

Unusual Fluorescence Behaviour of Sterically Congested Benzenehexacarboxylates

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Benzenehexacarboxylates with bulky alcohol moieties showed bulkiness-dependent dual fluorescence peaks with both small and substantial Stokes shifts, which are attributed to the decelerated conformational relaxation in the excited state due to steric hindrance between the adjacent bulky alcohol moieties.

Simple aromatic carboxylic esters like benzoates are non-fluorescent in fluid solutions at room temperature, although in low-temperature rigid matrices weak fluorescence has been detected along with fairly intense phosphorescence.¹⁻⁵ The poor fluorescence in fluid solutions has been attributed to rapid intersystem crossing to the n, π^* triplet state, which is close in energy to the lowest singlet excited π, π^* state.⁵ Nuclear substitution of benzoate with a highly electron-donating group, such as a hydroxy or an amino group, is known to enhance the fluorescence quantum yield, while electron-withdrawing groups have been believed to be ineffective in increasing the fluorescence quantum yield; hence the photophysical properties of benzenepolycarboxylates have not been investigated extensively. Here we report that extensive substitutions with alkoxy-carbonyl groups enhance the fluorescence efficiency considerably and, importantly, benzenehexacarboxylates with bulky alcohol moieties show dual fluorescence peaks originating from steric interaction between the adjacent bulky substituents.

The profiles of absorption and fluorescence spectra of some benzenepolycarboxylates are shown in Table 1 and Figure 1.† As expected, benzenemono-, 1,2-, 1,3- or 1,4-benzenedi-, and 1,3,5-benzenetricarboxylates did not emit any detectable

fluorescence in pentane solution at room temperature under our experimental conditions. However, 1,2,4,5-benzenetetracarboxylates emitted faint fluorescence around 331 nm and the fluorescence excitation spectra were in good agreement with the absorption spectra. The fluorescence lifetimes measured by the time-correlated single photon counting method were as short as 0.2–0.3 ns. Consequently, the sample solutions deaerated by argon bubbling showed no appreciable changes in shape or intensity of the fluorescence spectra. As expected, all 1,2,4,5-benzenetetracarboxylates with a variety of alcohol moieties afforded almost identical absorption 0–0 band maxima (*ca.* 292 nm), fluorescence maxima (*ca.* 331 nm) and lifetimes (*ca.* 0.3 ns), irrespective of the bulkiness of alcohol moieties.

By contrast, benzenehexacarboxylates behave quite differently. As can be seen from Figure 1, the methyl ester, having a longer fluorescence lifetime of 1.1 ns, exhibited a single fluorescence peak at 365 nm with a large Stokes shift up to 70 nm. The large Stokes shift clearly indicates that substantial conformational relaxation takes place in the excited state. Interestingly, the bornyl, *t*-butyl, and menthyl esters, although possessing comparable lifetimes of 0.8–1.1 ns, gave

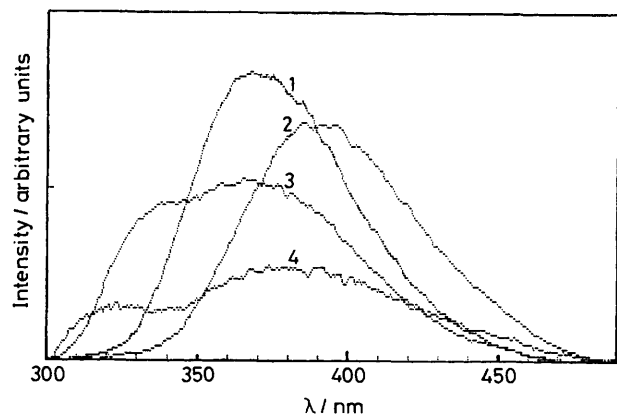


Figure 1. Uncorrected fluorescence spectra of (1) hexamethyl (1×10^{-5} mol l⁻¹), (2) hexa(-)-bornyl (2.1×10^{-5} mol l⁻¹), (3) hexa(-)-menthyl (1.8×10^{-5} mol l⁻¹), and (4) hexa-*t*-butyl benzenehexacarboxylate (2.1×10^{-5} mol l⁻¹) in pentane solutions at 25°C; excitation at 250 nm.

