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Published on Web 05/23/2002

Unique Dual Fluorescence of Sterically Congested Hexaalkyl Benzenehexacarboxylates: Mechanism and Application to Viscosity Probing

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Received August 16, 2001

Abstract: The static and dynamic fluorescence behavior of a series of hexaalkyl benzenehexacarboxylates (R_6BHC; R = methyl (Me), *tert*-butyl (tBu), (−)-menthyl (Men), (−)-bornyl (Bor), (−)-1-methylheptyl (MHp), neopentyl (neoPn), and 2-adamantyl (Ad)) was studied by steady-state and time-resolved fluorescence spectroscopy. Dual fluorescence from both the partially relaxed metastable Franck−Condon-like (FC′) and the fully relaxed (RX) state was observed for tBu_6BHC, Men_6BHC, Bor_6BHC, MHp_6BHC, $neoPn_6$BHC, and Ad_6BHC, whereas only single fluorescence from the RX state was observed for Me_6BHC. Picosecond time-resolved fluorescence spectroscopic measurements clearly demonstrated that the initially formed Franck−Condon (FC) state sequentially converts to the FC′ and then to RX state, with the relaxation hindered to such an extent that it shows variation with the steric bulk of the R groups. Thus, the fluorescence lifetimes (τ's) of FC′ and RX are critically dependent on the bulkiness of the R groups, varying from 17 to 130 ps and from 0.6 to 1.1 ns, respectively. The relative intensity of FC′ and RX fluorescence ($I_{RX}/I_{FC'}$) was found to be dependent on the excitation wavelength, suggesting that the conformational relaxation from the FC′ to RX state can compete with the vibrational relaxation of the FC′ state. The temperature and pressure dependences were studied by steady-state fluorescence spectroscopy to give the activation energies of 1−3 kcal/mol for the FC′-to-RX relaxation of congested R_6BHCs, as well as the activation volumes of 2.0, −0.62, and 7.4 mL/mol for tBu_6BHC, Men_6BHC, and Bor_6BHC at room temperature. The fluorescence anisotropy (ρ), as a measure of molecular motion, was also determined to be in the ranges of 0.03−0.3 for FC′ and 0.003−0.01 for RX. The much larger ρ's for the FC′ fluorescence by a factor of 2−100 are attributed to the shorter τ's. The $I_{RX}/I_{FC'}$ ratio was found to be insensitive to solvent polarity, but critically dependent on solvent viscosity, exhibiting an excellent linear relationship with the reciprocal viscosity. The potential use of these sterically congested R_6BHCs as microenvironmental viscosity probes is proposed.

Introduction

A variety of organic compounds have been reported to show dual fluorescence in fluid solution. The origin of the dual fluorescence reported so far may be assigned to one of the following mechanisms: (1) excited-state proton transfer or protonation/deprotonation,[1−25] (2) intramolecular/intermolecular excimer/exciplex formation,[26−31] (3) twisted intramolecular charge transfer (TICT) involving rotation around single or double bonds in the excited state,[32−54] (4) intramolecular electron transfer followed by conformational change and eventual intramolecular excimer formation in bridged electron donor−

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10.1021/ja016858l CCC: $22.00

acceptor systems (the "harpooning" process),[55,56] (5) excited-state conformational change leading to the formation of an excited state with extended conjugation (ESEC) in *N*-phenylnaphthalimides,[57,58] (6) intramolecular charge-transfer emission (ICT) (without the necessity of bond twisting, thus differing from TICT),[59−62] (7) excited-state cis−trans isomerization in 9-amino-6-chloro-2-methoxyacridine,[63,64] (8) excited-state charge separation and twisted charge resonance in tetraphenylethylene,[65−67] (9) excited-state bond-stretch isomerism in racked polysilanes,[68] (10) emission from two excited singlet states (S_2 and S_1),[69−71] and (11) independent excitation of ground-state conformers.[72−75]

More recently, we have reported that hexaalkyl benzenehexacarboxylates (R_6BHCs) with bulky alkyl (R) groups show dual fluorescence that could not be rationalized by conventional mechanisms.[76,77] The following mechanism has been proposed as a possible explanation for this unique dual fluorescence from sterically congested R_6BHCs: the Franck−Condon (FC) excited state generated upon absorption of light immediately relaxes to a partially relaxed metastable state (designated as Franck−Condon-like or FC′ state) prior to the full conformational relaxation. However, in the case of sterically congested R_6BHCs, further conformational relaxation to the fully relaxed (RX) singlet state is sterically hindered by the bulky R substituents, and therefore the fluorescence occurs from both the FC′ and the RX states.[76,77] To reveal the structural origin of the dual fluorescence, we have further determined the crystal structures of some R_6BHCs, which indicates that the alkoxycarbonyl, in particular *t*-butoxycarbonyl, groups are highly twisted against the benzene plane because of the steric hindrance between the adjacent alkoxycarbonyl groups.[78]

In this study, to elucidate the comprehensive picture of this unique dual fluorescence behavior, we wish to unequivocally establish the detailed mechanism of the relaxation and fluorescence pathways of the intervening FC, FC′, and RX states by performing time-resolved fluorescence spectroscopic measurements and by investigating the dual fluorescence of several R_6-BHCs (illustrated in Scheme 1) under varying conditions, including temperature, pressure, solvent, and excitation energy. We also demonstrate that these dual fluorescing compounds can be used as versatile molecular microviscosity probes.

Experimental Section

Materials. Hexamethyl benzenehexacarboxylate (Tokyo Kasei) was purified by repeated recrystallization from methanol. Hexa-*tert*-butyl, (−)-hexamenthyl, (−)-hexabornyl, (−)-hexakis(1-methylheptyl), hexaneopentyl, and hexa-2-adamantyl benzenehexacarboxylates (abbreviated as Me_6BHC, Men_6BHC, Bor_6BHC, MHp_6BHC, $neoPn_6$BHC, and Ad_6-BHC, respectively) were synthesized and purified as described previously.[77] Cyclohexane, pentane, decane, heptane, methanol, diethyl ether, and acetonitrile were purified prior to use. All R_6BHC solutions (0.10−0.16 mM) were air-saturated (nondegassed).

