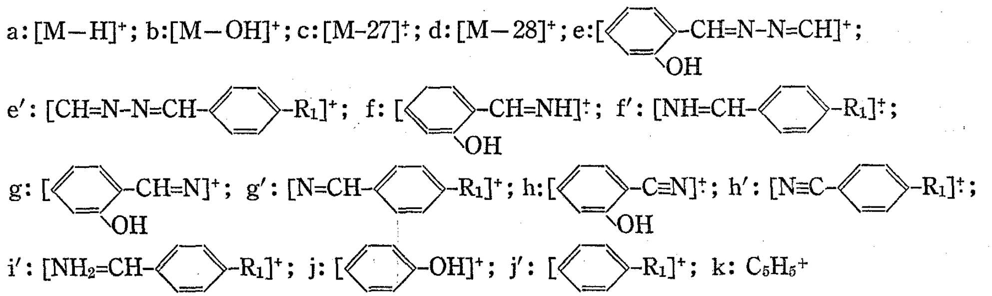
Compd. No.	$M^{+\cdot}$	Fragment ions[a]											
		a	b	c	d	e	f	g	h	i	j	k	l
I	100	65	—	12	21	93	6	23	7		41		—
II	100	15	49	4	6	29	44	28	6	8	20	20	—
III	91	50		14	19	100	10	45	8		17	35	—
IV	100	41	—	99	46	79	12	44	34		100	—	
V	49		5				100	30	14	16	10	—	32
VI	62	29	—	86	93	56	13	75	28		100	—	
VII	60		21				38	100	15	6	5	—	34

[a] Numerals in this table are relative intensities.
a: $[M-H]^+$; b: $[M-OH]^+$; c: $[M-27]^{+\cdot}$; d: $[M-28]^+$: e: $[M-Ar]^+$; f: $[M/2+H]^{+\cdot}$; g: $[M/2]^+$; h: $[M/2-H]^{+\cdot}$;
i: $[M/2+H_2]^+$; j: Ar^+; k: $C_5H_5^+$; l: $C_9H_7^+$; Ar: C_6H_5, C_6H_5O, $C_{10}H_7$, or $C_{10}H_7O$

TABLE III. The Results of Mass Spectral Measurements of S-Series

Compd. No.	R_1	Σ_{39} (>2%)	Fragment ions[a]															
			$M^{+\cdot}$	a	b	c	d	e	e′	f	f′	g	g′	h	h′	i′	j	j′	k
VIII	$N(CH_3)_2$	486	100	13	73		8	39[b]	10	5	22	14[b]	39[b]	11	11	19		14[b]	6
IX	CH_3	578	100	25	41	7	7	15	41	12	25[b]	17	53	25[b]		17[b]	11	33	28
X	Cl[c]	576	133	23	55	6	6	20	51	12	15	23	29	5		11	7	19	13
XI	Br[c]	1531	200	21	74	6	6	54	108	33	38	60	72	12	4	44[b]	25	44	53
XII	COOH	489	100	25	26	6	7	21[b]	45	12[b]	6	28	20	7	21[b]	6	9	12[b]	27
XIII	CN	426	100	25	31	7	7	20	34	10	5	28	12	9	3	6	5	19	12
XIV	NO_2	595	100	11	28	7	3	37	21	18		48	4	13	4	6	11		23

[a] Numerals in this table are relative intensities.



[b] the sum of intensities of two peaks having the same *m/e*

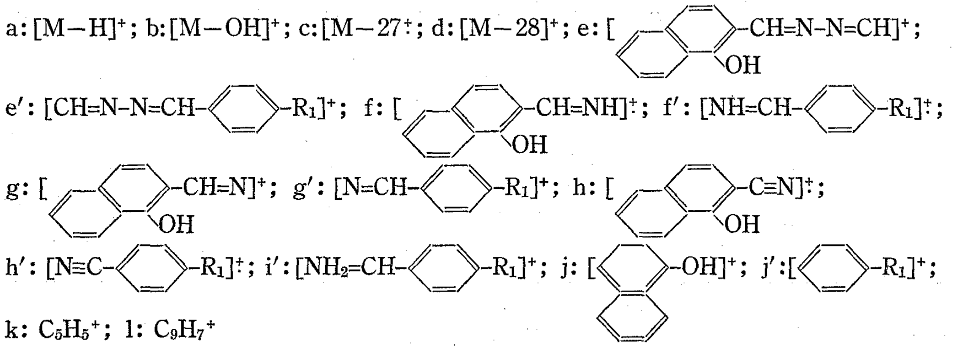
[c] the sum of intensities of two isotopic fragment ions

