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Electronic Spectra of α-Cyanobenzylideneanilines

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Electronic spectra of twenty four α-cyanobenzylideneanilines (I) were measured in ethanol. The effects of substituents on the spectra suggested that the electronic interaction of the two phenyl rings in I is stronger than that in the corresponding benzylideneanilines owing to the electron-withdrawing effect of the α-cyano group.

Keywords——α-cyanobenzylideneanilines; electronic spectra; substituent effects; molecular conformation; Schiff base

The molecular conformation of benzylideneanilines has been demonstrated as non-planar on the basis of electronic spectra,[2] X-ray crystal analyses,[3] and other physicochemical observations.[4] One exception is that of *p*-nitrobenzylidene–*p*-dimethylaminoaniline, where the intramolecular charge transfer interaction, caused by the strong electron-withdrawing nitro group on the *C*-phenyl ring and the strong electron-donating dimethylamino group on the *N*-phenyl ring, facilitates the delocalization of π-electrons over the whole molecule and makes a planar conformation energetically more favorable.[5] Since α-cyanobenzylideneanilines have a strong electron-withdrawing cyano group on the α-carbon atom, some of the compounds may have a similar possibility. This paper reports the effects of substituents on the electronic spectra of α-cyanobenzylideneanilines in ethanol, and the conformation of them is discussed.

Results and Discussion

The absorption maxima and the corresponding extinction coefficients of α-cyanobenzylideneanilines (Ia—x) are summarized in Table I, and some of the spectra are shown in Fig. 1 together with that of benzylideneaniline (II). The 311-nm band of II, which is sensitive to substitution on the *N*-phenyl ring but not to that on the *C*-phenyl ring, was assigned to an electronic transition to a benzene $^1B_{2u}$-type state in the aniline part of the molecule, and the 262-nm band, which is sensitive to substitution on the *C*-phenyl ring, was interpreted as a transition to a charge-transfer state in which the azomethine group acts as an electron acceptor and the *C*-phenyl ring as an electron donor.[2g] Thus a non-planar structure was proposed for II, in which the *N*-phenyl ring is twisted out of the molecular plane. The absorption bands of unsubstituted α-cyanobenzylideneaniline (Ia) at 361 nm (band I) and 280 nm (band II) can be compared to those of II at 311 nm and 262 nm, respectively, because the substituent

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[1] Location: *133-1, Yamadakami, Suita.*

[2] *a*) V.A. Ismailskii and E.A. Smirnov, *J. Gen. Chem. USSR*, **26**, 3389 (1956); *b*) N. Ebara, *Bull. Chem. Soc. Jpn.*, **33**, 534 (1960); *c*) *Idem*, *ibid.*, **34**, 1151 (1961); *d*) P. Brochlenhurst, *Tetrahedron*, **18**, 299 (1962); *e*) W.F. Smith, *ibid.*, **19**, 445 (1963); *f*) E. Haselbach and E. Heilbronner, *Helv. Chim. Acta*, **51**, 16 (1968); *g*) M.A. El-Bayoumi, M. El-Aasser, and F. Abdel-Halim, *J. Am. Chem. Soc.*, **93**, 586 (1971).

[3] H.B. Bürgi and J.D. Dunitz, *Chem. Commun.*, **1969**, 472; *idem*, *Helv. Chim. Acta*, **53**, 1747 (1970).

[4] V.I. Minkin, Yu.A. Zhdanov, E.A. Medyantzeva, and Yu.A. Ostroumov, *Tetrahedron*, **23**, 3651 (1967); J.W. Pavlik and A. van Putten, *ibid.*, **27**, 3007, 3301 (1971); K. Tabei and E. Saitou, *Bull. Chem. Soc. Jpn.*, **42**, 1440 (1969); A.S. Al-Tai, D. Muriel Hall, and A.R. Mears, *J. Chem. Soc. Perkin II*, **1976**, 133; M. Kobayashi, M. Yoshida, and H. Minato, *J. Org. Chem.*, **41**, 3322 (1976).

