The Phosphorescence Spectra of 2, 2'- and 4, 4'-Bipyridyls

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The blue-green phosphorescence spectra of 2, 2'-bipyridyl, and the blue phosphorescence spectra of 4, 4'-bipyridyl, in ethanol, carbon tetrachloride, and cyclohexane at 90°K, have been studied and the results are reported here. The phosphorescence spectra of 2, 2'- and 4, 4'-bipyridyls had not been observed previously. Kanda, Shimada, and Sakai[1] studied in detail the green-blue phosphorescence of biphenyl in EPA, petroleum ether, cyclohexane, and carbon tetrachloride at 90°K. Since the molecular structures of 2, 2'- and 4, 4'-bipyridyls are closely related to that of biphenyl, it was assumed that the phosphorescence spectra of the bipyridyls must be very similar to the spectrum of biphenyl. The vibrational analyses are discussed.

Experimental

2, 2'-Bipyridyl, from Tokyo Kasei Co., was recrystallized twice from ethanol. The melting point was 69.5°C. 4, 4'-Bipyridyl-dihydrochloride was obtained from K & K Laboratories.[2] Three grams of 4, 4'-bipyridyl-dihydrochloride was treated with 1.2 g. of caustic soda in water, and the 4, 4'-bipyridyl which precipitated was recrystallized twice from hot water; the product was 4, 4'-bipyridyl-dihydrate which was dried in air for 2 days and then in a desiccator over sulfuric acid for 20 days until a theoretical loss in weight corresponding to two molecules of water resulted. The melting point was 110.2—110.5°C. Solvent used in this study were ethanol, cyclohexane, and carbon tetrachloride which were purified as described previously.[1,3] The optical setup was the same as described previously.[3]

Results and Discussion

The triplet-singlet emission spectra of 2, 2'- and 4, 4'-bipyridyls in ethanol, carbon tetrachloride, and cyclohexane at 90°K have been observed, and the microphotometer tracing curves are shown in Figs. 1 and 2. Spectral data and the analyses are given in Tables I and III. The spectrum of 2, 2'-bipyridyl will be discussed first. This compound emitted blue-green phosphorescence with a lifetime of about 2 to 3 sec. by visual estimation. Exposure time ranged from 1 to 7 hr. with slit width of 100 μ and Kodak Tri-X film. The phosphorescence bands were broad in ethanol, somewhat resolved in carbon tetrachloride and very sharp and well resolved in cyclohexane. Therefore, the vibrational analyses ware made first with the spectrum in cyclohexane. The highest wave number band at 23545 cm^{-1} was taken as the 0, 0-band of the system and vibrational frequencies of 235, 325, 460, 605, 755, 815, 895, 995, 1155, 1235, 1310, 1460, and 1570 cm^{-1} were found; and the 1570 cm^{-1} frequency was seen to form the main progression of the system. These frequencies seem to correspond to the Raman frequencies of 615, 995, 1150, 1239, 1302, 1475, and 1574 cm^{-1}. The Raman data were obtained by us but unfortunately the frequencies corresponding to the phosphorescence bands of 235, 325, 755, 815, and 895 cm^{-1} have not yet been found. The phosphorescence band of 460 cm^{-1} may be explained as 2×235 cm^{-1}. For comparison, the infrared spectrum was also studied. The vibrational frequencies are listed in Table II.

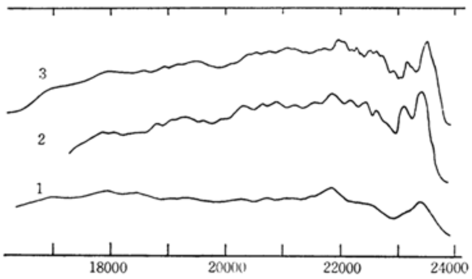

Fig. 1. Phosphorescence spectra of 2, 2'-bipyridyl at 90°K.
Concn.: 1×10^{-2} M, in ethanol (1), carbon tetrachloride (2) and cyclohexane (3)

4, 4'-Bipyridyl emitted blue phosphorescence and the lifetime was about 2 sec. by visual estimation. Exposure time ranged from 5 to 10 hr. with slit width of 100 μ and Kodak Tri-X film. The phosphorescence bands were broad in ethanol, somewhat resolved in carbon tetrachloride and very sharp and well resolved in cyclohexane as shown in Fig. 2. This behavior is very similar to that of 2, 2'-bipyridyl.