The mass spectra of compounds having the asymmetrical structure (Ar(OH)–CH=N–N=CH–Ar′–R) had the following characteristics: 1) The most abundant ions were molecular ions except two cases (XX and XXIII). 2) Fragment ions, $[Ar(OH)\text{–}CH{=}N]^+$, $[N{=}CH\text{–}Ar'\text{–}R]^+$, $[Ar(OH)\text{–}CH{=}N+H]^{+\cdot}$, $[N{=}CH\text{–}Ar'\text{–}R+H]^{+\cdot}$, $[Ar(OH)\text{–}CH{=}N-H]^{+\cdot}$, $[N{=}CH\text{–}Ar'\text{–}R+2H]^+$ of all compounds and $[M-OH]^+$ of S- and β-series compounds were abundant. 3) As similarly

Table IV. The Results of Mass Spectral Measurements of α-Series

Compd. No.	R_1	Σ_{39} (>2%)	$M^{+\cdot}$	a	b	c	d	e	e′	f	f′	g	g′	h	h′	i′	j	j′	k	l
			Fragment ions[a)]																	
XV	$N(CH_3)_2$	659	100	5	38		2		3	21	99	17	80	7	9	14	4	15	4	20
XVI	OCH_3	684	100	4	14			2	6	30	38	37	50	47	3	17	14	5	6	41
XVII	CH_3	559	100	5	8		2	3	8	20	9	44	20	70	4	25	9	17	12	33
XVIII	H	635	100	6	7				7	20	4	63	13	82	4	25	14	28	5	54
XIV	Cl[b)]	690	133	3	9			4	5	24	8	83	12	99		37		13	4	44
XX	Br[b)]	794	116	2	4			4	4	24	8	79	12	100		23	18	14	5	65
XXI	CN	554	100	3	4			3	3	19	4	71	8	61	6	8	13	10	4	49
XXII	NO_2	411	100		3					15		69	5	55		6	14		3	23

a) Numerals in this table are relative intensities.



a: $[M-H]^+$; b: $[M-OH]^+$; c: $[M-27]^{+\cdot}$; d: $[M-28]^+$; e: [-CH=N-N=CH]$^+$; OH

e′: [CH=N-N=CH- -R_1]$^+$; f: [-CH=NH]$^{+\cdot}$; OH; f′: [NH=CH- -R_1]$^{+\cdot}$;

g: [-CH=N]$^+$; OH; g′: [N=CH- -R_1]$^+$; h: [-C≡N]$^{+\cdot}$; OH

h′: [N≡C- -R_1]$^{+\cdot}$; i′: [NH_2=CH- -R_1]$^+$; j: [-OH]$^+$; j′: [-R_1]$^+$;