[5] K. Ezumi, H. Nakai, S. Sakata, K. Nishikida, M. Shiro, and T. Kubota, *Chem. Lett.*, **1974**, 1393.

TABLE I. Spectral Data of α-Cyanobenzylideneanilines in Ethanol
X(p)-C_6H_4-C(CN)=N-C_6H_4-Y(p)

Compounds (X, Y)		λ_{max} nm (ε) Band I	Band II	Other bands
Ia	(H, H)	361 (4920)	280 (14200)	222 (12100)
Ib	(H, Cl)	364 (6300)	282 (15400)	228 (15500)
Ic	(H, CN)	350 (5730)	283 (18500)	237 (16800)
Id	(H, Me)	371 (6690)	281 (14100)	226 (12700)
Ie	(H, OMe)	388 (9940)	284 (12200)	230 (11100)
If	(Cl, H)	365 (5960)	288 (16200)	222 (12500)
Ig	(CN, H)	373 (6030)	280 (19200)	221 (12100)
Ih	(Me, H)	361 (5950)	293 (15100)	223 (11800)
Ii	(OMe, H)	355s (9600)	320 (16600)	240 (10800), 222 (11500)
Ij	(NO_2, H)	377 (6500)	285 (18100)	220s (—)
Ik	(Cl, CN)	353 (6860)	294 (19600)	239 (19000)
Il	(CN, CN)	359 (5030)	279 (23400)	236 (16700)
Im	(Me, CN)	347s (7840)	299 (18900)	240 (19200)
In	(OMe, CN)	350s (—)	330 (19800)	246 (20300)
Io	(Cl, Cl)	367 (7470)	290 (17100)	229 (15400)
Ip	(CN, Cl)	375 (7310)	281 (19600)	226 (14000)
Iq	(Me, Cl)	362 (7770)	295 (17000)	230 (16600)
Ir	(OMe, Cl)	361 (11700)	323 (17200)	231 (14800)
Is	(Cl, Me)	374 (8180)	289 (16400)	225 (14200)
It	(CN, Me)	382 (8140)	281 (17200)	257 (12000), 222 (12000)
Iu	(Me, Me)	371 (7560)	292 (15100)	226 (13500)
Iv	(OMe, Me)	371 (10500)	318 (16000)	226 (13100)
Iw	(H, NMe_2)	456 (20800)		266 (14700)
Ix	(NMe_2, H)	403 (26800)		250 (12600)

TABLE II. Effect of Substituents on Band I and II[a]
X(p)-C_6H_4-C(CN)=N-C_6H_4-Y(p)

(a) Effects of Y on band I

X	Y H	Cl	CN	Me	OMe
H	Ia	+3	−11	+10	+27
Cl	If	+2	−12	+9	
CN	Ig	+2	−14	+9	
Me	Ih	+1	−14	+10	
OMe	Ii	+6	−5	+16	

(b) Effects of X on band I

Y	X H	Cl	CN	Me	OMe
H	Ia	+4	+12	0	−6
Cl	Ib	+3	+11	−2	−3
CN	Ic	+3	+9	−3	0
Me	Id	+3	+11	0	0

(c) Effects of Y on band II

X	Y H	Cl	CN	Me	OMe
H	Ia	+2	+3	+1	+4
Cl	If	+2	+6	+1	
CN	Ig	+1	−1	+1	
Me	Ih	+2	+6	−1	
OMe	Ii	+3	+10	−2	

(d) Effects of X on band II

Y	X H	Cl	CN	Me	OMe
H	Ia	+8	0	+13	+40
Cl	Ib	+8	−1	+13	+41
CN	Ic	+11	−4	+16	+47
Me	Id	+8	0	+11	+37

[a] This table should be read as follows; *e.g.*, in (a) the numerical value (−12) at the second row (Cl) and the fourth column (CN) means that the band I of compound I with X=Cl and Y=CN (Ik) shows a blue shift of 12 nm compared with that of compound I with X=Cl and Y=H (If).

effects are similar to one another (see, for example, Ia—e and If—j in Table I). Further inspection of the data, however, will reveal some differences between the substituent effects. The band I and II of compounds Ia—v are discernible, and the shifts of the two bands due to change in substituents are summarized in Table II. The spectra of Iw and x (Fig. 1) are somewhat different from the rest, and will be discussed later.

