Long-lived room temperature phosphorescence of a naphthalene—β-cyclodextrin—adamantane complex in the presence of oxygen

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Naphthalene-d_8—β-cyclodextrin—adamantane triple complexes were prepared in an aqueous solution at room temperature. Irradiation (λ = 285 nm) of the solution in the presence of molecular oxygen results in the long-lived (τ = 10.3 s) room temperature phosphorescence (RTP). The removal of oxygen from the solution increases the RTP intensity and phosphorescence lifetime by 1.5 times. The RTP spectrum contains a well-resolved vibrational structure, whose bands are assigned to full symmetric vibrations of naphthalene, their overtones, and the combination tones of full symmetric vibrations. The quantum-chemical calculation of the triple complex structure confirms that both naphthalene and adamantane can simultaneously be included into the β-cyclodextrin cavity and suggests that the role of the latter as the third component is the more efficient shielding of naphthalene from the oxygen effect due to both the formation of three-component complexes and their aggregation to form submicronic particles.

Key words: room temperature phosphorescence, absorption spectra, cyclodextrin—naphthalene—adamantane and cyclodextrin—naphthalene—cyclohexane triple complexes, quantum-chemical calculations.

The problem of development of organic systems with long-lived phosphorescence under standard conditions is far from being optimally solved. Our recent studies are aimed at searching for molecular organized systems of the host—guest type among arene—cyclodextrin (CD)—hydrocarbon triple complexes, which are characterized by long-lived room temperature phosphorescence (RTP). These systems are of theoretical and practical interest because the inclusion of a substrate into the CD cavity cannot easily and reliably be detected. In triple complexes of the considered type, the arene molecule acts as a "reporter" because the appearance of RTP unambiguously indicates the inclusion of the third component into the arene—CD binary complex. Many arenes are characterized by long lifetimes of phosphorescence. However, no RTP of arenes is observed, as a rule, in liquid solutions.[1] Long-lived phosphorescence requires the absence of phosphorescence quenchers, first of all, dissolved oxygen, in the solution to occur. The presence of dissolved oxygen results in quenching of the T_1 state of arene due to the exchange-resonance interaction from the arene to oxygen upon their interaction due to diffusion. Long-lived phosphorescence of arenes is observed in the case of rigid matrices, *e.g.*, boric acid or frozen solutions, when triplet arene molecules and quenchers cannot collide.

Molecular organized systems, in particular, host—guest inclusion complexes, provide new opportunities for observation of long-lived RTP of arenes. The use of β-cyclodextrin (βCD) as a "host," which is a cyclic compound whose shape resembles a basketball hoop with a large inner cavity (diameter ~8 Å), and arenes, *viz.*, acenaphthene, naphthalene (Naph), phenanthrene, fluorene, and their derivatives, as "guests" makes it possible to observe[2—8] RTP of these complexes in aqueous solutions when two conditions are fulfilled: (a) the third compound, whose role remains yet unclear, is added to the binary complex, and (b) molecular oxygen is removed from the sample. The longest phosphorescence (16.6 s) was observed[8] for the Naph-d_8—βCD—cyclohexane (CHex) triple complex at 284 K after oxygen was chemically eliminated from in the solution. Compounds containing heavy atoms were used as the third component in several works, but the phosphorescence lifetimes amounted to milliseconds.[2]

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To explain the effect of the third component, we calculated computer models of the Naph—βCD—CHex complex by the semiempirical quantum-chemical PM3 method. Analysis of the computer models showed[8] that after the formation of the Naph—βCD binary complex, the broad part of βCD remains large enough for inclusion of the third molecule, in particular, CHex. It turned out that CHex has the binding energy with βCD (E_{bind}) comparable with that of Naph, which favors the formation of a triple complex.[9] Accepting that the molecular volume plays a determining role in providing high E_{bind} for the third component, we assumed that adamantane (Ad), being more bulky than CHex to insert into the CD cavity where arene is already situated, should more efficiently shield arene from the interaction with O_2. The preliminary checking showed that the Naph-d_8—βCD—Ad triple complex exhibits long-lived RTP, which does not need the removal of oxygen from the solution to occur.