Instrumentation. Picosecond time-resolved fluorescence spectroscopic measurements were carried out at Hamamatsu Photonics. Sample

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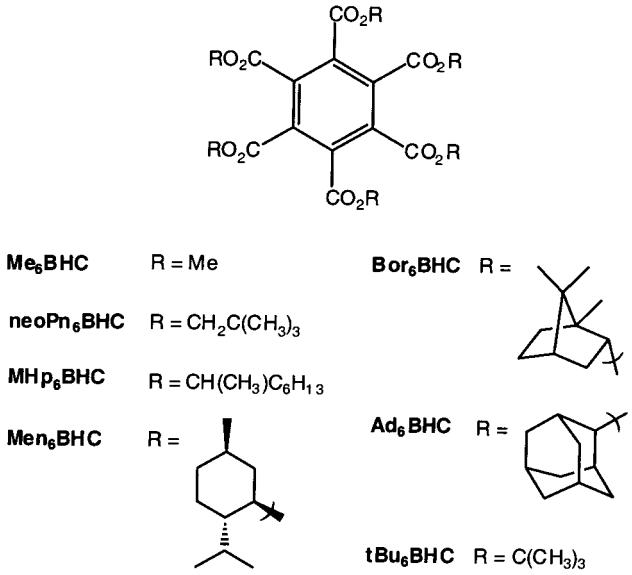
Scheme 1. Hexaalkyl Benzenehexacarboxylates (R_6BHCs)



solutions were irradiated using the second harmonics (270 nm) of a continuous wave (CW) cavity-dumped dye laser (Spectra-Physics 375B and 344S) which was synchronously pumped with a CW mode-locked argon ion laser (Spectra-Physics 2030-18). The pulse dye laser, oscillating at 540 nm, was operated at a 4 MHz repetition rate with a 10 ps full width at half maximum (fwhm). Fluorescence spectra and lifetimes were measured with a streak scope (Hamamatsu C4334) fitted with a polychromator (Chromex 250IS).[79]

Absorption and emission spectra were obtained by using a JASCO Ubest-50 spectrophotometer and a JASCO FP-770 spectrofluorimeter, respectively. Excitation wavelength was fixed at 250 nm, unless the effect of excitation energy was examined. Low-temperature emission spectra were taken at temperatures varying from 25 to −125 °C, by using an Oxford cryostat DN-1704 equipped with an ITC-4 temperature controller.

Fluorescence anisotropy was determined by using a matched set of polarizer and analyzer (JASCO), which were placed before and after the sample solution. The fluorescence anisotropy (ρ) is defined by eq 1, where $I_{\parallel}$ and $I_{\perp}$ are the intensities of the components of emitted light parallel and perpendicular to the electric vector of the exciting light, respectively.[80]

$$\rho = (I_{\parallel} - I_{\perp})/(I_{\parallel} + 2I_{\perp}) \quad (1)$$

To eliminate the effect of polarization arising from the instrumental optics, the emitted light intensities with vertical and horizontal polarizer/analyzer arrangements were measured, that is, I_{VV}, I_{VH}, I_{HV}, and I_{HH}, where the first and second subscripts refer to the incident and emitted light, respectively. The fluorescence anisotropy can then be determined for each band by eq 2, where the grating efficiency factor G is equal to I_{VH}/I_{HH}.[81]

$$\rho = (I_{VV}I_{HH} - I_{VH}I_{HV})/(I_{VV}I_{HH} + 2I_{VH}I_{HV}) = (I_{VV} - GI_{HV})/(I_{VV} + 2GI_{HV}) \quad (2)$$

All spectra under pressure were taken in a pressure vessel HKP-921208 designed and manufactured by Hikari Koatsu Co. (Hiroshima, Japan), which was equipped with three sapphire windows (5 mm i.d.)

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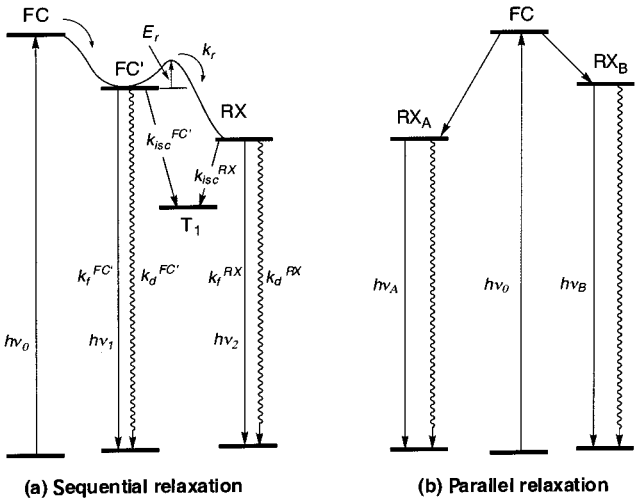

Figure 1. Two possible mechanisms for the dual fluorescence behavior of R_6BHC with bulky ester groups in solution.

for UV and fluorescence measurements and also with a coolant circulation system in the body of the vessel for constant temperature. For the spectral measurements at 25 °C, the pressure vessel containing a solution (11 mL) of fluorophore at ca. 0.1 mM was set in a fluorimeter and pressurized up to 350 MPa using a high-pressure pump KP5B (Hikari Koatsu Co.).

