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70. Masaru Nakamura, Kyoko Komatsu, Yoshiko Gondo, Kiyoko Ohta,*1 and Yo Ueda*2 : An Infrared Study of the C=N Stretching Frequency in N-Benzylideneaniline Derivatives.

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A series of 131 N-benzylideneaniline derivatives was prepared, and their infrared spectra were measured in the same conditions.

Statistical tests showed that differences of substitution in benzene ring of benzylidene group affected acceptably on the region of C=N stretching absorption peak, but those in benzene ring of aniline group had smaller effect on it.

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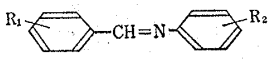
The infrared absorption band due to the stretching vibration of the C=N group in N-benzylideneaniline derivatives was assigned to the region 1626~1637 cm^{-1} by Fabian, *et al.*,[1] and 1613~1631 cm^{-1} by Clougherty, *et al.*[2]

Since the compounds studied were measured in various conditions, the effects of substituents on the band position have been remained uncertain.

The purpose of this investigation was to measure the infrared absorption spectra of N-benzylideneaniline derivatives in the same condition, and to clarify the effects of substituents on the absorption band due to C=N.

131 N-benzylideneaniline derivatives, including 43 new compounds, were prepared and their infrared spectra were measured in chloroform solutions and in potassium bromide tablets. Those compounds have no or only one substituent in each benzene ring of their molecules.

Table I. C=N Stretching Frequency in N-Benzylideneaniline Derivatives



R_1	R_2	in $CHCl_3$ (cm^{-1})	in KBr (cm^{-1})	R_1	R_2	in $CHCl_3$ (cm^{-1})	in KBr (cm^{-1})
2-Cl	2-OH	1621	1618	〃	4-Br	1623	1616
〃	4-OH		1616	——	2-Cl		1623
〃	2-Cl	1629	1618	2-OH	〃	1626	1616
〃	3-Cl		1618	4-OH	〃		1616
〃	4-Cl		1621	3-Cl	〃	1631	1623
〃	2-CH_3	1626	1613	4-Cl	〃	1637	1623
〃	4-CH_3	1623	1616	2-NO_2	〃		1629
〃	3-OCH_3	1623	1621	3-NO_2	〃	1634	1631
〃	4-OCH_3	1621	1618	4-NO_2	〃	1629	1626
〃	3-NO_2	1626	1621				
〃	2-Br		1621	3-Cl	2-OH	1631	1626
〃	3-Br	1623	1616	〃	4-OH		1621

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*2 Katakasu, Fukuoka (上田 陽).

1) J. Fabian, M. Legrand, P. Poirier : Bull. soc. chim. France, **1956**, 1499.

2) L. E. Clougherty, J. A. Sousa, G. M. Wyman : J. Org. Chem., **22**, 462 (1957).