In this work, we studied the phosphorescence of the Naph—βCD—Ad and Naph-d_8—βCD—Ad triple complexes at room and lowered temperatures and compared the results with the previously published data[8] on RTP of the Naph—βCD—CHex complexes. The structural parameters were calculated by the semiempirical quantum-chemical PM3 method. Since only the arene complexes characterized by the lifetimes of excited states ≥2 s were studied in this work, triple complexes containing heavy atoms were not considered.

Experimental

Naphthalene and its deuterated analog Naph-d_8 were used as "guests" for the complexes with βCD. Compounds were purified by recrystallization, and the purity was monitored by absorption and luminescence spectra. β-Cyclodextrin (Cyclolab, Hungary) was used without additional purification. Twice distilled water was used as the solvent. Adamantane was purified by sublimation *in vacuo* before experiments.

Preparation of complexes. Procedures for preparation of the triple complexes and measurements have been described previously.[10] Since adamantane is much more poorly soluble in water than CHex, the preparation procedure was somewhat changed. A preliminarily prepared aqueous solution of the Naph—βCD or Naph-d_8—βCD complex (concentrations $1 \cdot 10^{-4}$ and $5 \cdot 10^{-3}$ mol L^{-1}, respectively)* was poured in a quartz tube. The walls of the tube were covered with a thin layer of adamantane (prepared by evaporation of a solution in hexane), so that its concentration in the resulting solution was $1 \cdot 10^{-2}$ mol L^{-1}. A sealed tube with the solution was placed for 1 h in a water bath at 50 °C, and then the bath was slowly cooled to ~20 °C. The solution was periodically shaken. As a result, the solution became turbid due to the aggregation and crystallization of the formed triple complexes and βCD molecules. The RTP was observed in the formed aqueous suspension in which submicronic particles containing the Naph—βCD—Ad complexes were phosphorescence centers. Since the initial concentration of Ad exceeded the Naph concentration by ~2 orders of magnitude, we can believe that the aggregates contained ~100 Ad—βCD complexes per the triple complex.

Absorption and fluorescence spectra were recorded on a Specord M-40 spectrophotometer and an Elumin-2M spectrofluorimeter. Both instruments were attached to IBM personal computers, which provided recording and primary processing of spectra. The device for measuring lifetimes used previously[8] was modified. The number of discrete levels of the signal was brought to 1024, and the signal of fluorescence decay consisting of 350 experimental points was processed on an IBM PC using a program developed by one of the authors. The obtained luminescence spectra are shown in Fig. 1, and the frequencies in maxima are presented in Table 1.

Calculation procedures. Semiempirical quantum-chemical calculations of the substrate molecules (Naph, CHex, Ad), the 1 : 1 inclusion complexes with βCD, and the Naph—βCD—CHex and Naph—βCD—Ad triple complexes were performed by the MNDO/PM3 method (hereinafter PM3) with the standard set of parameters[12] using the PC GAMESS-99 program package.[13] The previously full-optimized structure close to the global minimum was used as the starting βCD molecule. Its heat of formation ΔH_{f} is −1468.4 kcal mol^{-1}.[14] The molecule has the C_7 symmetry and is stabilized by intramolecular O(2)—H...O(3′) hydrogen bonds between the secondary OH groups of the broad part of the cavity. The OH groups in position 2 of one glucose unit are proton donors, and the O atoms of the OH groups in position 3′ of the adjacent glucose unit are proton acceptors. The formation of inclusion compounds is characterized[15] by three types of energy: the total energy of interaction ΔE_{tot}, the binding energy ΔE_{bind}, and the perturbation energy of components ΔE_{pert}. The ΔE_{tot} values were calculated as differences between the heats of formation ΔH_{f} of the full-optimized complexes and the sum of ΔH_{f} of the full-optimized substrate molecules. The ΔE_{bind} values were obtained from ΔE_{tot} by subtraction of the sum of the ΔH_{f} values of the components of the complexes calculated with the same structural parameters, which they have in the complexes. The ΔE_{bind} values are the sum of

