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Studies of the π,π^* Absorption Bands of 2,6-Dimethyl-4-pyrone

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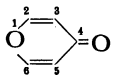
Synopsis. The π,π^* S-S absorption spectra of 2,6-dimethyl-4-pyrone in solutions up to the vacuum UV region were obtained. Based on the results of the MO calculations, the assignment and characterization of the observed π,π^* bands were studied, together with the assignment of the π,π^* bands near 250 nm of 4-pyrone.

Previously, we have theoretically and experimentally studied the π,π^* singlet-singlet absorption bands of *p*-[2] and *o*-quinones[3] and α-santonin[4] up to the vacuum UV region. 4-Pyrone is one of the fundamental unsaturated carbonyl compounds in organic and biological chemistry. As for the π,π^* absorption spectra of 4-pyrones, heretofore, only the π,π^* bands near 250 nm have been investigated.[5] In this work, we have studied the π,π^* absorption spectrum of 2,6-dimethyl-4-pyrone (II) up to the vacuum UV region in the same manner as in the previous works. The assignment of the π,π^* bands near 250 nm of 4-pyrone (I) has also been studied.



4-Pyrone (I)

The absorption spectra were measured in the same manner as in the previous works. The solvents used—heptane and 1,1,1,3,3,3-hexafluoro-2-propanol (HFP)—were the same as those used previously. Commercially available II was purified by the zone-melting method after being purified by vacuum sublimation (mp 133.6—134.5 °C).

As the electronic integral values in the Pariser-Parr-Pople method,[6] various kinds of integral values were tentatively used, based on the results obtained in the previous calculations.[2-4] Finally, the following integral values were chosen in this work. The core Coulomb integral of the carbonyl oxygen atom and the core resonance integral of the conventional C–C single bonds were taken as −14.00 and −1.50 eV, respectively. Otherwise, the intergral values used were the same as those used in the calculations of *p*-benzoquinone[2] and α-santonin.[4] For the oxygen atom of the 1-position, its core Coulomb integral, its Coulomb electron repulsion integral, and the core resonance integral of the C–O bonds were taken as −27.00, 19.46,[7] and −1.20 eV, respectively. As for the effect of methyl-group substitution, the core Coulomb integral of the substituted carbon atoms was taken as −9.00 eV, considering only the inductive effect of alkyl group, as in the previous works.[2,3] In the calculations, all the singly-excited configurations were included. As the dimention of the π-electronic system of I, that of the C_{2v} symmetry estimated by Norris *et al.*[8] from the microwave spectrum was used.

In Fig. 1, three π,π^* bands can be found, among which the strongest band is in the vacuum UV region.[9]

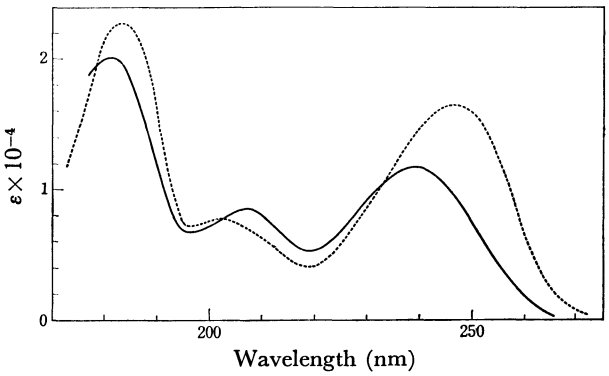


Fig. 1. Absorpion spectra of II in solutions.
——: Heptane, ------: HFP.

These three π,π^* bands are denoted as Bands A, B, and C in order of wavelength. A relatively large red-shift and a large intensity enhancement of Band A in the HFP solution in comparison with that in the heptane solution are noticeable. A strong hydrogen-bond between the oxygen atom of the 1-position of II and HFP may not be formed because of the steric hindrance caused by the two methyl groups of II. II is known to have a relatively strong basicity and this basicity is ascribed to the lone-electron-pair of the carbonyl oxygen atom.[5b,10] Therefore, the above-mentioned fact may be due to the strong hydrogen-bond formation between the carbonyl oxygen atom of II and HFP.

TABLE 1. WAVELENGTHS (λ), MOLAR ABSORPTION COEFFICIENTS (ε), AND OSCILLATOR STRENGTHS (f) OF THE ABSORPTION MAXIMA OF II

Heptane			HFP			Band name
λ(nm)	ε	f	λ(nm)	ε	f	
238.5	11800	0.25	246	16450	0.35	A
207	8550	≈0.17	202.5	7810	≈0.16	B
181	20200	0.5	183	22800	0.52	C

In Table 2, the first column denotes the numbering of the states in order of increasing excitation energies (calculated). In this table, the data on the higher excited states with small f values have been omitted. In view of the calculated results in Table 2, Band A is thought to consist of the $^1A_1$ (the No. 1 state)←$^1A_1$ and $^1B_2$ (the No. 2 state)←$^1A_1$ transition bands, but mostly of the former. On the other hand, in the spectrum of I in the hexane solution, obtained by Efimov *et al.*,[5e] the band near 250 nm corresponding to Band A has a shoulder on its long wavelength-side and the large distance (*ca.* 2800 cm^{-1}) between its peak and this shoulder shows that the main band and this shoulder belong to separate π,π^* bands. A similar spectrum for I in the

Table 2. Calculated excitation energies (E) and oscillator strengths (f) of the singlet π,π^* excited states of I and II and the corresponding observed π,π^* bands