Results and Discussion

Time-Resolved Fluorescence Spectroscopy. Dual fluorescence was first reported for the steady-state fluorescence spectra of Bor$_6$BHC, Ad$_6$BHC, Men$_6$BHC, and tBu$_6$BHC in fluid solution at room temperature.[76] As a likely, but tentative, mechanism for the dual fluorescence phenomenon, a sequential relaxation pathway from the FC to FC′ and then to RX state has been proposed (Figure 1a).[76] The fluorescence lifetime measurements at a 0.5 ns time resolution were performed using the conventional single photon counting technique, but the instrumental limitations precluded the reliable lifetime measurement of the short lifetime of FC′ fluorescence. Hence, an alternative parallel relaxation mechanism could not be ruled out in the previous study. As shown in Figure 1b, the FC state may relax concurrently to two independent relaxed states (RX_A and RX_B) which emit light at different wavelengths with different lifetimes, as was the case with the dual fluorescence of *N*-phenylnaphthalimides.[57,58] To definitely distinguish the two possibilities and elucidate the origin and comprehensive picture of the dual fluorescence of R_6BHC, it is absolutely necessary to directly monitor the fate(s) of excited state by the picosecond time-resolved fluorescence technique.

The time-resolved fluorescence spectra were recorded in a pentane solution of tBu$_6$BHC at room temperature. As can be seen from Figure 2, the FC′ (313 nm) and RX (382 nm) fluorescence exhibit distinctly different decay profiles. Thus, the FC′ fluorescence reaches the maximum immediately after the laser pulse and then rapidly decays, whereas the RX fluorescence develops more slowly to reach its maximum intensity after the FC′ fluorescence starts to decay, and then decays much more slowly. The relative fluorescence intensities, though not a simple measure of concentrations of the two fluorescing species, reflect the population changes of the FC′ and RX states. Time-resolved fluorescence measurements were also carried out with Men$_6$BHC, Bor$_6$BHC, MHp$_6$BHC, and

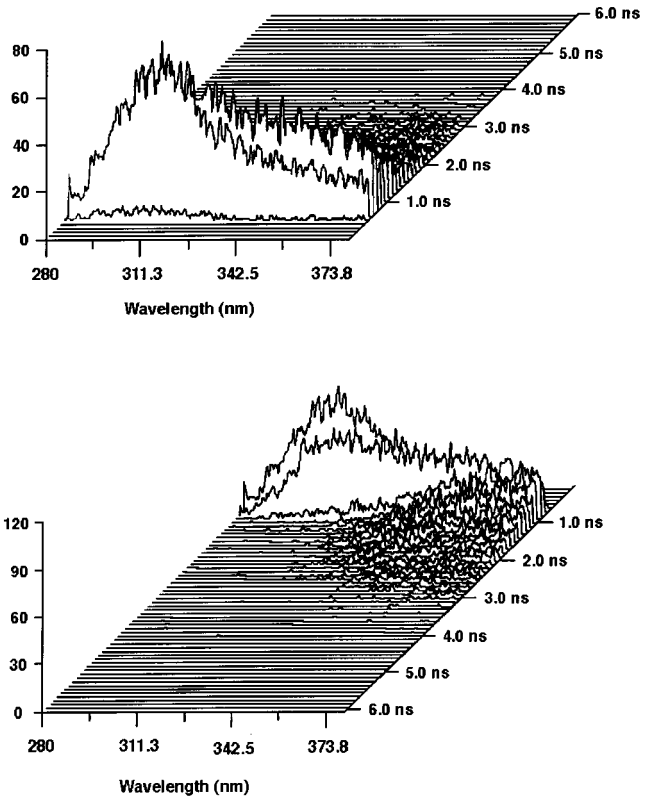

Figure 2. Picosecond time-resolved dual fluorescence spectra for tBu_6-BHC in pentane at room temperature; (a) "front" view, (b) "rear" view.

Table 1. Fluorescence Lifetimes (τ) and Fluorescence Anisotropies (ρ) of the Franck−Condon-like (FC′) and/or Relaxed (RX) States and Activation Energies (E_r) and Activation Volumes ($\Delta V_r^{\ddagger}$) for Relaxation from the FC′ to RX State of Hexaalkyl Benzenehexacarboxylates (R_6BHCs) and Naphthalene (as Reference)[a]

		τ/ns		E_r/kcal	ρ		$\Delta V_r^{\ddagger}$/mL
fluorophore	solvent	FC′	RX	mol^{-1}	FC′	RX	mol^{-1}
Me_6BHC	pentane	*b*	1.05	∼0	*c*	0.016	*c*
$neoPn_6$BHC	pentane	0.125	1.05	1.7	*d*	*d*	*d*
MHp_6BHC	pentane	0.049	0.89	2.7	*d*	*d*	*d*
Men_6BHC	pentane	0.11	0.80	1.2	0.028	0.013	−0.62
	decane	0.13	0.85	*d*	*d*	*d*	*d*
Bor_6BHC	pentane	0.040	1.05	2.1	0.31	0.0033	+7.4
Ad_6BHC	diethyl ether	0.017	0.94	1.4	*d*	*d*	*d*
tBu_6BHC	pentane	0.031	0.66	1.7	0.083	0.011	+2.0
	decane	0.036	0.62	*d*	*d*	*d*	*d*
naphthalene	pentane	*b*	14.2	∼0	*c*	0.0033	*c*

[a] Excited at 250 nm in air-saturated (nondegassed) solution of fluorophore (0.10−0.16 mM) at room temperature. [b] No FC′ fluorescence observed. [c] Not applicable. [d] Not determined.

Ad_6BHC to give similar results, that is, fast build-up and fast decay of the FC′ fluorescence signal and the subsequent growth of the RX fluorescence at the expense of the FC′ fluorescence, followed by a slower decay of the RX fluorescence signal. The fluorescence lifetimes of the FC′ and RX states of congested R_6BHCs as determined from the decay profiles are 31−130 ps and 0.66−1.05 ns, respectively, as listed in Table 1; a typical decay profile analysis for Men_6BHC is shown in Figure 3. In contrast, only the RX fluorescence lifetime was obtained for the less-congested Me_6BHC. The use of decane as a solvent gave somewhat longer and comparable lifetimes for FC′ and RX states, respectively, for both tBu_6BHC and Men_6BHC.

