BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 2693—2694 (1969)

Infrared Absorption Bands of Benzalanilines Observed in the 1200—850 cm^{-1} Region

Katsumi TABEI and Etsurou SAITOU

Tokyo College of Pharmacy, Kashiwagi, Shinjiku-ku, Tokyo

(Received December 24, 1968)

Previous infrared studies of the azomethine derivatives have dealt with their carbon-nitrogen double-bond stretching mode, but there have been few references to the other vibration of the compounds.[1] As a part of the infrared studies of the aromatic molecule,[2] the spectra of twenty-nine kinds of *N*-(*p*-substituted-benzal)-anilines and *N*-benzal-*p*-substituted-anilines were measured; it was found that three characteristic absorption bands appear in the 1200—850 cm^{-1} region. In the present report, we wish to present the observed data and to assign them qualitatively.

In comparison with the spectra of *N*-benzylaniline, *N*-propylidenecyclohexylamine, azobenzene, acetophenoneoxime, *p*-nitrostilbene, benzalacetone, and styrene, the three absorption bands which appeared at about 1190 cm^{-1}, 975 cm^{-1}, and 880 cm^{-1} in the spectra of the present type of compounds seem to be characteristic of the benzalaniline skeleton. The wave numbers of the above observed characteristic absorption bands are listed in Table 1.

TABLE 1. THE CHARACTERISTIC ABSORPTION BANDS OF BENZALANILINES

Compound	Mp (°C)	Frequencies in CCl_4 soln. (cm^{-1})		
		ν_{Ar-N}	δ_{CH} (in-plane)	δ_{CH} (out-of-plane)
$X-C_6H_4-N=CH-C_6H_5$				
$X=-N(CH_3)_2$	101—102	1210	965	880
$-OH$	182—183	1196	981	876
$-OCH_3$	71—71.5	1192	971	883
$-OC_2H_5$	72—73	1192	970	883
$-CH_3$	158—159**	1193	972	884
$-C_6H_5$*	148—149	1190	968	879
$-H$	52—53	1191	976	873
$-Cl$	63—63.5	1190	975	884
$-Br$	65—66	1190	974	883
$-I$	85—86	1192	975	880
$-COOH$*	191—193	1194	978	892
$-COOC_2H_5$*	47—48	1192	975	887
$-COCH_3$*	100—101	1193	975	885
$-SO_2NH_2$*	173—174.5	1195	956	892
$C_6H_5-N=CH-C_6H_4-Y$				
$Y=-N(CH_3)_2$***	99.5—100.5	1178	977	879
$-OH$*	191—193	1190	978	880
$-OCH_3$	63—64	1193	975	877
$-OC_2H_5$	61—62	1193	975	877
$-CH_3$	146—147**	1193	976	876
$-H$	52—53	1191	976	879
$-Cl$	63.5—64.5	1190	974	875
$-Br$	73—74	1191	974	874
$-I$	90—91	1189	976	880
$-COOH$*	224—225	1192	974	879
$-COOCH_3$***	125.5—126.5	1188	978	887
$-SO_2NH_2$*	176—179(d.)	1193	972	880
$-NO_2$***	92—93	1186	973	881
Miscellaneous				
p-$C_6H_4(-N=CH-C_6H_5)_2$*	141—141.5	1190	965	875
p-$C_6H_4(-CH=N-C_6H_5)_2$*	161.5—163	1186	973	866
$O_2N-C_6H_4-CH=N-C_6H_4-N(CH_3)_2$***	227—228	1235	950	883
$C_6H_{11}-N=CH-C_2H_5$	59—62****	1100	957	885

* measured in KBr disk
** bp under 3 mmHg
*** measured in $CHCl_3$ soln.
**** bp under 15 mmHg

A sharp band at 1191 cm^{-1} in *N*-benzalaniline may be assigned to the aryl carbon-nitrogen (Ar–N) bond-stretching vibration, since the band is not observed in the spectra of *N*-benzylaniline; the corresponding Ar–N stretching mode of *N*-benzylaniline can be assigned to a sharp and strong absorption band at 1322 cm^{-1}.

In addition, the above reference compounds do not have an absorption band in the 1200—1170 cm^{-1} region with the exception of a few medium bands in the 1170—1100 cm^{-1} region which may be due to the aromatic C–H in-plane deformation vibration.

N-propylidenecyclohexylamine, on the other hand, has its carbon-nitrogen single-bond-stretching band at 1100 cm^{-1}.

As is listed in the table, the Ar–N stretching frequency of benzalanilines is far lower than that of aromatic amine, and also the frequencies are kept

---

[1] E. Clougherty, J. A. Sousa and G. M. Wyman, *J. Org. Chem.*, **22**, 462 (1957); W. Kraws and C. G. J. Wagner, *Z. Naturforsch.*, **A 22** (5), 746 (1967); Yu. S. Ryabokobylko and B. M. Bolptin, *Chem. Abstr.*, **67**, 6486 (1967); G. Dudek, *J. Org. Chem.*, **32**, 882 (1967).

