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Spectroscopy and photophysics of bridged enone derivatives: effect of molecular structure and solvent

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Abstract

The spectroscopy and photophysics of several substituted enones with different bridged structures were studied in a variety of solvents. Results show that, in all cases, the non-radiative and radiative decay processes of the excited states are strongly influenced by the molecular structure and the solvent polarity. The "negative solvatokinetic effect" and "positive solvatokinetic effect" are observed for all four compounds. Compounds 3 and 4, with bridged double bond structures, have high fluorescence quantum yields and (especially compound 4 with a rigid structure even in non-polar solvents (cyclohexane, $\phi_f = 0.5$)), indicating that radiative decay is predominant during the decay of the excited states of these compounds. In contrast, the enone compounds with a free double bond have very low fluorescence quantum yields, indicating that non-radiative decay is important for these compounds.

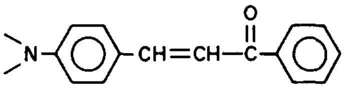
Keywords: Decay; Excited states

1. Introduction

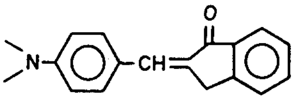
The photophysics and spectroscopy of molecules with intramolecular charge transfer (ICT) properties are of continuing theoretical and experimental interest [1–4]. The decay processes of excited molecules with ICT characteristics are strongly influenced by the molecular structure itself and the surrounding solvent molecules [5]. The determination of the decay processes of excited states is very important for an understanding of a series of theoretical problems, such as the twisted intramolecular charge transfer (TICT) phenomenon and the rotational relaxation dynamics of excited molecules [6–8], and also in the synthesis of laser and fluorescence dyes with desired properties [9–11]. Recently, the study of competing non-radiative decay channels has received more attention [12–16]. Lapouyade and coworkers [13–16] studied the radiative and non-radiative decay processes of several selectively bridged 4-dimethylamino-4′-cyanostilbenes, and found that bridging affects the photophysics dramatically.

Substituted enone derivatives are very effective photoinitiators and can be used to design highly sensitive photoimaging systems for hologram recording [17]. The photophysical behaviour and spectroscopy have been studied recently [18–20]. For instance, Devoe et al. [19] studied the characteristics of the excited states of bis[*p*-*N*,*N*-dimethylaminobenzylidene]acetone and found that the rate constants of non-radiative decay are slowest in strongly polar solvents and fastest in weakly polar solvents. We have studied the spectroscopy and photophysical behaviour of some chalcone derivatives, and have found that the decay processes of these compounds depend on the character of the substituents, the solvent polarity and temperature.

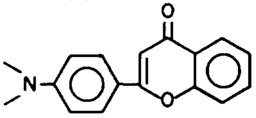
In the present paper, four enone derivatives with different bridged structures were synthesized; their structures are shown below.



4′-*N*,*N*-Dimethylaminochalcone (1)



2-[(4-*N*,*N*-Dimethylaminophenyl)methylene]-2,3-dihydro-1H-inden-1-one (2)



4′-*N*,*N*-Dimethylaminoflavone (3)

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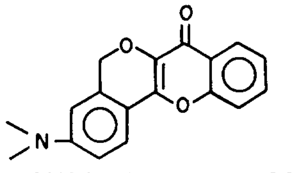

3-*N*,*N*-Dimethylamino-7-oxo[2]benzopyrano[4,3-b][1]benzopyran (**4**)

We report a survey of the emission parameters which reveals the role of the compound structure and the solvent properties on the competition between radiative and non-radiative decay of these enone derivatives. The results show that the bridging of different bonds in the enone molecules has an influence on the decay processes of the excited states.

2. Experimental details

Compounds **1**, **2**, **3** and **4** were prepared and purified as described previously [21]. Solvents were purified by standard procedures [22].

Absorption and fluorescence spectra were recorded on a Hitachi 330 UV–visible spectrophotometer and a Hitachi MPF-4 fluorescence spectrophotometer, equipped with a differential spectrum correction unit, respectively. The fluorescence quantum yield determination was carried out on a Perkin–Elmer LS-5 fluorescence spectrophotometer equipped with a data processing unit for calculating the integrated intensities. The standard for the fluorescence quantum yield determinations was fluorescein in 0.1 M sodium hydroxide ($\phi_f=0.93$). For the measurements, dilute samples (optical density (OD) maxima, less than 0.1) were employed with excitation at or near the absorption maxima. The fluorescence lifetimes were recorded on a Horiba NAES-1100 single-photon-counting apparatus.