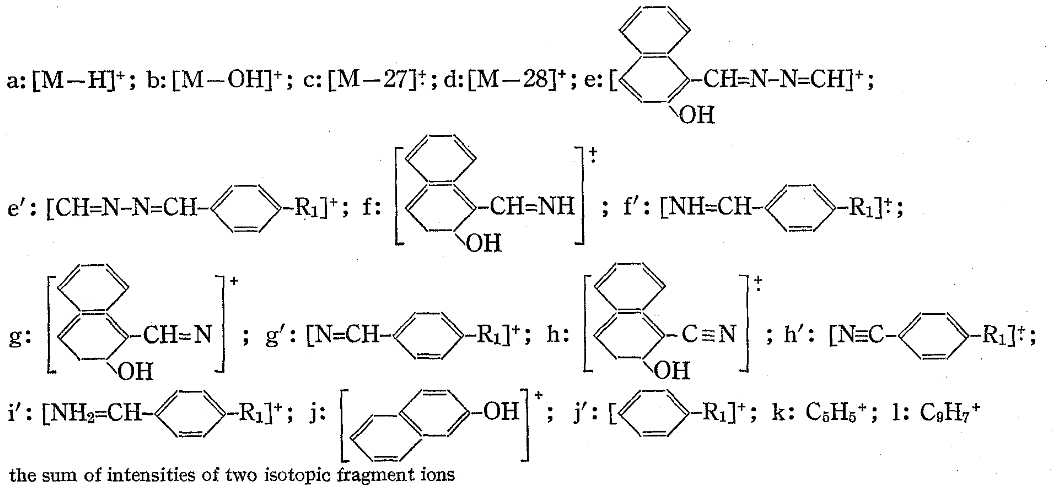
k: $C_5H_5^+$; l: $C_9H_7^+$

b) the sum of intensities of two isotopic fragment ions

Table V. The Results of Mass Spectral Measurements of β-Series

Compd. No.	R_1	Σ_{39} (>2%)	$M^{+\cdot}$	a	b	c	d	e	e′	f	f′	g	g′	h	h′	i′	j	j′	k	l
			Fragment ions[a)]																	
XXIII	$N(CH_3)_2$	429	86	3	100		2		3	2	40	8	36	3	4	5		6	2	6
XXIV	OCH_3	686	100	5	77		3		8	9	64	45	62	32	3	22	7	5	7	37
XXV	CH_3	805	100	9	53		5		12	9	15	58	28	74	5	29	8	22	18	39
XXVI	H	402	100	10	33				5	5	2	38	6	47		10	5			23
XXVII	Cl[b)]	529	133	9	53	2	3		5	8	5	56	8	64		21	6	7		22
XXVIII	Br[b)]	911	200	8	63	4	3		8	11	8	83	16	97		23	10	14	3	63
XXIX	COOH	507	100	11	29		5		7	12	13	59	9	59	3	11	7		7	31
XXX	CN	436	100	12	26		3		15	9	2	61	5	47	5	4	6	5		31
XXXI	NO_2	321	100	8	16					6		43		32		3	6			22

a) Numerals in this table are relative intensities.



a: $[M-H]^+$; b: $[M-OH]^+$; c: $[M-27]^{+\cdot}$; d: $[M-28]^+$; e: [-CH=N-N=CH]$^+$; OH

e′: [CH=N-N=CH- -R_1]$^+$; f: [-CH=NH OH]$^{+\cdot}$; f′: [NH=CH- -R_1]$^{+\cdot}$;

g: [-CH=N OH]$^+$; g′: [N=CH- -R_1]$^+$; h: [-C≡N OH]$^{+\cdot}$; h′: [N≡C- -R_1]$^{+\cdot}$;

i′: [NH_2=CH- -R_1]$^+$; j: [-OH]$^+$; j′: [-R_1]$^+$; k: $C_5H_5^+$; l: $C_9H_7^+$

b) the sum of intensities of two isotopic fragment ions as the results of *ortho*-hydroxy aromatic aldehyde azines having the symmetrical structure, fragment ions, $[M-1]^+$, $[M-27]^{+\cdot}$, $[M-28]^+$ and $[M-\text{aromatic ring}]^+$, were not abundant.

Correlation between Relative Ion Intensities of Fragment Ions, [Ar(OH)-CH=N]$^+$ (Abbreviated as the g Ion), [N=CH-Ar′-R]$^+$ (Abbreviated as the g′ Ion) and [M—OH]$^+$ (Abbreviated as the b Ion), and the Substituent Effect

Among several kinds of characteristic fragment ions of aromatic aldehyde azines having the asymmetrical structure only such ions as g, g′ and b ions were considered to be adequate to investigate the relationship between the relative ion intensities and the substituent effects, because other major ions are all rearrangement ions.

