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Spectroscopic and Theoretical Studies on the Protonation to Xanthone Derivatives

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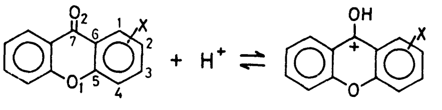
Ultraviolet absorption, fluorescence, and excitation spectra of xanthone and its hydroxyl and methoxyl derivatives were measured in sulfuric acid solutions of various acidities. The basicities (pK_a's) of these compounds were obtained from the spectral change. Variable-β type molecular orbital calculations of the π-systems were performed, assignment of the absorption spectra being made. It was confirmed that protonation occurs at the carbonyl oxygen atom. A method for obtaining the equilibrium constant without knowing the absolute intensity is proposed.

It has been established that in strong acidic media protonation occurs at the carbonyl oxygen atom of γ-pyrone and its derivatives.[1,2] As a dibenzo derivative of γ-pyrone, xanthone (or 9H-xanthen-9-one, **1**: X=H) is also expected to be protonated at the carbonyl oxygen atom forming hydroxyxanthylium ion (**2**: X=H).



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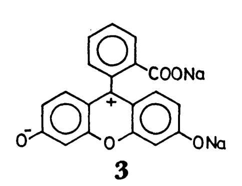
Actually xanthone is known to be stable in concentrated sulfuric acid showing strong emission,[3] and the basicity of xanthone has been obtained from the change of the ultraviolet absorption spectra.[4-6] The basic and emissive characters of xanthone are expected to vary with the number and positions of the substituent such as a hydroxyl group, according to reports on the features of the substitution effect on the absorption and emission of xanthone derivatives.[3,5,7] These phenomena have close resemblance to those of the hydroxyl derivatives of anthraquinone forming the alizarin dye group where electron donating power of the hydroxyl group and the competitive intramolecular hydrogen bonding are the major factors determining basic and emissive characters. It should also be noted that the emissive character of xanthone is related to that of fluorescein (**3**).



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We have studied in detail the acidity dependence of the electronic absorption and emission spectra and the basicities of mono-hydroxyl and methoxyl derivatives of xanthone (**1**: X=OH, OCH_3) and interpreted the results with the molecular orbital calculations of the π-electronic structures.

Experimental

Materials. Commercial G.R. grade of xanthone was purified by recrystallization from ethanol. 1-, 2-, 3-, and 4-methoxyxanthones and the corresponding hydroxyxanthones were synthesized after Ullmann and Zlokasoff[8] and purified by recrystallization from aqueous ethanol. Concentrated sulfuric acid of high special grade (Wako Pure Chemical Industries, Ltd.) was used without further purification.

Measurement. A Shimadzu multiconvertible spectrophotometer D40R was used to measure the ultraviolet and visible absorption spectra with stopcocked fused quartz 1 cm cells. A Hitachi MPF-2A fluorescence spectrophotometer was used for the excitation and fluorescence spectra. Fluorescence spectra were automatically corrected with Rhodamine B by use of the spectrum correction attachment. Absorption and emission spectra were measured in ethanol and in sulfuric acid of various acidities at room temperature. All the solutions were prepared just before the measurement, the concentration of the solute being about 10^{-4}—10^{-5} M. The acid concentrations were determied by titration with a standard aqueous solution of sodium hydroxide. The value of Hammett's acidity function were taken from the table by Jørgensen and Hartter.[9] The basicities (pK_a) of the xanthone derivatives were determined from the change of the ultraviolet absorption spectra by the iterative least squares calculation for the sigmoid curve of ε-H_0 plot.[10] Although the absolute intensity of excitation spectra was not obtained, we could obtain fairly accurate values of pK_a from the relative change of the excitation spectra at two different wavelengths. Details are given in the Appendix.

Results and Discussion

Ultraviolet Absorption Spectra. Ultraviolet absorption spectra of the neutral (**1**, in EtOH) and protonated (**2**, in conc. H_2SO_4) xanthone are shown in Fig. 1 and Table 1, the former spectrum being in accordance with the previous results.[7,11,12] The spectra of the hydroxyl and methoxyl derivatives are given in Figs. 2 and 3 and Table 1. The spectra of the hydroxyl and the corresponding methoxyl derivatives, except for the 1-derivatives are so similar that the spectra of 2-,

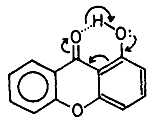

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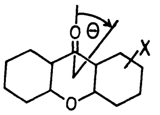
Table 1a. OBSERVED AND CALCULATED ABSORPTION SPECTRA OF XANTHONE DERIVATIVES