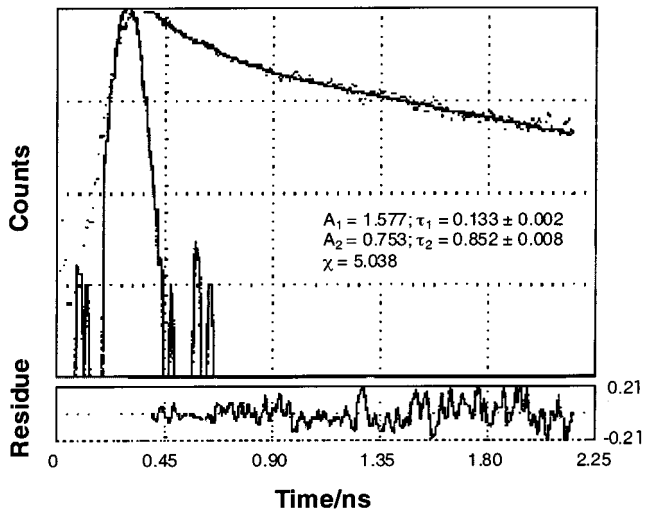

Figure 3. Typical double-exponential fit of dual fluorescence decay of Men_6BHC (0.1 mM) in decane at room temperature.

The coupled FC′-decay and RX-growth behavior observed in the initial stages of the fluorescence profile unambiguously supports the sequential formation of the two fluorescing states, where the relaxation of the initially produced FC′ state results in the RX state with accompanying conformational changes of the alkoxycarbonyl groups. Equations 3−8 are derived from the sequential mechanism shown in Figure 1a:

$$dI_{FC'}/dt = k_f^{FC'} I_0 \exp(-t/\tau_{FC'}) \quad (3)$$

$$dI_{RX}/dt = [k_f^{RX} k_r/(1/\tau_{FC'} - 1/\tau_{RX})] I_0 [\exp(-t/\tau_{RX}) - \exp(-t/\tau_{FC'})] \quad (4)$$

$$\tau_{FC'} = 1/(k_f^{FC'} + k_d^{FC'} + k_{isc}^{FC'} + k_r) \quad (5)$$

$$\tau_{RX} = 1/(k_f^{RX} + k_d^{RX} + k_{isc}^{RX}) \quad (6)$$

$$dI_{RX}/dt \approx k_f^{RX} k_r \tau_{FC'} I_0 [1 - \exp(-t/\tau_{FC'})] \quad (\text{when } t \approx \tau_{FC'} \ll \tau_{RX}) \quad (7)$$

$$\approx k_f^{RX} k_r \tau_{FC'} I_0 \exp(-t/\tau_{RX}) \quad (\text{when } t \approx \tau_{RX} \gg \tau_{FC'}) \quad (8)$$

where k_f, k_d, and k_{isc} with superscript FC′ or RX are rate constants for the fluorescence, radiationless decay (internal conversion), and intersystem crossing from the FC′ or RX state, while k_r for the FC′-to-RX relaxation, I_{RX} and $I_{FC'}$ the fluorescence intensities from the RX and FC′ states at a specific wavelength, $\tau_{FC'}$ and τ_{RX} the apparent lifetimes of the FC′ and RX fluorescence, I_0 the intensity of light absorbed by the molecule, and $dI_{FC'}/dt$ and dI_{RX}/dt the fluorescence intensity changes evaluated from the time-resolved fluorescence spectra shown in Figure 2. As indicated by eq 3, the FC′ fluorescence signal decays exponentially with a time constant of $1/\tau_{FC'}$. For RX fluorescence, eq 4 is simplified during the initial building-up period because $\tau_{FC'}$ is much smaller than τ_{RX}. Thus, the development of RX fluorescence is approximated by a single-exponential growth with a time constant of $1/\tau_{FC'}$, which is identical to the decay time constant of the FC′ fluorescence. This concurrent decay-growth relationship between the FC′ and

RX fluorescence was explicitly confirmed by the experimental data shown in Figure 2, but curve-fitting of the RX growth is virtually impossible or unreliable because of the very limited data points available for the initial stage of RX fluorescence. After the initial building-up period, the RX fluorescence signal decays exponentially as formulated by eq 4, or by simplified eq 8, with a time constant of $1/\tau_{RX}$.

For Me_6BHC, the relaxation of the FC′ state to the RX state is presumably so fast that fluorescence from the FC′ state is negligible, or the FC′ state does not exist at all because the methoxycarbonyl groups can rotate freely. As the size of alkyl group increases, rotation of the alkoxycarbonyl groups is slowed or restricted because of the steric hindrance between the adjacent alkoxycarbonyl groups; thus the conformational relaxation of alkoxycarbonyl groups is decelerated. Thus, the metastable FC′ state comes into existence as an emissive state prior to further full conformational relaxation of alkoxycarbonyl groups. In other words, the FC′ fluorescence is in competition with the further conformational relaxation process, and the relative rate is kinetically controlled.

The dual fluorescence systems reported so far may be classified into two categories, that is, "chemical" and "physical," according to the nature of the changes involved. The majority of dual fluorescence systems involve some chemical changes upon light absorption, for example, proton transfer, charge transfer, charge separation, cis−trans isomerization, and excimer/exciplex formation. Molecular conformation changes upon excitation can also lead to dual fluorescence behavior through the formation of relaxed states with extended conjugation,[57,58] excited-state bond-stretching isomerism,[68] and sequential relaxation of the FC state to conformationally different metastable and fully relaxed states.[76,77] Excited-state conformers can also be formed by independent excitation of ground-state conformers.[72−75] All of the latter examples are not accompanied by any chemical changes, but rather involve excited-state conformation changes and therefore are thought "physical," although the nature, mechanism, and requirements for the occurrence of dual fluorescence are entirely different in each case.

