

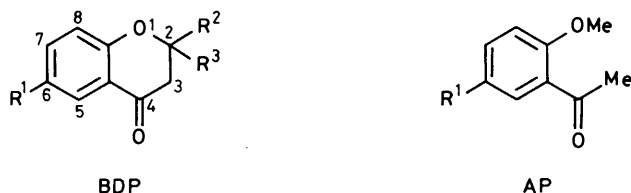
Structural and Solvent Effects on the Fluorescence Properties of Benzodihydropyranones

Ryoka Matsushima,* Yoshiharu Hiramatsu, and Tatsuya Kitanishi

Department of Applied Chemistry, Faculty of Engineering, Shizuoka University, Hamamatsu 432, Japan

Fluorescence properties of benzodihydropyranones (BDP) varied markedly with substituents and solvents. 6-Methoxy-BDP (**3**) showed $\phi_f = 0.2$ – 0.4 while 7-methoxy-BDP was non-fluorescent in methanol. Both unsubstituted BDP (**1**) and 6-methyl-BDP (**2**) were weakly fluorescent ($\phi_f = 10^{-3}$ – 10^{-2}) in methanol, but (**2**) had high ϕ_f (0.2–0.4) in aqueous methanol. The fluorescence wavenumber of (**3**) was decreased linearly, while ϕ_f increased with solvent polarity E_T (30). 2-Aryl-BDP showed a lower ϕ_f than 2-alkyl-BDP. Compared with BDP, substituted acetophenones had a lower ϕ_f by one order of magnitude. The results are discussed in terms of relative ordering of low-lying excited states, intramolecular charge transfer in S_1 (π, π^*), heterolytic C–O bond cleavage, meta-transmission effects of the methoxy group, etc.

Flavanones have been shown to undergo C–O bond cleavage of the dihydropyranone ring from triplet π, π^* states and/or bimolecular hydrogen-atom abstraction from triplet n, π^* states, depending on the substituents and solvents.¹ This work was



undertaken to elucidate the structural effects of benzodihydropyranones (BDP) on their singlet excited state properties, using a variety of substituents. The fluorescence and phosphorescence properties of chroman-4-one have been studied in some detail by Gallivan,² though the structural effects for a series of BDP have been little investigated.

The methoxy substituent (R^1) is expected to exhibit 'meta-transmission' effects³ to enhance ring–carbonyl charge transfer in the singlet π, π^* states, while R^2 and R^3 may alter significantly the excited state properties without substantial influence on the absorption spectra. In order to infer the effects of the cyclic structure of BDP, comparison with acetophenones (AP) has also been made.

Results

Structural Effects on Fluorescence Efficiencies.—Table 1 summarizes the fluorescence properties of BDP and AP measured in methanol and in aqueous methanol solution, for excitation at 313 nm. All BDP were non-fluorescent in non-polar solvents such as benzene, hexane, and ether. In acetonitrile solution (**1a**), (**2a**), and (**4a**) showed extremely weak or nil fluorescence though (**3a**) was moderately fluorescent (ϕ_f 0.057). The fluorescence spectra and yields were substantially unchanged with excitation wavelengths, e.g., ϕ_f for (**3e**) 0.47, 0.47, and 0.42 in methanol on excitation at 405, 365, and 313 nm, respectively; the values were 0.31, 0.39, and 0.32 in aqueous methanol on excitation at 365, 334, and 313 nm, respectively. Mean errors are assumed to be > 10%.

Some remarkable features are noted for the structural effects on the fluorescence quantum yields. (1) R^1 has a large effect: the ϕ_f values of (**1a**), (**2a**), and (**4a**) are low in methanol but become higher by one or two orders of magnitude in aqueous methanol

