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# The Nuclear Magnetic Resonance and Infrared Spectra of Aromatic Azomethines

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Theoretical and experimental studies have suggested that the molecular structure of benzalaniline is not planar and that the benzene ring of the aniline part is distorted from the plane of the *trans*-benzalamino skeleton, as is shown in Fig. 1; it has also been disclosed that the substituent in the benzaldehyde ring has more effect on the electronic structure of azomethine group than that in the aniline part does.[1-7] Although a few papers suggest the above molecular geometry from the point of view of infrared spectral studies, there has been very little work on the nuclear magnetic resonance spectra of aromatic azomethines.

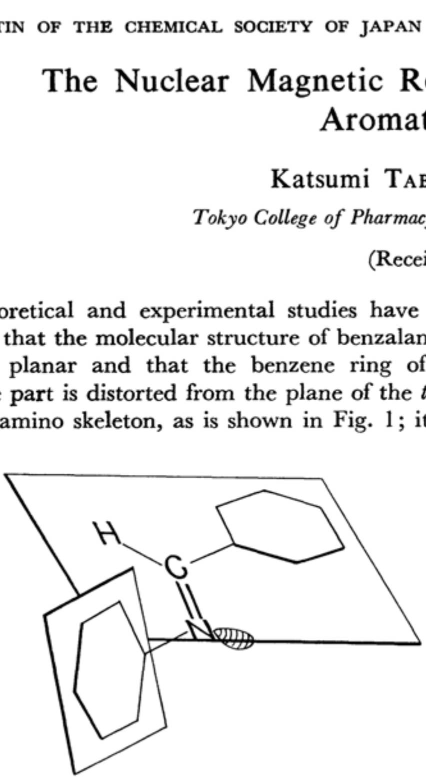

Fig. 1

In the present work, the nuclear magnetic resonance spectra of more than twenty kinds of *p*-substituted benzalaniline were newly measured; the characteristic Hammett relation in the NMR and

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[1] V. A. Izmail'skii and E. A. Smirnov, *Zh. Obshch. Khim.*, **26**, 3042 (1956); V. A. Izmail'skii and Yu. A. Fedorov, *Zh. Fiz. Khim.*, **39**, 768 (1965).

[2] N. Ebara, This Bulletin, **33**, 534, 540 (1960); **34**, 1151 (1961).

[3] M. Uehara, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **86**, 901 (1961).

[4] W. F. Smith, *Tetrahedron*, **19**, 445 (1963).

[5] L. E. Clougherty, J. A. Sousa and G. M. Wyman, *J. Org. Chem.*, **22**, 462 (1957).

[6] J. D. Margerum and J. A. Sousa, *Appl. Spectry*, **19**, 91 (1965).

[7] W. Kraws and C. G. J. Wagner, *Z. Naturforsch.*, **A22**, 746 (1967).