3. Results and discussion

From the molecular structures of these compounds (shown above), it can be seen that they have the same electron-donating and electron-withdrawing groups, but different bridged structures. For compound **1**, all bonds in the molecule are in the free condition. For compound **2**, there are two bridged C–C single bonds, one free C=C double bond and one free C–C single bond. For compound **3**, all bonds between the two benzene rings, except for one single bond, are bridged, while all bonds between the two rings are bridged for compound **4**. The change in molecular structure has a very strong influence on the spectroscopic properties and the radiative and non-radiative decay processes of the excited states of these compounds. Table 1 shows the absorption maxima and molar extinction coefficients of these compounds in a variety of solvents. A red shift in the absorption maxima is observed in polar solvents in all cases. The solvent-induced shifts in the absorption bands of these compounds are consistent with a transition having significant charge transfer character [23].

Fig. 1 shows the fluorescence spectra of compound **1** in different solvents; the others show the same characteristics as compound **1**. In polar solvents, the fluorescence maxima are dramatically shifted to the red. Since neither solvent nor solute may rearrange during the course of the electronic transition, any solvent stabilization of the ground state is revealed by a shift in the absorption spectrum. Similarly, the solvent stabilization of the excited state is revealed by a shift in the fluorescence spectrum. We observed a larger solvent-induced shift in the fluorescence maxima of compounds **1**, **2**, **3** and **4** than in the absorption maxima (see Table 1). This suggests that the molecules are solvated significantly in the S_1 excited state, resulting in a large difference in dipole moment between the S_1 excited state and the ground state [24].

The peak wavenumbers in the fluorescence spectra of the compounds can be correlated with the empirical Dimroth polarity parameter $E_T(30)$ of the solvents [25], as shown in Fig. 2, and a good linear relationship is obtained. The solvent-induced shifts of the emission and absorption spectra (Stokes shift) can be linearly correlated with the Bilot–Kawski (BK) values (solvent polarity parameter) [26].

$$\Delta\tilde{\nu}_s=\tilde{\nu}_a^{\max}-\tilde{\nu}_f^{\max}=\frac{(\mu_e-\mu_g)^2}{hca^3}\,\mathrm{BK}+\mathrm{constant}$$

with

$$\mathrm{BK}=\frac{\{(\epsilon-1)/(2\epsilon+1)\}-\{(n^2-1)/(2n^2+2)\}}{\{1-\beta(n^2-1)/(2n^2+2)\}^2\{1-\beta(\epsilon-1)/(2\epsilon+2)\}}$$

where $\Delta\tilde{\nu}_s$ is the Stokes shift, h is Planck's constant,

Table 1
Absorption and emission maxima (nm) and molar extinction coefficients of the compounds in different solvents

Solvent	$E_T(30)$ (kcal mol^{-1})	1			2			3			4		
		λ_{abs}	λ_{em}	log ϵ	λ_{abs}	λ_{em}	log ϵ	λ_{abs}	λ_{em}	log ϵ	λ_{abs}	λ_{em}	log ϵ
Toluene	33.9	393	468	4.57	411	467	4.45	362	417	4.33	385	441	4.30
Ethyl acetate	38.1	399	498	4.49	413	497	4.44	366	442	4.34	388	464	4.36
Acetonitrile	46.0	415	536	4.56	427	534	4.44	373	474	4.32	396	489	4.37

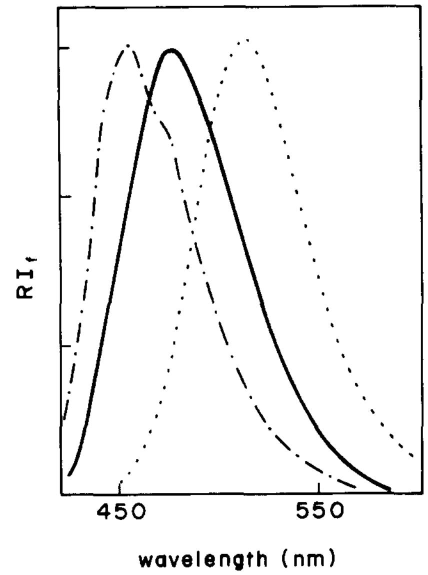

Fig. 1. Fluorescence spectra of compound **1**: – · –, in benzene; ——, in ethyl acetate; · · · · ·, in acetonitrile.