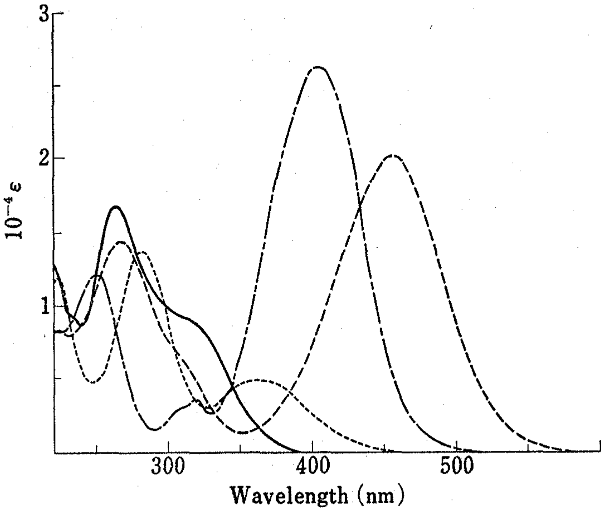

Fig. 1. Absorption Spectra of Ia, Iw, Ix, and II

--------, Ia; – – – –, Iw; —·—·—, Ix; ———, II.

From Table II following substituent effects will be seen:

Effects on band I; (1) Substitution on the *N*-phenyl ring (change in Y) brings about larger shifts than that on the *C*-phenyl ring (change in X). (2) Substitution of a cyano group on the *N*-phenyl ring results in considerable blue shifts. (3) Contrary to (2), red shifts of -700 to $-900\ \mathrm{cm}^{-1}$ are caused by substitution of a cyano group on the *C*-phenyl ring. (4) Practically no or, if any, small blue shifts are caused by electron-donating groups on the *C*-phenyl ring.

Effects on band II; (5) Change in X causes larger shifts than change in Y, in contrast to the effects on band I. (6) Electron-donating groups on the *C*-phenyl ring bring about marked red shifts. (7) The sensitivity of the band to change in X is maximal with *p*-cyanoaniline derivatives (Y $=$CN).

Effects (1) and (5), which are similar to those observed on the spectra of benzylideneanilines, suggest that the two phenyl rings in I are electronically isolated to some extent. However, the degree of isolation will be smaller than that in corresponding benzylideneanilines because the effects of change in X on band I and the effects of change in Y on band II are appreciable in contrast to the case of benzylideneanilines, where essentially no effect was observed.[2g] In the case of I with a cyano group on the *C*-phenyl ring, strong electron-withdrawing effects of the two cyano groups can lower the energy of the intramolecular charge-transfer and increase the interaction of both phenyl rings as suggested by Kubota, *et al.*[5] (effect (3)). On the other hand, when an electron-donating group is on the *C*-phenyl ring, charge-transfer to the azomethine part of the molecule will take place mainly from the *C*-phenyl ring, and the degree of isolation of the two phenyl rings will be larger (effects (4) and (6)). In compounds I with a cyano group on the *N*-phenyl ring, the isolation of the two phenyl rings will be further enhanced owing to the strong electron-withdrawing effects of the two cyano groups. Consequently, band I of these compounds shifts to shorter wave length (effect (2)), and band II is most sensitive to change in X (effect (7)).