Excitation-Wavelength Dependence. The effects of excitation energy on the relative intensities of two fluorescence bands ($I_{RX}/I_{FC'}$) were examined by steady-state fluorescence spectroscopy with tBu_6BHC (in pentane, cyclohexane, heptane, decane, acetonitrile, and methanol), Men_6BHC (in pentane, cyclohexane, heptane, decane, and acetonitrile), Bor_6BHC (in pentane, cyclohexane, heptane, and decane), MHp_6BHC (in pentane, cyclohexane, heptane, and decane), $neoPn_6$BHC (in pentane, cyclohexane, heptane, and decane), and Ad_6BHC (in ethyl ether) at room temperature. Figure 4 shows the results for tBu_6BHC, Men_6BHC, and MHp_6BHC in pentane. The $I_{RX}/I_{FC'}$ ratio was moderately dependent on the excitation wavelength and appreciably increased at shorter excitation wavelengths. Analogous excitation-wavelength dependence of the $I_{RX}/I_{FC'}$ ratio was also observed for other R_6BHCs in all solvents studied. These results are reasonably accounted for by assuming that some of the excess vibrational energy of the FC state is carried over to the FC′ state, which in turn accelerates further relaxation of the "hot" FC′ state to the RX state in competition with the internal vibrational relaxation within it. Such a competition may not be unrealistic, as the rate constant for the FC′ fluorescence (τ 31−130 ps) and the diffusion rate constant in pentane (10^{10} s^{-1}) are of the same order. The monotonic decrease of the $I_{RX}/I_{FC'}$ ratio with decreasing excitation energy (Figure 4) is compatible with the hot FC′ state, or energy-carry-over, mechanism proposed above. It is also pointed out that the six bulky alkoxycarbonyl groups surrounding the benzene chromophore significantly decelerate the collisional deactivation by solvent molecules, preserving the excess vibrational energy in and around the chromophore.

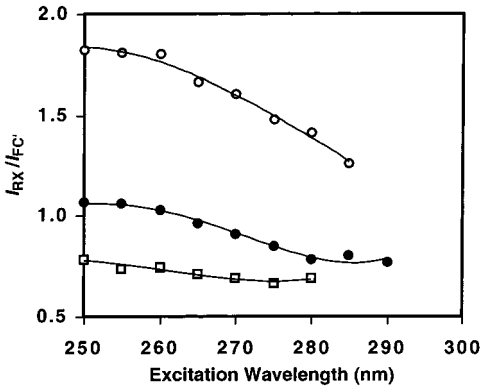

Figure 4. Relative fluorescence intensity ($I_{RX}/I_{FC'}$) as a function of excitation wavelength in pentane at room temperature for tBu_6BHC (○), Men_6BHC (●), and MHp_6BHC (□, data scaled to 1/10).

Temperature Dependence. The effects of temperature on the $I_{RX}/I_{FC'}$ ratio were examined by steady-state fluorescence spectroscopy for tBu_6BHC, Men_6BHC, Bor_6BHC, MHp_6BHC, and $neoPn_6$BHC in pentane and for Ad_6BHC in diethyl ether. The $I_{RX}/I_{FC'}$ ratio was found to decrease gradually with decreasing temperature for all R_6BHCs studied. Equations 9−12 are derived for the quantum yields of the two fluorescing processes ($\Phi_{FC'}$ and Φ_{RX}) and the activation energy of relaxation from the FC′ to RX state (E_r). Assuming that the peak positions and widths of the two fluorescence bands are not significantly affected by temperature, we represented the relative quantum yield $\Phi_{RX}/\Phi_{FC'}$ by the $I_{RX}/I_{FC'}$ ratio to give eq 13.

$$\Phi_{FC'} = k_f^{FC'}/(k_f^{FC'} + k_d^{FC'} + k_{isc}^{FC'} + k_r) \quad (9)$$

$$\Phi_{RX} = [k_r/(k_f^{FC'} + k_d^{FC'} + k_{isc}^{FC'} + k_r)] \times [k_f^{RX}/(k_f^{RX} + k_d^{RX} + k_{isc}^{RX})] \quad (10)$$

$$k_r = k_{r0} \exp[-E_r/RT] \quad (11)$$

$$\ln(\Phi_{RX}/\Phi_{FC'}) = -E_r/RT + \ln k_{r0} - \ln[k_f^{FC'}(k_f^{RX} + k_d^{RX} + k_{isc}^{RX})/k_f^{RX}] \quad (12)$$

$$\ln(I_{RX}/I_{FC'}) = -E_r/RT + \ln k_{r0} - \ln[k_f^{FC'}(k_f^{RX} + k_d^{RX} + k_{isc}^{RX})/k_f^{RX}] \quad (13)$$

Further assuming marginal temperature dependence of $k_f^{FC'}$, k_f^{RX}, k_d^{RX}, and k_{isc}^{RX}, we obtained the activation energy of relaxation (E_r) as a slope of the plot of $\ln(I_{RX}/I_{FC'})$ against $1/T$ (eq 13). The $\ln(I_{RX}/I_{FC'})$-versus-$1/T$ plots gave good straight lines for all of the systems studied. The E_r values thus obtained are listed in Table 1, which are in the range of 1−3 kcal/mol for congested R_6BHC. In view of the assumptions made and other factors that have not been taken into account (e.g., solvent

viscosity change with temperature), these estimates are tentative. However, it is reasonable to think that the E_r values, though close to the activation energy for the viscosity of pentane, reflect the bulkiness effect of the alkoxycarbonyl group upon rotational relaxation in the excited singlet R_6BHC, because the least-bulky Me_6BHC gives no barrier for the rotation.