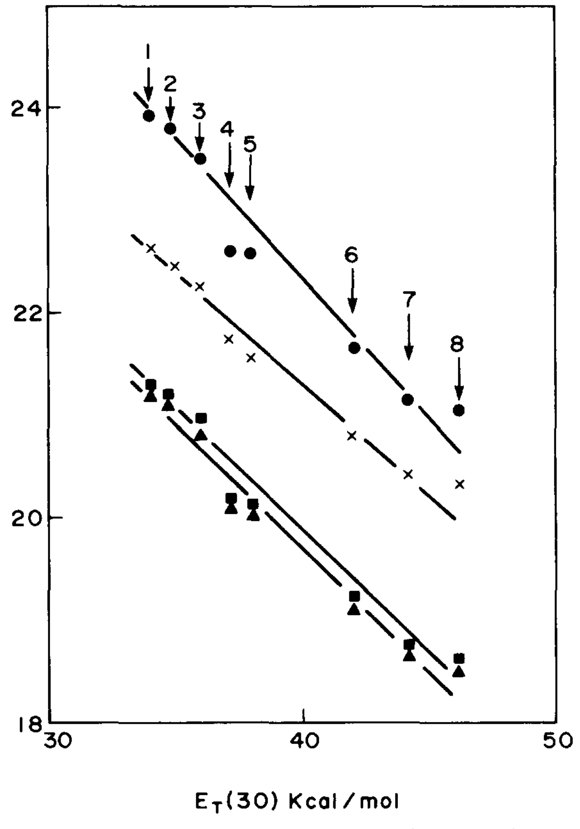

Fig. 2. Change in the wavenumber of the emission maximum of compounds **1** (▲), **2** (■), **3** (●) and **4** (×) as a function of the $E_T(30)$ values of the solvents: 1, toluene; 2, ethyl ether; 3, 1,4-dioxan; 4, tetrahydrofuran (THF); 5, ethyl acetate; 6, acetone; 7, dimethylformamide (DMF); 8, acetonitrile.

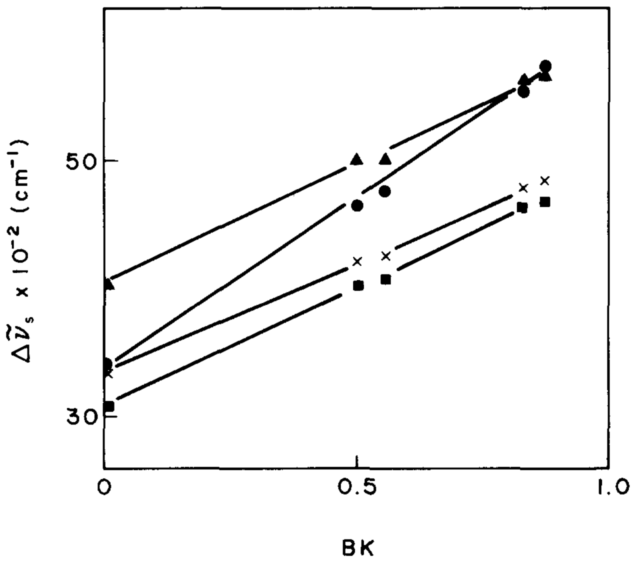

Fig. 3. Plot of the Stokes shifts of compounds **1** (▲), **2** (■), **3** (●) and **4** (×) vs. the BK values.

Table 2

Differences between the dipole moments of the excited and ground states ($\Delta\mu$) of the compounds

	1	2	3	4
$\Delta\mu$ (D)	5.9	5.6	8.2	5.8

Table 3

Fluorescence quantum yields (ϕ_f) of the compounds in different solvents

Solvent	$E_T(30)$ (kcal mol^{-1})	ϕ_f			
		1	2	3	4
Cyclohexane	31.2	0.0007	$<10^{-4}$	0.007	0.50
Toluene	33.9	0.037	0.039	0.76	1
Ethyl ether	34.6	0.054	0.046	0.87	1
Ethyl acetate	38.1	0.21	0.11	1	0.95
THF	37.4	0.24	0.12	1	0.91
Acetone	42.2	0.33	0.077	–	–
Acetonitrile	46.0	0.13	0.045	1	0.86

c is the velocity of light, a is the Onsager cavity radius and ϵ and n are the static dielectric constant and the refractive index of the solvent respectively. The β factor approximates to unity in the case of isotropic polarizability. The Stokes shifts obtained for the compounds in the different solvents are plotted against the BK parameter in Fig. 3. An excellent linear correlation is observed. From the slopes of the straight lines in Fig. 3, the differences between the dipole moments of the excited and ground states were obtained and are listed in Table 2.