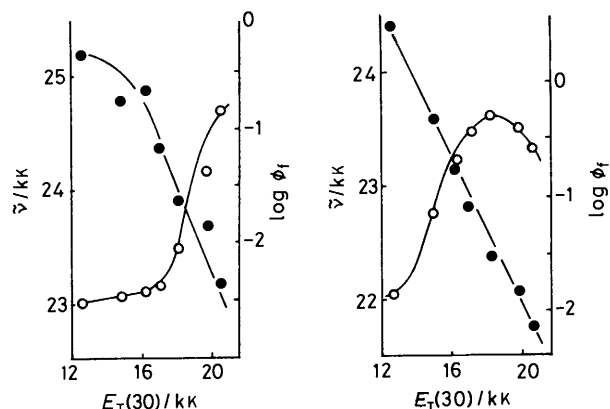


Figure 1. Effects of solvent polarity on $\bar{\nu}_f$ (●) and ϕ_f (○). Left, (**2b**); right, (**3b**) in dioxane–water

solution. The ϕ_f values of (**3a**–**e**) are high in both solvents, with some lowering in aqueous methanol solution. Contrary to (**3b**), 7-methoxyflavanone is non-fluorescent in methanol and only moderately fluorescent in aqueous methanol (4:1) solution (ϕ_f ca. 10^{-2}). Thus, the *meta*- and *para*-methoxy substituents exert contrasting effects. (2) The ϕ_f values with aryl substituents R^2 and R^3 are lower than those for hydrogen or alkyl substituents. (3) The ϕ_f values of BDP (**1**) and (**3**) are significantly higher than those of the corresponding AP (**5**) and (**6**), respectively.

Absorption Spectra.—The u.v. absorption maxima and coefficients of the longer wavelength bands are listed in Table 2. The spectra of BDP are substantially changed with R^1 , but only to a small degree with R^2 and R^3 . In cyclohexane weak but distinct shoulders are found for (**1**) and (**2**), though not for (**3**). By changing the solvent to methanol, the band maxima are red-shifted and the weak shoulders are hidden. On the other hand, (**3**) show no shoulders in the longer wavelength region. Compared with (**1**) and (**3**), acetophenones (**5**) and (**6**) show higher energy transitions, respectively, suggesting some conformational effect.

Solvent Effects on Fluorescence Properties.—Figure 1 illustrates plots of the fluorescence wavenumber ($\bar{\nu}_f$) and quantum yield (ϕ_f) as a function of solvent polarity, E_T (30),⁴ for (**2b**) and (**3b**) in dioxane–water. While (**3b**) shows a linear decrease in $\bar{\nu}_f$ reflecting a π, π^* transition, (**2b**) shows inflection at ca. 16 which suggests a switch in the electronic state in S_1 from n, π^* to π, π^* .

Table 1. Fluorescence properties of BDP and AP^a

BDP or AP	Substituent		Quantum yield (λ /nm)	
	R ¹	R ² ,R ³	Methanol	Methanol-water (1:4)
(1a)	H	H,H	0.9×10^{-3} (410)	3.8×10^{-2} (410)
(1b)	H	H,Ph	1.2×10^{-3} (420)	2.3×10^{-2} (410)
(1c)	H	H, <i>p</i> -MeOC ₆ H ₄	<i>b</i>	1.5×10^{-3} (410)
(1d)	H	H, <i>p</i> -HOC ₆ H ₄	<i>b</i>	0.9×10^{-3} (410)
(2a)	Me	-(CH ₂) ₅ -	3.9×10^{-2} (425)	0.44 (440)
(2b)	Me	H,Ph	9.6×10^{-3} (430)	0.16 (440)
(3a)	MeO	-(CH ₂) ₅ -	0.43 (462)	0.34 (485)
(3b)	MeO	H,Ph	0.29 (460)	0.11 (475)
(3c)	MeO	Me,Me	0.42 (463)	0.31 (482)
(3d)	MeO	H, <i>p</i> -MeOC ₆ H ₄	0.25 (465)	<i>c</i>
(3e)	MeO	-(CH ₂) ₄ -	0.42 (463)	0.32 (480)
(4a)	Cl	-(CH ₂) ₅ -	1.4×10^{-3} (410)	0.14 (430)
(4b)	Cl	H,Ph	0.6×10^{-3} (410)	<i>c</i>
(5)	H		<i>b</i>	1.9×10^{-2} (410)
(6)	MeO		4.1×10^{-2} (460)	1.0×10^{-2} (480)

^a Excited at 313 nm. Quinine sulphate in aqueous sulphuric acid solution was used as standard. Absorbances at 313 nm were 0.048 ± 0.002 for both BDP and quinine sulphate solution. 2'-Methoxyacetophenone (5) and 2',5'-dimethoxyacetophenone (6) were included for comparison. ^b Too weak to be determined. ^c Not measured because of very low solubility.