X	Observed value		Calculated value		
	ΔE (eV)	f	ΔE (eV)	f	θ(°)a)
H	3.69	0.09	4.07	0.19	00
	4.31	0.02	4.51	0.00	90
	4.38	0.02			
	4.79	0.16	4.78	0.08	90
	5.21	0.37	5.23	0.14	0
			5.25	1.46	90
	5.64	0.31	5.66	0.04	90
			5.67	0.13	0
1-OCH$_3$	3.60	0.11	3.91	0.19	43
	4.21	0.04	4.33	0.11	−35
	4.50	0.08	4.56	0.00	23
			4.98	0.43	−76
	5.21	0.81	5.25	0.27	54
			5.33	0.89	−80
			5.67	0.09	−9
2-OCH$_3$	3.44	0.09	3.80	0.23	−10
	4.16	0.05	4.35	0.11	4
			4.69	0.23	83
	4.98	0.46	5.14	0.10	−49
	5.25	0.60	5.21	0.06	77
			5.28	0.43	−75
			5.62	0.03	−5
3-OCH$_3$	4.08	0.32	4.08	0.14	−16
	4.63	0.14	4.48	0.05	63
			4.63	0.10	−52
			4.98	0.82	−80
	5.23	0.71	5.29	0.73	59
			5.58	0.30	−39
			5.72	0.26	−66
4-OCH$_3$	3.59	0.09	3.90	0.19	26
	4.28	0.03	4.36	0.09	−58
			4.65	0.03	−83
	5.01	0.66	5.08	0.58	−66
			5.26	0.82	83
			5.33	0.16	−50
			5.59	0.14	3

a) Direction of the transition moment.



3-, and 4-hydroxyxanthones have been omitted. The spectra of 1-hydroxy- and 1-methoxyxanthones are quite different from each other indicating an intramolecular hydrogen bonding in 1-hydroxyxanthone (**4**). The n→π* bands of these compounds were not observed in the polar solvents used in this study.[12] The spectra of the neutral compounds are generally seen to shift to the red on protonation, *viz.*, the 340 nm band of xanthone is shifted to 400 nm. The electronic structures of forms **1** and **2** of the 1-, 2-, and 4-derivatives seem very similar to those of xanthone, while those of the 3-derivatives are modified by the electron flow from the substituent etherial lone pair electrons.[7] This anomaly is also reflected in the basicity.

Table 1b. OBSERVED AND CALCULATED ABSORPTION SPECTRA OF PROTONATED XANTHONE DERIVATIVES

X	Observed value		Calculated value		
	ΔE (eV)	f	ΔE (eV)	f	θ(°)a)
H	3.16	0.05	3.37	0.17	0
	3.71	0.31	3.84	0.48	90
			4.02	0.00	90
	4.61	0.04	4.91	0.10	0
	4.93	0.46	5.00	1.05	90
	5.69	0.39	5.34	0.06	0
			5.64	0.61	90
1-OCH$_3$	2.95	0.11	2.97	0.19	41
	3.79	0.23	3.75	0.30	−69
			3.95	0.07	81
	4.63	0.09	4.68	0.79	84
	4.79	0.33	4.95	0.14	−49
			5.24	0.14	62
	5.64	0.29	5.51	0.67	−75
			5.85	0.03	72
2-OCH$_3$	2.99	0.06	2.99	0.18	−24
	3.62	0.14	3.75	0.18	76
	3.94	0.16	3.89	0.23	−78
	4.82	0.55	4.71	0.82	82
			4.86	0.16	29
	~5.6	~0.5	5.14	0.73	82
			5.37	0.13	−80
			5.70	0.07	−84
3-OCH$_3$	3.52	0.37	3.41	0.28	65
	3.94	0.02	3.61	0.52	−65
			4.15	0.01	−66
	4.55	0.05	4.75	0.06	−5
	5.01	0.56	5.01	0.74	−73
			5.22	0.40	48
	~5.6	~0.3	5.61	0.69	85
4-OCH$_3$	2.99	0.06	2.90	0.13	31
	3.72	0.24	3.79	0.28	66
			3.91	0.03	52
	4.82	0.58	4.56	0.96	88
			4.80	0.21	−54
	~5.6	~0.3	5.25	0.14	53
			5.45	0.37	−66
			5.73	0.22	37

a) See the footnote in Table 1a.