The results shown in Tables III—V indicate that the relative ion intensities of these three fragment ions must be strongly dependent on the substituent. It has been known that the ion intensity of a common fragment ion in the mass spectra of a series of substituted aromatic compounds correlates with the substituent constant in many cases. Bursey, *et al.*[8] explained the substituent dependence of the ion intensity of a common fragment ion from the standpoint of the kinetic approach, and introduced the so-called log Z/Z_0 method (the equation 1). Where k refers to the rate constant of the formation of $[A]^+$ ion from the molecular ion, and $[A^+]$ and $[M^{+\cdot}]$ refer to the relative ion intensities of $[A]^+$ and $[M]^{+\cdot}$ ions detected on the mass spectra. The suffix 0 indicates the case of the standard compound.

$$\log\frac{Z}{Z_0}=\log\frac{[A^+]/[M^{+\cdot}]}{[A_0^+]/[M_0^{+\cdot}]}=\log\frac{k_A}{k_{A_0}}\propto\sigma\ (\text{or }\sigma^+)\qquad(1)$$

According to the idea presented by Chin, *et al.*[9] the ion intensity of the molecular (or the fragment) ion initially formed in the ion source ($[^tM^{+\cdot}]_0$ or $[^tA^+]_0$; in this case the suffix 0 means the earliest stage of the formation of an ion) can be divided into two groups. One is the molecular (or fragment) ion having sufficient internal energy to decompose ($[^dM^{+\cdot}]_0$ or $[^dA^+]_0$), and the other is the molecular (or fragment) ion having insufficient energy to undergo fragmentation ($[M^{+\cdot}]_0$ or $[A^+]_0$). And these authors expressed the linearity between the logarithmic ratio of the relative ion intensity of a fragment ion formed by the unimolecular reaction to that of the molecular ion having sufficient energy to decompose and the substituent constant by the equation (2). Here, f_i refers to the fraction of the instrumental loss[8] and its magnitude

$$\log\frac{(1-f_i)[A^+]_0}{(1-f_i)[^dM^{+\cdot}]_0}=\log\frac{[A^+]}{[^dM^{+\cdot}]}=\log\frac{f_A[^tA^+]}{[^dM^{+\cdot}]}=\log\frac{f_Ak_A}{k_t}\propto\sigma\ (\text{or }\sigma^+)\qquad(2)$$

is assumed to be independent on the kind of ion. $[^dM^{+\cdot}]$ is considered to be the fraction of $[^tM^{+\cdot}]$ (the equation 3). And f_A is the fraction of the $[^tA]^+$ ion appearing as $[A]^+$ (the equation 4). k_t is the sum of all rate constants resulting in decomposition of the molecular ion.

$$[M^{+\cdot}]=f_M[^tM^{+\cdot}]=f_M([^dM^{+\cdot}]+[M^{+\cdot}])\qquad(3)$$

$$[A^+]=f_A[^tA^+]=f_A([^dA^+]+[A^+])\qquad(4)$$

In the present investigation, the equation (2) was applied to the examination of the substituent dependences of the relative ion intensities of three fragment ions mentioned before, because the values of f_M's were found to be neither constant nor correlative with the substituent constant in all of three series compounds and the equation (2) does not include the term f_M. The magnitude of $[^dM^{+\cdot}]$ was calculated by the summation of relative ion intensities of all peaks having those values larger than 2% and locating between *m/e* (M−1) and 39. Because, it was difficult to estimate the extent of the contribution of the background in the region of *m/e* less than 39 and to determine the relative intensity of weak peaks accurately.

The results shown in Table VI indicate that the relative ion intensity of the g ion is remarkably dependent on the substituent constant, σ^+, in all of three series compounds. The linear

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[8] M.M. Bursey and F.W. McLafferty, *J. Am. Chem. Soc.*, **88**, 529 (1966).

[9] M.S. Chin and A.G. Harrison, *Org. Mass Spectrom.*, **2**, 1073 (1969).

correlations between the relative ion intensities of the g′ ions of α- and β-series compounds and σ^+ are somewhat inferior to that of the case of the g ion. And those between the relative ion intensities of the g′ ion of S-series compounds and of the b ions of all of three series compounds and σ^+ are fairly inferior to the above two cases.

