Fluorescence Emission and Conformation of 6-*O*-α-(1-Naphthylmethyl)-2,3-di-*O*-pentylcellulose in Dilute Solution[1]

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ABSTRACT: The fluorescence property and molecular structure of a specifically substituted cellulose derivative, 6-*O*-α-(1-naphthylmethyl)-2,3-di-*O*-pentylcellulose (NPeC), were investigated. Steady-state and time-resolved measurements of fluorescence spectra were carried out for a dilute solution of NPeC in tetrahydrofuran at different temperatures. It was found that the cellulose derivative forms a naphthyl excimer intramolecularly via a dynamic process requiring quite a small activation energy (E_a = 2.8 kcal mol^{-1}). The intramolecular excimer formation in NPeC is interpreted as a consequence of the short-range approach of two adjacent naphthyl chromophores after photoexcitation of one of them; possibly, the substituents are originally allowed to be fairly close to each other, owing to a special arrangement of the carbohydrate backbone. In combination with the conformational analysis performed on a model disaccharide as a dimer unit of NPeC, it is suggested that the backbone chain of this polymer prefers to assume a "twisted" structure.

Introduction

As is well-known,[2−6] many cellulose derivatives are capable of forming a liquid-crystalline phase in concentrated solutions with appropriate solvents and/or in a fluid state without any solvent. Numerous reports have centered around the optical, thermal, rheological, and other physical properties of cellulosics, occasioned by their mesomorphic, supramolecular ordering. Attention has also been directed to the morphological features and mechanical characteristics of the solid films and fibers of cellulosics prepared from the liquid-crystalline state.

The liquid crystallinity of cellulosic polymers may be considered to be essentially due to the semirigidity inherent in the carbohydrate backbone constructed by β(1→4) linkage of glucose residues. However, the molecular structure of liquid-crystalline cellulosics in fluid media has not yet been elucidated in detail, in contrast to the situation of many polypeptides whose molecular chains can assume an α-helical conformation to be a rigid rod. The propose of this present paper is to provide some significant informations about the chain conformation and rigidity of cellulosic molecules in solution.

The cellulose derivative studied in this work is a specifically substituted polymer, 6-*O*-α-(1-naphthylmethyl)-2,3-di-*O*-pentylcellulose, abbreviated as NPeC below. This polymer forms a chiral nematic mesophase in a condensed state showing a certain degree of fluidity.[7] The previous work was mainly concerned with the chiroptical properties of NPeC, examined by means of circular dichroism (CD) spectrophotometry. Of particular interest was the indication of a spiral arrangement of naphthyl substituents along the cellulose backbone, as evidenced by dilute-solution CD studies. This suggests that the polymer may have a helical or twisted secondary structure in fluid solution. In the present paper, we would like to give further insight into the molecular structure of the cellulose derivative NPeC in solution, through measurements of the fluorescence which is emitted from photoexcited naphthyl chromophores attached onto the carbohydrate backbone. It is shown that this polymer is readily capable for intramolecular formation of an excited dimer (excimer) of naphthalene. Detailed analysis of the temperature-dependent, fluorescence emission spectrum of NPeC in dilute solution is carried out. Molecular force-field calculations are also conducted on a dimer-unit model of NPeC, to deduce a chain conformation of this polymer consistent with the interpretation of the fluorescence spectroscopic data.

Experimental Section

Materials. The structural formula of the cellulose derivative sample 6-*O*-α-(1-naphthylmethyl)-2,3-di-*O*-pentylcellulose (NPeC) is shown in Figure 1. The degree of substitution (DS) for the naphthylmethyl group was approximately 1.0 and the DS for the pentyl group was 1.82, for a total side-group DS of 2.82. This sample was synthesized from 6-*O*-tritylcellulose as a starting material, via the preparation of 6-*O*-trityl-2,3-di-*O*-pentylcellulose (DS(trityl) = 1.03, DS(pentyl) = 1.82, for a total DS of 2.85), with a mass-average molecular weight of 144 000 corresponding to a degree of polymerization of ca. 265. Details of the preparation and characterization of NPeC have been described previously.[7] Reagent-grade 1-ethylnapthalene (Tokyo Kasei Kogyo Co., Ltd.) was used as a reference sample in the fluorometry. Tetrahydrofuran (THF) was used as a solvent, which was purified by vacuum distillation after preliminary distillation over sodium metal.