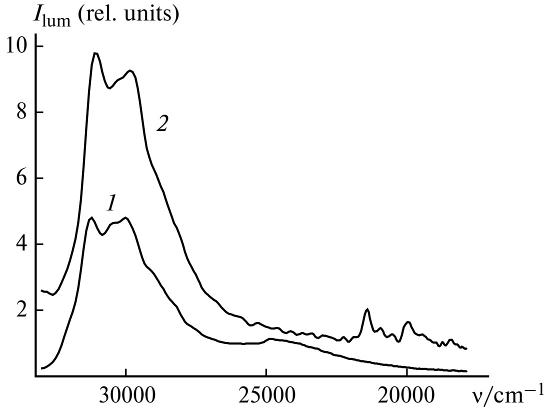

Fig. 1. Luminescence spectrum of the naphthalene-d_8—β-cyclodextrin complex at 293 K in the absence (*1*) and after addition of adamantane (*2*).

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* As known, naphthalene is rather volatile, therefore, its real concentration somewhat differed from the calculated value and its exact value was determined from the absorption spectra of solutions of the binary complexes.

Table 1. Experimental frequencies of transitions (ν/cm^{-1}) in the phosphorescence spectra of naphthalene and naphthalene-d_8 and assignments of vibrational satellites in the phosphorescene spectra

Number of band	Naph-d_8—βCD—CHex		Naph-d_8—βCD—Ad		Naph-h_8—βCD—Ad		Type of symmetry, assignment
	ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$	
1	21302	0—0	21430	0—0	21301	0—0	0—0
2	—	—	21142	—	—	—	—
3	20806	496 (495)	20947	483 (495)	20793	508 (512)	A_{1g}, ν_9
4	20486	816 (833)	20609	821 (833)	20297	1004 (1025)	A_{1g}, ν_7
5	20323	979	—	—	—	—	A_{1g}, $2\nu_9$
6	—	—	—	—	20161	1140 (1145)	A_{1g}, ν_6
7	19931	1371 (1383)	20054	1376 (1383)	—	—	A_{1g}, ν_4
8	—	—	—	—	19932	1369 (1376)	A_{1g}, ν_5
9	19754	1548 (1550)	19888	1542 (1550)	19737	1564 (1577)	A_{1g}, ν_3
10	19448	1854 (1878)	19574	1856 (1878)	—	—	A_{1g}, $\nu_9 + \nu_4$
11	—	—	—	—	19419	1882 (1888)	A_{1g}, $\nu_9 + \nu_5$
12	19277	2025 (2045)	19407	2023 (2045)	19226	2075 (2089)	A_{1g}, $\nu_9 + \nu_3$
13	19123	2179	19225	2205	—	—	A_{1g}, $\nu_7 + \nu_4$
14	—	—	—	—	18988	2313 (2335)	A_{1g}, $\nu_8 + \nu_3$
15	—	—	—	—	18931	2370 (2391)	A_{1g}, $\nu_5 + \nu_7$
16	18933	2369 (2373)	19063	2367 (2373)	—	—	A_{1g}, $\nu_4 + 2\nu_9$
17	—	—	—	—	18776	2525 (2541)	A_{1g}, $\nu_7 + 2\nu_8$
18	18573	2729	18672	2758 (2766)	—	—	A_{1g}, $2\nu_4$
19	—	—	—	—	18576	2725 (2752)	A_{1g}, $2\nu_5$
20	—	—	—	—	18363	2938 (2976)	A_{1g}, $\nu_4 + 2\nu_8$
21	18406	2896 (2933)	18500	2930 (2933)	—	—	A_{1g}, $\nu_3 + \nu_4$
22	18226	3076 (3100)	18337	3093 (3100)	—	—	A_{1g}, $2\nu_3$
23	18087	3215 (3278)	—	—	—	—	A_{1g}, $\nu_3 + 2\nu_6$
24	17924	3378	—	—	—	—	A_{1g}, $\nu_3 + \nu_4 + \nu_9$
25	17727	3575	—	—	—	—	A_{1g}, $2\nu_3 + \nu_9$
26	17586	3716	—	—	—	—	A_{1g}, $\nu_3 + \nu_4 + \nu_7$
27	17418	3884 (3843)	—	—	—	—	A_{1g}, $\nu_1 + \nu_3$
28	17214	4088	—	—	—	—	
29	17044	4258	—	—	—	—	
30	16867	4435	—	—	—	—	
31	16698	4604 (4586)	—	—	—	—	A_{1g}, $2\nu_1$