Fluorescence and Excitation Spectra. We did not measure the phosphorescence spectra of xanthones, since a number of studies have been reported.[12–14] Fluorescence spectra of xanthone in concentrated sulfuric acid is exemplified in Fig. 1 as the most typical of the compounds studied. That the conjugate acid **2** fluoresces more strongly than the neutral compound **1** reminds one of the structure of the fluorescent form **3** of fluorescein.

For a series of the protonated xanthone derivatives the values of the Stokes shift are scattered in the range 3500—7000 cm^{-1}, revealing a drastic change in the geometry of the compounds on protonation. However, no apparent correlation was observed between the values of the Stokes shift and the basicity of the parent compound.

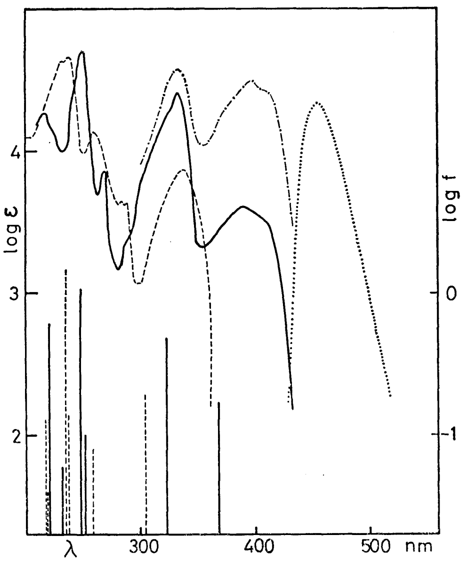


Fig. 1. Observed and calculated spectra of neutral (**1**) and protonated (**2**) xanthones
----: Absorption spectrum in EtOH and calculated transition energies of **1**, X=H.
——: Absorption spectrum in conc. H_2SO_4 and calculated transition energies of **2**, X=H.
-·-·: Excitation spectrum of **1** (2.66×10^{-5}M) in conc. H_2SO_4. Excited at 456 nm.
······: Fluorescence spectrum (corrected) of **1** (~10^{-5} M) in conc. H_2SO_4. Emitted at 420 nm.

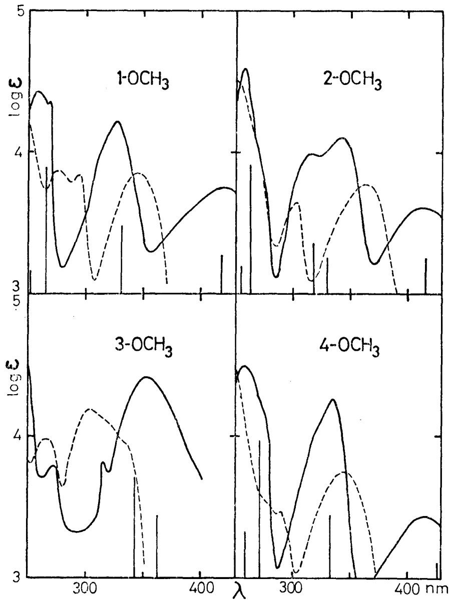


Fig. 2. Ultraviolet absorption spectra of methoxyxanthones in ethanol (----) and in concentrated sulfuric acid (——) solutions. The spectra of hydroxyxanthones are essentially the same as the corresponding methoxyl derivatives except for 1-substituted compounds (See Fig. 3). The calculated spectra of the protonated compounds are shown with solid bars.

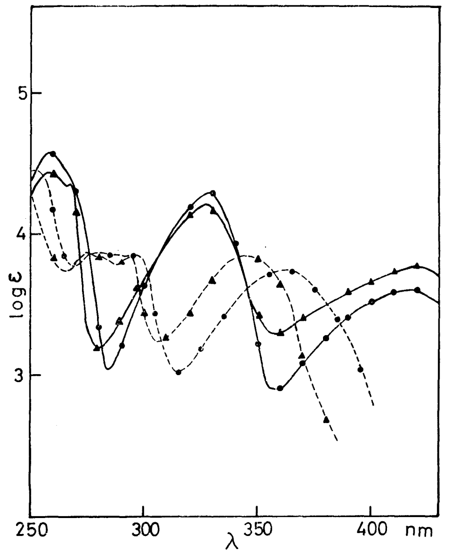


Fig. 3. Ultraviolet absorption spectra of 1-hydroxy- (●) and 1-methoxyxanthones (▲) in ethanol (----) and in concentrated sulfuric acid (——) solutions.