1) Y. Kanda, R. Shimada and Y. Sakai, *Spectrochim. Acta*, **17**, 1 (1961).
2) K & K Laboratories, Inc. 177—10 93rd Avenue, Jamaica 33, N. Y., U. S. A.
3) Y. Kanda and R. Shimada, *Spectrochim. Acta*, **15**, 211 (1959).

TABLE I. PHOSPHORESCENCE SPECTRUM OF 2, 2′-BIPYRIDYL
ν: Wave number in cm^{-1}

In cyclohexane			In CCl_4			In ethanol			Analysis
ν	Rel. int.	$\Delta\nu$	ν	Rel. int.	$\Delta\nu$	ν	Rel. int.	$\Delta\nu$	
23545	10	0	23450	10	0	23420	8	0	0,0
23310	6.5	235							0-235
23220	7	325	23130	8.5	320				0-325
23085	5.5	460							0-235×2
22940	6.5	605	23860	6.5	590				0-615
22790	8.5	755	22685	8	765				0-760
22730	8.5	815							
22650	8.5	895				22525	7	895	0-895
22550	9	995	22465	9	985				0-995
22390	9	1155							0-1150
22310	9	1235	22205	9	1245				0-1239
22235	9	1310							0-1302
22085	10	1460							0-1460
21975	10	1570	21880	10	1570	21865	10	1555	0-1574
21740	9	1805							0-1574-235
21640	9	1905	21555	9	1895	21495	9	1925	0-1574-325
21405	9	2140	21240	8.5	2210				
21215	9	2330	21125	8.5	2325	21120	9	2300	0-1574-760
21075	9.5	2470							0-1574-895
20980	9	2565	20875	9	2575	20790	9	2630	0-1574-995
20830	8.5	2715							0-1574-1150
20745	9	2800	20655	8.5	2795				0-1574-1239
20650	8.5	2895							0-1574-1302
20515	8.5	3030							0-1574-1460
20405	8.5	3140	20310	8.5	3140	20330	9	3090	0-1574×2
20130	7	3415	19980	7	3470				
19500	7	4045	19645	7	3805				
19220	7	4325	19315	7.5	4135	19450	9	3970	
18950	6.5	4595	19070	7	4380	19040	9	4380	
18555	6.5	4990	18830	6.5	4620				
17940	6.5	5605	18430	6	5020	18530	9	4890	
			18070	6	5380				
			17880	6	5570	17930	9	5490	
16935	7	6610				17045	9	6375	

TABLE II. VIBRATIONAL FREQUENCIES OF 2, 2′-BIPYRIDYL (cm^{-1})

Raman		Infrared	Raman		Infrared
In CS_2	In CCl_4	KBr disk	In CS_2	In CCl_4	KBr disk
		405 m	1190(1)	1187(2)	
		428 w			1210 w
	615(3)	621 s	1240(3)	1239(4)	1250 s
		655 m			1268 vw
		741 w	1307(2)	1302(3)	
		757 vs			1397 w
		894 w			1418 vs
		975 vw	1455(3)	1475(3)	1454 vs
1003(3)	995(5)	993 s	1490(3)	1490(3)	1507 w
1050(1)	1045(2)	1040 s			1529 w
		1065 m			1559 s
		1084 s	1575(3)	1574(3)	
		1089 s	1595(3)	1595(3)	1582 vs
	1150(2)	1140 m			3051 vw