〃	3-Cl		1626
〃	4-Cl		1621
〃	2-CH_3	1631	1626
〃	4-CH_3	1631	1621
〃	4-OCH_3	1629	1621
〃	3-NO_2	1634	1631
〃	2-Br	1637	1629
〃	3-Br	1634	1631
〃	4-Br	1634	1626
——	3-Cl	1634	
2-OH	〃		1618
3-OH	〃		1623
4-Cl	〃		1626
2-NO_2	〃	1634	1629
3-NO_2	〃	1634	1621
4-NO_2	〃	1634	1626
〃	——	1634	1626
〃	2-OH	1626	1626
〃	4-OH		1621
〃	4-Cl		1623
〃	2-CH_3		1629
〃	3-CH_3	1634	1626
〃	4-CH_3	1631	1626
〃	2-OCH_3	1631	1626
〃	3-OCH_3		1626
〃	4-OCH_3		1618
〃	3-NO_2	1637	1626
〃	4-NO_2	1634	1626
〃	2-Br	1637	1626
〃	3-Br	1634	1626
〃	4-Br		1623
——	4-Cl	1631	1629
2-OH	〃	1626	1616
3-OH	〃		1623
2-NO_2	〃	1623	1618
3-NO_2	〃	1634	1623
4-NO_2	〃	1637	1623
2-NO_2	——	1623[a]	1626
〃	2-OH	1623	1616
〃	4-OH	1623	1626
〃	2-CH_3	1623	1623
〃	3-CH_3	1623	1626
〃	4-CH_3	1623	1618
〃	2-OCH_3	1618	
〃	3-OCH_3	1623	1623
〃	4-OCH_3	1621	1618
〃	2-NO_2	1637	
〃	3-NO_2	1634	1623
〃	4-NO_2	1637	1623
〃	2-Br	1629	1634
〃	3-Br	1626	1626
〃	4-Br	1626	1621
3-NO_2	2-NO_2	1645	1637
3-NO_2	——	1637	1629
〃	2-OH	1634	1629
〃	4-OH		1623
〃	2-CH_3	1637	1626
〃	3-CH_3	1631	1626
〃	4-CH_3	1637	1619
〃	3-OCH_3	1634	1623
〃	4-OCH_3		1621
〃	3-NO_2	1645	1639
〃	4-NO_2	1642	1631
〃	3-Br	1637	1631
〃	4-Br	1631	1631
——	3-NO_2	1634	1631
2-OH	〃		1618
3-OH	〃		1626
4-OH	〃		1623
4-NO_2	〃		1629
4-NO_2	——	1629	1623
〃	2-OH	1623	1626
〃	4-OH	1629	1623
〃	2-CH_3	1637	1629
〃	3-CH_3	1634	1629
〃	4-CH_3	1634	1626
〃	2-OCH_3	1631	1626
〃	3-OCH_3	1634	1629
〃	4-OCH_3	1629	1623
〃	4-NO_2	1637	1629
〃	2-Br		1629
〃	3-Br	1634	1631
〃	4-Br	1637	1631
2-OH	4-NO_2	1629	1616
2-OH	——	1631	1623
〃	2-OH	(1624)[2]	1631
〃	3-OH		1623
〃	4-OH		1621
〃	2-CH_3	1623	1613
〃	3-CH_3	1623	1616
〃	4-CH_3	1626	1621
〃	2-OCH_3	1621	1616
〃	3-OCH_3	1626	1616
〃	4-OCH_3	1623	1621
〃	2-Br		1613
〃	3-Br	1623	1621
〃	4-Br	1626	1613
——	2-OH	1631	1623
4-OH	〃		1613
3-OH	——		1626
〃	4-CH_3	1631	1626
〃	4-OCH_3	1631	1626
〃	3-Br		1618
〃	4-Br		1621
4-OH	4-OH		1613
〃	2-OCH_3		1621
〃	3-Br		1613
——	4-OH		1623

a) 1621 cm^{-1} [2]

Results and Discussion

As shown in Table I, most of the compounds exhibited rather strong peaks in the region of 1618~1645 cm^{-1} in chloroform solutions, and of 1613~1639 cm^{-1} in solid states.

The assignment of C=N absorption band is not always simple, but the facts that the regions mentioned above coincided with the reported ones, and most of the N-benzylideneaniline derivatives didn't show any complex pattern in a range of 1610~1650 cm^{-1} made us comparatively easy to assign these bands to C=N stretching mode of vibrations.