Excitation spectrum of xanthone in concentrated sulfuric acid changes with the solute concentration as shown in Fig. 4. For the solutions with solute concentration lower than 10^{-5} M, 330 and 400 nm bands undoubtedly correspond to the absorption spectrum. As the solute concentration increases the relative intensities of these two bands become reversed, and reabsorption is gradually observed around 330 nm. As a result, solutions with concentration higher than 10^{-3} M give a quite different spectral shape. However, at lower concentrations no secondary change such as energy transfer seems to occur. We therefore adjusted the concentration below 10^{-4} M for the measurement of the excitation spectra for obtaining the basicities of the xanthone derivatives. The change of the excitation spectra of xanthone with the solvent acidity is shown in Fig. 5.

Basicities. The basicities (pK_a's) of xanthone and

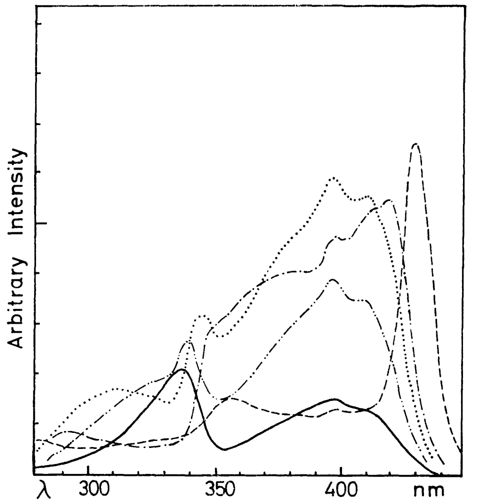


Fig. 4. Concentration dependence of the excitation spectrum of xanthone in concentrated sulfuric acid. Emitted at 452 nm.
Concentrations are
——: 2.66×10^{-5}M, -··-: 1.06×10^{-4}M,
······: 2.66×10^{-4}M, -·-: 5.32×10^{-4}M,
----: 2.66×10^{-3}M.

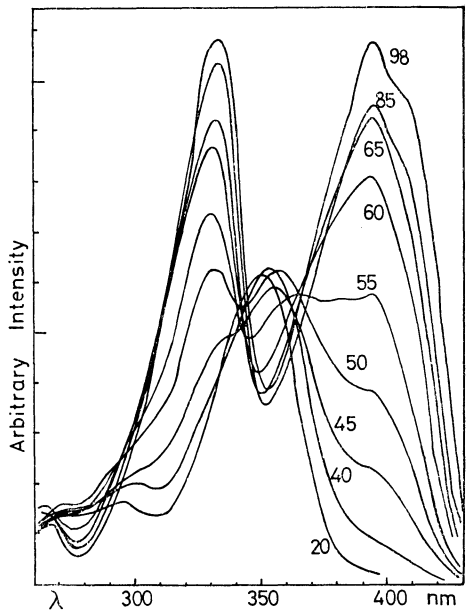


Fig. 5. Solvent acidity dependence of the excitation spectrum of xanthone in concentrated sulfuric acid. The numbers indicate the weight per cent of sulfuric acid. Excited at 452 nm.

Table 2. Basicities and π-electron densities of xanthone derivatives

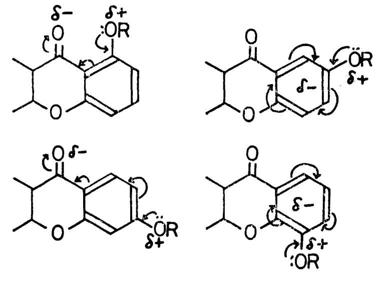
X	$-\mathrm{p}K_a$		π-Electron density	
	Absorption	Excitation	Carbonyl O	Ethereal O
H	4.1	4.0	1.425	1.772
1-OH	4.1	4.3	1.455	1.769
1-OCH_3	2.2	2.2		
2-OH	3.9	3.8	1.428	1.773
2-OCH_3	3.7	3.7		
3-OH	3.0	2.6	1.434	1.771
3-OCH_3	2.8	2.5		
4-OH	4.2	4.2	1.425	1.777
4-OCH_3	4.2	4.4		

its eight derivatives were determined both from the absorption and excitation spectra (Table 2). The values for xanthone, −4.1 (absorption) and −4.0 (excitation), are in agreement with the reported values, −4.08,4) −4.12,5) and −4.2,6) all from the ultraviolet absorption measurement, but no report can be found for the derivatives studied here. Comparing these values with those for benzophenone (−6.4), anthrone (−5.0), 4,4′-dimethoxybenzophenone (−4.4), and 4,4′-dihydroxybenzophenone (−4.2),15) we find these data suggest that protonation occurs at the carbonyl oxygen atom of xanthone. The electron donating ethereal oxygen lone pair of xanthone acts as a bridge for the conjugation of the π-electron between the two benzene rings and also an electron supplier to the carbonyl oxygen atom, placing the basicity of xanthone as high as that of dihydroxybenzophenone. All the hydroxyl and methoxyl derivatives are no less basic than xanthone.