Note. Experimental vibrational frequencies[11] of Naph and Naph-d_8 are given in parentheses.

the electrostatic and van der Waals energies. The difference $\Delta E_{\text{tot}} - \Delta E_{\text{bind}} = \Delta E_{\text{pert}}$ characterizes the energy of perturbation of the components. Since complexation is energetically favorable, the ΔE_{tot} and ΔE_{bind} values are negative, while ΔE_{pert} is positive. The ΔE_{tot}, ΔE_{bind}, and ΔE_{pert} are presented in Table 2. The structures of the Naph—βCD—Ad and Naph—βCD—CHex triple complexes are shown below.

Results and Discussion

RTP spectra of triple complexes. The luminescence spectrum of the Naph-d_8—βCD complex in water at 293 K (spectral pattern *1*) is presented in Fig. 1. The spectrum clearly represents excimer fluorescence at 24000 cm^{-1} along with fluorescence at 30000 cm^{-1}. After Ad was added to the binary complex, the excimer fluorescence disappeared from the spectrum, the intensity of monomeric fluorescence increased at 30000 cm^{-1}, and RTP bands appeared at $\nu < 22000$ cm^{-1}, although oxygen was not removed from the sample (pattern *2*). The changes in the luminescence spectrum of the solution are likely caused by the formation of the Naph-d_8—βCD—Ad triple complex.

The equilibrium constant of the reaction Ad + Naph-d_8—βCD → Naph-d_8—βCD—Ad was calculated from the change in the RTP fluorescence at 21400 cm^{-1} with a change in the concentration of Ad in the triple complex and amounted to 680 L mol^{-1}. The addition of sodium sulfite to the sample containing the triple complex in order to chemically bind dioxygen increases the amplitude of the RTP signal by 1.5 times and the RTP lifetime from 10.3 to 15.5 s. In the presence of dioxygen, the RTP of the Naph—βCD—Ad complex was also observed, but the increase in the signal amplitude and RTP lifetime after chemical elimination of dioxygen was at most 10%.

The efficiency of Ad introduction to obtain the long-lived RTP of the triple complex was estimated from the

Table 2. Heats of formation (ΔH_f) and binding energies (ΔE_{bind}) of the complexes and isolated molecules calculated by the PM3 method

Compound or complex	$-\Delta H_f$	$-\Sigma(\Delta H_f)_c{}^a$	$-\Delta E_{tot}{}^b$	$-\Delta E_{bind}$	ΔE
	kcal mol^{-1}				
βCD	1468.4	—	—	—	—
2βCD	2949.1	2936.8	12.6^c	—	—
Cyclohexane	31.0	—	—	—	—
Adamantane	35.0	—	—	—	—
Naphthalene	–40.7	—	—	—	—
βCD—Naph	1440.1	1427.7	12.4	—	—
βCD—CHex	1510.0	1499.4	10.6	—	—
βCD—Ad	1522.0	1503.4	18.6	—	—
βCD—Naph—CHex	1469.6	1458.7	10.9	55.1	1.5^d
		(1414.5)^e			(44.2)^f
βCD—Naph—Ad	1500.7	1462.7	38.3	52.1	25.6^d
		(1448.6)^e			(13.8)^f
2βCD—Naph—CHex	2963.5	2939.4	24.9^g	—	23.9^h
2βCD—Naph—Ad	2973.5	2943.4	30.1^g	—	2.0^h

[a] Sum of contributions from different components.

[b] Energy of formation of the binary and triple complexes.

[c] Energy of dimerization of βCD.

[d] Energy of inclusion of the third particle into the binary complex.

[e] Sum of ΔH_f of the components of the triple complexes perturbed due to complexation.

[f] Energy of perturbation of the components of the triple complexes is presented in parentheses.