[2] K. Tabei and C. Ito, This Bulletin, **41**, 514 (1968).

in a narrow range (1186—1196 cm^{-1}), even when a subsitutent is introduced into the para position of either the aniline or benzaldehyde ring. This fact can reasonably be understood by taking the non-planar structure of the benzalaniline molecule into account; the conjugation effect between the aniline ring and the benzalamino skeleton may be substantially interrupted, since the plane of the aniline ring is twisted from that of the benzalamino part, as is shown in Fig. 1.[3)]

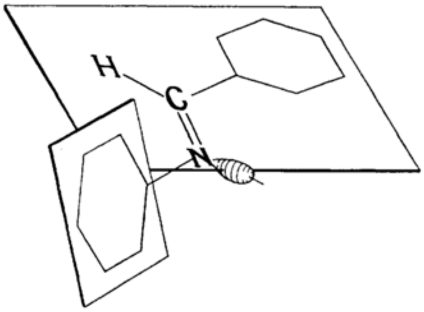

Fig. 1

That is to say, the above frequency region can safely be assigned to the stretching vibration of the non-conjugated sp^2 carbon-sp^2 nitrogen single bond which is expected to appear in the intermediate region between the C–N stretching frequency of aromatic amine and that of aliphatic amine.[4)]

A strong electron-donating *p*-substituent in the aniline ring can, however, increase the Ar–N bond order by releasing an electron to the lone-pair lobe of the azomethine nitrogen, as is shown in Fig. 2. The $\nu_{\mathrm{Ar-N}}$ of such derivative as *N*-benzal-*N'*, *N'*-dimethyl-*p*-phenylenediamine will then appear at a little higher frequency (1210 cm^{-1}). When this group is in the benzaldehyde ring, on the other hand, the $\nu_{\mathrm{Ar-N}}$ shifts to a little lower frequency; the Ar–N stretching band of *p*-dimethylaminobenzal-aniline then appears at 1178 cm^{-1}. The above frequency shift is probably due to the fact that the electron-rich azomethine nitrogen can repel the aromatic ring of the aniline part.

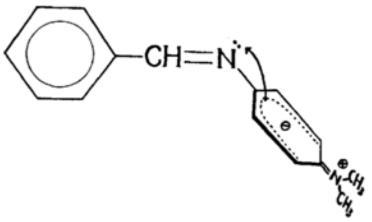

Fig. 2

It was also confirmed that the sharp absorption bands at about 972 cm^{-1} and 883 cm^{-1} give spectral information about the azomethine skeleton. The former is probably due to the C–H in-plane deformation vibration of the azomethine group, and the latter, to the C–H out-of-plane deformation mode, since the above pair of bands do not appear in the spectra of *N*-benzylaniline and other reference compounds. In the case of *N*-propylidenecyclohexylamine, the bands are observed at 956 cm^{-1} and at 845 cm^{-1} respectively. However, they have not been verified.

Experimental

Materials. Twenty-nine kinds of aromatic azomethines were prepared by usual condensation reactions between the corresponding aldehyde and amine, and were purified by recrystallization from methanol or ethanol or by distillation under reduced pressure.[5)]

N-Propylidenecyclohexylamine was also prepared by the condensation of cyclohexylamine and propionaldehyde and was distilled repeatedly under reduced pressure. The purity of the materials was checked by thin-layer chromatography.

Infrared Spectra. The IR spectra of the above compounds were measured by using a JASCO DS-301 infrared spectrophotometer in a carbon tetrachloride or chloroform solution or in a disk of potassium bromide. The wave numbers determined in the present experiment are listed in Table 1, along with their physical constants.

The authors wish to express their deep gratitude to Mrs. Moriharu Nagase of the Tokyo College of Pharmacy for her helpful measurement of the infrared spectra.

[3)] V. A. Izmail'skii and R. A. Smirnov, *Zhur. Obshch. Khim.*, **26**, 3042 (1956); V. A. Izmail'skii and Yu. A. Fedorov, *Zh. Fiz. Khim.*, **39**, 768 (1965); N. Ebara, This Bulletin, **33**, 534, 540 (1960), **34**. 1151 (1961); M. Uehara, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **86**, 901 (1961); W. F. Smith, *Tetrahedron*, **19**, 445 (1963); V. I. Minkin, Yu. A. Zhdanov, E. A. Medyantzeva and Yu. A. Ostroumov, *ibid.*, **23**, 3651 (1967); K. Tabei and E. Saitou, This Bulletin, **42**, 1440 (1969).

[4)] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley & Sons, Inc., New York (1964), p. 248.

[5)] H. Gilman, "Organic Syntheses," Coll. Vol. **I**, p. 80 (1956); A. Skita and C. Wulff, *Ann.*, **453**, 190 (1927).