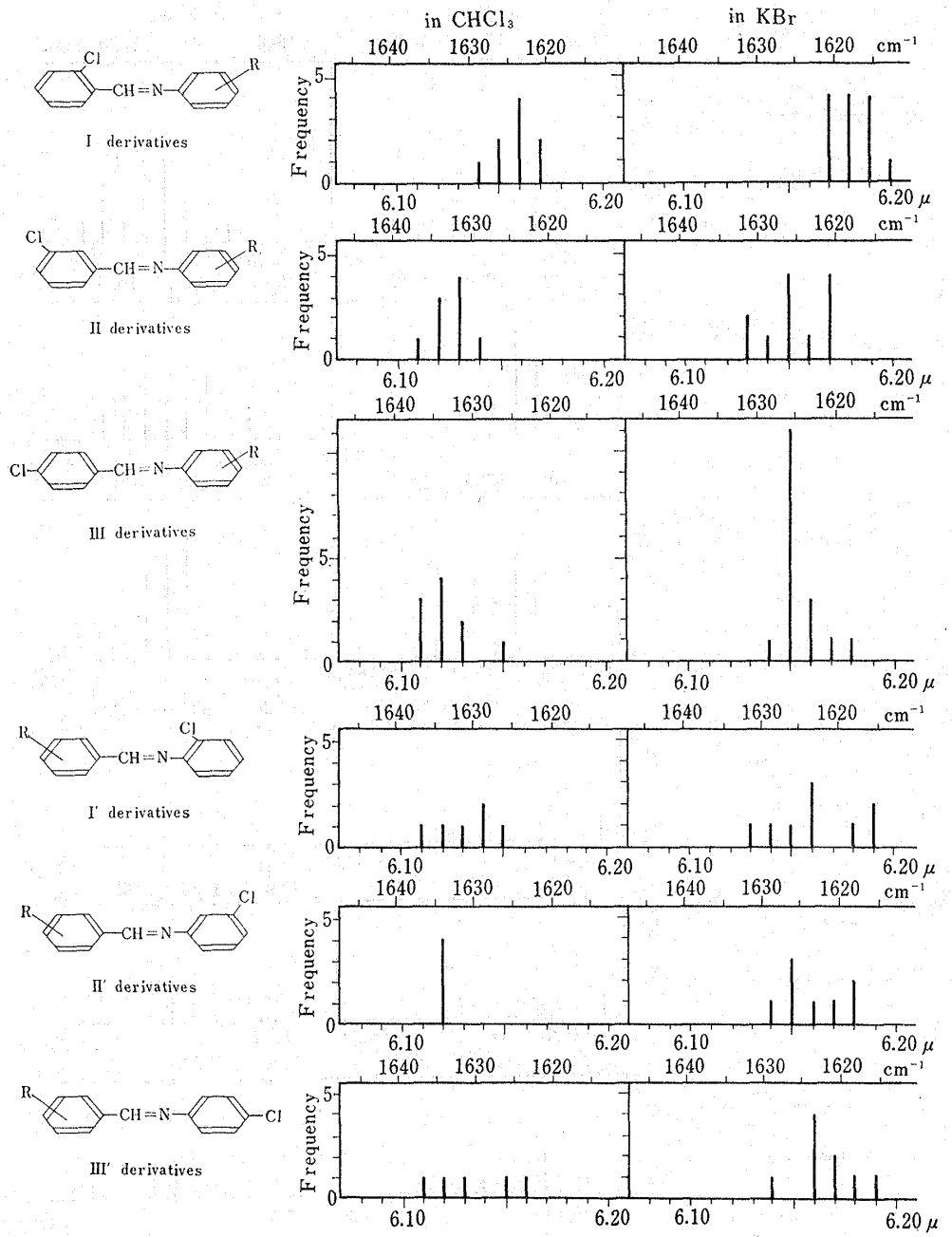


Fig. 1. Distributions of the Data of C=N Stretching Frequency in I, II, III, I′, II′, and III′ Derivatives

N-(2-Chlorobenzylidene)aniline (I) derivatives showed the absorption peaks in lower frequency region than N-(3-chlorobenzylidene)aniline (II), and N-(4-chlorobenzylidene)-aniline (III) derivatives as shown in Fig. 1.

Statistical tests of the differences between mean wave numbers of C=N stretching absorption bands of I, II, and III derivatives, using the table of Fisher's distribution and a 5% level of significance, showed that the population of the data of I derivatives was different from those of II and III derivatives, and that of II derivatives was not different from that of III derivatives. On the contrary, those of N-benzylidene-2-chloroaniline (I′) derivatives, N-benzylidene-3-chloroaniline (II′) derivatives, and N-benzylidene-4-chloroaniline (III′) derivatives were not different from each other.

