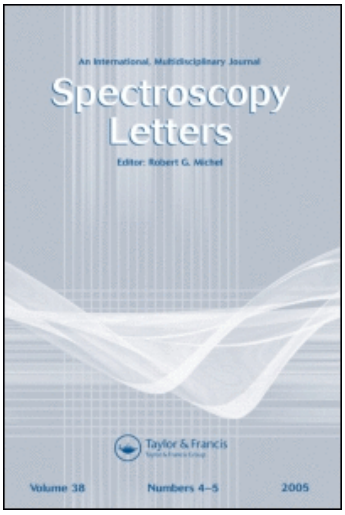

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Ultraviolet Spectrum of Some N,N-Dimethyl-N'Phenylformamidine Derivatives

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ULTRAVIOLET SPECTRUM OF SOME N,N-DIMETHYL-N'PHENYLFORMAMIDINE DERIVATIVES

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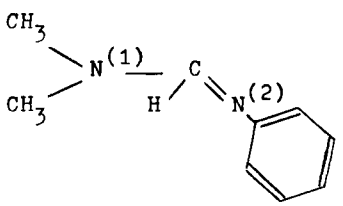
I. INTRODUCTION

The influence of the substituent on the ultraviolet spectrum of benzene derivatives has been extensively examined but the ultraviolet spectrum of phenylformamidine derivatives has not yet been investigated. N,N-Dimethyl-N'Phenylformamidines (DMPF)



are molecules characterized by a strong conjugation between the amino-$N^{(1)}$ and imino$^{(2)}$ nitrogen atoms; the phenyl ring adopts a non-planar configuration with respect to the $N^{(1)} - C = N^{(2)}$ plane[1,2]. In this work, we report the U.V. Spectrum of some DMPF and discuss the influence of the substituent implanted on the aromatic ring, on the λ_{max} and ε_{max} values of the absorption located at 270 nm.

2. EXPERIMENTAL

The spectra were registered on a Unicam SP 700 Spectrophotometer in cyclohexane at 25°C. The concentrations of DMPF derivatives varied between 6 and 9.10^{-4} mole/dm^3.

The intensities of the absorption band were measured by the Ramsay method[3] :

$$I = \frac{1}{cl} \ln \left(\frac{I_o}{I}\right) d\nu = \frac{S}{cl}$$

where the symbols have their usual meaning. The area of the band S was calculated by the formula of Simpson :

$$S = 2.3 \frac{h}{3} (y_o + 4\, y_1 + 2\, y_2 + 4\, y_4 + \ldots)$$

where h = the interval of $d\nu$ and y = the absorption for a given wavenumber.

The oscillator strength f, may be calculated by the relation

$$f = 4.315 \cdot 10^{-9} \int \varepsilon \, d\nu$$

The amidine was synthetisized according to the method described by Bredereck[4]. The amidine was extracted by benzene and dried on potassiumcarbonate. It was then further purified by vacuumdistillation.

3. RESULTS AND DISCUSSION

Fig. 1 shows the U.V. spectrum of DMPF and 4-Cl DMPF. The spectrum is characterized by two absorption bands. The first one lying at $\pm$ 200 nm with ε = 20.000 probably corresponds to the

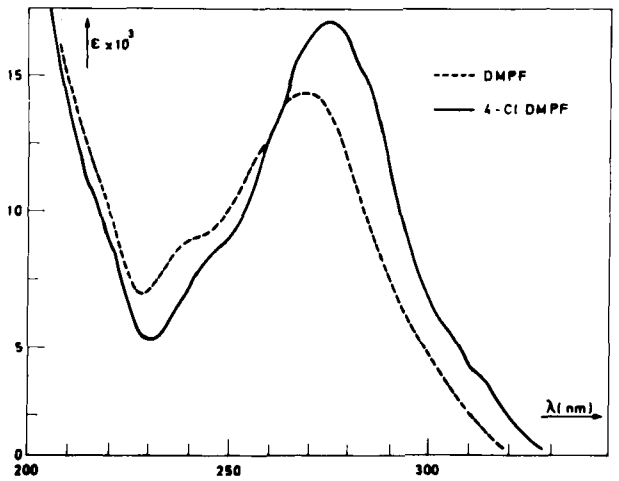


Fig. 1. : U.V. spectrum of DMPF ($c = 8.5 \times 10^{-4}$ mole/dm^3) and 4-Cl DMPF ($c = 6.5 \times 10^{-4}$ mole/dm^3); ($S = C_6H_{12}$, $T = 25°C$).

^1B transition. Table 1 indicates the values of λ(nm) and of the displacements $\Delta\nu$(nm) and $-\Delta\nu(cm^{-1})$ with respect to the unsubstituted DMPF for the second band. Table 1 also reports the values of $\Delta\nu(cm^{-1})$ observed for the benzene derivatives characterized by the same degree of substitution[5].