TABLE 1. IR AND NMR SPECTRA OF BENZALANILINE AND ITS DERIVATIVES

| Substituent X | Hammett's $\sigma_p$ * | $X-C_6H_4-CH=N-C_6H_5$ (type A) | | | | $C_6H_5-CH=N-C_6H_4-X$ (type B) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | mp (°C) | $\nu_{C=N}$ ($cm^{-1}$) | | $\tau$ in $CDCl_3$ | mp (°C) | $\nu_{C=N}$ ($cm^{-1}$) | | $\tau$ in $CDCl_3$ |
| | | | in KBr | in $CCl_4$** | | | in KBr | in $CCl_4$** | |
| $-N(CH_3)_2$ | −0.83 | 99.5—100.5 | 1600 | 1617 | 1.73 | 101—102 | 1619 | 1630 | 1.51 |
| $-OH$ | −0.46 | 191—193 | 1616 | 1630** | — | 182—183 | 1624 | — | — |
| $-OCH_3$ | −0.27 | 63—64 | 1624 | 1635 | 1.65 | 71—71.5 | 1627 | 1630 | 1.55 |
| $-OC_2H_5$ | −0.25 | 61—62 | 1621 | 1635 | 1.65 | 72—73 | 1629 | 1633 | 1.55 |
| $-CH_3$ | −0.17 | 146—147*** | 1630**** | 1638 | 1.66 | 158—159*** | 1630**** | 1637 | 1.61 |
| $-H$ | 0.00 | 52—53 | 1629 | 1635 | 1.60 | | | | |
| $-C_6H_5$ | +0.01 | | | | | 148—149 | 1630 | 1635 | 1.52 |
| $-Cl$ | +0.23 | 63.5—64.5 | 1627 | 1635 | 1.64 | 63—63.5 | 1629 | 1635 | 1.61 |
| $-Br$ | +0.23 | 73—74 | 1624 | 1634 | 1.64 | 65—66 | 1630 | 1636 | 1.60 |
| $-I$ | +0.28 | 90—91 | 1621 | 1629 | 1.64 | 85—86 | 1628 | 1635 | 1.64 |
| $-COOH$ | +0.27 | 224—225 | 1623 | — | — | 191—193 | 1625 | — | — |
| $-COOR$***** | +0.45 | 125.5—126.5 | 1622 | 1632 | 1.53 | 47—48 | 1632 | 1635 | 1.60 |
| $-COCH_3$ | +0.52 | | | | | 100—101 | 1630 | 1635** | 1.60 |
| $-SO_2NH_2$ | +0.57 | 176—179 (d.) | 1619 | — | — | 173—174.5 | 1628 | 1634** | — |
| $-NO_2$ | +0.78 | 92—93 | 1620 | 1629** | 1.46 | | | | |
| *N*,*N*-Dibenzal-*p*-phenylenediamine | | | | | | 141—141.5 | 1618 | 1631** | 1.51 |
| Terephthalaldehyde dianil | | | | | | 161.5—163 | 1615 | 1628** | 1.52 |
| *N*,*N*-Dimethyl-*N'*-(*p*-nitrobenzal)-*p*-phenylenediamine | | | | | | 227—228 | 1619 | 1629** | 1.42 |

* H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).
** Solvent is chloroform.
*** Bp at 3 mmHg.
**** Measured in liquid film.
***** R is methyl in type A and ethyl in type B respectively.

IR spectra of the azomethine group will be discussed in order to clarify the molecular geometry.

## Experimental

**Materials.** Twenty-nine kinds of benzalaniline were prepared by the usual condensation reaction either from aniline and *p*-substituted benzaldehydes or from *p*-substituted anilines and benzaldehyde.[8,9] The crystalline compounds were purified by repeated recrystallization from methanol or ethanol, but *N*-(*p*-methylbenzal)-aniline, *N*-benzal-*p*-toluidine, and ethyl *p*-(*N*-benzalamino)-benzoate were distilled under reduced pressure. The purity of the products was checked by thin-layer chromatography.

**Nuclear Magnetic Resonance Spectra.** The NMR spectra of the above compounds were measured by using a JNM-4H-100 NMR spectrometer in a deuteriochloroform solution at a 0.2—0.5 mol/*l* concentration. The spectra of the hydroxyl, carboxyl, and sulfonamido derivatives, however, could not be measured, since the compounds are not satisfactorily soluble in deuteriochloroform.

**Infrared Spectra.** The IR spectra of the above benzalanilines were also measured by using a JASCO DS-301 infrared spectrophotometer in a carbon tetrachloride or chloroform solution and in a disk of potassium bromide. The spectra of *p*-(*N*-benzalamino)-benzoic acid and *p*-(*N*-benzalamino)-benzenesulfonamide were not measured in the solution because of their poor solubility in the above solvents.

The $\tau$ values and the wave numbers so measured are listed in Table 1, together with the physical constants.

## Results and Discussion

***N*-(*p*-Substituted-benzal)-anilines (Type-A compounds).** The NMR proton signals of the azomethine group of the *N*-(*p*-substituted-benzal)-anilines appear in the region of 1.46 $\tau$ (*p*-nitrobenzalaniline)- 1.73 $\tau$ (*p*-*N*,*N*-dimethylaminobenzalaniline) as a singlet peak; the introduction of an electron-donating or of an electron-withdrawing group into the para position of the benzaldehyde ring of a type-A compound brings about a small shift of the signal to a higher or to a lower field respectively.

The plot of the $\tau$ values against Hammett's $\sigma_p$ constant (Fig. 2) shows a characteristic Hammett relationship between the chemical shift of an azomethine proton signal and the electronic effect of a substituent in type-A compounds.