Table VI. Least Squares Analyses of the Logarithmic Values of Ratios of the Relative Ion Intensities of Ions *vs.* σ^+

Ratio	S-Series				α-Series				β-Series			
	σ[a]	r[b]	m[c]	k[d]	σ[a]	r[b]	m[c]	k[d]	σ[a]	r[b]	m[c]	k[d]
$[g^+]/[^dM^{+\cdot}]$	0.03	0.98	0.41	−1.35	0.05	0.98	0.33	−0.94	0.06	0.97	0.35	−0.96
$[g'^+]/[^dM^{+\cdot}]$	0.19	−0.84	−0.80	−1.12	0.09	−0.96	−0.43	−1.54	0.12	−0.92	−0.40	−1.56
$[b^+]/[^dM^{+\cdot}]$	0.11	−0.77	−0.18	−1.05	0.13	−0.90	−0.36	−1.86	0.09	−0.87	−0.22	−1.00
$[e^+]/[^dM^{+\cdot}]$	0.02	0.98	0.33	−1.41								
$[e'^+]/]^dM^{+\cdot}]$	0.18	0.62	0.18	−1.14	0.17	0.14	0.03	−2.04	0.14	0.68	0.19	−1.77
$[g'^+]/[g^+]$	0.18	−0.93	−1.24	0.22	0.11	−0.98	−0.75	−0.60	0.11	−0.98	−0.77	−0.61
	(0.08	−0.99	−0.80	−0.57)[e]								
$[b^+]/[g^+]$	0.10	−0.88	−0.52	0.27	0.12	−0.97	−0.69	−0.92	0.11	−0.97	−0.57	−0.04

a) standard deviation
b) correlation coefficient
c) slope
d) intercept
e) for only four compounds having the substituents of OCH_3 CH_3, H and NO_2.

Linear correlations obtained seem to suggest that each one of three ions, g, g′ and b, was formed by a single process from the molecular ions. However, the mass spectra were measured in the present investigation by utilizing 75 eV ionizing electrons, then the two-step formation processes of the g and g′ ions, $[M]^{+\cdot}\rightarrow e\rightarrow g$, $[M]^{+\cdot}\rightarrow e'\rightarrow g'$ and $[M]^{+\cdot}\rightarrow b\rightarrow g'$, must also be possible to exist.

A logarithmic relative ion intensity ratio of a common fragment ion, $[B]^+$, formed by a two-step fragmentation process of the molecular ions of a series of compounds, $[M]^{+\cdot}\rightarrow[A]^+\rightarrow[B]^+$, can be shown to correlate also linearly with the substituent constant when the $[A]^+$ ion has no substituent. In the step of $[A]^+\rightarrow[B_A]^+$, where $[B_A]^+$ means the $[B]^+$ ion formed from the $[A]^+$ ion, the logarithmic relative ion intensity ratio, $\log [^tB_A{}^+]/[^dA^+]=\log [B_A{}^+]f_A/[A^+](1-f_A)f_{B_A}$, may be assumable to be kept approximately constant (c) throughout a series of compounds. And also both f_A and f_{B_A} are assumable to vary only slightly with the substituent constant[9] to give an approximately constant values (c') of $\log f_A/(1-f_A)f_{B_A}$. Then, the equation (5) is derived. By the way, it can be expected that the logarithmic relative ion intensity ratio, $\log [A^+]/[^dM^{+\cdot}]$, is in a linear correlation with the substituent constant, for instance σ^+ (the equation 6). From equations (5) and (6) one can derive the equation (7) which shows the linear relationship between the value of $\log [B_A{}^+]/[^dM^{+\cdot}]$ and the substituent constant.

$$\log\frac{[B_A{}^+]}{[A^+]}\simeq(c-c') \tag{5}$$

$$\log\frac{[A^+]}{[^dM^{+\cdot}]}\propto\sigma^+ \tag{6}$$

$$\log\frac{[B_A{}^+]}{[^dM^{+\cdot}]}+(c'-c)\propto\sigma^+ \tag{7}$$

Next, the case where the $[A]^+$ and $[B_A]^+$ ions have substituents is considered. If there exists a relationship expressed by the equation (6) and if the logarithmic relative ion intensity ratio, $\log[^tB_A{}^+]/[^dA^+]$, is assumed to correlate linearly with the substituent constant, for instance σ^+ (the equation 8), the equation (9) is derived. This equation means that the value of log $[B_A{}^+]/[^dM^{+\cdot}]$ does not correlate linearly with the substituent constant, because, even if the logarithmic values of both f_A and f_{B_A} are assumed to correlate linearly with the substituent constant,[9] the value of log $(1-f_A)$ cannot correlate linearly with the substituent constant.