Except for the 1-substituted derivatives the basicities of hydroxyl and the corresponding methoxyl derivatives are almost the same. The basicities of the methoxyxanthones are in the following order:

$$1 > 3 > 2 > 0\ (=\text{xanthone}) > 4.$$

Note a gap between the 3- and 2-methoxyxanthones. This can be explained by the resonance theory as in the following scheme:



More quantitative correlation can be obtained from the molecular orbital calculation. In Table 2 the π-electron densities on the carbonyl and ethereal oxygen atoms of the xanthone derivatives are compared with the basicity data, which are correlated well with the π-electron densities on the carbonyl oxygen atom (Fig. 6) but not with the ethereal oxygen atom. Although a similar argument has been given by Efimov and Komarov for the basicities of xanthone and γ-pyrone derivatives, it is based on the Hückel molecular orbital.16) It should be noted that for π-electron systems with many heteroatoms the Hückel method often gives unreasonable π-electron densities.17)

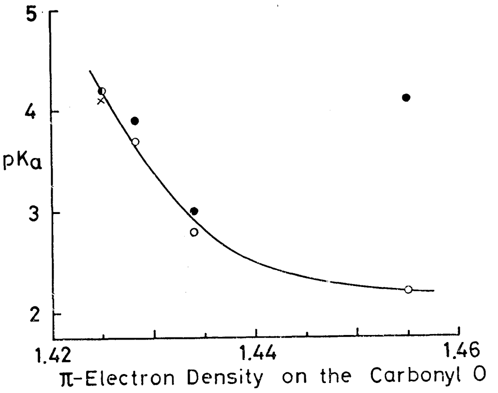


Fig. 6. Correlation between the basicities ($\mathrm{p}K_a$'s) and the π-electron densities on the carbonyl oxygen atom of xanthone derivatives

× : xanthone ●: hydroxyxanthone

○: methoxyxanthone

The $\mathrm{p}K_a$ values are taken from the UV absorption data.

On the other hand, as evident from **4** the excess π-electron on the carbonyl oxygen atom of 1-hydroxyxanthone is pulled away through the hydrogen bond, causing no net effect on the value of the basicity.

If no side-reaction intervenes in the excited states of fluorescent molecules the basicities can be obtained fairly accurately from the change of the excitation spectra.

Calculation of the π-Electronic Structures of Xanthone and Its Derivatives. In order to get theoretical support for the mechanism of protonation to xanthone derivatives and to interpret the observed electronic spectra, the π-electronic structures of the ground and lower excited states of the neutral and protonated xanthone derivatives were calculated with the variable-β approximation proposed by Nishimoto and Forster,[21] in which the consistency of the bond order-bond length relation is attained automatically with the PPP type molecular orbital framework. No accurate geometry of a molecule is therefore necessary for the input data.[22] No distinction was taken between the hydroxyl and methoxyl derivatives. For the protonated xanthones the protonated carbonyl oxygen atom was treated simply as a hydroxyl oxygen atom. No parametrization was tried for the different electronegativities of positively charged carbon atoms. Extensive singly excited configuration interaction was carried out. The parameters and details of the calculation are after Nishimoto.[23]

Electronic Structures of Xanthone and Its Derivatives. The net π-electron charge densities and the calculated bond lengths of the two forms of xanthone (**1**,**2**: X=H) are shown in Fig. 7. In both cases the charge distribution over the central three atoms lying on the molecular axis (z-axis) is rather uneven, while electron is uniformly populated over the wing benzene moiety. For the hydroxyl and methoxyl derivatives, the π-electron densities on the carbonyl oxygen atom are found to be correlated well with their basicities (Table 2 and Fig. 6), but not the total π-electron energies of **1** and **2**.

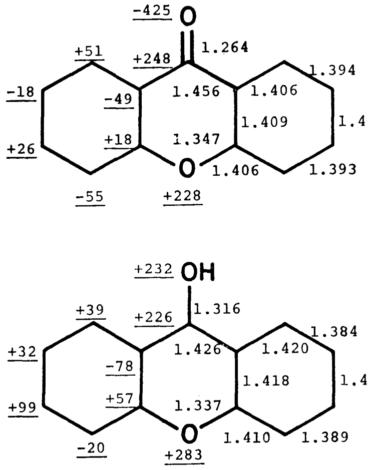


Fig. 7. The bond lengths and the net charge densities of the ground state of the neutral and protonated xanthones. The charge densities in the unit of 10^{-3} electron are underlined.