Fluorescence Anisotropy. The fluorescence anisotropies obtained in nondegassed pentane and/or decane at room temperature are listed in Table 1. Rotation of excited-state molecules during their lifetimes causes fluorescence depolarization, and therefore the fluorescence anisotropy (ρ) can be used as a measure of rotational relaxation of the whole molecule. Short fluorescence lifetimes (τ's) usually correlate with large ρ's, while long τ's associate with small ρ's. Naphthalene, employed as a reference compound with a long τ (14.2 ns), gave a very small ρ as low as 0.003. For the compounds studied here possessing short τ's of 30−110 ps, the FC′ fluorescence gave fairly large ρ's of 0.03−0.3, whereas the RX fluorescence afforded much smaller ρ's of 0.003−0.01, owing to the longer τ's. Interestingly, the FC′ fluorescence anisotropy critically depends on the ester groups (Table 1), indicating that the rotational motion of excited molecule is affected by the ester groups.

It may be interesting to examine the validity of the Perrin equation in the present system: $\rho_0/\rho = 1 + 6D_R\tau$, where ρ_0 represents the limiting anisotropy factor, and D_R represents the rotatory diffusion constant.[81] The Perrin equation is known to be valid for ellipsoids of revolution. However, the plot of $1/\rho$ versus τ for the FC′ and RX fluorescence did not give a good linear relationship but a scattered plot, for which the nonellipsoidal form or the continuous structural changes of R_6BHC in the excited state would be responsible.

Pressure Effects. The effects of pressure on dual fluorescence were examined for tBu_6BHC, Men_6BHC, and Bor_6BHC in pentane at room temperature. Assuming the same shape for each fluorescence band over the entire pressure range employed, we derived eqs 14 and 15 from eqs 9, 10, and 12:

$$(\partial \ln k_r/\partial P)_T \approx -\Delta V_r^{\ddagger}/RT \quad (14)$$

$$[\partial \ln(I_{RX}/I_{FC'})/\partial P]_T \propto -\Delta V_r^{\ddagger}/RT - (\partial \ln[k_f^{FC'}(k_f^{RX} + k_d^{RX} + k_{isc}^{RX})/k_f^{RX}]/\partial P)_T \quad (15)$$

where P is the pressure (MPa), and $\Delta V_r^{\ddagger}$ is the activation volume (mL/mol) at constant temperature.

Neglecting the pressure effect on $k_f^{FC'}$, k_f^{RX}, k_d^{RX}, and k_{isc}^{RX}, we obtain eq 16, with the activation volume $\Delta V_r^{\ddagger}$ calculated from a plot of $\ln(I_{RX}/I_{FC'})$ against P at a given temperature. The results are shown in Figure 5 and Table 1.

$$\ln(I_{RX}/I_{FC'}) \propto -[\Delta V_r^{\ddagger}/(RT)]P - \ln[k_f^{FC'}(k_f^{RX} + k_d^{RX} + k_{isc}^{RX})/k_f^{RX}] \quad (16)$$

The activation volume is the difference in partial volume between the FC′ state and the transition state for the relaxation to the RX state. Because no bond breaking or formation is involved in the present system, the activation volume is anticipated to be small, reflecting only the change in molecular packing density through the rotational relaxation of alkoxycarbonyl moieties. As shown in Table 1, tBu_6BHC and Bor_6BHC gave moderately/highly positive $\Delta V_r^{\ddagger}$ values of 2.0 and 7.4 mL/mol, respectively, for which the bulky, rigid, spherical *tert*-butyl, and bornyl groups would be responsible, because the rotational relaxation of these rigid moieties inevitably causes volume expansion at the transition state. On the contrary, a more flexible, aspherical menthyl group gave a slightly negative activation volume of −0.6 mL/mol, indicating that the volume change upon rotational relaxation can be minimized through the higher conformational adjustability of a less-rigid R_6BHC case.

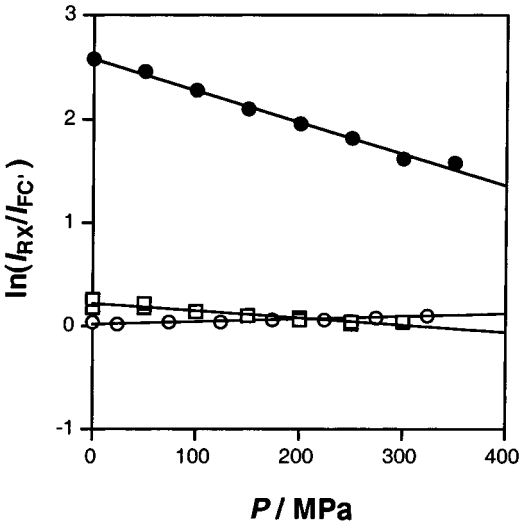

Figure 5. Relative fluorescence intensity ($I_{RX}/I_{FC'}$) as a function of pressure in pentane at room temperature for tBu_6BHC (□), Men_6BHC (○), and Bor_6BHC (●).

Table 2. Fluorescence Maxima and Relative Intensities of the FC′ and RX Peaks of tBu_6BHC in Various Solvents at Room Temperature[a]

			λ_{max}/nm		
solvent	η[b]/mPa s	E_T[c]/kcal mol^{-1}	FC′	RX	$\Phi_{RX}/\Phi_{FC'}$
(1) pentane	0.225	30.9	331	382	1.82
(2) hexane	0.299	30.9	331	382	1.72
(3) heptane	0.397	30.9	329	379	1.52
(4) isooctane	0.47	30.9	329	385	1.41
(5) octane	0.515	30.9	328	383	1.39
(6) decane	0.861	30.9	327	379	1.20
(7) cyclohexane	0.898	30.9	326	379	1.14
(8) dodecane	1.34	30.9	327	379	1.00
(9) tetradecane	2.18	30.9	328	379	0.90
(10) hexadecane	3.34	30.9	328	380	0.83
(a) diethyl ether	0.23	35.3	330	379	2.04
(b) acetonitrile	0.34	45.6	330	389	1.59
(c) methanol	0.545	55.5	330	382	1.45
(d) ethanol	1.076	51.9	325	379	1.04
(e) isopropanol	2.2	48.6	326	386	1.08
(f) butanol	2.62	50.2	325	382	0.75
(g) isobutanol	3.91		325	389	0.93

[a] Excitation wavelength, 250 nm; tBu_6BHC concentration, 0.1 mM. [b] Viscosity (ref 82b). [c] Polarity parameter (ref 82b).