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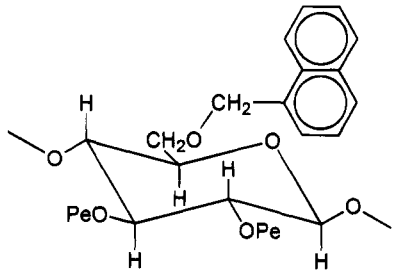

Figure 1. Structural formula of 6-*O*-α-(1-naphthylmethyl)-2,3-di-*O*-pentylcellulose, abbreviated as NPeC. Pe = pentyl group.

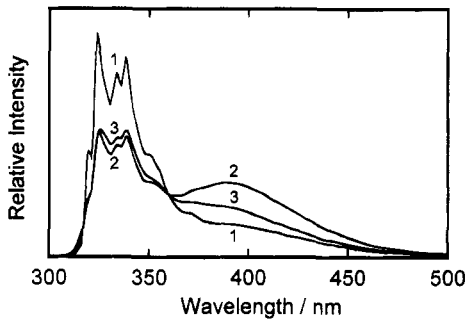

Figure 2. Fluorescence spectra of NPeC in THF at different temperatures: (1) −90 °C; (2) −30 °C; (3) +5 °C. The excitation wavelength is 282 nm.

Measurements. UV-absorption spectra were measured with a Hitachi U-2000 spectrophotometer. Steady-state fluorescence spectra and excitation spectra were recorded with a Hitachi 850 fluorescence spectrophotometer. The fluorescence measurements were carried out for a dilute NPeC solution in THF in a temperature range of ca. −95 to +50 °C. The polymer concentration in the solution was adjusted so that the concentration of naphthyl chromophores was less than 10^{-4} M, and the sample was deaerated by freeze–thaw cycles at 10^{-5} mmHg. A quartz Dewar equipped with a thermocouple was utilized for measurements at temperatures below 20 °C. The quantum yields of fluorescence emission were determined relative to that of quinine bisulfate in 1.0 N sulfuric acid.[8] Time-resolved fluorescence spectra were also measured with a picosecond laser system as the excitation light pulse. Details of the apparatus for measurements have been described elsewhere by Yamamoto et al.[9] The full-width at half-maximum of the overall excitation pulse was 500 ps in the present study.

Conformational Energy Calculations. Molecular force-field calculations were performed on a model disaccharide (shown in Figure 6) by using CHARMm program.[10] The total potential energy was calculated according to the definition described in ref 10b, including bond stretching, bond angle bending, torsional potentials, and van der Waals and electrostatic interactions. Energy-minimized structures were visualized by QUANTA program.[10a] For the calculations an effective dielectric constant was set equal to 3. All the atoms making up the model compound were treated explicitly, and no specific geometrical constraint was applied to the molecule.

Results and Discussion

Fluorescence Emission Characteristics. The cellulose derivative NPeC gave an absorption spectrum almost identical with that of 1-ethylnaphthalene (1EN), when measured in dilute solutions (chromophore concentration ≤ 10^{-4} M) in THF. Figure 2 depicts selected fluorescence spectra of NPeC in THF, obtained at different temperatures. Each spectrum consists of a mixture of two emission bands. The structured shorter wavelength band is due to the ordinary fluorescence emission from monomeric excited naphthyl groups. The longer wavelength band, centered at ca. 390 nm, may

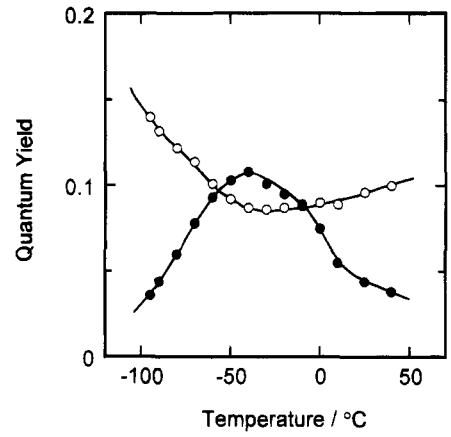

Figure 3. Temperature dependence of the fluorescence quantum yields of monomer emission (○) and excimer emission (●) of NPeC in THF.