Assignment of the Electronic Spectrum of Xanthone. In order to discuss the assignment, the higher occupied and lower vacant π-molecular orbitals given in Table 3 should be considered. Both the HOMO and LUMO are symmetric (S) with respect to the plane passing through the molecular axis, and perpendicular to the molecular plane (yz-plane) to which the symmetry notations S and A will be referred unless otherwise stated. Assignment of the electronic spectra is given in Table 4. Pownall and Huber (abbreviated as PH) gave the assignment based on their phosphorescence excitation measurement.[12] There are a few discrepancies between their assignment and ours. Although σ-electron is not taken into this calculation we can expect that the lowest ,n→π* transition (Band I according to PH) is roughly expressed as (n→9) and x-polarized, *i.e.*, perpendicularly to the molecular plane, as both the π-LUMO 9 and σ-HOMO n have S symmetry. That this band is observed by PH as z-polarized may be an outcome of possible vibrational perturbation. The most dominant contribution to the lowest π→π*

Table 3. Higher occupied and lower vacant π-orbitals of xanthone

AO[a)]	Occupied MO		Vacant MO	
	7	8	9	10
C_1	0.3451	0.1363	−0.3050	0.1599
C_2	0.0597	0.3500	−0.0220	−0.3888
C_3	−0.2905	0.1064	0.3188	0.1872
C_4	−0.3405	−0.2773	−0.1863	0.2142
C_5	−0.0192	−0.2714	−0.1985	−0.4145
C_6	0.2961	−0.2632	0.1896	0.2656
C_7	−0.0532	−0.0288	0.4459	0.0000
O_1	0.0333	0.3930	0.1565	0.0000
O_2	−0.4171	0.3167	−0.4077	0.0000
Symmetry	S	S	S	A
Energy (eV)	−10.4359	−9.3827	−2.2098	−1.3450

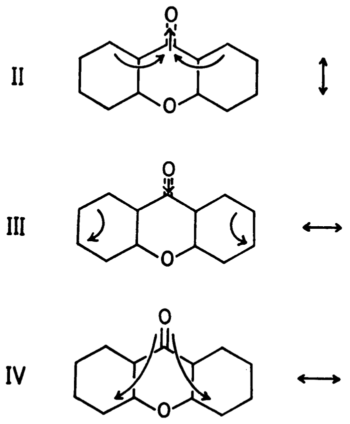
a) For numberings see formula **1** in the text.

Table 4. Assignment of the electronic spectra of xanthone

Band[a)]	Observed values[b)]		Calculated values[b)]	Polarization[c)]	Assignment	
	in EtOH	in 3-Methylpentane[a)]			Configuration	Character
I	—	3.37 (—)[d)]	—	x (z)[a)]	n→9[e)]	n→π*[f)]
II	3.69 (0.09)	3.69 (0.10)	4.07 (0.19)	z (z)	8→9	CT
III	{4.31 (0.02) 4.38 (0.02)}	4.39 (0.02)	4.51 (0.00)	y (y)	8→11 {5→9} 7→10	LE
IV	4.79 (0.16)	4.84 (0.10)	4.78 (0.08)	y (z)	8→10	Back CT
V	5.21 (0.37)	5.29 (0.50)	{5.23 (0.14) 5.25 (1.46)}	z y} (z)	{7→9 6→9}	LE

a) Ref. 12. b) Energies are in eV. The values in parentheses are oscillator strengths. c) Choice of axis is explained in the text. d) log ε_{max}~0.8.[12] e) For notations see Table 3 and the text. 5, 6, 10, and 11 are S and 7—9 are A. f) CT: Charge-transfer, LE: Locally excitation.

transition (Band II) is denoted by (8→9) and polarized along the molecular axis. Inspection of the wave functions indicates that this is a charge-transfer band, in which electron flows into the carbonyl oxygen atom from the ring moiety. The next higher band (Band III) is a mixture of several transitions with y-polarization, most of which are locally-excited in the ring moiety. In contrast to the tentative assignment by PH that Band IV is a z-polarized charge-transfer band, our calculation shows that it is a y-polarized *back*-charge-transfer band due to transition (8→10). The upper orbital 10 has A symmetry with no coefficient on the carbonyl group. The electron flow associated with the electronic transitions II, III, and IV in xanthone are shown in the diagram below, in which the two-headed arrow shows the direction of the transition moment.



