The Electronic Spectra of 6,6′-Diamino-2,2′-bipyridine

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Synopsis. The lowest-energy π-π^* band of 6,6′-diamino-2,2′-bipyridine (dabp) appeared at near-UV region, and was found to suffer a characteristic solvent effect. The results were discussed in terms of its electronic structure calculated by ab initio method using a STO-3G basis set.

Electronic structures of polyazabiphenyls and their derivatives, particularly 2,2′-bipyridine (bpy) and its derivatives, have been studied in relation to their physical, chemical, and physiological importances.[1,2] However, the effect of substituent(s), especially at 6,6′-positions, on the electronic structures and photochemical properties of bpy have not been so well understood though ligands of the bpy family are familiar in inorganic chemistry. We previously reported the synthesis, properties, and complexability of 6,6′-diamino-2,2′-bipyridine (dabp)[3] and its derivatives.[4] Introduction of the amino groups at 6,6′-positions of bpy causes a large red shift of the π-π^*-transition band, appearing in the near-UV region (320—340 nm) with a strong intensity ($\log\varepsilon>4$).[3] Furthermore, the absorption band has been found to suffer a characteristic solvent effect. In this report, a detailed study on the electronic spectra of dabp has been carried out, and the photometric and some related properties of dabp has been discussed in terms of the effect of amino substituents at 6,6′-positions.

Experimental

6,6′-Diamino-2,2′-bipyridine (dabp) was prepared and purified according to the method previously reported.[3] For spectral measurements, dabp was further purified by reprecipitation with a KOH-methanol/water system to remove a trace amount of acid salt and subsequent sublimation under reduced pressure. 2,2′-Bipyridine (bpy), 6,6′-dimethyl-2,2′-bipyridine (dmbp), and 2-aminopyridine (amp) were obtained from Wako Pure Chem. Ind., Ltd, and purified by usual procedures. 6,6′-Dibromo-2,2′-bipyridine (dbbp) were prepared according to the literature's method.[5] The electronic spectra were recorded on a JASCO UVIDEC-505 spectrophotometer at 20 °C. ^{13}C and ^{1}H NMR spectra were measured with a JEOL JNM-GX270 Spectrometer (67.8 and 270 MHz, respectively) at 27 °C.

Ab initio calculation with a STO-3G basis set was carried out at The Computer Center of The University of Tokyo, using GAUSSIAN 80 HITAC Version. To avoid prohibitive geometry optimizations, the reported geometries of the bpy ring having s-trans planar structure in the Ref. 6 and of the amino group of 2-aminopyridine (amp) in Ref. 7 were used in the calculation.

Results and Discussion

The measured absorption maxima at the longest wavelength of bpy and some of its 6,6′-disubstituted derivatives in methanol appear in the order of bpy ($\lambda_{\max}$=281 nm, $\log\varepsilon$=4.13), dmbp (289 nm, 4.18), dbbp (303 nm, 4.19), and dabp (334 nm, 4.08). Dabp has a strong absorption band ($\log\varepsilon>4$) at around 330 nm, at much longer wavelength than other compounds. These absorption bands of bpy derivatives undergo a large red shift without decrease in the intensity upon protonation to the ring nitrogens in an acidic medium, i.e., the absorption maxima at the longest wavelength appear in the order of bpy ($\lambda_{\max}$=302 nm, $\log\varepsilon$=4.21), dmbp (311 nm, 4.20), and dabp (358 nm, 4.19) in acidic methanol.[8] These results indicate that the bands are not due to a n-π^* but to a π-π^* transition band.[9,10]

Table 1. The absorption Maxima at the Longest Wavelength in Various Solvents

Solvent	$\lambda_{\max}$/nm				
	dabp	bpy	dmbp	dbbp	amp
Cyclohexane	326	281	290	306	288
Chloroform	329	282	291	305	291
Acetone	334	—	—	—	—
Dioxane	334	281	291	306	295
DMF[a)]	339	281	291	305	297
DMSO[b)]	341	282	292	305	300
Ethanol	335	281	289	304	296
Methanol	334	280	289	303	296
Water[c)]	325	279	287	—[d)]	287

a) Dimethyl formamide. b) Dimethyl sulfoxide. c) pH 9.3 buffer solution (0.2 mol dm^{-3} of pottasium borate). d) Insoluble.