be assigned to the excimer fluorescence emission originating from the attractive interaction of an excited naphthyl group with another naphthyl group in the ground state. Both naphthyl chromophores associated with the excimer formation should be considered to be attached onto the same polymer chain of NPeC, since the polymer solution sample is so dilute that the intermolecular excimer formation is virtually negligible. The absence of interactions between naphthyl groups in the ground state and of photoactive impurities was ascertained by measurements of excitation spectra; i.e., the excitation spectra monitored at an arbitrary wavelength ranging from 390 to 470 nm were substantially the same as that for the monomer emission (monitored at 339 nm), and they also agreed well with the absorption spectrum. In Figure 2, it should be noted that the excimer emission band of NPeC is, in fact, blue-shifted by ca. 15 nm, compared with the fluorescence spectra of stable naphthyl excimers such as are formed intramolecularly in poly(vinylnaphthalene) and its model compounds (dinaphthylalkanes) in THF solutions.[11,12] This observation will be discussed later, in relation to the thermodynamic stability of the excimer structure in NPeC.

Figure 3 shows a result of the measurements of the quantum yield of excimer fluorescence (Φ_D) and that of monomer fluorescence (Φ_M), plotted as a function of temperature. To evaluate the quantum yields, the area of each fluorescence spectrum of NPeC was divided into monomer and excimer contributions using a monomer fluorescence spectrum of 1EN as reference. As the temperature is raised to −40 °C, quenching of the monomer emission and accompanying enhancement of the excimer emission are clearly observed. This indicates an increase in frequency of the encounter between an excited naphthyl chromophore and one in the ground state during the lifetime of the excitation. In the temperature region higher than −40 °C, however, the quantum yield Φ_D decreases monotonically with increasing temperature, while Φ_M tends to increase gradually after passing through a minimum at around −30 °C. This observation may be interpreted as due to the increasing importance of the dissociation of excimer once formed, kinetically competing with the association into excimer.

To confirm directly the dynamics of the intramolecular excimer formation in NPeC, time-resolved fluorescence spectra were measured at two representative temperatures: −40 °C, at which a maximal value of the quantum yield ratio Φ_D/Φ_M was obtained, and +25 °C,

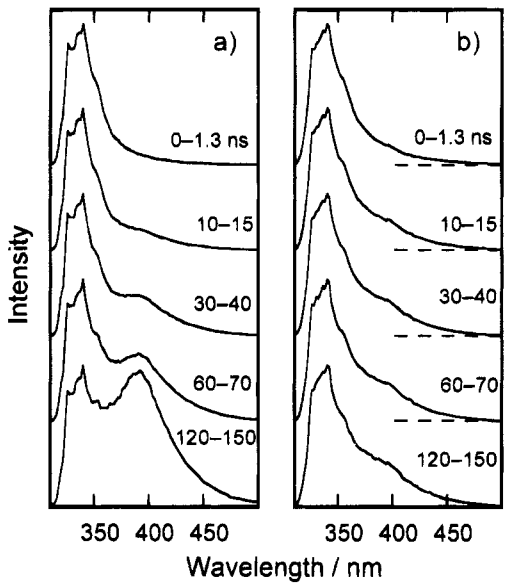

Figure 4. Time-resolved fluorescence spectra of NPeC in THF, measured at (a) −40 and (b) +25 °C. The excitation wavelength is 296 nm, and the bandwidth is 2 nm. Numerals show the observation times in nanosecond units after the time of maximum intensity of the excitation pulse.

at which the apparent efficiency of excimer emission was much lower. The result is shown in Figure 4; here all the spectra are normalized to the same maximum intensity, after accumulation of photon counting over a time period t_1 to t_2 in nanoseconds. Time zero corresponds to the time when the excitation laser pulse shows the maximum intensity. In the data obtained at −40 °C (Figure 4a), we can see a dramatic spectral change with the elapse of time after the pulsed excitation. The marked growth in relative intensity of excimer fluorescence with observation time demonstrates clearly that the initial excited species is in the monomeric state and the excimer is formed via a dynamic process, which is possibly accompanied by only a little conformational rearrangement in an NPeC molecular after photoexcitation, as discussed below. In contrast to the emission behavior at −40 °C, at 25 °C there is less evolution of excimer fluorescence with time after excitation, as can be seen in Figure 4b. The intensity of excimer fluorescence relative to that of monomer fluorescence remains almost constant at any time longer than 15 ns, indicating that the interconversion between the excited monomeric and dimeric states appears to be nearly equilibrium.