TABLE III. PHOSPHORESCENCE SPECTRUM OF 4, 4'-BIPYRIDYL

ν: Wave number in cm^{-1}

In cyclohexane			In CCl_4			In ethanol			Analysis
ν	Rel. int.	$\Delta\nu$	ν	Rel. int.	$\Delta\nu$	ν	Rel. int.	$\Delta\nu$	
24530	10	0	24530	10	0	24585	8	0	0,0
24385	9	145							0–145
24240	5	290	24240	7	290				0–290
24055	4	475							0–475
23955	5	575	23960	6	570				0–575
23775	8	755	23775	7	755	23750?	7	835	0–755
23635	8	895							0–755–145
23525	9	1005	23530	8.5	1000	23500?	8	1085	0–1005
23380	8.5	1150							0–1005–145
23260	9.5	1270	23260	9.5	1270	23275	9.5	1310	0–1270
23110	9	1420							0–1270–145
22920	10	1610	22925	9.5	1605	22975	10	1610	0–1610
22780	9	1750							0–1610–145
22525	8.5	2005	22575	8	1955				0–1610–475
22265	8.5	2265	22250	8	2280	22290	7	2295	0–1610–755
21955	9	2575	21985	8.5	2545	21980	7.5	2605	0–1610–1005
21790	8	2740							0–1610–1005–145
21660	9	2870	21660	8.5	2870	21685	7	2900	0–1610–1270
21500	8	3030							0–1610–1270–145
21330	8	3200	21340	7	3190	21350	5	3235	0–1610×2
21180	6	3350							0–1610×2–145
20960	4	3570	21030	2.5	3500				0–1610×2–475
20710	3	3820	20705	1	3825	20715	1	3870	0–1610×2–755
20395	1	4135	20390	0.5	4140	20380	0.5	4205	0–1610×2–1005
20070	0.5	4460	20080	0.2	4450	20060	0.3	4525	0–1610×2–1270

The vibrational analysis was made with the spectrum in cyclohexane. Each strong band was accompanied by a weak satellite band with a separation of 145 cm^{-1}. The highest wave number band at 24530 cm^{-1} was taken as the 0, 0-band of the system and the vibrational frequencies of 290, 475, 575, 755, 1005, 1270, and 1610 cm^{-1} were found. The frequency of 1610 cm^{-1} was seen to form the main progression of the system. These frequencies seem

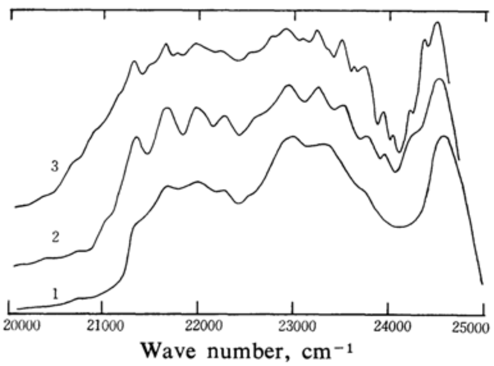

Fig. 2. Phosphorescence spectra of 4, 4'-bipyridyl at 90°K.

Concn.: 1×10^{-2} M, in ethanol (1), carbon tetrachloride (2) and cyclohexane (3)

to correspond to the Raman frequencies of 575, 755, 1002, 1295, and 1595 cm^{-1}. The Raman data were obtained by us but unfortunately the frequencies corresponding to the phosphorescence bands of 145, 290, and 475 cm^{-1} have not yet been found. For comparison, the infrared spectrum was also studied. The vibrational frequencies are listed in Table IV. Because of symmetry relations the infrared data may sometimes be useless. However, we can not neglect them, if the presence of any anomalous vibrational band structures in the spectrum is to be checked. Incidentally, anomalous band structures had been found in the phosphorescence spectra of aromatic compounds, such as benzoic acid and aniline.[4)] It seems that both the spectra of 2, 2'- and 4, 4'-bipyridyls show no anomalous vibrational structure. The overall spectral features of the bipyridyls are very similar to those of biphenyl.[1)]

We also studied the near ultraviolet absorption spectrum of 2, 2'-bipyridyl in cyclohexane and observed the change of the spectrum

4) Y. Kanda, R. Shimada, Y. Gondo, M. Nakamizo, K. Hanada, M. Koyanagi and Y. Takenoshita, *Proc. Intern. Symp. Mol. Struct. Spectry., Tokyo*, **1962** (B303); Y. Kanda, R. Shimada and Y. Takenoshita, *Spectrochim. Acta*, **19**, 1249 (1963).