Although Ledbetter, Kramer, and Miller suggested that the electronic spectra of I show steric hindrance to coplanarity due to the cyano group,[6] the observed substituent effects on the spectra of I lead us to conclude that the conformation of I is somewhat more planar compared with that of corresponding benzylideneanilines. The conjugation of the two phenyl rings will be more enhanced with the more electron-withdrawing substituent on the *C*-phenyl ring and the more electron-donating substituent on the *N*-phenyl ring. Thus the spectrum

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[6] J.W. Ledbetter, D.N. Kramer, and F.M. Miller, *J. Org. Chem.*, **32**, 1165 (1967); Our present view is not completely concordant with the suggestion of these authors, but their discussion was limited on the longest wavelength band (band I) for which explicit assignment had not been made (*cf.* ref. 2*g*)).

of α-cyanobenzylidene-*p*-dimethylaminoaniline (Iw) (Fig. 1) is closely related to that of *p*-nitrobenzylidene-*p*-dimethylaminoaniline which shows strong absorption at 275 and 440 nm in acetonitrile,[5] indicating that Iw has an almost coplanar structure.

The 403-nm band of Ix can be regarded as band II because the spectrum of Ix (Fig. 1) is similar to that of *p*-dimethylaminobenzylideneaniline in which the 262-nm band of II exhibits a large red shift owing to the strong electron-donating effect of the dimethylamino group and eventually becomes the longest wavelength band.[2g] Band I of Ix can be expected around the same wave length as that of Ia, but may be hidden by the strong absorption of band II.

Experimental

α-Cyanobenzylideneanilines, Ia—v and x, were prepared from the corresponding nitrones by the method of Krönke and Krönke,[7] and Iw was prepared from *p*-nitrosodimethylaminoaniline and benzylcyanide by the method of Ehrlich and Sachs.[8] All compounds gave expected analytical results.

Spectral data were obtained using Hitachi type 124 and type 100-40 spectrometers.

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7) F. Krönke and G. Krönke, *Chem. Ber.*, **91**, 1474 (1958).
8) P. Ehrlich and F. Sachs, *Chem. Ber.*, **32**, 2431 (1899).

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Studies on *Cerbera*. II.[1] Cerbinal and Its Derivatives, Yellow Pigments in the Bark of *Cerbera manghas* L.

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Cerbinal, yellow pigment having iridoid skeletal with $\Delta^{3,5,7,9(1)}$-tetraene, and 10-formyl and 11-carbomethoxy residues, was isolated along with 10-carboxy- (cerberic acid) and 11-carboxy- (cerberinic acid) derivatives from the bark of *Cerbera manghas* L.

Keywords——*Cerbera manghas*; Apocynaceae; iridoids; iridoid pigments; theviridoside

In the preceding paper, we reported on the cardenolides in the kernels,[1,3] bark,[1] and leaves[1] of *Cerbera manghas*. On the iridoid constituents of this plant, theviridoside and theveside have been isolated from the leaves by Inouye, *et al.*[4] This paper deals with the isolation and structure elucidation of cerbinal (CL), cerberic acid (CA), and cerberinic acid (CNA), yellow pigments with iridoid skeletal, in the stem and root barks.

When the methanol percolate of the dried powdered bark was concentrated, diluted with water and partitioned with a variety of solvents, CL was isolated as yellow needles by the crystallization with methanol of the benzene fraction. On column chromatography of

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1) Part I: F. Abe and T. Yamauchi, *Chem. Pharm. Bull.* (Tokyo), **25**, 2744 (1977).
2) Location: *Nanakuma 11, Nishi-ku, Fukuoka*; *a*) To whom, all inquiries should be addressed.
3) *a*) T. Matsubara, *Nippon Kagakukaishi*, **58**, 1104 (1939); *b*) S. Rangaswami and E. Venkata Rao, *J. Sci. Ind. Res.* (India), **16B**, 209 (1957); E. Venkata Rao, B.S. Sastry, and M.N. Narayanan, *Ind. J. Pharm.*, **36**, 75 (1974); E. Venkata Rao and M. Appa Rao, *Phytochemistry*, **15**, 848 (1976).
4) H. Inouye and T. Nishimura, *Phytochemistry*, **11**, 1852 (1972).