Table 2. Absorption properties in the near-u.v. region^a

BDP or AP	λ_{\max} /nm (ϵ /l mol ⁻¹ cm ⁻¹)		
	Cyclohexane	Methanol	Methanol-Water ^b
(1a)	312 (360), 363sh	318 (367)	322 (366)
(1b)	312 (360), 362sh	317 (360)	322 (392)
(1c)	<i>c</i>	318 (367)	322 (392)
(1d)	<i>c</i>	318 (370)	322 (392)
(2a)	324 (331), 375sh	335 (340)	335 (348)
(2b)	322 (368), 363sh	330 (332)	333 (361)
(3a)	344 (421), <i>d</i>	354 (385)	353 (371)
(3b)	343 (436), <i>d</i>	350 (391)	352 (400)
(3c)	343 (398), <i>d</i>	353 (397)	352 (400)
(3d)	<i>c</i>	350 (380)	352 (400)
(3e)	<i>c</i>	353 (382)	354 (392)
(4a)	328 (340), 385sh	<i>c</i>	<i>c</i>
(4b)	324 (345), 367sh	328 (329)	334 (371)
(5)	297 (562), 347sh	303 (355)	307 (350)
(6)	322 (447), 365sh	330 (355)	333 (476)

^a Concentration of BDP or AP was *ca.* 0.1M for the measurement or detection of the weak shoulders. ^b Methanol-water 1:4. ^c Not measured. ^d No shoulder (sh) was detected.

The slope of the $\tilde{\nu}_f$ plots is -0.36 for (2b) and -0.43 for (3b), respectively, as a measure of the polarity or the degree of charge transfer during the transitions compared with those for the negatively solvatochromic pyridinophenolate.⁴ While ϕ_f values substantially increase with solvent polarity, (3b) shows a decrease above *ca.* 19. Similarly, (3a–e) and (6) show slight decreases in ϕ_f as the solvent changes from methanol to aqueous methanol (Table 1), suggesting new radiationless decay or quenching channels pertinent to increased charge separation or stronger solvation as will the quenching of charge-transfer exciplexes in polar solvents.⁵

Approximate Fluorescence Lifetimes.—Table 3 lists the approximate radiative (τ^0) and actual (τ) lifetimes. The former were estimated from the maximum wavenumbers of and the areas under the first absorption bands, using convenient approximate relationships.^{6a,*} In polar solvents τ^0 values are in the range 15–30 ns which correspond to $\pi \rightarrow \pi^*$ transitions, whereas τ^0 for (1b) and (2b) in cyclohexane solution is of the order of 10^{-4} – 10^{-5} s which implies $n \rightarrow \pi^*$ transitions.

Table 3. Approximate fluorescence lifetimes

BDP or AP	Solvent ^a	τ^0 /ns ^b	τ /ns ^c
(1a)	A	25	0.023
	W	23	0.88
(1b)	A	24	0.029
	W	22	0.50
(2a)	A	29	1.13
	W	27	12
(2b)	A	27	0.26
	W	24	3.8
(3a)	A	27	12
	W	27	9.0
(3b)	A	28	8.1
	W	24	2.7
(5)	A	20	—
	W	20	0.37
(6)	A	19	0.78
	W	15	0.15

^a A: Methanol, W = aqueous methanol (4:1). ^b Radiative lifetime estimated from the maximum wavenumber and the area of the first absorption band. From the weak shoulders, the order of magnitude of τ^0 for (1b) and (2b) in cyclohexane solution was estimated to be *ca.* 2×10^{-4} and 8×10^{-5} s, respectively, though much less accurate. ^c Actual lifetime $\tau = \tau^0 \cdot \phi_f$.