$$\log\frac{[B_A{}^+]f_A}{[A^+](1-f_A)f_{B_A}} \propto \sigma^+ \tag{8}$$

$$\log\frac{[B_A{}^+]}{[{}^dM^{+\cdot}]} + \log\frac{f_A}{(1-f_A)f_{B_A}} \propto \sigma^+ \tag{9}$$

In the present investigation, the results shown in Table VI indicate the following facts: 1) The two-step formation pathway of the g ion may be probable in S-series compounds, but nothing can be said about this pathway of α- and β-series compounds. Because the e ion ($[\mathrm{Ar(OH)\text{–}CH{=}N\text{–}N{=}CH}]^+$) was not abundant enough to examine the possibility in both α- and β-series compounds. 2) The two-step formation pathway of the g′ ion *via* the e′ ion ($[\mathrm{CH{=}N\text{–}N{=}CH\text{–}Ar'\text{–}R}]^+$) may be improbable in all of three series compounds. Because, the correlation between log $[e'^+]/[{}^dM^{+\cdot}]$ and σ^+ had a very poor correlation coefficient and had the slope of opposite sign to that of the slope of the correlation between log $[g'^+]/[{}^dM^{+\cdot}]$ and σ^+, namely there was no such relationship as that expressed by the equation (6). 3) With regard to the two-step formation pathway of the g′ ion *via* the b ion any distinct supposition is impossible, because the linearity between log $[b^+]/[{}^dM^{+\cdot}]$ and σ^+ was fairly good in all of three series compounds.

Next, a brief comment is made on the probability of the coexistence of two fragment ions, $[B_A]^+$ and $[B_M]^+$, the latter means the $[B]^+$ ion formed from the molecular ion. There may be little doubt that the logarithmic relative ion intensity ratio, log $[B_M{}^+]/[{}^dM^{+\cdot}]$, correlates with σ^+ linearly (the equation 10). If the $[B]^+$ ion detected on the mass spectra is a mixture of $[B_M]^+$ and $[B_A]^+$ ions and the value of log $[B^+]/[{}^dM^{+\cdot}]$ correlates with σ^+ linearly, three equations (7), (10) and (11) must be formed at the same time. This requirement can be fulfilled only when $[B_M{}^+]$ is equal to $[B_A{}^+]$, and in this case all of these three linear correlations must have the same slope. In the case of the g ion of S-series compounds the slope of the correlation between the value of log $[g^+]/[{}^dM^+]$ and σ^+ was 0.41. The slope of the correlation between the value of log $[g_e{}^+]/[{}^dM^+]$ and σ^+ can be assumed to be approximately equal to that of the correlation between the value of log $[e^+]/[{}^dM^+]$ and σ^+ having the value of 0.33 from the consideration mentioned before (the equations (5)—(7)). Then it may be considered that the g ion of S-series compounds must be formed primarily by either one of the two probable pathways, $[M]^{+\cdot}\rightarrow g$ or $[M]^{+\cdot}\rightarrow e\rightarrow g$. It was not possible to examine the cases of the g ion of α- and β-series compounds and of the g′ ion of all three series compounds, because the probability of the two-step formation pathways of these ions could not be clarified as mentioned before.

$$\log\frac{[B_M{}^+]}{[{}^dM^{+\cdot}]} \propto \sigma^+ \tag{10}$$

$$\log\frac{([B_M{}^+]+[B_A{}^+])}{[{}^dM^+]} \propto \sigma^+ \tag{11}$$

Contribution of the Ionization Potentials to the Substituent Effects

In the approach to substituent effects on the logarithmic Z-value ratios Bentley, *et al.*[10] derived an equation (12) by using a simplified equation obtainable from the quasi-equilibrium theory for the rate constant. Here, IP refers to the ionization potential. This equation involves the approximation that the excess internal energy of the molecular ion (E) does not vary with the substituents (Y).

$$\ln\frac{Z_Y}{Z_0} = \ln\frac{k_Y}{k_0} \simeq \frac{(N-1)}{E}[\mathrm{IP}(M_Y)-\mathrm{IP}(M_0)] \tag{12}$$

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[10] T.W. Bentley, R.A.W. Johnstone, and D.W. Payling, *J. Am. Chem. Soc.*, **91**, 3978 (1969).