[g] Energy of inclusion of the substrates into the βCD dimer.

[h] Energy of "closure" of the three-component complexes by the second βCD molecule.

presented data on the lifetimes. As previously,[16] we assume that the lifetimes of RTP in the presence of dioxygen (τ_1) and after its binding (τ_2) can be presented by the expressions

$$1/\tau_1 = k_{ph} + k_{nr} + k_q[O_2]$$

and

$$1/\tau_2 = k_{ph} + k_{nr} + \alpha k_q[O_2], \qquad (1)$$

where k_{ph} and k_{nr} are the rate constants of radiative and nonradiative transitions, respectively; k_q is the rate constant of phosphorescence quenching by dioxygen, and $\alpha \ll 1$ characterizes the efficiency of chemical binding of dioxygen dissolved in water. A simple transformation of Eqs. (1) gives the formula

$$1/\tau_1 - 1/\tau_2 = k_q(1 - \alpha)[O_2] \approx k_q[O_2]$$

and

$$k_q \approx (1/\tau_1 - 1/\tau_2)/[O_2]. \qquad (2)$$

After substitution of the reference value[17] $[O_2] = 2.9 \cdot 10^{-4}$ mol L^{-1} and lifetimes $\tau_1 = 10.3$ s and $\tau_2 = 15.5$ s, we obtain $k_q \approx 112$ L mol^{-1} s^{-1}. Thus, the rate constant of phosphorescence quenching by dioxygen was an order of magnitude lower than $k_q \approx 1000$ L mol^{-1} s^{-1} obtained[16] for the Naph-d$_8$—βCD—CHex complex. This explains why RTP can be observed in the Naph-d$_8$—βCD—Ad complex in the presence of dioxygen.

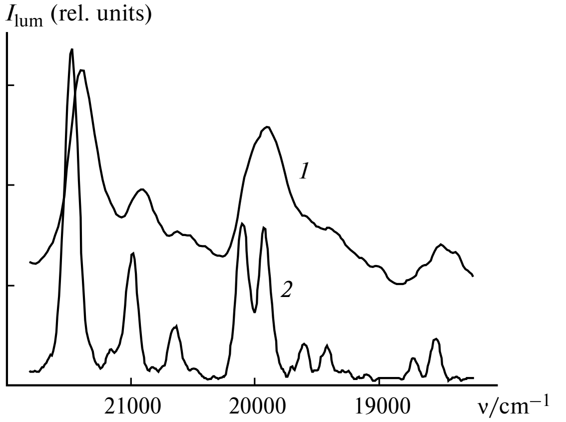

Fig. 2. Phosphorescence of the naphthalene-d$_8$—β-cyclodextrin—adamantane complex (concentrations $1 \cdot 10^{-4}$, $5 \cdot 10^{-3}$, and $1 \cdot 10^{-2}$ mol L^{-1}, respectively) at 293 (*1*) and 77 K (*2*).

Interpretation of the RTP spectrum. The RTP spectrum of the Naph-d$_8$—βCD—Ad complex contains the pronounced vibrational structure in addition to the most intense band of the 0—0-transition, which can be seen by a comparison of the spectra of the same sample detected at 293 and 77 K (Fig. 2). The frequencies in maxima of the phosphorescence bands measured at 77 K are presented in Table 1. A comparison of the frequencies of vibrational transitions in the RTP spectra of the Naph—βCD—Ad and Naph-d$_8$—βCD—Ad complexes shows that deuteration results in the red shift of the bands in the spectrum of the latter due to the substitution of the H atoms by the D atoms. Analysis of the values $\Delta\nu = \nu_{0-0} - \nu_i$ allowed us to assign the observed bands of vibrational transitions to full symmetric vibrations, their overtones, and the combination tones of full symmetric vibrations of the A$_1$ type of the Naph and Naph-d$_8$ molecules.[11] The shifts of the bands due to deuteration confirm this conclusion. We ascribe the appearance of vibrations of the A$_1$ type only in the phosphorescence spectrum to the fact that the Naph molecule can easily be placed in the cavity and weakly interacts with the βCD walls without a loss of high symmetry (D_{2h}), which is inherent in this molecule in the free state. The calculated structure of the triple complex also shows that the Naph molecule retains the planar conformation. However, the conclusion about the retention of symmetry of Naph in the cavity needs to be verified by a more sensitive method, for example, the Raman spectroscopy.