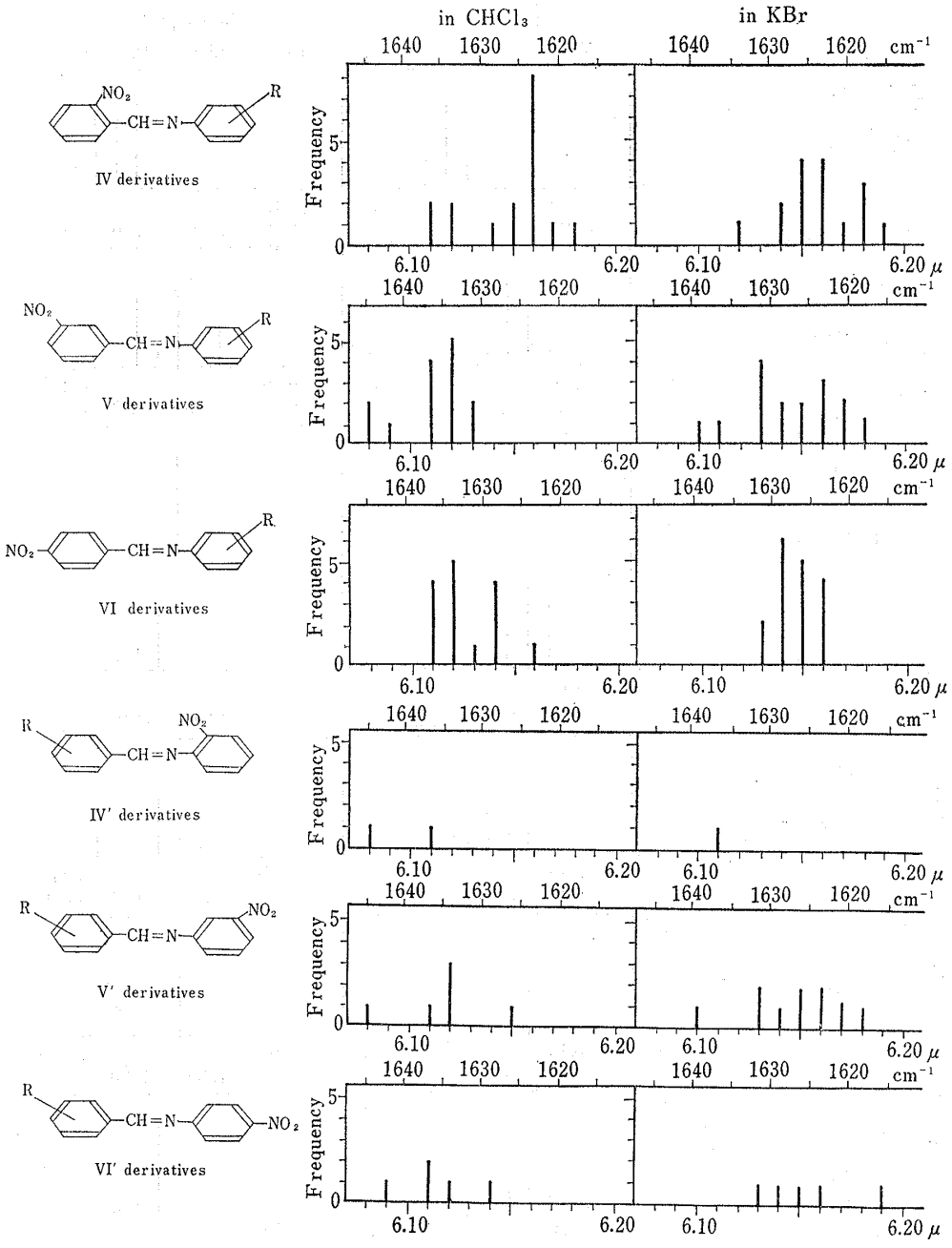


Fig. 2. Distributions of the Data of C=N Stretching Frequency in IV, V, VI, IV′, V′, and VI′ Derivatives

Populations of the data of wave number of C=N stretching absorption bands in N-(2-nitrobenzylidene)aniline (Ⅳ) derivatives, N-(3-nitrobenzylidene)aniline (Ⅴ) derivatives, and N-(4-nitrobenzylidene)aniline (Ⅵ) derivatives were different from each other, while those of the data of N-benzylidene-3-nitroaniline (Ⅴ′) derivatives and N-benzylidene-4-nitroaniline (Ⅵ′) derivatives were not different. N-Benzylidene-2-nitroaniline (Ⅳ′) derivatives available were not enough for calculation.

Distributions of the data of Ⅳ, Ⅴ, Ⅵ, Ⅳ′, Ⅴ′, and Ⅵ′ derivatives are shown in Fig. 2.