Solvent Effects. The effects of solvent polarity and viscosity on dual fluorescence were also examined. The fluorescence maxima and relative intensities of the FC′ and RX peaks of tBu_6BHC in various solvents are shown in Table 2. In nonpolar solvents such as aliphatic hydrocarbons (entries 1−10), the FC′ and RX fluorescence maxima show only small irregular changes in the fairly narrow wavelength ranges. In contrast, the $I_{RX}/I_{FC'}$ ratio varies significantly. Because the polarity of these solvents is essentially the same,[82b] the change in $I_{RX}/I_{FC'}$ should be attributed to the solvent viscosity.[82b]

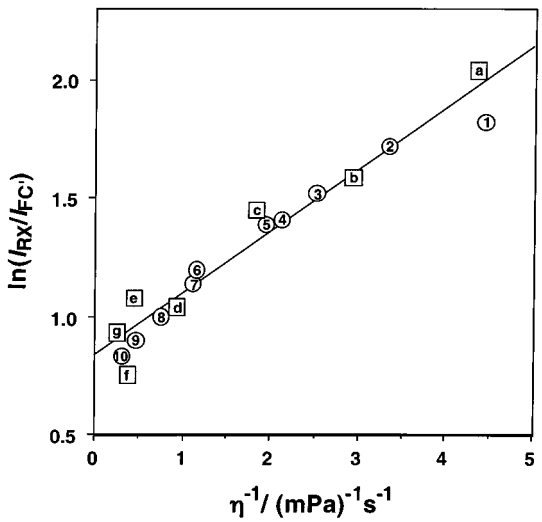

Figure 6. Relative fluorescence intensity ($I_{RX}/I_{FC'}$) as a function of reciprocal viscosity ($1/\eta$) in various solvents (see Table 2 for entry numbers/characters of relevant solvents) at room temperature for tBu_6BHC.

The viscosity dependence observed is reasonable from a qualitative point of view, as the rotational relaxation of bulky alkoxycarbonyl moieties, leading to the RX state, accompanies intra- and intermolecular frictions with adjacent alkoxycarbonyls as well as surrounding solvent molecules. Equation 17 is derived from eqs 9 and 10 for the relative intensity of RX and FC′ fluorescence.

$$\Phi_{RX}/\Phi_{FC'} = k_r k_f^{RX}/[k_f^{FC'}(k_f^{RX} + k_d^{RX} + k_{isc}^{RX})] \quad (17)$$

In this equation, the rotational relaxation rate constant, k_r, is most sensitive to solvent viscosity (η), while the other radiative and nonradiative processes, involving little conformational or rotational changes, are thought to be much less sensitive to η. Assuming that the fluorescence ($k_f^{FC'}$, k_f^{RX}), nonradiative decay (k_d^{RX}), and intersystem crossing rate constants (k_{isc}^{RX}) are independent of viscosity and that the friction upon rotational relaxation is analogous to that of diffusion in the same solvent, we found that $F_{RX}/F_{FC'}$ is proportional to k_r, which is in turn inversely proportional to the solvent viscosity (η in mPa s) (eq 18).[82a]

$$\Phi_{RX}/\Phi_{FC'} \propto k_r = 8RT/(3 \times 10^5 \eta) \quad (18)$$

Hence, the $I_{RX}/I_{FC'}$ values are plotted against the reciprocal viscosity to give a good straight line shown in Figure 6.

Interestingly, the use of polar solvents did not cause any bathochromic shift of FC′ or RX fluorescence. Thus, the fluorescence maxima in alcohols, acetonitrile, and ether appear at 325−330 nm for FC′ and 379−389 nm for RX (Table 2), which are almost comparable to those in nonpolar solvents. Furthermore, the $I_{RX}/I_{FC'}$ values obtained in the protic and aprotic polar solvents (entries a−g) fall on the same regression line obtained for nonpolar hydrocarbons, as shown in Figure 6. The relative fluorescence intensity, which is insensitive to solvent polarity but highly sensitive to solvent viscosity giving a linear relationship with $1/\eta$, prompted us to employ tBu_6BHC and other bulky R_6BHCs as in-situ molecular viscosity probes, not only for conventional fluid solutions but also for organized media such as micelles, vesicles, and liquid crystals.

Microenvironmental Viscosity. In the present study, the microenvironmental viscosity of sodium dodecyl sulfate (SDS) micelle was evaluated by solubilizing tBu_6BHC, as an in-situ fluorescent viscosity probe, in aqueous SDS solutions above the critical micelle concentration (cmc). The concentration of fluorophore was fixed at 0.15 mM, which is sufficient for statistically distributing one fluorophore molecule per one micelle at the cmc, considering the average aggregation number of SDS (ca. 60).[83] The microviscosity of SDS micelle interiors was evaluated by plotting the $I_{RX}/I_{FC'}$ values obtained with aqueous solutions of SDS at concentrations 3, 5, and 10 times higher than the formal cmc (8 mM)[83] on the regression line in Figure 6 and then by reading the corresponding $1/\eta$ value. At these SDS concentrations of 3, 5, and 10 times cmc, the fluorophore/micelle ratios are 0.33, 0.2, and 0.1, respectively. It should be noted that the estimated microenvironmental viscosity critically depends on the SDS concentration, varying from 0.27 mPa s at a concentration that is 3 times higher than the cmc, up to 2.0 mPa s at 10 times cmc.