Structure of complexes and complex formation energy. The data presented indicate that in the aggregated

Naph—βCD—Ad triple complexes the phosphorescence centers are most efficiently shielded from the attack of dissolved molecular oxygen. This could not be achieved by the addition of other saturated hydrocarbons, such as CHex or isooctane. To reveal the mechanism of appearance of the long-lived RTP, one has to clarify the role of the third component in the complexes, because in the arene—βCD binary complexes no RTP virtually occurs even after the removal of oxygen from the sample, which fact was confirmed by numerical experiments. Since the RTP is observed for the aggregated complexes, we can assume that two types of species are the structural units of these aggregates: Naph—Ad—βCD three-component complexes and Naph—βCD—CHex and/or βCD—Naph—Ad—βCD and βCD—Naph—CHex—βCD complexes. In these complexes, both substrates are placed in the cavity of the βCD dimer as "head-to-head," and the energy of formation of this dimer is rather high.**14** We performed calculations for the complexes of both types. The Naph—βCD, Ad—βCD, and CHex—βCD binary complexes were also calculated for comparison. As can be seen from the data in Table 2, the highest binding energy is inherent in the Ad—βCD complex with such an orientation of the Ad molecule that the C—H tertiary bond is almost perpendicular to the C_7 axis of βCD (Fig. 3). The E_{bind} value obtained by us agrees satisfactorily with the mean energy of complexation for bromoadamantane with βCD (~15.0 kcal mol^{-1}), which has been calculated previously**18** by the molecular mechanics method with MM3 parametrization. As the structures of the triple complexes show (see Fig. 3), the third molecule can always occupy, in fact, a free site remained in the broad part of the cavity after Naph was inserted.

The inclusion of Ad as the third component is characterized by a higher binding energy E_{bind} (−25.6 kcal mol^{-1}) and is accompanied by a lower perturbation of the structures of the all three components, which is expressed in the minimum perturbation energy (13.8 kcal mol^{-1}) compared to that for the Naph—βCD—CHex (see Table 2). The stick models show that in the Naph—βCD—CHex complex the bottom, narrower part of βCD more tightly embraces the Naph molecule than in the Naph—βCD—Ad complex. This is expressed in the fact that the cone of the "basket" of the first complex is more pronounced than that of the second complex. However, in any case, embracing of the Naph molecule by the narrow bottom part of βCD prevents its expulsion by the third particle and prevents Naph from direct collisions from the bottom. The spherical models (see Fig. 3) show that the Ad molecule closes the top part of the cavity more tightly than CHex, favoring a greater prevention of Naph from external effects.