Kinetic Treatment and Thermodynamic Data Analysis. The ratio of the quantum yield of excimer fluorescence to that of monomer fluorescence, Φ_D/Φ_M, serves as a measure of an apparent efficiency of excimer formation. To analyze the temperature dependence of Φ_D/Φ_M more quantitatively, we consider a conventional photophysical kinetic scheme involving excimer formation and dissociation processes, as follows:[13]

$$M^* \rightarrow M + h\nu_M \qquad k_M^f$$

$$M^* \rightarrow M + \text{heat} \qquad k_M^n$$

$$M^* + M \rightleftarrows D^* \qquad k_{DM} \text{ (for association)}; \quad k_{MD} \text{ (for dissociation)}$$

$$D^* \rightarrow 2M + h\nu_D \qquad k_D^f$$

$$D^* \rightarrow 2M + \text{heat} \qquad k_D^n$$

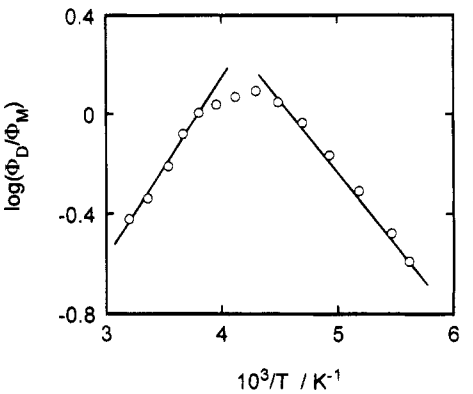

Figure 5. Logarithm plot of the quantum yield ratio Φ_D/Φ_M against the reciprocal of temperature. Two solid lines indicate the slopes in the low- and high-temperature regions.

where M and M* represent the naphthyl chromophore in the ground state and the excited monomeric state, respectively, and D* ≡ (MM)* is the intramolecular excimer. Rate parameters are also indicated in the scheme for each of the corresponding energy dissipation processes.

Through analysis with the steady-state approximation, we can derive a relationship between the quantum yield ratio Φ_D/Φ_M and the rate parameters in the following form.

$$\Phi_D/\Phi_M = (k_D^f/k_M^f)[k_{DM}/(k_D^f + k_D^n + k_{MD})] \qquad (1)$$

At low temperatures where k_{MD} and k_D^n are regarded as negligibly small compared with k_D^f, Φ_D/Φ_M is almost solely determined by the association rate constant k_{DM}, since k_M^f and k_D^f are generally independent of temperature. This may be the case for the temperature dependence of the fluorescence quantum yields observed below −40 °C in Figure 3. Then, eq 1 reduces to

$$\Phi_D/\Phi_M \propto k_{DM} = A \exp(-E_a/RT) \qquad (2)$$

where E_a is the activation energy for the excimer formation, and A and R are the Arrhenius factor and the gas constant, respectively. In the higher temperature region, possibly above −40 °C in Figure 3, the dissociation of excimer becomes conspicuous and therefore the condition $k_{MD} \gg k_D^f + k_D^n$ is satisfied. Then, it can be seen from eq 1 that the temperature dependence of Φ_D/Φ_M is governed mainly by the photodissociation equilibrium constant $K_{eq} = k_{DM}/k_{MD}$, and consequently

$$\Phi_D/\Phi_M \propto K_{eq} = \exp(-\Delta G/RT) \qquad (3)$$

where ΔG is the change of free energy accompanying the excimer formation and satisfies the thermodynamic relation $\Delta G = \Delta H - T\Delta S$ with the enthalpy and entropy changes.