The values of ε_{max}, I and f are given in Table 2 for the same DMPF derivatives. The values of ε are of the same order of magnitude as these for the ^1L_a transition in disubstituted benzene derivatives (as for example $\varepsilon = 11.7$ for $ClC_6H_4NH_2$)[7]; this fact suggests that the absorption observed at 270 nm for the DMPF derivatives is mainly a ^1L_a transition and the ^1L_b transition is presumably hidden beneath it. In some di- or trisubstituted benzene derivatives, the ^1L_b transition is seen only as an inflec-

TABLE 1. : WAVELENGTH AND DISPLACEMENT $-\Delta\nu$ OBSERVED FOR DMPF DERIVATIVES

SUBSTITUENT OF DMPF	λ(nm)	$\Delta\lambda$(nm)	$-\Delta\nu(cm^{-1})$	$-\Delta\nu(cm^{-1})$ in C_6H_6 derivatives
H	269	0	0	0
4 CH_3	272	3	410	1400
4 Cl	275	6	811	2500
4 Br	276	7	943	3500
3 Cl	272	3	410	—
3,4 diCl	277	8	1173	—
3,5 diCl	275	6	811	3600
3,4 diCH_3	273	4	544	1900
4 F	268	-1	-139	550
4 I	277	8	1173	5600
OCH_3	275(6)	7	811	3400

(6) observed in acetonitrile.

tion on the blue side of the ^1L_a transition[8]. The values of $\tilde{\nu}$ are, however, lower for DMPF than for the para-aniline derivatives ($\tilde{\nu}$ = 41.000 cm^{-1}) and the bathochromic shift can be explained by a stronger conjugation due to the electrons of the $N^{(1)} - C = N^{(2)}$ skelet in the DMPF derivatives. As shown in figure 2, a relationship is found between the $\Delta\nu$ values for the DMPF and benzene derivatives but the relation is not linear.

TABLE 2. : ε_{max}, I AND f VALUES CALCULATED FOR THE DMPF DERIVATIVES.

SUBSTITUENT OF DMPF	$\varepsilon_{max} \times 10^{-3}$ ($l.mole^{-1}cm^{-1}$)	$I \times 10^{-6}$ ($l.mole^{-1}cm^{-1}$)	f
H	14.2	120.7	0.52
4 CH_3	14.6	122.7	0.53
4 Cl	18.3	156.6	0.65
4 Br	17	150.8	0.53
3 Cl	14.6	123.1	0.67
3,4 diCl	19.1	155.6	0.56
3,5 diCl	16.4	130.6	0.49
3,4 diCH_3	13	114.3	0.46
4 F	12.6	114.1	0.77
4 I	20	177.4	

It has frequently been generalized that the resonance, but not the inductive effects of substituents, affects the spectrum of the aromatic molecules but, as pointed out by Jaffé[9], it is probably an oversimplification. For most of the monosubstituted benzene, the molar orbital calculations performed by Matson[10], show that the spectroscopic properties are adequately described in terms of the resonance effect alone. The ability of a substituent to undergo resonance interaction may be expressed by the Taft resonance parameter $\sigma - \sigma'$[11]. Figure 3 reports the variation of $\Delta\lambda$ and ε_{max} as a function of $\sigma - \sigma'$.

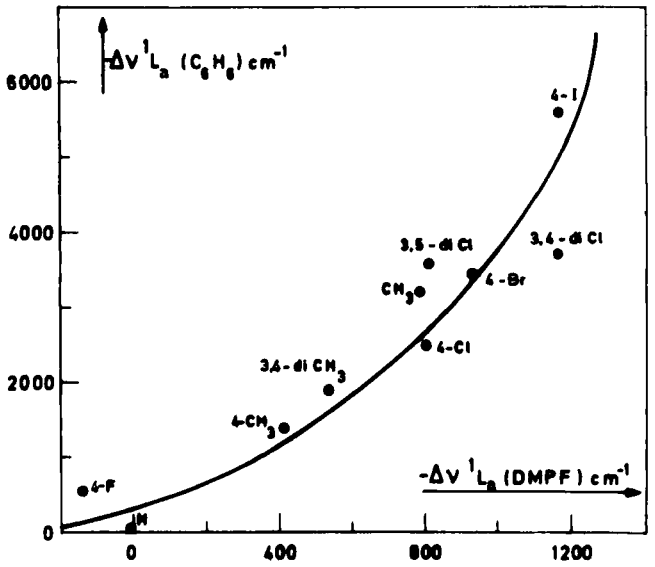


Fig. 2. : $-\Delta\nu\ ^1L_a\ (C_6H_6)$ as a function of $-\Delta\nu\ ^1L_a$(DMPF).