TABLE IV. VIBRATIONAL FREQUENCIES OF 4, 4'-BIPYRIDYL (cm^{-1})

Raman		Infrared
In $CHCl_3$	In C_6H_6	KBr disk
	575(0)	
	660(3)	
		733 m
755(1)		745 w
		760 w
		806 vs
		850 m
		879 m
		968 m
		976 w
		988 s
1002(2)		1006 w
		1037 w
		1075 m
		1097 w
		1127 w
1155(2)		
1217(3)		1217 s
1295(2)	1297(3)	
		1325 w
	1357(1)	
		1409 vs
		1493 m
1530(1)	1535(1)	1535 s
1595(1)		1592 vs
		1943 w
		2780 w
		3015 s

through addition of trichloroacetic acid. The spectrum showed a remarkable red shift as can be seen in Fig. 3. This shows that the broad band with maximum at 284 mμ belongs to a π-π* type transition.[5] The compound can be assumed to consist of two pyridine rings. The lowest excited level of pyridine is of an n-π* type and its second one is of a π-π* type. Now, because of the interaction of π-electron systems the lowest excited state of 2, 2'-bipyridyl is not of an n-π* type but a π-π* type. The spectral features of 2, 2'-bipyridyl do not resemble those of biphenyl. This has been clearly explained in a theoretical work by

5) M. Kasha, *Discussions Faraday Soc.*, **9**, 14 (1950).

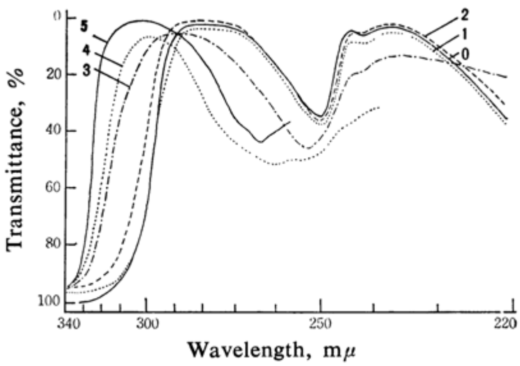

Fig. 3. Ultraviolet absorption spectra of 2, 2'-bipyridyl with trichloroacetic acid in cyclohexane.
2, 2'-Bipyridyl: 1×10^{-4} M,
CCl_3COOH: 0; without acid, 1; 1×10^{-5} M, 2; 1×10^{-4} M, 3; 1×10^{-3} M, 4; 1×10^{-2} M, 5; 1×10^{-1} M

Gondo.[6] If the 2, 2'-bipyridyl molecule is assumed to be trans-coplanar,[7,8] the lowest excited singlet state is a ^1B_u, and the lowest triplet state is a ^3B_u state. Thus, a π-π* type excited triplet state is believed to be responsible for the phosphorescence of 2, 2'-bipyridyl, and may also be the case with 4, 4'-bipyridyl. The similarity found between the phosphorescence spectra of biphenyl,[1] 2, 2'- and 4, 4'-bipyridyl seems to support this interpretation. The rather long lifetimes of 2, 2'- and 4, 4'-bipyridyls are also compatible with the above interpretation.[5]

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6) Y. Gondo, Dissertation submitted to the Graduate School, Kyushu University, 1964, and *J. Chem. Phys.*, in press.
7) P. E. Fielding and R. J. W. Le Fèvre, *J. Chem. Soc.*, **1951**, 1811.
8) L. L. Merritt, Jr., and E. D. Schroeder, *Acta Cryst.*, **9**, 801 (1956).