As shown in Fig. 3, N-(3-hydroxybenzylidene)aniline (Ⅷ) derivatives showed a C=N stretching absorption band in a comparatively higher frequency region than N-(2-hydroxybenzylidene)aniline (Ⅶ) derivatives and N-(4-hydroxybenzylidene)aniline (Ⅸ) derivatives. Population of the data of Ⅷ derivatives was different from those of Ⅶ and Ⅸ derivatives, but that of Ⅶ derivatives was not different from that of Ⅸ

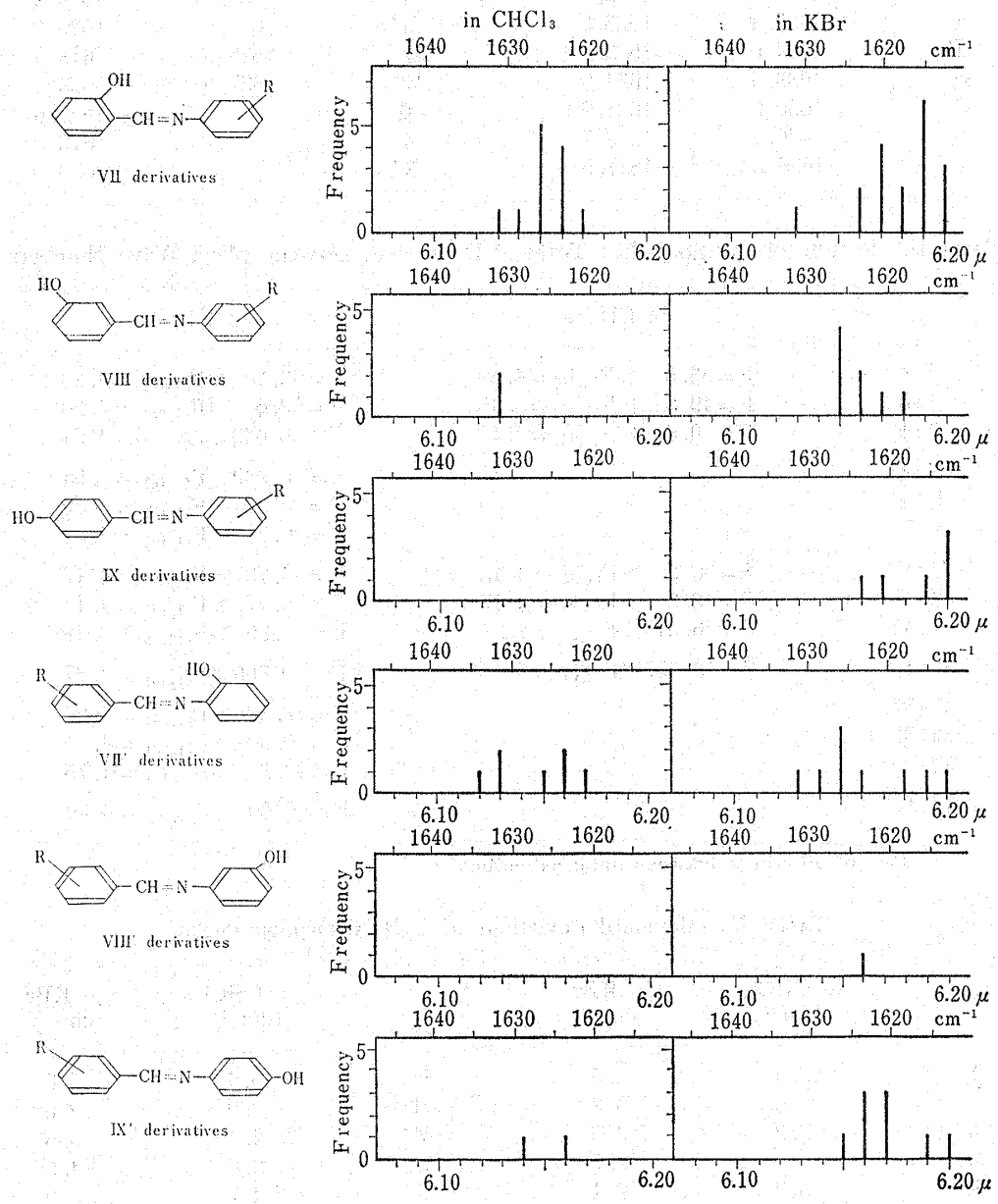


Fig. 3. Distributions of the Data of C=N Stretching Frequency in Ⅶ, Ⅷ, Ⅸ, Ⅶ′, Ⅷ′ and Ⅸ′ Derivatives

derivatives. While, those of N-benzylidene-2-hydroxyaniline (Ⅶ′) derivatives and N-benzylidene-4-hydroxyaniline (Ⅸ′) derivatives were not different. N-Benzylidene-3-hydroxyaniline (Ⅷ′) derivatives available were not enough for calculation.