The present NMR data permit only a qualitative discussion; however, it seems reasonable that the chemical shift of an azomethine proton signal is

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[8] L. Gattermann, "Die Praxis des Organischen Chemikers," 40 Aufl., 150 (1961).

[9] H. Gilman, "Organic Syntheses," Coll. Vol. I, p. 80 (1956).

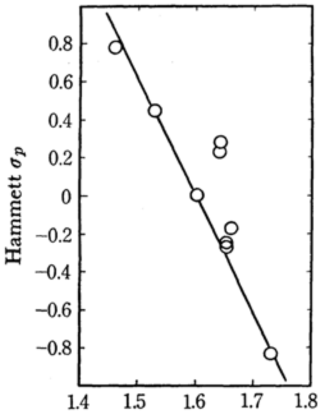
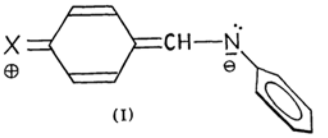
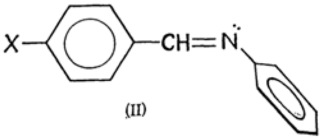


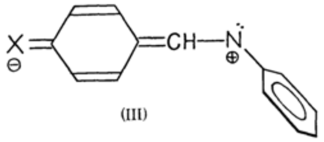
Fig. 2. τ value of azomethine proton *vs.* Hammett's $\sigma_p$ in type A compounds.

mainly determined by the change in the electron density on the carbon atom in the azomethine double bond, supposing that the magnetic anisotropy of a substituent can be neglected as in the case of styrene and phenylacetylene derivatives.[10,11]

Consequently, the present chemical shift of the azomethine proton signal can be understood by taking the following resonance structures (I)—(III) into account; since an increase in the contribution of the polar structure (I) to the ground state (II) makes for an increase in the electron density of the azomethine carbon as well as in that of nitrogen,[12] the introduction of an electron-donating group to the para position of the benzaldehyde ring makes for a small shift of the azomethine proton signal to the higher-field side. The substituent effect of an electron-withdrawing group corresponding to the increase in the contribution of the polar structure (III), on the other hand, decreases the electron density at the azomethine group and, therefore, makes for a small shift of the signal to the lower-field side.


(I)


(II)


(III)

From the above discussion, it can also be expected that an increase in the contribution of either polar structure will bring about a decrease in the carbon-nitrogen bond order of the azomethine group. Previous infrared studies have not satisfactorily treated the substitution effect upon the change in the C=N bond order; therefore, the C=N stretching frequency of many kinds of type-A compounds were also measured.

When an electron-donating or electron-withdrawing group is introduced into the para position of the benzaldehyde ring, the C=N stretching band of benzalaniline, 1635 $cm^{-1}$ in a $CCl_4$ solution and 1629 $cm^{-1}$ in a KBr disk, is, as expected, shifted more or less to the longer wavelength side. The present characteristic trend is confirmed by plotting the $\nu_{C=N}$ against the Hammett's $\sigma_p$ constant, as is shown in Fig. 3. The relationship obtained can also safely be explained by taking the polar structures (I) and (III) into consideration, as has been mentioned previously.

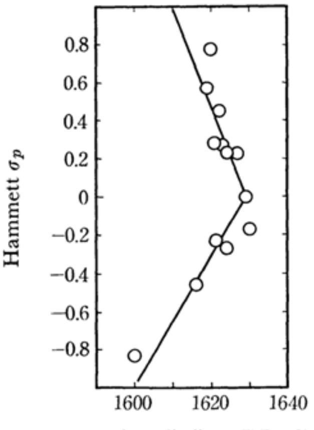


Fig. 3. $\nu_{C=N}$ *vs.* Hammett's $\sigma_p$ constant in type A compounds.

**$p$-Substituted $N$-benzalanilines (Type-B Compounds).** The preceding discussion does not take the effect of the aniline part into account, since the aniline ring may be distorted from the plane of the benzalamino skeleton. In order to substantiate the above description, the NMR and IR spectra of $p$-substituted $N$-benzalanilines were also studied. It was revealed that the proton signal and the C=N stretching band of the azomethine group of type-B

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10) H. Kasiwagi and J. Niwa, This Bulletin, **36**, 405, 411 (1963).

