[Chem. Pharm. Bull. 27(5)1120—1124(1979)]

UDC 547.551.2.03.08 : 543.426.06

Studies on the Phosphorimetric Determination of Amines with Halonitro Compounds. II.[1] Substituent Effect on the Fluorescence and Phosphorescence of 4′-Substituted 4-Nitrodiphenylamines and 2-(Substituted Anilino)-5-nitropyridines

Kazumasa Hirauchi and Tameyuki Amano

Shionogi Research Laboratory, Shionogi and Co., Ltd.[2]

(Received October 28, 1978)

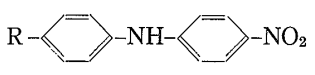
Substituent effects on the fluorescence and phosphorescence of 4′-substituted 4-nitrodiphenylamines and 2-(substituted anilino)-5-nitropyridines at 77°K were examined, and satisfactory linear relationships between Hammett's substituent constant σ and the lowest excited singlet energy levels, the lowest excited triplet energy levels, and the triplet decay constants of the compounds were obtained.

Keywords——Hammett-type correlation; fluorescence; phosphorescence; 4′-substituted 4-nitrodiphenylamines; 2-(substituted anilino)-5-nitropyridines

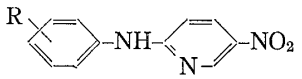
Many Hammett-type correlations have been found for excited state molecules. For example, satisfactory correlations have been obtained for triplet decay constants[3] and triplet energy levels[4] of substituted benzophenones, quenching of 1,4-dimethoxybenzene fluorescence by 4-substituted benzyl chlorides and benzyl acetates,[5] hydrogen abstraction of substituted toluene by benzophenone triplets,[6] quenching of fluorenone triplets by 4-substituted anilines,[7] and quenching of biacetyl fluorescence and phosphorescence by phenols and anilines.[8]

This paper presents some Hammett-type correlations for excited state aromatic nitro compounds, which probably have the lowest excited singlet and triplet of π,π^* configurations[9] in ethanol at 77° K.

4′-Substituted 4-nitrodiphenylamines (I—VII) and 2-(substituted anilino)-5-nitropyridines (VIII—XVI) were synthesized by treating aniline and substituted anilines with 4-fluoronitorobenzene and 2-chloro-5-nitropyridine, respectively.



R	R
I: NH_2	V: H
II: OH	VI: Cl
III: OCH_3	VII: NO_2
IV: CH_3	



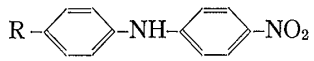
R	R
VIII: *p*-OH	XIII: *p*-Cl
IX: *p*-OCH_3	XIV: *m*-Cl
X: *p*-CH_3	XV: *p*-COOH
XI: *m*-CH_3	XVI: *p*-NO_2
XII: H	

Chart 1

1) Part I: K. Hirauchi and T. Amano, *Chem. Pharm. Bull.* (Tokyo), **25**, 1326 (1977).
2) Location: *Sagisu, Fukushima-ku, Osaka, 553, Japan.*
3) G. Favaro, *Chem. Phys. Lett.*, **21**, 401 (1973).
4) D.R. Arnold, "Advances in Photochemistry," Vol. 6, ed. by W.A. Noyes, Jr., G.S. Hammond, and J.N. Pitts, Jr., Wiley-Interscience, New York, 1968, pp. 330—331.
5) F.A. Carroll, M.T. McCall, and G.S. Hammond, *J. Am. Chem. Soc.*, **95**, 315 (1973).
6) C. Walling and M.J. Gibian, *J. Am. Chem. Soc.*, **87**, 3361 (1965).
7) G.H. Parsons, Jr. and S.G. Cohen, *J. Am. Chem. Soc.*, **96**, 2948 (1974).
8) N.J. Turro and T. Lee, *Mol. Photochem.*, **2**, 185 (1970).
9) O.S. Khalil, H.G. Bach, and S.P. McGlynn, *J. Mol. Spectrosc.*, **35**, 455 (1970).

The fluorescence and phosphorescence data for 4′-substituted 4-nitrodiphenylamines and 2-(substituted anilino)-5-nitropyridines are summarized in Tables I and II, and Hammett-type correlations are given in Figs. 1 to 6.