Comparison of the RTP spectra of the Naph—βCD—Ad and Naph—βCD—CHex triple com-

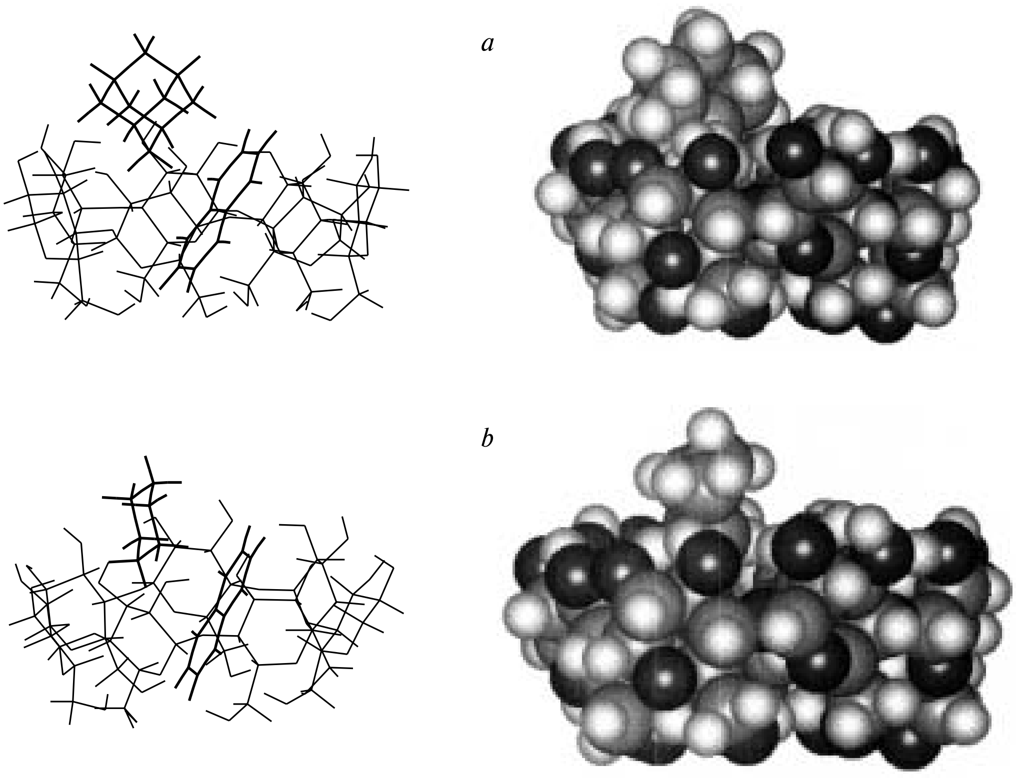

Fig. 3. Stick and volume models of structures of the Naph—βCD—Ad (*a*) and Naph—βCD—CHex (*b*) triple complexes calculated by the PM3 method.

plexes[19] at 77 K shows that the spectrum of the latter is characterized by narrower bands and a smaller Stokes shift. We attribute this fact to the tighter embracing of the substrate by the bottom part of CD in the Naph—βCD—CHex triple complex than in the Naph—βCD—Ad complex. As a result, the Naph molecule in the complex with CHex is in a more "rigid" environment than that in the Naph—βCD—Ad complex. The latter decreases the non-homogeneous spectrum-line broadening and is energetically manifested in a higher energy of perturbation of the components (see Table 2, $E_{\text{pert}} = 44.2$ and 13.8 kcal mol^{-1}) for the formation of the Naph—βCD—CHex complex than for the Naph—βCD—Ad complex formation.

Calculation of the complexes of the second type shows that they also exist. In these complexes, a pair of components, *viz*., Ad and Naph or CHex and Naph, are included into the "head-to-head" βCD dimer, so that each of them is situated in the cavity of its "own" βCD. The energy of formation of these complexes was calculated by two methods: as the energy of inclusion of the pair of isolated components into the dimer ($^1\Delta E_{\text{tot}}$) or as the energy of "closure" of the three-component complex with the "cap" of the free βCD molecule ($^2\Delta E_{\text{tot}}$). As can be seen from the data in Table 2, for the βCD—Naph—CHex—βCD and βCD—Naph—Ad—βCD complexes, both $^1\Delta E_{\text{tot}}$ values are approximately of the same order of magnitude, and $^1\Delta E_{\text{tot}}$ for the Naph—βCD—Ad complex is only by ~5 kcal mol^{-1} higher than that for the Naph—βCD—CHex complex. On the contrary, $^2\Delta E_{\text{tot}}$ for the Naph—βCD—CHex complex is by an order of magnitude higher than that for the Naph—βCD—Ad complex. These data can be interpreted as follows. First, the behavior of Ad and CHex as the third components differ substantially, but this is not consistent with the small difference in $^1\Delta E_{\text{tot}}$. Hence, the complexes βCD—Naph—CHex—βCD or βCD—Naph—Ad—βCD can hardly be RTP centers in the aggregates. Second, a rather low $^2\Delta E_{\text{tot}}$ value for the βCD—Naph—Ad—βCD complex implies that the Naph—βCD—Ad triple complex, unlike Naph—βCD—CHex, is not likely prone to add the second βCD molecule. Based on these facts, we concluded that the triple complexes are the RTP centers in the aggregates.