No.	Calculated: Symmetry	Calculated: E(eV)	Calculated: f	Observed[a]: Band name	Observed[a]: E(eV)	Observed[a]: ε,f[b]
			(1) I			
1	$^1B_2$	4.306	0.055		≈4.75[5e]	3000[5e]
2	$^1A_1$	4.367	0.365		5.09[5e]	12600[5e]
3	$^1B_2$	5.445	0.056			
4	$^1A_1$	6.095	0.029			
5	$^1A_1$	6.612	0.077			
6	$^1B_2$	6.946	0.071			
7	$^1A_1$	7.422	1.157			
			(2) II			
1	$^1A_1$	4.456	0.372	A	5.20	0.25
2	$^1B_2$	4.512	0.048			
3	$^1B_2$	5.362	0.063	B	5.99	≈0.17
4	$^1A_1$	6.178	0.038			
5	$^1A_1$	6.681	0.051			
6	$^1B_2$	7.045	0.070			
7	$^1A_1$	7.438	1.180	C	6.85	0.5

a) The data for I and II are those in the hexane and heptane solutions, respectively. b) The values for I and II are molar absorption coefficient and oscillator strength, respectively.

ethanol solution has been reported by Franzosini *et al.*[5a,11] Therefore, as is shown in Table 2, the main band and the shoulder may be reasonably assigned to the $^1B_2$ (the No. 1 state)←$^1A_1$ and $^1A_1$ (the No. 2 state)← $^1A_1$ bands of I, respectively.

As for Band B, the assignment based on the calculated results is not clear. Band C may be safely assigned to the $^1A_1$ (the No. 7 state)←$^1A_1$ band, in view of the large f value of this transition, as is shown in Table 2. Therefore, it may be concluded that both Bands A and C are polarized almost along the symmetry axis of II. According to the calculated results, Band A has the character of the intermolecular charge-transfer band[12] from the oxygen atom of the 1-position to the carbonyl group, and the excited state of Band C is greatly localized in two vinyl groups, as in the case of Band D of α-santonin.[4] In the HFP solution, the strong hydrogen-bond formation between II and HFP, mentioned above, may intensify this character of Band A. So, the noticeable solvent effect for Band A in the HFP solution, mentioned above, may be reasonably explained on the basis of this characteristic of Band A.

As is seen in Table 2, the calculated excitation energy of the lowest $^1A_1$ state (the No. 1 state) of II is 0.09 eV greater than that of the corresponding state (the No. 2 state) of I. On the other hand, the corresponding state of 3,5-dialkyl-4-pyrone is 0.153 eV smaller than that of I. Based on the calculated results, therefore, the main band near 250 nm of I may be expected to be at longer wavelengths than Band A and at shorter wavelengths than the corresponding band of 3,5-dialkyl-4-pyrone, respectively. This expectation is verified in the case of Band A, as is seen in Table 2.

References

1) Permanent address: The Tokyo Metropolitan Industrial Technology Center, Kita-ku, Tokyo.

2) A. Kuboyama, S. Matsuzaki, M. Takagi, and H. Arano, *Bull. Chem. Soc. Jpn.*, **47**, 1604 (1974); *Tokyo Kogyo Shikensho Hokoku*, **69**, 492 (1974).

3) a) A. Kuboyama, F. Kobayashi, and S. Morokuma, *Bull. Chem. Soc. Jpn.*, **48**, 2145 (1975); *Tokyo Kogyo Shikensho Hokoku*, **71**, 180 (1976); b) A. Kuboyama and H. Arano, *Bull. Chem. Soc. Jpn.*, **49**, 1401 (1976).

4) A. Kuboyama, Y. Sato, and F. Kobayashi, *Bull. Chem. Soc. Jpn.*, **48**, 3381 (1975); *Tokyo Kogyo Shikensho Hokoku*, to be published.

5) a) P. Franzosini, G. Trauerso, and M. Senesi, *Ann. Chim. (Rome)*, **45**, 128 (1955); M. Rolla and P. Franzosini, *ibid.*, **46**, 582 (1956); b) H. Tsubomura, *Nippon Kagaku Zasshi*, **78**, 106 (1957); c) K. Yamada, *Bull. Chem. Soc. Jpn.*, **35**, 1323 (1962); d) R. Zahradnik, C. Parkanyi, and J. Koutecky, *Collect. Czech. Chem. Commun.*, **27**, 1242 (1962); e) A. A. Efimov, R. N. Nurmuchametov, and A. I. Tolmachev, *Opt. Spektrosk.*, **29**, 6 (1970); f) J. Gayoso, H. Bouanani, and A. Boucekkine, *Bull. Soc. Chim. Fr.*, **1974**, 553.

6) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953); J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

7) S. Nagakura, "Yuuki Denshi Riron," Baifuukan, Tokyo (1966), 283.

8) C. L. Norris, R. C. Benson, P. Beak, and W. H. Flygare, *J. Am. Chem. Soc.*, **95**, 2768 (1973).

9) The n, π^* absorption bands of I[5e] and II are found near 300 nm in the heptane solutions.

10) L. F. Cavalieri, *Chem. Rev.*, **41**, 525 (1947).

11) In Yamada's paper,[5c] the existence of two shoulders on the long wavelength-side of the main peak is described, but no data about the absorption intensity are given.

12) S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954); S. Nagakura, *Pure Appl. Chem.*, **7**, 79 (1963).