Based on the kinetic treatment described above, the plot of the logarithm of Φ_D/Φ_M versus the reciprocal of absolute temperature ($1/T$) was constructed for the present system, as shown in Figure 5. From the slope in the low-temperature side of the plot, the activation energy E_a for the excimer formation can be evaluated, while the slope in the higher temperature region provides the enthalpy change ΔH accompanying the excimer formation. The values thus obtained were E_a = 2.8 kcal mol^{-1} and ΔH = −3.4 kcal mol^{-1}, and additionally the activation energy (E_d) for the dissocia-

Table 1. Values of Activation Energy (E_a) and Enthalpy Change (ΔH) Estimated for the Excimer Formations of NPeC and Several Other Naphthyl Compounds

compound [solvent][a]	E_a, kcal mol^{-1}	ΔH, kcal mol^{-1}
NPeC [THF]	2.8[b]	−3.4[b]
1-ethylnaphthalene		
[THF]		−4.6[b]
[MTHF]	3.8[c]	−5.8[c]
2-ethylnaphthalene [MTHF]	3.2[d]	−4.5[d]
1-(1-naphthyl)-3-(2-naphthyl)-propane [hexane]	2.0[e]	−2.1[e]
1,3-di-2-naphthylpropane [THF]	5.1[f]	
2,4-di-2-naphthylpentane [THF]	4.8 (*meso* isomer)[f]	
	5.5 (*racemo* isomer)[f]	
poly(2-vinylnaphthalene) [THF]	5.3[g]	

[a] THF = tetrahydrofuran, MTHF = 2-methyltetrahydrofuran. [b] Evaluated in this work. [c] From ref 14. [d] From refs 12 and 15. [e] From refs 12 and 16. [f] From ref 11. [g] From ref 12.

tion of excimer is calculated as $E_d = E_a - \Delta H = 6.2$ kcal mol^{-1}.

In Table 1, the values of E_a and ΔH estimated for the excimer formation in NPeC are compared with the corresponding values for several other naphthyl compounds studied previously by Ito et al.[11,12,14-16] Interestingly, $E_a = 2.8$ kcal mol^{-1} for NPeC is much smaller than the activation energies (4.8−5.5 kcal mol^{-1}) required for the intramolecular excimer formations of poly(2-vinylnaphthalene) (PVN) and its model compounds, dinaphthylalkanes such as 1,3-di-2-naphthylpropane (1,3-DNPr). The E_a value for NPeC is rather close to the corresponding values of 3.2−3.8 kcal mol^{-1} for the intermolecular excimer formation of ethylnaphthalenes (1EN and 2EN) in concentrated solutions, where the association reaction is controlled solely by the translational diffusion of the fluorescent molecules.

It is well established that a symmetrical parallel sandwich arrangement of two aromatic rings with an interplanar spacing of 3−4 Å is the most favorable geometry for a stable excimer, and the diffusion-controlled encounter is, in general, the governing mechanism for the intermolecular formation.[13] In the case of intramolecular excimer formation, the probability of a suitable association should be greatly affected by the configuration and microstructure of the molecules to which fluorescent groups are attached. For the intramolecular excimer formations in diarylalkanes such as diphenyl-[17,18] and dinaphthylalkanes,[15,19] it has been ascertained that the preferred excimer alignment specified above can be achieved when two aromatic groups are separated by three carbon atoms along the alkane chain, as in 1,3-DNPr. Then, the rate of excimer formation is directly controlled by the internal rotations of the skeletal methylene chains. This conformational relaxation process corresponds to the mutual diffusion in the case of intermolecular excimer formation of monomeric fluorescent compounds.

As far as NPeC is concerned, however, it seems difficult to ascribe the primary factor controlling the intramolecular excimer formation to the dynamics of the cellulose backbone with a repeating distance of ca. 5.2 Å between glycosidic linkages, based on the relatively low value of E_a estimated for this polymer. It is more plausible that the excimer interaction is controlled by a little conformational change of C6 side chains with a naphthyl moiety dangling at the individual ends. This situation would require a specific structure of the carbohydrate backbone of NPeC in the equilibrium ground state, in which two adjacent naphthyl chromophores may already be in close proximity to each other; however, the intramolecular excimer formation occurs persistently as a result of a dynamic process, i.e., mutual approaching of the pair of naphthyl groups after photoexcitation of one of the two.