An approximative linear relationship is observed for the substituents like 4 CH_3, 3,4 diCH_3, 3 Cl, 3,4 diCl, but strong deviations appear for the halogens in para position. It has been argued that the inductive effect of the substituent can not be neglected when the resonance effect is large[12,13]. As pointed out by other spectroscopists, the excitation energy may be governed by the polarizability of the substituents[14,15] or by the interaction of the d orbitals of the halogens with electronically excited states of the aromatic ring[16]. Both effects contribute in giving values in the order I > Br > Cl > F.

In the DMPF 4-halogeno derivatives the resonance effect must be large and the intramolecular charge transfer between the

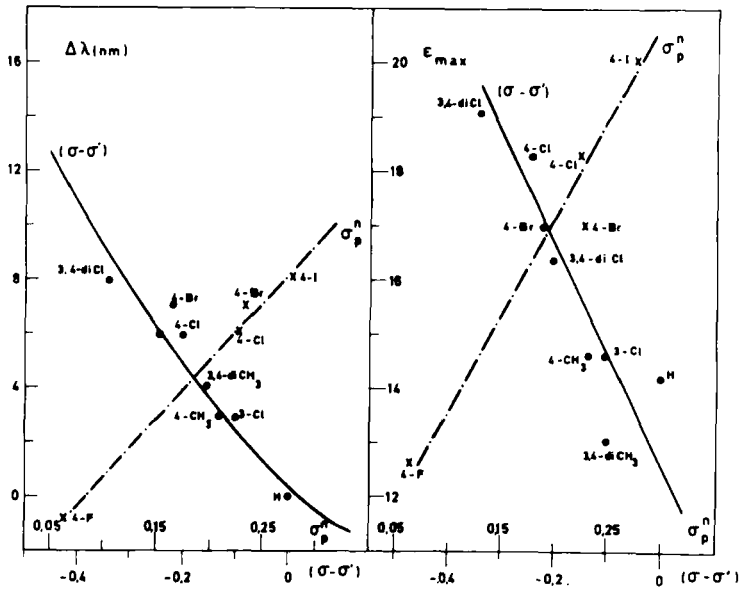


Fig. 3 : $\Delta\lambda$(nm) and ε_{max} as a function of $\sigma - \sigma'$ (●) and of σ_p^n (x).

electron donor group ($N^{(1)} - C = N^{(2)}$) and the halogens in para position must be important. As a matter of fact, the $\Delta\lambda$ and ε_{max} values are better correlated with the Hammett normal values σ_p for the four 4-halogen derivatives (figure 3); these normal values, including both inductive and resonance effects, are related to the net effect of the substituent and are found to decrease in the order I > Br > Cl > F. Recently Tomasik[17] has presented a new set of spectral substituent constants ($\sigma_{uv,p}$) based on the experimental shift of the ^1L_a band in the UV spectra of p.disubstituted benzene derivatives. These substituent constants

decrease on going from iodine ($\sigma_{uv,p}$=0.37) to fluorine ($\sigma_{uv,p}$ = 0.10).

Figure 4 shows that as for monosubstituted benzene derivatives [18,19] there is a relationship between the -Δν values and I_D - the ionization potential of the substituent[20]. The energy required to transfer an electron from the substituent to the ring is directly related to the I_D values of the substituent. The -Δν values are thus expected to increase as the values of I_D decreases. The resonance effect moves negative charge to the ring, thereby lowering the energy to remove an electron. Such rela-

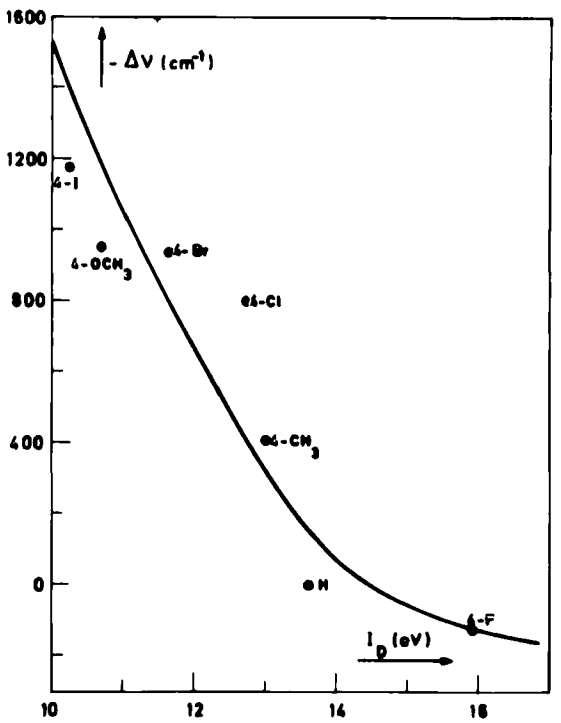


Fig. 4. : $-\Delta\nu(cm^{-1})$ as a function of I_D of the substituent.

tions are however difficult to establish owing to the considerable scatter of the I_D values recorded in the literature.

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