In the micelle, the dodecyl chains of SDS are assembled to form a spherical hydrophobic core, which behaves like semi-ordered *liquid* hydrocarbon.[83] Fluorescence probes have been frequently used to measure the microenvironmental viscosity of micelles.[84] For SDS micelles, the microviscosity has been estimated as 193 mPa s (determined at 23 °C by intermolecular excimer formation),[85] 15 mPa s (by intermolecular excimer formation),[86] 16 mPa s (by fluorescence depolarization),[87] 10 mPa s (20 °C by intramolecular excimer formation),[88] 9 mPa s (20 °C by intramolecular excimer formation),[89] 11.5 mPa s (25 °C by intramolecular excimer formation),[90] 21−22 mPa s (25 °C by intramolecular excimer formation),[91] 3.2 mPa s (by fluorescence quenching),[92] ∼2 mPa s (by measurement of nonradiative decay rate),[93] 4.3 mPa s (by excited-state torsional relaxation),[94] 19 mPa s (by intramolecular excimer formation),[95] 24 mPa s (30 °C, by intramolecular excimer formation),[96] and 3.6 mPa s (by fluorescence quantum yield measurement).[97] The large divergence is presumably because of the different modes of molecular motions of the probe molecules employed and the assumptions made for calculating the microviscosity in each method. Thus, fluorescence depolarization monitors the rotational motion of whole probe molecules, while excimer formation and fluorescence quenching monitor the translational motion of the probes. On the other hand, nonradiative decay and torsional relaxation in the excited state accompany only small or negligible molecular motions and monitor the excited-state properties of the probes. Apart from the extremely large value

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reported by Pownall and Smith,[85] two sets of values, that is, 2−5 and 9−24 mPa s, have been reported as the microviscosity of SDS micelles. This apparent discrepancy may be accounted for in terms of the differences in methodologies used for probing the microviscosity. The smaller values have been obtained by fluorescence quenching, nonradiative decay measurement, excited-state torsional relaxation, and fluorescence quantum yield measurement, while the larger values have been obtained by fluorescence depolarization and inter/intramolecular excimer formation. Thus, such probing methods that involve global or translational molecular motions tend to give the larger viscosity values, while those with little or no molecular motions or conformational changes give the smaller viscosity values.

Our estimations using the dual fluorescent probe give the lower values of 0.27−2 mPa s, with a dependence on the SDS concentration. The increasing microviscosity with increasing SDS concentration is unprecedented and somewhat unexpected, because similar attempts to measure the microviscosity at different SDS concentrations have not been made.[84−97] For pure SDS micelles at concentrations above the cmc, the size and aggregation number of the micelles are believed to be independent of the SDS concentration.[83] If the size and aggregation state of SDS micelles were unaffected upon addition of tBu_6BHC as a probe, we would expect the same fluorescence behavior at all SDS concentrations above the formal cmc. To explain the observed dependence of the $I_{RX}/I_{FC'}$ value upon SDS concentration, we need to postulate some structural change of SDS micelles in the presence of the fluorescent probe. It is likely that, although the tBu_6BHC molecule is much smaller in size than the SDS micelle, the accommodation of tBu_6BHC leads to a more loosely packed, less ordered micellar structure than that of the pure SDS micelle. The obtained microviscosities of 0.27, 0.36, and 1.92 mPa s at SDS concentrations 3, 5, and 10 times higher than the formal cmc are comparable to those of pure hexane, heptane, and tetradecane, respectively. This means that the dodecyl chains of SDS molecules are only loosely assembled around the probe molecule particularly at the low SDS concentrations, which facilitates the rotational relaxation of the excited probe, accompanying the synchronized reorganization of SDS molecules. At higher SDS concentrations, tBu_6BHC is considered to be surrounded by more tightly packed SDS molecules, for which we have no plausible rationale at present, but a possible formation of larger micelles would be responsible. The resulting rigid micellar structure should decelerate the relaxation of excited tBu_6BHC to give lower $I_{RX}/I_{FC'}$ values at higher SDS concentrations. Thus, the estimated microviscosity reflects the microenvironmental response "sensed" by the probe molecule, as was the case with the preceding probes.

The dual fluorescence of tBu_6BHC does not sense the rotation or the translational movement of the excited molecule, but rather monitors the conformational relaxation (presumably rotation) of alkoxycarbonyl groups. This feature would be more suitable for detecting even the small microviscosity changes arising from changes in the aggregation state.

Conclusion

Using picosecond time-resolved fluorescence spectroscopy, we have demonstrated that the relaxation of the FC state of sterically congested R_6BHCs occurs sequentially to a partially relaxed FC′ and then to a fully relaxed RX state. The lifetimes of FC′ and RX fluorescence are in the ranges of 17−130 ps and 0.6−1.1 ns, respectively. The relaxation from the FC′ to RX state is accelerated by the excess vibrational energy in the FC′ state. The relaxation energy barrier E_r is in the range of 1−3 kcal/mol for the sterically congested R_6BHCs. The activation volume of relaxation $\Delta V^{\ddagger}$ depends on the ester groups and can be positive or negative, depending on the shape and conformational rigidity of the alkyl group. Larger fluorescence anisotropies of 0.03−0.3 for FC′ fluorescence and smaller fluorescence anisotropies of 0.003−0.01 for RX fluorescence have been obtained, which are consistent with the shorter and longer lifetime of each fluorescent state. The relative intensity $I_{RX}/I_{FC'}$ is insensitive to solvent polarity, but is proportional to the reciprocal of solvent viscosity, which makes these sterically congested R_6BHCs suitable as microscopic viscosity probes as demonstrated for the SDS micelle.

Acknowledgment. We appreciate the preliminary laser examinations for obtaining time-resolved fluorescence spectra made by Professor Tadashi Okada and Dr. Hiroshi Miyasaka at Osaka University. We also thank Dr. Guy A. Hembury for assistance in the preparation of this manuscript.

JA016858L