Further, the τ^0 values in Table 3 are essentially constant with the changes in substituent and solvent, thus implying that the variation in ϕ_f in Table 1 substantially reflects the variation in the fluorescence lifetime.

Discussion

The pronounced effect of R¹ may be explained in terms of relative ordering of the low-lying excited states, as illustrated in Figure 2 for (1a)–(3a). The n, π^* and π, π^* characters of the S₁ state were assigned from u.v. absorption coefficients, solvent shifts, and the magnitude of τ^0 , while those for T₁ were from low-

* The fluorescence lifetimes should be measured directly, *e.g.* from decay rates, rather than the indirect and approximate estimation from absorption spectra and emission quantum yields. Because of the non-availability of equipment to carry out direct measurements, an indirect estimation has been used in this work.

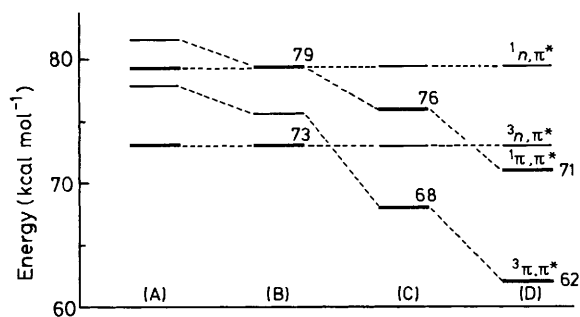


Figure 2. Relative ordering of low-lying excited states of (1a)–(3a). (A) refers to (1a) in cyclohexane solution, (B)–(D) refer to methanol solutions of (1a)–(3a), respectively. The locations of S_1 and T_1 (thick line) were estimated from u.v. absorption and fluorescence maxima, and from low-temperature phosphorescence 0–0 bands, respectively.¹ The locations of S_2 and T_2 (thin line) are qualitative

temperature phosphorescence spectra in rigid glasses.^{1,2} The locations of S_2 and T_2 are only qualitative. Further, the changes in the n,π^* levels (both singlet and triplet) were ignored as a first approximation, since the n,π^* levels of phenyl ketones feature much less variation compared with the π,π^* levels.⁷

Figure 2(A) represents (1) or (2) in a non-polar solvent where no fluorescence is observed, reflecting the forbidden nature of the radiative transition of S_1 (n,π^*) as well as allowed and rapid intersystem crossing to T_2 (π,π^*).^{6c} Figure 2(B) refers to the methanol solution of (1) where fluorescence is very weak, since singlet n,π^* and π,π^* states are very close or nearly degenerate. Figure 2(C) refers to a methanol solution of (2), where significant fluorescence is observable because of the allowed radiative transition of S_1 (π,π^*) but still weak due to the allowed intersystem crossing to T_2 (n,π^*). Similar ordering may also be assumed for aqueous methanol solution of (1) and acetonitrile solution of (3). Figure 2(D) refers to a methanol solution of (3) where strong fluorescence is observed because of the allowed radiative transition of S_1 (π,π^*) and the forbidden intersystem crossing to T_1 (π,π^*). A similar ordering is assumed for aqueous methanol solution of (2).

The remarkable effects of the 6-methoxy substituent of (3) may be rationalized as 'meta-transmission' effects, as recognized in the solvolytic photoreaction of benzyl derivatives.³ Both *ortho*- and *meta*-alkoxy groups can assist in enhancing ring-carbonyl charge transfer in the singlet π,π^* states. In a more polar solvent, charge separation and solvation would be stronger. This may facilitate solvent quenching or induce a new deactivation channel such as heterolytic C–O bond cleavage (7) which may either give ring-opening products or rapidly recombine to lead to the starting material, both resulting in a decrease in ϕ_f or τ . In support of this assumption, the partial involvement of C–O bond cleavage from singlet excited states has been implied. Thus, Stern–Volmer plots with triplet quenchers gave curvature for photochemical ring opening of (3b) in propan-2-ol (Figure 3), whereas straight lines were obtained for (3b) in benzene or with (1b) and (2b) in propan-2-ol.¹ Since singlet π,π^* states generally feature polar or zwitterionic character and triplet states have biradical character,^{6c} heterolytic cleavage (7) is likely from S_1 (π,π^*) and homolytic cleavage (8) from T_1 (π,π^*) (Scheme). A back-recombination of (7) leading to starting material (overall photochromic process) would occur in competition with proton migration leading to ring-opening products. The lower ϕ_f values for flavanones (R^2 or $R^3 = \text{aryl}$), compared with those for chroman-4-ones (R^2 and/or $R^3 = \text{alkyl}$ or H), are ascribable to the enhanced stabilization of (7) which accelerates cleavage, though vibrational motions or vibronic coupling effects^{6b} may be partly involved.