Table I. Corrected Fluorescence and Phosphorescence Spectral Data for 4′-Substituted 4-Nitrodiphenylamines in EtOH–Glass at 77°K



R	Fluorescence			Phosphorescence			
	$E_{x.\,max}$ nm	$E_{m.\,max}$ nm (cm^{-1})	RFI[a]	$E_{x.\,max}$ nm	$E_{m.\,max}$ nm (cm^{-1})	RPI[b]	τ[c] (sec)
$-NH_2$	403	586 (17065)	0.7	Not detectable			
$-OH$	401	564 (17730)	4	Not detectable			
$-OCH_3$	404	544 (18382)	16	Not detectable			
$-CH_3$	406	511 (19569)	27	408	560 sh 582 (17182) 614	0.6	0.28
$-H$	406	494 (20243)	34	403	540 sh 569 (17575) 600	11	0.32
$-Cl$	405	490 (20408)	109	406	530 560 (17857) 596	31	0.31
$-NO_2$	354 413 433	448 (22321) 471	244	353 410 429	514 (19455) 550 590	1431	0.46

a) Relative fluorescence intensity. For comparison of fluorescence intensity, that of anthracene solution (2×10^{-5} M in EtOH) was taken as 100 (at 376/402 nm).
b) Relative phosphorescence intensity. For comparison of phosphorescence intensity, that of carbazole solution (2×10^{-5} M in EtOH) was taken as 100 (at 340/437 nm).
c) Mean lifetime.
sh=shoulder.

As shown in Figs. 1—4, linear plots are obtained for fluorescence and phosphorescence maximum wavelength *vs.* the Hammett substituent constant, σ.

The correlations are satisfactory for the compounds examined and indicate that the lowest excited singlet and triplet energy levels are lowered by electron-donating substituents and raised by electron-withdrawing substituents. The trends observed in Figs. 2 and 4 are just the reverse of those of the lowest excited triplet energy levels of substituted benzophenones, which have the lowest excited triplet of n,π^* configuration.[4]

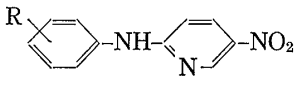
The linear plots in Fig. 3 give two lines with different slopes; the one in the electron-donating region has a steep slope and the other in the electron-withdrawing region has a moderate slope. The difference in slope indicates that the electronic effects of substituents on the lowest excited singlet energy levels are different in the electron-donating region and the electron-withdrawing region.

As for 4′-substituted 4-nitrodiphenylamines, the relative fluorescence and phosphorescence intensities are also increased by electron-withdrawing substituents and decreased by electron-donating substituents, but are not correlated with σ.

Conversion of the observed lifetime data into the corresponding deactivation constants ($K=1/\tau$) gives linear plots for log K *vs.* σ, as shown in Figs. 5 and 6.

The correlations are satisfactory for the compounds examined and indicate that the solvent quenching rate is accelerated by electron-donating substituents and decreased by electron-withdrawing substituents. The trends observed in Figs. 5 and 6 are also just the reverse of those of triplet decay constants of substituted benzophenones.[3]

TABLE II. Corrected Fluorescence and Phosphorescence Spectral Data for 2-(Substituted Anilino)-5-nitropyridines in EtOH–Glass at 77°K



R	Fluorescence			Phosphorescence			
	$E_{x.\,max}$ nm	$E_{m.\,max}$ nm (cm^{-1})	RFI[a]	$E_{x.\,max}$ nm	$E_{m.\,max}$ nm (cm^{-1})	RPI[b]	τ[c] (sec)
p-OH	315 406	566 (17668)	3	Not detectable			
p-OCH_3	318 400	501 sh 541 (18484)	27	Not detectable			
p-CH_3	318 392	475 sh 522 (19157)	38	317 385	540 sh 571 (17513)	0.4	0.14
m-CH_3	320 389	465 sh 490 (20408)	28	318 386	534 sh 562 (17794)	2	0.19
H	320 388	460 sh 486 (20576)	211	318 386	525 sh 559 (17889)	20	0.20
p-Cl	320 388	448 sh 482 (20747)	257	317 385	518 sh 550 (18182) 565 sh	85	0.24
m-Cl	319 390	449 472 (21186)	289	318 384	507 538 (18587) 566 sh	741	0.25
p-COOH	320 392	454 sh 479 (20877)	244	318 385	507 535 (18692) 570 sh	280	0.27
p-NO_2	341 sh 392 410	438 451 (22173)	26	339 sh 392 412	495 528 (18939) 564	1507	0.32