The reliability of the variable-β calculation especially for the assignment of the electronic spectra of heteroatomic systems has been tested with a number of molecules.[21,24] As evident from Figs. 1 and 2 and Table 1 this is also the case for the xanthone derivatives. Agreement between calculation and observation is generally better for the protonated xanthone derivatives than the neutral compounds.

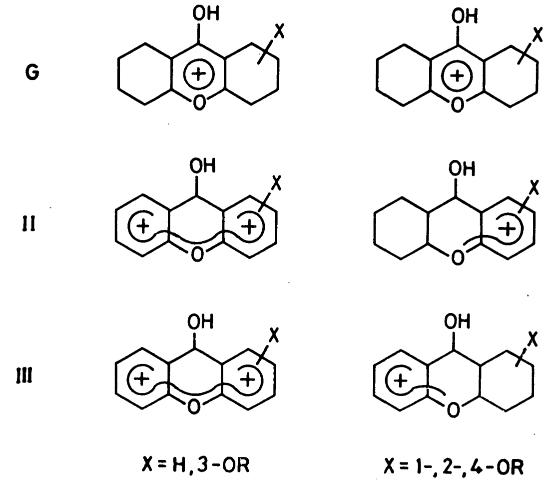


Fig. 8. Illustrative sketches of the charge densities of the ground and lower excited states of the protonated xanthone derivatives
G: Ground state II: Lowest $\pi \rightarrow \pi^*$ state
III: Second lowest $\pi \rightarrow \pi^*$ state

The 3-substituted derivatives show quite different spectral patterns, which are reproduced fairly well by the molecular orbital calculation. Charge densities of the ground and lower excited states of the protonated xanthone derivatives are given in Fig. 8. The 3-derivatives again behave quite differently from other derivatives, *viz.*, in xanthone and 3-derivatives the lowest two $\pi \rightarrow \pi^*$ excitations are delocalized all over the molecules, while in other derivatives the excitations are localized. Of the four derivatives of the protonated xanthone the 3-derivative has the lowest value of the total π-electron energy.

The authors are indebed to Dr. T. L. Kunii, the University of Tokyo, for allowing them to use the variable-β program on a Hitac 5020E computer at the Computer Centre, the University of Tokyo. Part of this study was supported by a grant from the Ministry of Education.

Appendix

Determination of the Equilibrium Constant without Knowing the Absolute Intensity. Let us assume that following acid-base equilibrium takes place.

$$B + H^+ = A, \tag{A1}$$

where B and A are, respectively, an organic base and the conjugate acid. If the analytical concentration of B is c, of which fraction x is protonated to form A, the dissociation constant K_a of the conjugate acid A is expressed as

$$K_a = \frac{c(1-x)h_0}{cx} = \frac{h_0(1-x)}{x}, \tag{A2}$$

where the acid concentration h_0 is related to Hammett's acidity function H_0 as

$$H_0 = -\log h_0. \tag{A3}$$ [25]

By definition the basicity of B or its pK_a value is expressed as

$$\begin{aligned} pK_a &= -\log K_a \\ &= H_0 + \log \frac{x}{1-x}, \end{aligned} \tag{A4}$$

A physical quantity Q for an equilibrated system is assumed to be additive of the components as in

$$Q = \alpha\{c(1-x)q_b + cxq_a\}, \tag{A5}$$

where q is the molar quantity of the component, such as molar extinction coefficient and the emission intensity per mole expected with a unit quantum yield, and α is a factor dependent on experimental conditions. Namely, factor α is the length of the cell in the case of electronic absorption measurement, while for emission spectra it is a function of the quantum yield, cell length, quenching mechanism, *etc.* and is usually left unknown.

Let us consider the latter case with unknown α. By choosing two different abscissae, or wavelengths, λ_1 and λ_2 (Fig. 9), we get

$$\begin{aligned} Q_1 &= \alpha\{c(1-x)q_{b1} + cxq_{a1}\} \\ Q_2 &= \alpha\{c(1-x)q_{b2} + cxq_{a2}\}. \end{aligned} \tag{A6}$$

For the ratio R, we get

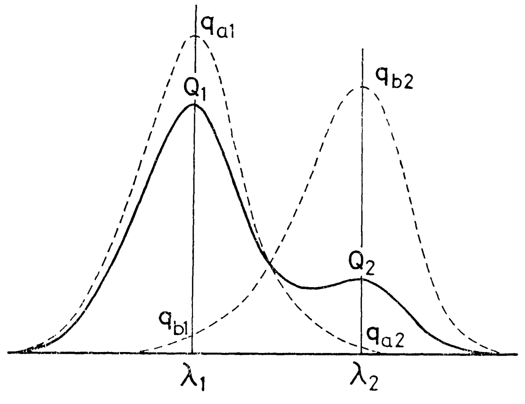


Fig. 9. Illustration for obtaining the equilibrium constant by measureing the absorbances at two different wavelengths