Thus, in Ⅰ, Ⅱ, ……, Ⅸ derivatives the populations of the data were different in seven of nine calculated couples, while in Ⅰ′, Ⅱ′, ……, Ⅸ′ derivatives there was no different couple in five calculated ones. The mean wave numbers and results of the statistical tests of differences between mean wave numbers are shown in Table Ⅱ and Ⅲ, respectively.

Table Ⅱ. Mean Wave Numbers of C=N Absorption Peaks

	in $CHCl_3$ (cm^{-1})	in KBr (cm^{-1})		in $CHCl_3$ (cm^{-1})	in KBr (cm^{-1})
Ⅰ	1623.9	1617.9	Ⅴ′	1635.0	1626.7
Ⅰ′	1631.0	1622.8	Ⅵ	1632.5	1626.9
Ⅱ	1632.4	1625.2	Ⅵ′	1635.8	1625.0
Ⅱ′	1634.0	1623.4	Ⅶ	1625.3	1618.4
Ⅲ	1633.5	1624.9	Ⅶ′	1627.0	1623.1
Ⅲ′	1630.2	1621.9	Ⅷ		1623.6
Ⅳ	1626.2	1623.7	Ⅸ		1616.5
Ⅴ	1636.6	1627.5	Ⅸ′		1620.8

Table Ⅲ. Results of the Statistical Tests of Differences between Mean Wave Numbers

	in $CHCl_3$	in KBr
Ⅰ:Ⅱ	$\bar{F}=53.5 > F_{(1,16)}=4.49$	$\bar{F}=33.2 > F_{(1,23)}=4.28$
Ⅰ:Ⅲ	$\bar{F}=49.3 > F_{(1,19)}=4.38$	$\bar{F}=62.6 > F_{(1,28)}=4.20$
Ⅱ:Ⅲ	$\bar{F}=0.65 < F_{(1,17)}=4.45$	$\bar{F}=0.049 < F_{(1,27)}=4.21$
Ⅰ′:Ⅱ′		$\bar{F}=0.049 < F_{(1,15)}=4.54$
Ⅰ′:Ⅲ′		$\bar{F}=0.22 < F_{(1,16)}=4.49$
Ⅱ′:Ⅲ′		$\bar{F}=0.71 < F_{(1,15)}=4.54$
Ⅳ:Ⅴ	$\bar{F}=30.2 > F_{(1,29)}=4.18$	$\bar{F}=4.73 > F_{(1,30)}=4.17$
Ⅳ:Ⅵ	$\bar{F}=12.2 > F_{(1,30)}=4.17$	$\bar{F}=6.57 > F_{(1,30)}=4.17$
Ⅴ:Ⅵ	$\bar{F}=6.61 > F_{(1,27)}=4.21$	$\bar{F}=4.96 > F_{(12,16)}=2.42^{a)}$
Ⅴ′:Ⅵ′	$\bar{F}=0.057 < F_{(1,9)}=5.12$	$\bar{F}=0.306 < F_{(1,13)}=4.67$
Ⅶ:Ⅷ		$\bar{F}=8.32 > F_{(1,24)}=4.26$
Ⅶ:Ⅸ		$\bar{F}=0.901 < F_{(1,22)}=4.30$
Ⅷ:Ⅸ		$\bar{F}=13.3 > F_{(1,12)}=4.75$
Ⅶ′:Ⅸ′		$\bar{F}=0.90 < F_{(1,16)}=4.49$

a) Test of difference between unbiased estimates.