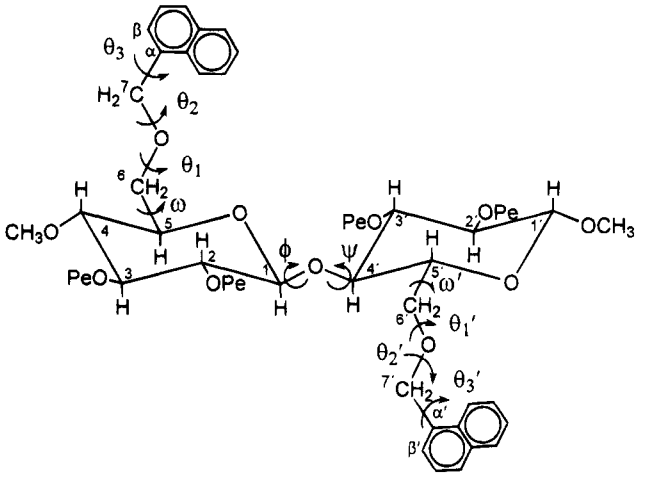

Figure 6. Model disaccharide as the dimeric unit of NPeC, used for conformational energy calculations. Pe = pentyl group. Dihedral angles ϕ, ψ, and ω refer to the rotations about H1C1−O1C4′, C1O1−C4′H4′, and O6C6−C5O5 linkages, respectively, and similarly θ_1, θ_2, and θ_3 denote the rotations about C5C6−O6C7, C6O6−C7Cα, and O6C7−CαCβ, respectively.

From the data of association enthalpy (ΔH) listed in Table 1, it is found that the degree of stability of the NPeC excimer is intermediate between those of ethylnaphthalene excimers ($-\Delta H \geq 4.5$ kcal mol^{-1}) and an unstable excimer formed intramolecularly in 1-(1-naphthyl)-3-(2-naphthyl)propane (αβ-DNPr). In αβ-DNPr, a sandwichlike arrangement is possible, but the axes of the two naphthalene rings never become parallel due to the configurational restriction,[12,19] resulting in quite a small enthalpy gain of 2.1 kcal mol^{-1} in the excimer state. As has often been experienced, fluorescence spectra of such unstable excimers tend to shift to the blue side, compared with those of stable excimers of the corresponding aromatic chromophore. In the fluorescence spectra of NPeC (Figure 2), the wavelength (λ_D^{max}) for the maximum intensity of the excimer emission was ca. 390 nm, as mentioned previously. This wavelength is shorter than $\lambda_D^{max} \cong 405$ nm,[11,15] reported for fluorescence emission from the stable excimers of ethylnaphthalenes and 1,3-DNPr, but longer than $\lambda_D^{max} \cong 375$ nm[12] for the unstable αβ-DNPr excimer. The difference in λ_D^{max} between the different naphthyl compounds may be ascribed to the difference in the binding energy between their excimeric structures. This observation is consistent with the above estimation of the stability of excimer based on the ΔH data. From these results, it is at least reasonable to assume that the sandwich arrangement of two naphthalene rings in the NPeC excimer is not a perfectly overlapped type, although the rings are able to gain access to each other without a high potential barrier.

Molecular Modeling. The most familiar conformational model for unsubstituted cellulosic chains is a flat ribbon structure with 2_1 symmetry,[20,21] in which C5−C6 bonds in individual anhydroglucose residues are placed alternately from side to side along the ribbon composed of a linkage of pyranose rings. NMR spectroscopic studies on a few β-1,4-linked di- and polysaccharides, e.g., methyl β-cellobioside[22] and cellulose