11) Y. Yukawa and H. Yamada, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **85**, 501 (1964).

12) V. I. Minkin, Yu. A. Zhdanov, E. A. Medyantzeva and Yu. A. Ostroumov, *Tetrahedron,* **23**, 3651 (1967).

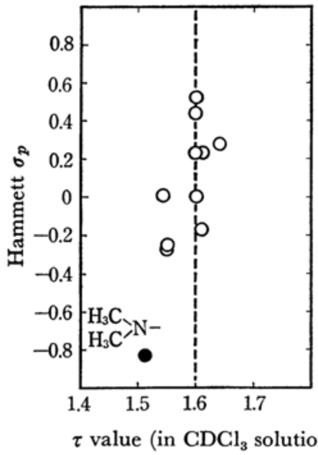


Fig. 4. τ value of azomethine proton *vs.* Hammett's $\sigma_p$ in type B compounds.

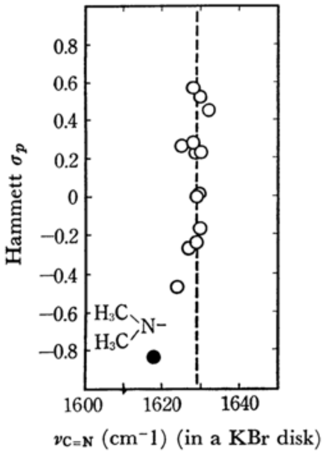
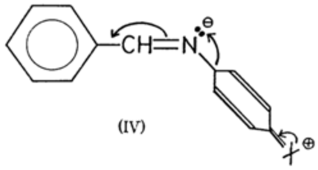


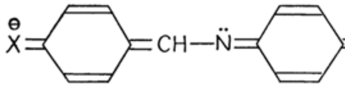
Fig. 5. $\nu_{C=N}$ *vs.* Hammett's $\sigma_p$ constant in type B compounds.

compounds appear within a narrower range than those of type-A compounds do. That is, a substituent in the para position of the aniline ring can not exert any appreciable electronic effect upon the azomethine group, and the Hammett relation is not obtained, as is depicted in Figs. 4 and 5. The present results can reasonably be understood by accepting the previous non-planar structure for the benzalaniline molecule in which an aniline ring can not conjugate with a benzalamino π system.

A strong electron-donating group such as *N,N*-dimethylamino, however, shifts the proton signal considerably to the lower-field side, and at the same time shifts the C=N stretching band to the longer wavelength side. The above rather exceptional shift found in the dimethylamino derivative can be understood by considering the electron-repelling effect of the electron-rich azomethine nitrogen atom. Since an electron is concentrated on one of the $sp^2$ lobes, the lone-pair lobe, from the dimethylaminophenyl group, the electron-rich azomethine nitrogen atom can repel its π-electron to the benzaldehyde part inductively, as in the structure (IV), and can, therefore, increase the electron density at the azomethine carbon and at the same time decrease the bond order of the azomethine bond.



(IV)



(V)

If an electron can transfer from an aniline part to a benzaldehyde one conjugatively, as is shown in the planar structure (V), the azomethine proton signal and the C=N stretching band of *N*-(*p*-nitrobenzal)-*N′*,*N′*-dimethyl-*p*-phenylenediamine can be expected to appear in a far lower-field side and in a far longer wavelength region than those of other benzalanilines. The observed values, however, are 1.42 τ in the $CDCl_3$ solution, 1629 $cm^{-1}$ in the $CHCl_3$ solution, and 1619 $cm^{-1}$ in the KBr disk. The present shifts are merely larger than those of *p*-nitrobenzalaniline; 1.46 τ in the $CDCl_3$ solution, 1630 $cm^{-1}$ in the $CHCl_3$ solution, and 1621 $cm^{-1}$ in the KBr disk.

The above results suggest that dimethylamino, a strong electron-donating group, in the para position of the aniline ring can not conjugate directly with the nitro group through the benzalaniline skeleton and that it can not greatly change the electron density and bond order of the azomethine bond. Thus, the non-planar structure of benzalaniline, the so-called Brocktehurt model, is also supported with respect to the Hammett relationship in NMR and IR spectra.

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