From Table 2, it can be seen that the change in the dipole moment of compound **3** is larger than those of compounds **1**, **2** and **4**. It is suggested that this result can be attributed to the larger conformational change of compound **3** than of the other compounds [27].

Table 4
Photophysical constants of the compounds in ethyl acetate (EtOAC) and acetonitrile (AN)

Compound	**1**		**2**		**3**		**4**	
	EtOAC	AN	EtOAC	AN	EtOAC	AN	EtOAC	AN
$k_{nr} \times 10^{-9}$ (s^{-1})	1.1	1.2	1.5	3.3	0	0	0.019	0.049
$k_f \times 10^{-8}$ (s^{-1})	2.9	1.8	1.9	1.5	4.8	3.9	3.7	3.0
τ (ns)	0.74	0.70	0.57	0.29	2.3	2.5	2.5	2.9

The fluorescence quantum yields of the compounds in various solvents are listed in Table 3. The data reveal a significant dependence on the solvent properties, especially on $E_T(30)$. In all four compounds the ϕ_f values increase with solvent polarity over a wide range of solvent polarity; with a further increase in $E_T(30)$ the ϕ_f values decrease with solvent polarity. In a previous study [20], it was found that, for enone compounds, there are two mechanisms involved during the course of increasing solvent polarity. One mechanism, which involves the enone structure, is the increase in the fluorescence quantum yield with a suitable enhancement of ICT: the so-called "negative solvatokinetic effect". Several suggestions, such as "biradicaloid charge transfer" [28], "proximity effect" [29] and "conformational changes" [30], have been proposed to explain the behaviour of the "negative solvatokinetic effect". In other words, in non-polar solvents, the three effects described above will result in effective non-radiative decay of the excited state. The other mechanism, which is usually observed in molecules with ICT character, is a reduction in the fluorescence quantum yield by strong ICT: the so-called "positive solvatokinetic effect". From the fluorescence quantum yields in non-polar solvents (cyclohexane), it can be seen that ϕ_f is very low, except for compound **4** with a rigid structure ($\phi_f = 0.5$); ϕ_f of compound **3**, in which the double bond is bridged, is larger than that of compounds **1** and **2**. Therefore, for compound **4**, the "proximity effect" leads to non-radiative decay due to the rigid structure. For compound **3**, "biradicaloid charge transfer" is impossible due to the fact that the double bond is bridged in the ring. Therefore the "proximity effect" and "conformational change" are the main causes of non-radiative decay. For compounds **1** and **2**, all three effects exist simultaneously, resulting in a very low ϕ_f value (**1**, $\phi_f = 0.0007$; **2**, $\phi_f < 10^{-4}$). These effects are reduced with increasing solvent polarity. Table 3 also shows that the "negative solvatokinetic effect" can be observed only in slightly polar solvents (in toluene, $E_T(30) = 33.9$ kcal mol^{-1}) for compound **4**, but in strongly polar solvents (in acetonitrile, $E_T(30) = 46.0$ kcal mol^{-1}) for compound **1**, indicating that the "positive solvatokinetic effect" plays a predominant role for compound **4** and the "negative solvatokinetic effect" is more important for compound **1** during the course of increasing solvent polarity.

From the fluorescence lifetime (τ) and fluorescence quantum yield (ϕ_f), and the relations $\phi_f = (k_f/k_f + k_{nr})$ and $k_f = \phi_f/\tau$, the radiative rate constants (k_f) and non-radiative rate constants (k_{nr}) were calculated for the compounds and are listed in Table 4. From this table it can be seen that, for compounds **3** and **4**, the non-radiative rate constants are very low in polar solvents, indicating that the radiative decay process is predominant. This result infers that the bridging of the double bond in the ring is very important in decreasing the non-radiative decay process. In contrast, the inhibition of the single bond, e.g. for compound **2**, plays a less important role in the reduction of the non-radiative decay of the excited state.

4. Conclusions

From the results presented in this work, the following conclusions may be drawn. The non-radiative and radiative decay processes of the enone derivatives depend dramatically on the molecular structure and the solvent polarity. Bridging has a strong influence on the photophysics of these compounds. Compounds **3** and **4** with bridged double bonds have strong fluorescence emission. Compound **4** with a rigid structure shows high fluorescence emission in both polar and non-polar solvents. In contrast, compounds **1** and **2** with free double bonds have very low fluorescence quantum yields.

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