——: Observed spectrum
----: Spectrum of the component A
······: Spectrum of the component B

$$R=\frac{Q_1}{Q_1+Q_2}=\frac{(1-x)q_{b1}+xq_{a1}}{(1-x)(q_{b1}+q_{b2})+x(q_{a1}+q_{a2})}$$
$$=\frac{q_{b1}+(q_{a1}-q_{b1})x}{(q_{b1}+q_{b2})+(q_{a1}+q_{a2}-q_{b1}-q_{b2})x}$$
$$=\frac{F+Gx}{D+Ex}, \tag{A7}$$

which is a function of x (Eq. (A4)) and can be changed by varying the acidity H_0 of the solvent. By plotting R against H_0 we get a sigmoid curve whose limits are F/D and $(F+G)/(D+E)$ (Fig. 10).

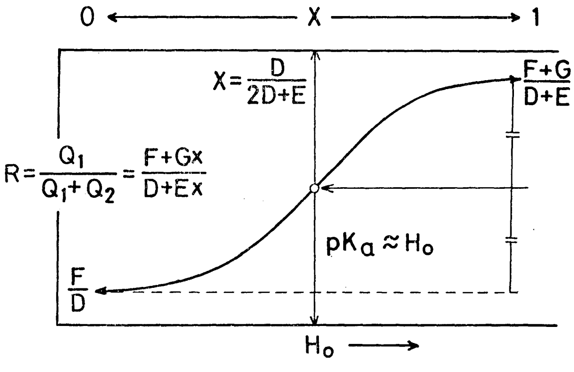


Fig. 10. Graphical method for obtaining the inflexion point of a sigmoid curve. Inflexion point is marked with ○.

Now let us find the inflexion point of this curve. By means of the relations[10]

$$\frac{dx}{dh_0}=\frac{(1-x)^2}{K_a} \tag{A8}$$

$$\frac{dh_0}{dH_0}=-2.303h_0 \tag{A9}$$

we get

$$\frac{dR}{dH_0}=-\frac{2.303h_0(1-x)^2(DG-EF)}{K_a(D+Ex)^2} \tag{A10}$$

$$\frac{d^2R}{dH_0{}^2}=\frac{2.303^2h_0(1-x)^2(DG-EF)\{D-(2D+E)x\}}{K_a(D+Ex)^3} \tag{A11}$$

By equating the identity (A11) to be zero, we get

$$x=\frac{D}{2D+E}=\frac{q_{b1}+q_{b2}}{(q_{b1}+q_{b2})+(q_{a1}+q_{a2})}, \tag{A12}$$

with which the identity (A10) is not zero. Thus Eq. (A12) certifies the inflexion point. Substitution of Eq. (A12) into Eq. (A4) gives

$$pK_a=H_0+\log\frac{q_{b1}+q_{b2}}{q_{a1}+q_{a2}}, \tag{A13}$$

This means that if $q_{b1}+q_{b2}$ is nearly equal to $q_{a1}+q_{a2}$ the basicity pK_a is obtained as the H_0 value at the inflexion point of the curve $Q_1/(Q_1+Q_2)$ against H_0. Usually the quantities q's are unknown. However, if the maxima of Q for components A and B are of the same order of magnitude, the second term of the right hand side of Eq. (A13) would be negligible by choosing these peak wavelengths as λ_1 and λ_2 as in Fig. 9. This is shown in Table 2 for the case of xanthone derivatives, where the pK_a values estimated from the excitation spectra by using this method are very close to the values obtained from the ultraviolet absorption spectra.

When it is difficult to read the inflexion point of a sigmoid curve, the following additional relations are helpful. As evident from Eqs. (A10) and (A11), the slope of the curve R–H_0 is maximum at the inflexion point. It can easily be shown that the R value at the inflexion point is the arithmetic mean of the two asymptote readings

$$\left(F+G\frac{D}{2D+E}\right)\Big/\left(D+E\frac{D}{2D+E}\right)=\left(\frac{F}{D}+\frac{F+G}{D+E}\right)\Big/2. \tag{A14}$$

The present method is not restricted to the case of an acid-base equilibrium (A1) and is also applicable to other types of equilibrium such as that of monomer-dimer

$$2A=A_2. \tag{A15}$$

Analysis is straightforward.[26]

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