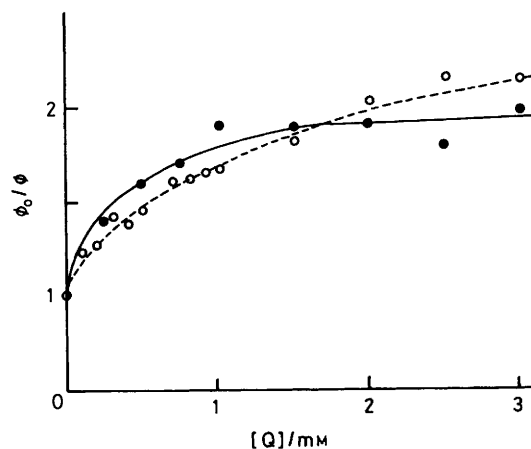
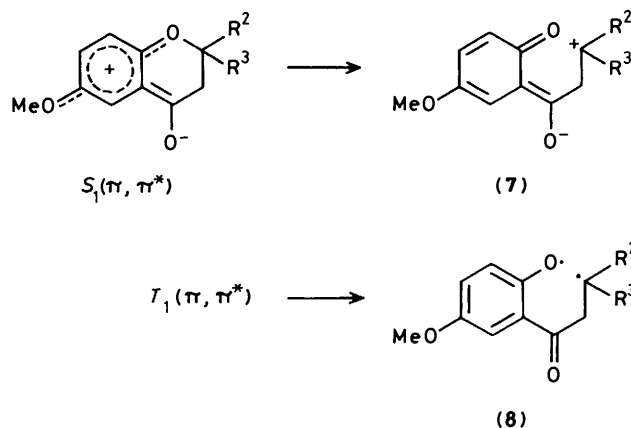


Figure 3. Stern–Volmer quenching plots for the photochemical ring opening reaction of (3b) in propan-2-ol. (○) With 313–366 nm light and ferrocene as triplet quencher, (●) with 365–366 nm light and *trans*-stilbene as triplet quencher. Straight and steeper lines were obtained with (1b) and (2b) in propan-2-ol or with (3b) in benzene¹



Scheme.

Since molecular rigidity can suppress radiationless deactivation,^{6b} the higher ϕ_f values of (3) compared with that of (6) are attributable to the more rigid cyclic structure of BDP compared with the acyclic AP system. The different features in the absorption spectra are also attributable to the effects of the cyclic *versus* acyclic structures. The quasi-coplanar and rigid conformation of the BDP system would allow favourable orbital overlap or extensive conjugation of the π -chromophores, whereas the acyclic and flexible AP system would consist of an equilibrium mixture of rotational isomers. As a result, S_1 (π,π^*) of BDP would be more stable than AP.

Experimental

Flavanones⁸ and chroman-4-ones⁹ were prepared by reported methods, while commercial acetophenones (Wako Chemicals) were purified by column distillation. Commercially available solvents of the purest grade were distilled before use. U.v. absorption and fluorescence spectra were recorded on a Hitachi 200–100 spectrophotometer and a 204 fluorescence spectrometer, respectively. Correction of the fluorescence spectra and evaluation of the fluorescence quantum yields were carried out using aqueous acid solutions of quinine sulphate as standard.¹⁰ Solutions of both BDP and the fluorescence standard were diluted so that the optical densities at the excitation wavelength

were $0.048 \pm 0.002 \text{ cm}^{-1}$, and were measured in a 1.0 cm cell (right angle observation of the centre of the cell) without removal of the dissolved oxygen.

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