Table 2. Chemical Shifts in NMR Spectra of dabp in Various Solvents

Solvent	^{13}C[a)]					^{1}H[a)]
	2,2′	3,3′	4,4′	5,5′	6,6′	$\delta_{3,3'}-\delta_{5,5'}$[b)]
Chloroform-d	155.1	111.6	138.4	108.6	157.9	1.04
Acetone-d_6	155.7	110.5	138.4	108.9	159.9	1.09
DMSO-d_6[c)]	154.1	108.6	137.4	107.9	158.9	1.00
Methanol-d_4	156.1	111.9	139.5	110.0	160.8	0.72
Methanol-d_4+D_2O (1 : 3 v/v)	155.1	113.1	140.4	111.0	159.9	0.55

a) Chemical shift δ/ppm from TMS. b) Differences of chemical shifts between 3,3′-positions and 5,5′-positions. c) Dimethyl-d_6 sulfoxide.

Relatively few has been known as to the solvent effect on the electronic spectra of 6,6′-disubstituted bpy derivatives, and that of bpy has been reported to be little.[10,11] Those of dmbp and dbbp also suffered only a small solvent effect (Table 1). On the contrary, a larger and characteristic solvent effect was observed in the spectrum of dabp, i.e., an aprotic solvent of higher polarity caused a larger red shift to the π-π^* transition band of dabp, while water caused a blue shift. As the absorption maximum of this band suffered no change over the wide range of dabp concentration (10^{-4}—10^{-5} mol dm^{-3}) in any solvent, the solvent-dependent shifts were not due to a solute-solute interaction.[7] The imino-type tautomer of dabp is unlikely to contribute to the solvent-induced shifts, since the ^{13}C NMR spectra of dabp suffered only a small solvent effect in several different solvents (Table 2), indicating that dabp was presumably in the amino-form in these solvents.[3] The change in the conformation of two pyridine rings as a possible origin of the shifts[11] can be also ruled out from the ^{1}H NMR studies in several different solvents. The extent of the lower-field shift of the 3,3′-protons compared with the 5,5′-protons is known to be a good measure of the ring conformation of bpy moiety, and that of dabp was essentially the same as that of bpy in all solvents studied (Table 2),[11] confirming that dabp was in s-trans planar conformation.[3,4,12] Therefore, the solvent-induced shift of the absorption band may be attributed to the direct electronic effect of the amino substituents. Almost similar solvent-induced shift was observed for amp (Table 1).[7,13]

In order to understand the electronic structure of dabp, ab initio calculation with a STO-3G basis set was carried out. Bpy has six higher-lying occupied MO's, four π-MO's (π_3—π_6) and two n-MO's (n+ and n−), and four unoccupied π-MO's (π_1^*—π_4^*), which play essential role in the photochemical properties and complexability of bpy.[1,2,6] Dabp had also the same set of the corresponding MO's (Fig. 1). The MO levels of dabp were generally higher than the corresponding MO levels of bpy. In particular π_5 and π_6 levels of dabp were higher than the corresponding MO levels of bpy presumably due to an antibonding character between the amino-nitrogens and the 6,6′-carbons (Fig. 1, Table 3). However, the π_1^*-MO of dabp has small coefficients at the amino-nitrogens, affecting little to the energy level of this MO, thus lowering the energy gap between occupied π_5 or π_6-MO's and unoccupied π_1^*-MO (Fig. 1, Table 3). As the strong absorption band at the longest wavelengths are thought to have large weight on the allowed transition from the π_6 (B_g, HOMO) to the π_1^* (A_u, LUMO),[1,14] it is not surprising that the large red shift of this band was observed for dabp by introduction of amino substituents.

The solvent effect on the absorption band can be interpreted in terms of the calculated MO coefficients of π_6 (Fig. 1, Table 3). Hydrogen-bond formation by the amino-hydrogen of dabp to aprotic polar solvents may cause an increase in the electron density on the amino-nitrogens, raising the energy-level of π_6 and resulting in the red shift of the absorption band. While, the opposite effect may be resulted from hydrogen bonding of the amino-nitrogen of dabp with protons of the protic solvents (Fig. 2),[13] explaining the observed blue shift in water.