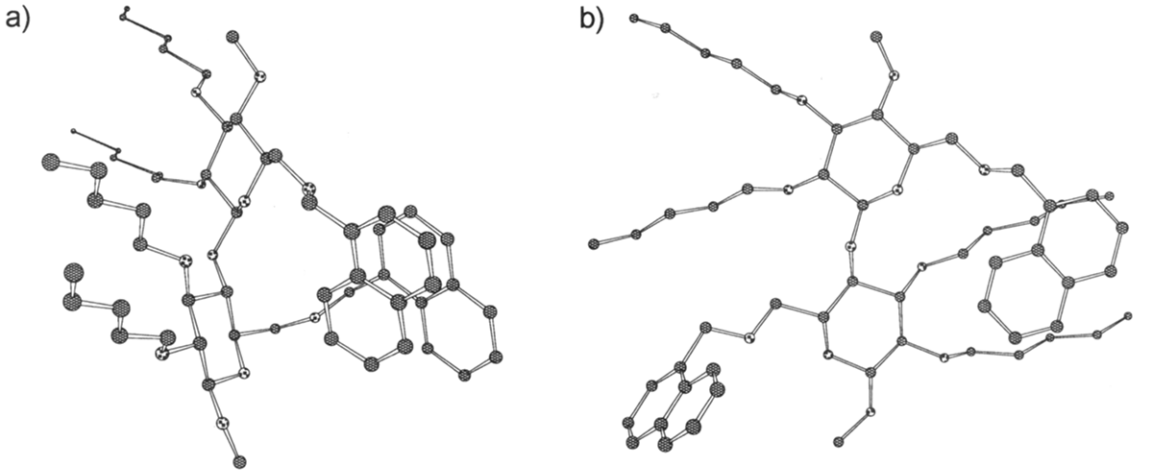

Figure 7. Energy-minimized conformations of the dimeric model of NPeC: (a) twisted form at $(\phi, \psi) = (78.1°, -9.9°)$ and (b) flat ribbonlike form at $(\phi, \psi) = (0.5°, -42.7°)$.

Table 2. Values of Dihedral Angles for Energy-Minimized Conformations of the Dimer Model of NPeC

	dihedral angle, deg									
conformation	ϕ	ψ	ω	θ_1	θ_2	θ_3	ω'	θ_1'	θ_2'	θ_3'
twisted[a]	78.1	−9.9	68.5	−159.4	−169.4	113.9	−63.2	−154.4	167.5	−96.4
flat ribbonlike[b]	0.5	−42.7	61.5	−167.0	180.0	−67.7	54.9	175.7	175.4	−110.9

[a] Corresponding to Figure 7a. [b] Corresponding to Figure 7b.

triacetate,[23] have suggested that such a ribbonlike structure may be substantially maintained even in solution state. On the other hand, recent studies[21,24] with X-ray diffractometry in combination with conformational analysis have indicated a general tendency in which cellulose derivatives with relatively bulky substituents prefer a helical chain conformation with n-fold ($n \geq 3$) screw symmetry at least in their crystalline state.

In the present system, the flat ribbon-type of conformation would be inapplicable to the cellulose derivative molecule NPeC, because the antiparallel orientation of the C5−C6 and C5′−C6′ bonds anchoring on adjacent pyranose rings should prevent two naphthyl chromophores from standing face to face with each other at a distance of less than 4 Å. To deduce a more preferable conformation of NPeC, molecular force-field calculations were performed for a model disaccharide whose structural formula is depicted in Figure 6. In this model compound, the hydroxyl groups at the reductive and nonreductive ends of the original cellobiose unit are replaced by methoxyl groups. The relative orientation of the two glucopyranose units, which were taken to remain the usual $^4C_1$ chair conformation, can be represented by two dihedral angles ϕ and ψ. Each angle is defined in terms of a sequence of four atoms and refers to a rotation of a bond vector connecting the 3rd and 4th atoms relative to another bond vector connecting the 1st and 2nd atoms, around the middle bond. If the rotation is clockwise when viewed from the 2nd to the 3rd atom, it is defined to be of positive sense and the rotational angle (ϕ or ψ) is also positive.[25] For this model compound, the angular alignment of $(\phi, \psi) = (0°, 0°)$ denotes that the bonds C1−H1 and C4′−H4′ are *cis* to O1−C4′ and O1−C1, respectively.