a) Relative fluorescence intensity. For comparison of fluorescence intensity, that of anthracene solution (2×10^{-5} M in EtOH) was taken as 100 (at 376/402 nm).
b) Relative phosphorescence intensity. For comparison of phosphorescence intensity, that of carbazole solution (2×10^{-5} M in EtOH) was taken as 100 (at 340/437 nm).
c) Mean lifetime.
sh=shoulder.

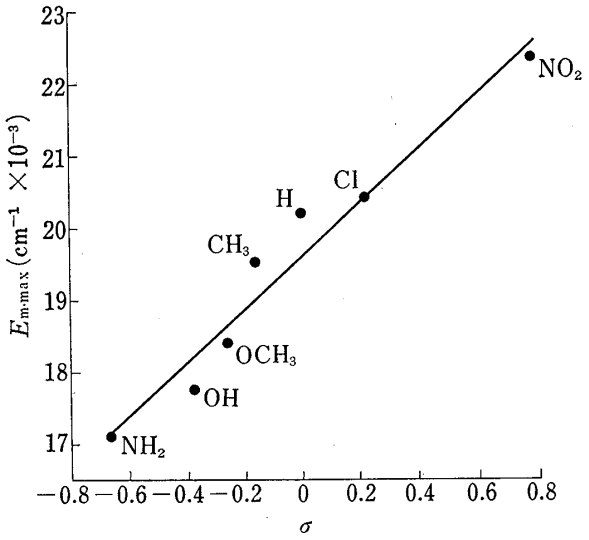


Fig. 1. Hammett Plot for Fluorescence Emission Maxima of 4′-Substituted 4-Nitrodiphenylamines in EtOH–Glass at 77° K

$E_{m.max}(cm^{-1})=19638+3770\,\sigma$, $r=0.972$

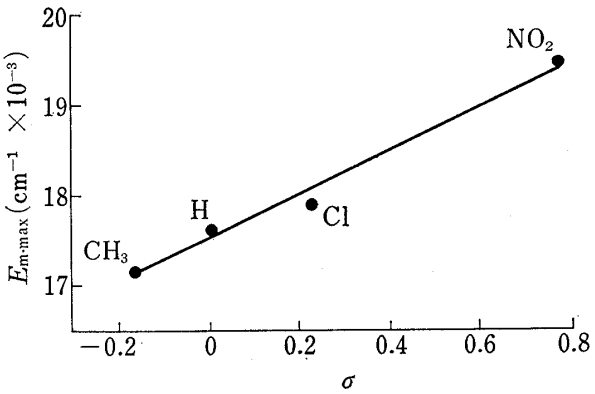


Fig. 2. Hammett Plot for Phosphorescence Emission Maxima of 4′-Substituted 4-Nitrodiphenylamines in EtOH–Glass at 77° K

$E_{m.max}(cm^{-1})=17518+2394\,\sigma$, $r=0.991$

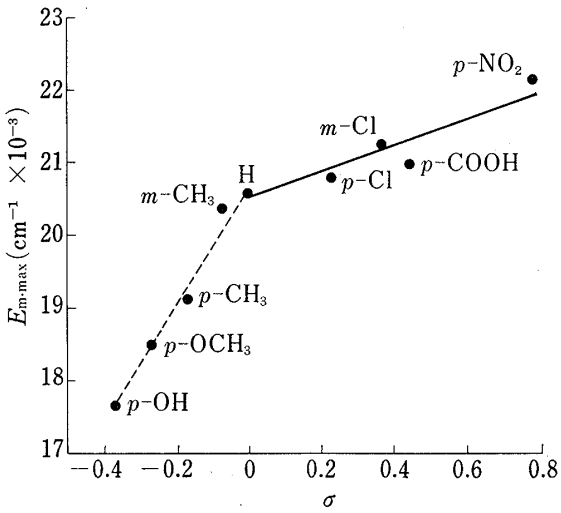


Fig. 3. Hammett Plot for Fluorescence Emission Maxima of 2-(Substituted Anilino)-5-nitropyridines in EtOH–Glass at 77° K