Table Ⅳ. Standard Deviations of C=N Absorption Peaks

	in $CHCl_3$ (cm^{-1})	in KBr (cm^{-1})		in $CHCl_3$ (cm^{-1})	in KBr (cm^{-1})
Ⅰ	2.4	2.5	Ⅴ′	5.5	5.8
Ⅰ′	3.6	5.2	Ⅵ	3.9	2.6
Ⅱ	2.2	3.7	Ⅵ′	4.4	5.5
Ⅱ′		3.7	Ⅶ	2.6	4.6
Ⅲ	3.2	2.4	Ⅶ′	4.7	5.9
Ⅲ′	5.0	3.5	Ⅷ		2.7
Ⅳ	5.5	4.6	Ⅸ		4.2
Ⅴ	4.2	5.7	Ⅸ′		3.9

As shown in Table Ⅳ, most of the standard deviations of I, Ⅱ, ……, Ⅸ derivatives were smaller than corresponding values of I′, Ⅱ′,……, Ⅸ′ derivatives.

As shown in Fig. 4, a linear relation seemed to exist between Hammett's substiuent constants, σ values, and mean wave numbers of C=N stretching absorption band measured in solid states for a series of compounds, of which benzylidene nucleus was substituted by Cl, NO_2, and OH, groups except 4-OH derivatives. However, the steep slope indicated that the effect of substituents on absorption bands was not so serious.

When σ values were plotted against mean absorption frequencies of a series of compounds, where aniline nucleus was substituted by Cl, NO_2, OH, CH_3, OCH_3, and Br groups no such linear relation was found.

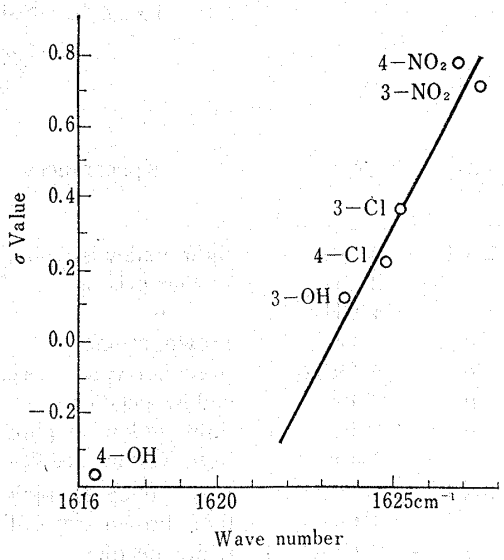


Fig. 4. Hammett's Substituent Constants, σ, plotted against the Mean Wave Numbers of C=N Stretching Absorption Bands

These results revealed that differences of substitution in benzene ring of benzylidene group affected acceptably on the region of infrared absorption due to the C=N stretching vibration, but those in benzene ring of aniline moiety had smaller effect on it.

It is interesting that this conclusion is similar to a result of a polarographic investigation that substituents in benzylidene group of N-benzylideneaniline derivatives have significant effect on half wave potentials of C=N, while those in aniline group have no effect on them.[3)]

Experimental

The N-benzylideneaniline derivatives were prepared by standard procedures.

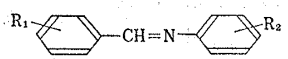
The purity of the compounds was checked by their melting points, data of elementary analyses and gas chromatographic tests on columns utilizing SE-30 at 200°. Appearances, melting points, and data of elementary analyses of new compounds are shown in Table Ⅴ.

The infrared spectra were measured from 1667 to 1538 cm^{-1} in chloroform solutions using Koken DS-301 Infrared Spectrophotometer, and from 5000 to 667 cm^{-1} in potassium bromide tablets using Hitachi EPI-S Infrared Spectrophotometer.

The authors are grateful to Prof. T. Momose and Dr. Y. Ohkura of Faculty of Pharmaceutical Sciences, Kyushu University for their encouragement during the present work, and they also extend their gratitude to Miss K. Soeda and Mr. H. Matsui for measurements of infrared spectra in chloroform solutions, and to Miss Y. Takahashi, Miss T. Tahara, Mr. M. Abe, and Mr. M. Shido for elementary analyses.

3) M. Uehara : Nippon Kagaku Zasshi **86**, 901 (1965).