Einolf, *et al.*[11] considered that the rate constant ratio of two fragmentation reactions of the same molecular ion giving the ions $[A]^+$ and $[B]^+$ can be correlated with the activation energies of these two reactions. And they also showed that the relative ion intensity ratio is equal to the rate constant ratio. This correlation can be expressed by the equation (13).

$$\log\frac{[A^+]}{[B^+]}=\log\frac{k_A}{k_B}=\log\frac{\nu_A}{\nu_B}+(N-1)\log\frac{E-E_A^\circ}{E-E_B^\circ} \qquad (13)$$

Here, ν is the frequency factor; E° is the activation energy; N is the effective number of harmonic oscillators. When E is assumable to be much larger than the difference of E_A° and E_B°, this equation can be approximated by the equation (14).[12] This equation can be rewritten

$$\log\frac{[A^+]}{[B^+]}\simeq\log\frac{\nu_A}{\nu_B}+\frac{0.43(N-1)}{E}(E_B^\circ-E_A^\circ) \qquad (14)$$

$$\log\frac{[A^+]}{[B^+]}\simeq\log\frac{\nu_A}{\nu_B}+\frac{0.43(N-1)}{E}[\mathrm{AP}(B^+)-\mathrm{AP}(A^+)]$$

$$=\log\frac{\nu_A}{\nu_B}+\frac{0.43(N-1)}{E}[\{\mathrm{IP}(B^\cdot)-\mathrm{IP}(A^\cdot)\}+(D_B-D_A)] \qquad (15)$$

as the equation (15) by substituting either the difference of appearance potentials (AP) of two ions or the sum of the difference of ionization potentials of radicals corresponding to the ions and the difference of dissociation energies (D) of bonds to be broken to give the ions for the difference of activation energies. Of course, the value of the left-hand side of this equation will correlate linearly with the substituent constant, if values of both log $[A^+]/[^dM^{+\cdot}]$ and log $[B^+]/[^dM^{+\cdot}]$ are in linear correlations with the substituent constant.

Richards, *et al.*[13] recognized that the values of log $[YC_6H_4CO^+]/[C_6H_5CO^+]$, both of these two ions were believed to be formed from the substituted benzyl molecular ions $[(YC_6H_4COCOC_6H_5]^{+\cdot})$, correlated linearly with the difference of appearance potentials of these two ions. And they explained that the substituent (Y) affects the ratio of the relative ion intensities mainly by changing the activation energies for the competing decompositions of the molecular ions.

This kind of approach seems to be helpful to find out any reason of the substituent effects found in this study. But, none of the values of the frequency factor, the ionization potential and the dissociation energy was available from the known data, therefore, they must be estimated by any means. Among them the ionization potentials of radicals can be calculated by the molecular orbital method and the value of the difference of dissociation energies is able to assume to vary very slightly by the change of substituent, because the bond to be broken is located at the far position from the substituent in all of the cases of fragmentations forming g, g′ and b ions.[14] However, the value of the frequency factor is impossible to estimate. Moreover, the formation pathways of both g and g′ ions are ambiguous, although metastable ions indicating the presence of the pathway, $[M]^{+\cdot}\rightarrow g$, were observed on the mass spectra of each three compounds of α- and β-series compounds which were measured again at 20 eV electron energy for the particular purpose of looking for the metastable ions.[15] This situation made the examination of the reason of the substituent effects found in this study

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[11] N. Einolf and B. Munson, *Org. Mass Spectrom.*, **5**, 397 (1971).

[12] $\log\frac{E-E_A^\circ}{E-E_B^\circ}=-0.43\left[\frac{(E_A^\circ-E_B^\circ)}{E}+\frac{(E_A^{\circ2}-E_B^{\circ2})}{2E^2}+\frac{(E_A^{\circ3}-E_B^{\circ3})}{3E^3}+\cdots\right]$

[13] K.E. Richards, B.N. McMaster, and G.J. Wright, *Org. Mass Spectrom.*, **10**, 295 (1975).