●——●: $E_{m.max}(cm^{-1})=20712+8289\sigma$, $r=0.991$
●——●: $E_{m.max}(cm^{-1})=20386+2014\sigma$, $r=0.913$

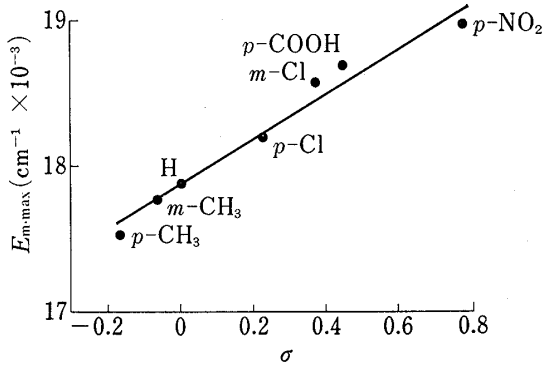


Fig. 4. Hammett Plot for Phosphorescence Emission Maxima of 2-(Substituted Anilino)-5-nitropyridines in EtOH–Glass at 77° K

$E_{m.max}(cm^{-1})=17877+1544\sigma$, $r=0.980$

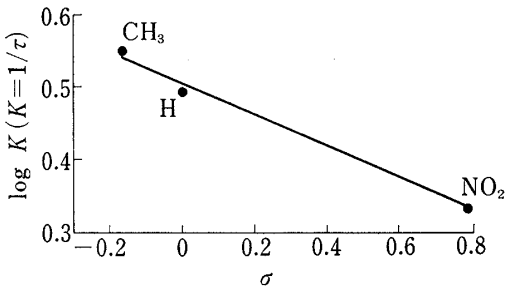


Fig. 5. Hammett Plot for Triplet Decay Constants of 4′-Substituted 4-Nitrodiphenylamines in EtOH–Glass at 77° K

$\log K=0.506-0.220\sigma$, $r=-0.996$

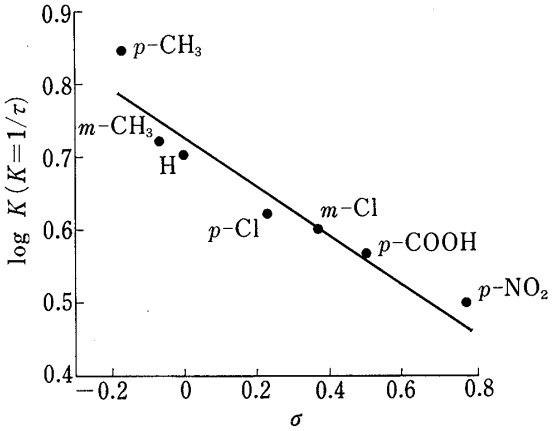


Fig. 6. Hammett Plot for Triplet Decay Constants of 2-(Substituted anilino)-5-nitropyridines in EtOH–Glass at 77° K

$\log K=0.727-0.333\sigma$, $r=-0.948$

The plot in Fig. 5 does not include the K value for the chloro derivative because it is too high to fit the linear relationship. This high K value may be due to the heavy-atom enhancement of radiationless transition from the lowest excited triplet state to the ground state.

We cannot speculate on the exact significance of the Hammett-type correlations for excited state molecules, but it should be emphasized that correlations between σ-values and excited state molecules seem to be possible.

Experimental

Apparatus——Phosphorescence excitation and emission spectra, and intensity were measured with a Hitachi MPF-2A spectrofluorometer equipped with a Hitachi phosphoroscope attachment, and the lifetime was measured with the same apparatus equipped with a Hitachi V-104 synchroscope.

Fluorescence excitation and emission spectra, and intensity were also measured with the same apparatus without the chopper in the phosphoroscope and synthroscope. Phosphorimetric and fluorometric measurements were done at liquid-nitrogen temperature using a fused quartz microsample tube of 2 mm inner diameter. The concentration of sample solutions was 2×10^{-5} M.