The dimer model has a number of rotatable bonds, and hence suitable sets of initial conformations were prerequisite to finding out the stable molecular form. Three initial sets of the rotational angles of ϕ and ψ, $(\phi, \psi) = (52.7°, 12.7°)$, $(88.6°, 48.5°)$, and $(149.2°, 13.9°)$, were picked from the corresponding values for several energy-minimized structures constructed preliminarily for a permethylated cellobiose. The pentyl side-chain conformation was set equal to *all-trans*, but a slight deformation was noted inherent in the refined energy minimization for the model disaccharide. The conformation of an O6C6−C5O5 sequence, which is designated by a dihedral angle ω in Figure 6, was initially assumed to be either of two possible *gauche* states.[26] (The angle ω is taken as 0° in the *cis* conformation.) It follows that the interrelation in conformation around a C5−C6 bond between the two atomic sequences, O6C6−C5O5 and O6C6−C5C4, can be expressed as *gg* or *gt* in terms of conventional character codes; *g* indicates a *gauche* and *t* a *trans* conformation. The conformations around the other rotatable bonds of the C6 side chain, designated as C5C6−O6C7, C6O6−C7Cα, and O6C7−CαCβ in Figure 6, were specified by dihedral angles θ_1, θ_2, and θ_3, respectively. The angles θ_1 and θ_2 were initially taken as 180°, indicating a *trans* conformational state of the corresponding bond sequences, and the initial value of θ_3 was set at +90° or −90°. Thus, we treated 48 initial conformations in the combinations of three pairs of dihedral angles (ϕ, ψ), (ω, ω'), and (θ_3, θ_3'), and found two different types of spatial arrangement of the glucopyranose units for the model disaccharide by energy minimization. The most stable conformation in each type is depicted in Figure 7, and the details of the rotational angles of the main chain and C6 and C6′ side chains are summarized in Table 2.

In a molecular form given in Figure 7a, the dihedral angles around the glycosidic linkage were calculated as $(\phi, \psi) = (78.1°, -9.9°)$. This angular alignment gives rise to a definitely "twisted" structure between the pyranose rings. The conformational states around the C5−C6 and C5′−C6′ bonds are *gt* ($\omega = 68.5°$) and *gg* ($\omega' = -63.2°$), respectively. The two naphthalene moieties locate close to each other at an interplanar distance of about 4 Å. In the other stable conformation shown in Figure 7b, the dihedral angles ϕ and ψ are 0.5° and −42.7°, respectively, and the conformational states around the C5−C6 and C5′−C6′ bonds are both *gt* (see Table 2). In this alignment, the two pyranose

rings construct a so-called flat ribbon structure, but steric interactions between the bulky substituents (−Pe's and $-CH_2Naph$) caused some extent of deviation from the usual type[21] adopted as a crystalline conformation of the cellulose backbone.

Comparing the total potential energy between the two structural forms shown in Figure 7, the flat ribbon form was, in fact, slightly more stable than the twisted one; however, the energy difference was only 0.6 kcal mol^{-1}, which is small enough to allow the twisted form as a sterically permissible conformation. The result of the fluorescence measurements indicated that the intramolecular excimer interaction in NPeC may be controlled primarily by a little conformational transition of C6 side chains. Overlapping of two adjacent naphthyl rings with an interspacing of less than 4 Å, essential to excimer formation, via a short-range approaching process can be fulfilled in such a twisted structure of the carbohydrate backbone as demonstrated in Figure 7a for the model disaccharide.

Conclusions

The fluorescence emission behavior and molecular structure of a cellulose derivative, 6-O-α-(1-naphthylmethyl)-2,3-di-O-pentylcellulose (NPeC), in dilute solution were investigated. The major conclusions to be drawn from the results of this study are summarized as follows.

The cellulose derivative NPeC forms a naphthyl excimer intramolecularly via a dynamic process accompanied by some local conformational rearrangement after photoexcitation: From the estimation of a considerably low activation energy (E_a = 2.8 kcal mol^{-1}), it can be deduced that the intramolecular excimer formation is attained by short-range approaching of two adjacent naphthyl chromophores; i.e., they are originally allowed to be in fairly close vicinity to each other, owing to a specific structure of the cellulose backbone. From the estimation of a relatively small enthalpy gain (ΔH = −3.4 kcal mol^{-1}) and the observation of somewhat blue-shifted spectra of the excimer emission, compared with the case for other stable naphthyl excimers, it can be deduced that the sandwich arrangement of two naphthalene rings in the excimer state of NPeC is not a perfectly overlapped type.

In the molecular force-field calculations performed on a model compound as the dimeric unit of NPeC, a sterically stable, "twisted" type of conformation was found out, which permits close contact of two naphthyl chromophores. By the combined use of this result of the conformational analysis and that of the fluorescence measurements, it seems reasonable to assume that the cellulose backbone of NPeC prefers to assume a twisted structure in the solution state.

References and Notes

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