[14] T.L. Cottrell, "The Strength of Chemical Bonds," 2nd ed., Butterworths, London, 1958; F.W. McLafferty, T. Wachs, C. Lifshitz, G. Innorta, P. Irving, *J. Am. Chem. Soc.*, **92**, 6867 (1970).

[15] Any distinct metastable ions indicating the direct formation pathway of the g ion from the molecular ion could not be detected on the mass spectra of three compounds of S-series compounds. And metastable ions indicating the pathway, $[M]^{+\cdot}\rightarrow g'$, could not be detected at all on the mass spectra of all of three series compounds.

impossible. Therefore, only the relationships between the differences of ionization potentials and the logarithmic values of the relative ion intensity ratios of two combinations, g′ to g and b to g, were examined.

The ionization potentials of radicals were calculated by subtracting the total energies of radicals calculated by the unrestricted INDO method from those of the corresponding cations calculated by the restricted INDO method,16) but in some cases the calculation of total energies was unsuccessful. Therefore, ionization potentials obtained were limited to the case of three kinds of g radicals, four kinds of g′ radicals having the substituents of OCH_3, CH_3, H and NO_2 and four kinds of b radicals having the same kinds of substituents. These ionization potentials are shown in Table VII.

Table VII. Ionization Potentials of Radicals (eV)

g· radicals		g′· radicals	
S-Series compounds	9.623	·N=CH–Ar′–OCH_3	9.763
α-Series compounds	9.229	·N=CH–Ar′–CH_3	9.847
β-Series compounds	9.103	·N=CH–Ar′–H	10.107
		·N=CH–Ar′–NO_2	10.848

	b· radicals	
	α-Series compounds	β-Series compounds
·Ar–CH=N–N=CH–Ar′–OCH_3	8.788	8.659
·Ar–CH=N–N=CH–Ar′–CH_3	8.802	8.699
·Ar–CH=N–N=CH–Ar′–H	8.847	8.772
·Ar–CH=N–N=CH–Ar′–NO_2	9.208	9.120

Table VIII. Least Squares Analyses of the Differences of Ionization Potentials *vs.* σ^+

	S-Series	α-Series	β-Series
[IP(g·) – IP(g′·)] *vs.* σ^+			
Standard deviation	0.11	0.11	0.11
Correlation coefficient	–0.97	–0.97	–0.97
Slope	–0.73	–0.72	–0.72
Intercept	–0.60	–0.97	–1.09
[IP (g·) – IP (b·)] *vs.* σ^+			
Standard deviation		0.12	0.11
Correlation Coefficient		–0.97	–0.97
Slope		–0.69	–0.57
Intercept		–0.92	–0.04

In both cases of the ratios of $[g'^+]/[g^+]$ and $[b^+]/[g^+]$, their logarithmic values were found to be in linear correlations with σ^+ (Table VI). Differences of ionization potentials were also found to correlate linearly with σ^+ in α- and β-series compounds (Table VIII).18) From these

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16) g, g′, and b radicals were assumed to have the structures, [Ar(OH)–CH=N]·, [N=CH–Ar′–R]·, and [Ar(OH)–CH=N–N=CH–Ar′–R]·, respectively. In the restricted INDO calculation a cation was considered to have as same geometry as that of the corresponding radical.7,17)

17) M.J.S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill Book Company, New York, 1969.

18) Ionization potentials of b· radicals of S-series compounds were not calculated, because this group of compounds does not include the derivatives having the substituents of OCH_3 and H.

two linear relationships it became clear that the ratio of relative ion intensities of two fragment ions, g′ and g or b and g, correlates linearly with the difference of ionization potentials of two radicals corresponding to the two ions.

The results obtained indicate that the substituents affect the ionization potential of the radical corresponding to each fragment ion and that the variation of ionization potentials is reflected on the logarithmic values of relative ion intensity ratios of fragment ions. But, since the formation pathways of g and g′ ions could not be clarified, any more conclusion can not be derived from the results.