Introduction of amino substituents also affected the

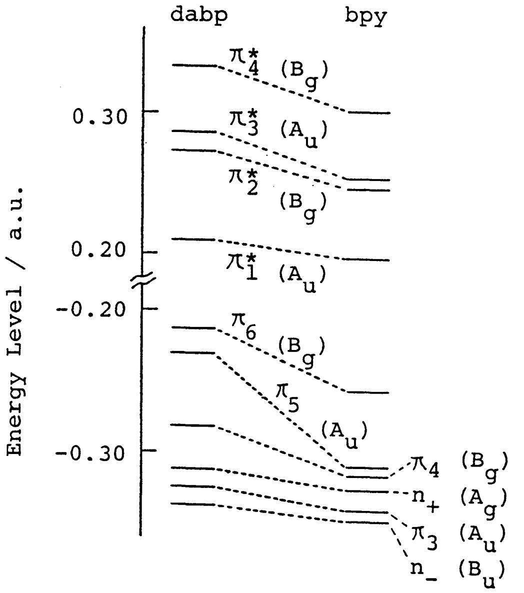
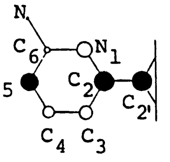


Fig. 1. The energy diagram of calculated MO of dabp and bpy.

Table 3. Energy Levels and Coefficients of the Calculated π_5, π_6, and π_1^* of dabp and bpy

Material	Orbital	Energy level/a.u.	Coefficient						
			N_1	C_2	C_3	C_4	C_5	C_6	N_{amino}
	$\pi_1^*(A_u)$[a]	0.209	−0.38	0.42	−0.22	−0.27	0.40	−0.07	0.04
dabp	$\pi_6(B_g)$[b]	−0.214	−0.07	−0.22	−0.37	−0.03	0.36	0.22	−0.35
	$\pi_5(A_u)$[c]	−0.230	−0.29	0.12	0.31	0.10	−0.23	−0.24	0.43
	$\pi_1^*(A_u)$	0.197	−0.35	0.42	−0.26	−0.24	0.43	−0.10	—
dpy	$\pi_6(B_g)$	−0.257	−0.18	−0.35	−0.31	0.07	0.37	0.23	—
	$\pi_5(A_u)$	−0.311	0.30	−0.10	−0.35	−0.28	0.05	0.34	—

a)



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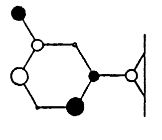

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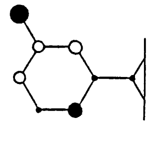

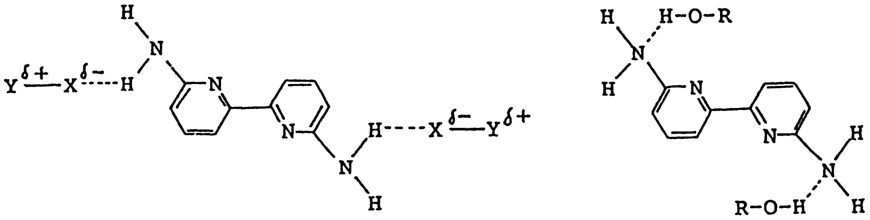

Fig. 2. The solute-solvent interactions of dabp.

basicities (proton affinities) of the nitrogen atoms of dabp, which were estimated from their ls-electron levels according to the method of Catalán et al.[15,16] The calculated proton affinities for dabp and bpy in this work[17] showed that the proton affinity of the ring-nitrogens of dabp (9.80×10^2 kJ mol^{-1}) were much higher than either those of bpy (9.22×10^2 kJ mol^{-1}) or the amino-nitrogens of dabp (8.67×10^2 kJ mol^{-1}), being in agreement with the results reported in Ref. 3.

Thus, the amino substituents at 6,6′-positions increased the σ-donating ability of the ring-nitrogens though they affected little to the lowest π^*-level (π_1^*). Since the σ-donor and π-acceptor capacities of the ligand interact synergistically in the transition-metal complexes,[18] the results described above explain the high stability of 1 : 1 complexes of dabp with divalent transition-metal ions.[3]

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