Table V. N-Benzylideneaniline Derivatives



R_1	R_2	Appearances	m.p. (°C)	Formula	Analysis, N(%) Calcd.	Found
2-Cl	4-OH	light yellowish pink prisms	145	$C_{13}H_{10}ONCl$	6.05	5.93
〃	2-CH_3	yellow prisms	77	$C_{14}H_{12}NCl$	6.11	6.10
〃	4-CH_3	〃	52	〃	6.11	6.03
〃	3-OCH_3	brown prisms	38	$C_{14}H_{12}ONCl$	5.71	5.68
〃	4-OCH_3	greenish yellow prisms	62	〃	5.71	5.45
〃	2-Br	yellow needles	119	$C_{13}H_9NBrCl$	4.76	4.62
〃	3-Br	light yellowish pink needles	38	〃	4.76	4.72
〃	4-Br	light yellow needles	65	〃	4.76	4.51
3-Cl	2-OH	light yellowish pink leaflets	83	$C_{13}H_{10}ONCl$	6.05	6.02
〃	4-OH	light brown crystalline powder	143	〃	6.05	5.83
〃	2-Cl	white needles	52	$C_{13}H_9NCl_2$	5.58	5.53
〃	3-Cl	〃	47	〃	5.58	5.58
〃	4-Cl	light brown needles	42	〃	5.58	5.63
〃	4-CH_3	light brown plates	55	$C_{14}H_{12}NCl$	6.11	6.11
〃	4-OCH_3	light green leaflets	68	$C_{14}H_{12}ONCl$	5.71	5.68
〃	3-NO_2	light yellow needles	109	$C_{13}H_9O_2N_2Cl$	10.73	10.36
〃	2-Br	light yellow prisms	65	$C_{13}H_9NBrCl$	4.76	4.82
〃	3-Br	light yellowish pink needles	49	〃	4.76	4.77
〃	4-Br	light yellow needles	61	〃	4.76	4.71
4-Cl	2-OH	yellowish brown needles	116	$C_{13}H_{10}ONCl$	6.05	5.94
〃	4-OH	light brown prisms	179	〃	6.05	5.88
〃	2-OCH_3	yellow plates	73	$C_{14}H_{12}ONCl$	5.71	5.75
〃	3-OCH_3	brown prisms	28	〃	5.71	5.49
〃	4-OCH_3	light gray leaflets	122	〃	5.71	5.80
〃	3-NO_2	light yellowish pink needles	125	$C_{13}H_9O_2N_2Cl$	10.73	10.73
〃	4-NO_2	yellow needles	161	〃	10.73	10.62
〃	2-Br	yellow plates	46	$C_{13}H_9NBrCl$	4.76	4.74
〃	3-Br	white needles	71	〃	4.76	4.74
〃	4-Br	light yellow leaflets	120	〃	4.76	4.91
2-NO_2	3-NO_2	light yellow needles	128	$C_{13}H_9O_4N_3$	15.50	15.38
〃	4-NO_2	yellowish orange needles	144	〃	15.50	15.41
3-NO_2	2-Cl	yellow needles	102	$C_{13}H_9O_2N_2Cl$	10.72	10.72
〃	3-OCH_3	yellow plates	77	$C_{14}H_{12}O_3N_2$	10.93	10.61
〃	4-OCH_3	yellow prisms	80	〃	10.93	10.92
〃	3-Br	white needles	124	$C_{13}H_9O_2N_2Br$	9.18	8.88
4-NO_2	3-CH_3	yellow plates	94	$C_{14}H_{12}O_2N_2$	11.64	11.51
〃	3-OCH_3	yellowish orange prisms	96	$C_{14}H_{12}O_3N_2$	10.93	10.62
3-OH	3-Cl	light yellowish pink prisms	124	$C_{13}H_{10}ONCl$	6.05	6.06
〃	4-Cl	light brown needles	135	〃	6.05	6.07
〃	4-OCH_3	〃	122	$C_{14}H_{13}O_2N$	6.16	6.12
〃	3-NO_2	yellow prisms	148	$C_{13}H_{10}O_3N_2$	11.11	11.32
〃	3-Br	light orange prisms	138	$C_{13}H_{10}ONBr$	5.08	4.72
〃	4-Br	light yellow needles	141	〃	5.08	4.98