Ethanol: Reagent grade EtOH (1000 ml) was distilled after dissolving 10 g of Na metal in it.

Correction of the Measured Values of Fluorescence and Phosphorescence——Excitation spectra: These were corrected by both the Argauer method[10] using the thermopile technique and the Lippert method[11] using β-naphthol, quinine sulfate, and *m*-(dimethylamino)nitrobenzene.

Emission spectra: These were corrected by the Lippert method.

Intensities: These were corrected by both the Argauer method and the Lippert method.

Preparation of 4′-Substituted 4-Nitrodiphenylamines (I—VII)——The compounds were prepared by the reported methods:[12,13] 4′-amino- (I), mp 210—211° (lit.,[12] 211°); 4′-hydroxy- (II), mp 186—187° (lit.,[13] 183—184°); 4′-methoxy- (III), mp 153° (lit.,[12] 154°); 4′-methyl- (IV), mp 138° (lit.,[12] 137.5°); 4-nitro- (V), mp 134—135° (lit.,[13] 135—136°); 4′-chloro- (VI), mp 182—183° (lit.,[13] 181—182°); 4′-nitro- (VII), mp 220—222° (lit.,[13] 218—219°).

Preparation of 2-(Substituted Anilino)-5-nitropyridines (VIII—XVI)——A mixture of 1 mmol of 2-chloro-5-nitropyridine and 1.2 mmol of amine in 1 ml of dimethyl sulfoxide was heated at 100° for 2 hr. The mixture was poured into 60 ml of cold water, then the precipitate was collected by filtration, and recrystallized from MeOH: 2-(4-hydroxyanilino)- (VIII), mp 212—213° (lit.,[14] 211—212°); 2-(4-methoxyanilino)- (IX), mp 162° (lit.,[14] 160—161°); 2-(4-methylanilino)- (X), mp 137—138° (lit.,[14] 137—138°); 2-(3-methylanilino)- (XI), yield 0.16 g (64%), brown needles, mp 128—129°. *Anal.* Calcd. for $C_{12}H_{11}N_3O_2$: C, 62.87; H, 4.84; N, 18.33. Found: C, 62.73; H, 4.73; N, 18.24. 2-Anilino- (XII), mp 136—137° (lit.,[14] 135—136°); 2-(4-chloroanilino)- (XIII), yield 0.15 g (60%), yellow needles, mp 165°. *Anal.* Calcd. for $C_{11}H_8ClN_3O_2$: C, 52.92; H, 3.23; Cl, 14.20; N, 16.83. Found: C, 53.00; H, 3.33; Cl, 14.26; N, 16.70. 2-(3-Chloroanilino)- (XIV), yield 0.16 g (64%), brown needles, mp 191—192°. *Anal.* Calcd. for $C_{11}H_8ClN_3O_2$: C, 52.92; H, 3.23; Cl, 14.20; N, 16.83. Found: C, 52.92; H, 3.27; Cl, 13.99; N, 16.70. 2-(4-Carboxyanilino)- (XV), yield 0.17 g (65%), yellow needles, mp 258—260°. *Anal.* Calcd. for $C_{12}H_9N_3O_4$: C, 55.60; H, 3.50; N, 16.21. Found: C, 55.49; H, 3.61; N, 16.00. 2-(4-Nitroanilino)- (XVI), yield 0.14 g (53%), brown needles, mp 272—274°. *Anal.* Calcd. for $C_{11}H_8N_4O_4$: C, 50.78; H, 3.10; N, 21.53. Found: C, 51.04; H, 3.08; N, 21.34.

10) R.J. Argauer and C.E. White, *Anal. Chem.*, **36**, 368 (1964).
11) E. Lippert, W. Nägele, I. Seibold-Blankenstein, U. Staiger, and W. Voss, *Z. Anal. Chem.*, **170**, 1 (1959).
12) R. Lants and P. Obelliane, *Bull. Soc. Chim. Fr.*, **1956**, 311.
13) H.J. Backer and S.K. Wadman, *Rec. Trav. Chim. Pays-Bas*, **68**, 595 (1949).
14) A. Mangini, *Ricerca Sci.*, **8**, 427 (1937) [*C.A.* 33, 9305 (1939)].