† Benzenepolycarboxylates were synthesized from the corresponding carboxylic chlorides and alcohols, and were purified by repeated recrystallizations. Absorption and fluorescence spectra were recorded on a Jasco Ubest 50 spectrophotometer and an FP-770 spectrofluorimeter, respectively. Fluorescence lifetimes were measured by the time-correlated single photon counting method using a Horiba NAES 1100 instrument equipped with a pulsed H₂ light source; the radiation from the lamp was made monochromatic (270 nm) by a Jobin-Yvon 10 cm monochromator, and the emission was filtered by a Toshiba UV-39 filter [0% transmittance (*T*) at <360 nm; 50% *T* at 390 nm].

Table 1. Absorption and fluorescence spectra of some aromatic esters.^a

Aromatic ester	Absorption maximum ^b /nm	Fluorescence		
		Maximum /nm	Stokes shift/nm	Lifetime /ns
Benzoate				
Methyl	280	— ^c		
Phthalate				
Dimethyl	282	— ^c		
Dimethyl	282	— ^c		
Isophthalate				
Dimethyl	288	— ^c		
Terephthalate				
Dimethyl	295	— ^c		
1,3,5-Benzenetricarboxylate				
Trimethyl	293	— ^c		
1,2,4,5-Benzenetetracarboxylate				
Tetramethyl	291	331	40	0.2
Tetra(-)-bornyl	293	331	38	0.2
Tetra(-)-menthyl	292	332	40	0.3
Benzenehexacarboxylate				
Hexamethyl	295	365	70	1.1
Hexa(-)-bornyl	292	320, 390 (0.03 : 1) ^d	28, 98	1.1
Hexa- <i>t</i> -butyl	295	325, 380 (0.56 : 1) ^d	30, 85	
Hexa(-)-menthyl	296	340, 360 (0.95 : 1) ^d	44, 64	0.8

^a Measured in aerated pentane solution at room temperature.

^b Apparent 0–0 band. ^c Fluorescence not detected under the conditions employed. ^d Relative intensity between two maxima.

two peaks at different wavelengths, which are apparently related to the alcohol moiety introduced. Since the absorption 0-0 band maxima do not differ substantially among these hexacarboxylates, the observation of dual fluorescence peaks indicates that, in these sterically congested esters, at least two excited states of different energies are involved, and also that the conversion from one to another is decelerated to a rate which is comparable with those of the radiative and non-radiative deactivation processes. Only the sterically congested esters showed dual peaks and virtually no concentration effect was observed over 10^{-4} – 10^{-6} mol l⁻¹. Hence the different states involved are not a monomer/excimer fluorophore pair but are most likely the conformational isomers of the excited singlet, rotational relaxation of which is restricted by the steric hindrance between the adjacent bulky alcohol moieties.

From the observed absorption 0-0 bands which are very similar to those of terephthalates, the hexacarboxylates are taken to have a staggered, less conjugating structure with respect to the alkoxy carbonyl groups owing to the steric hindrance. The antibonding nature of some excited state orbitals may ease rotational relaxation about some bonds, which has been restricted in the ground electronic state. Thus, the short and long wavelength fluorescence peaks are assigned to the emission from the Franck-Condon-like and relaxed singlet, respectively; the relative intensity of the two peaks, shown in parentheses in Table 1, is a certain measure of both the population of the Franck-Condon-like and relaxed singlets and the feasibility of the rotational relaxation in the excited state.

Since the hexacarboxylates provide a novel dual fluorescence system involving a mechanism different from those of the excimer formation, protonation/deprotonation or twisted intramolecular charge transfer,⁶⁻¹⁰ further study is in progress on the origin and the mechanism of this bulkiness-dependent dual fluorescence system.

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