Thus, at the chosen concentrations of the components, the Naph—βCD two-component complex can has a composition of 1 : 1 and 2 : 2, which follows from the observed luminescence spectrum (see Fig. 1). The 2 : 2 composition corresponds to the structure of the βCD dimer, whose cavity contains two Naph molecules exhibiting the excimer fluorescence with a maximum at 25000 cm^{-1}.[10,20] The addition of the third component, *viz*., Ad or CHex, affords (a) triple complexes from the 1 : 1 complexes when Ad or CHex is inserted, (b) triple complexes from the decomposed 2 : 2 complexes, and (c) many Ad—βCD or CHex—βCD binary complexes, which produce aggregates from these complexes and result in their precipitation as microparticles from an aqueous solution. These microparticles contain ~1% triple complexes responsible for the appearance of RTP. The formation of microparticles is a condition for the long-lived RTP.[21] The structure and size of the aggregates are presently being refined. Note that our calculation ignores the solvent effect and does not show the structure and sizes of the aggregates. Therefore, the data on the geometry and high stability of the complex are insufficient for understanding the mechanism of the third component effect.

Role of the third component in the appearance of RTP. To explain the role of Ad in the appearance of RTP in the presence of oxygen, let us compare the following facts. There are two types of aggregates consisting mainly of the βCD—CHex and βCD—Ad binary complexes and containing ~1% triple complexes, *viz*., Naph—βCD—CHex and Naph—βCD—Ad, respectively, of the number of the binary complexes. The both aggregates contain dioxygen. In the first case, oxygen should be removed to observe RTP, and in the second case, it should not be removed. As follows from the calculation, the three-component complexes act as RTP centers in the aggregates. The difference between them is that Ad more tightly than CHex closes the broad (upper) part of the cavity due to the higher binding energy. In addition, Ad jumps out above the upper cut of the cavity to a greater extent than CHex. Therefore, being, in addition, more poorly soluble in water than CHex, Ad forms more compact aggregates in which diffusion of oxygen and its accessibility to the Naph molecule are more hindered than in the aggregates of the Naph—βCD—CHex triple complexes.

A large volume of the third component, which more reliably protects Naph from dioxygen in the triple complexes, is necessary but insufficient condition for RTP observation. We found that the replacement of Ad by its structural analog urotropin (Ur), which is highly soluble in water and its addition to the system does not change the absorption and luminescence spectra of the Naph-d$_8$—βCD complex: the excimer fluorescence retains and no RTP is observed after dioxygen eliminating. This means that the presence of Ur does not produce a sufficiently stable Naph-d$_8$—βCD—Ur triple complex, whose formation could result in the appearance of RTP. In addition, a solution of the Naph-d$_8$—βCD binary complex remains transparent after addition of Ur. Therefore, no bulky aggregates necessary for the appearance of the long-lived RTP are formed in the presence of Ur.[21]

Several conclusions can be drawn from the data obtained. First, the RTP can appear only when the third component is presented by compounds with the lowest solubility in water, thus favoring the aggregation of the triple complexes to larger particles. Second, the volume of the third component should be large enough to obtain a high binding constant of the third component with the Naph—βCD binary complex and to prevent most reliably Naph from collisions with dioxygen molecules in the broad part of the cavity. In this respect, as with respect to the low solubility in water, Ad excels all liquid hydrocarbons used previously, including CHex and isooctane.

The third conclusion is that the aggregates containing the triple complexes should be sufficiently dense to impede diffusion of molecular oxygen in the aggregates. Their structure and density should not allow dioxygen molecule to approach the arene molecule at a distance necessary for phosphorescence quenching for the lifetime of the Naph molecule in the excited triplet state.

The use of Naph-d_8 as arene, whose lifetime is ~20 s in frozen solutions, imposes the greatest requirements on the molecular organized system for observation of the long-lived RTP in the presence of oxygen. Presently, among the CD-based systems, only the Naph-d_8—βCD—Ad aggregated complex satisfies these requirements.

Thus, the RTP with a lifetime of 10.3 s was observed for the first time in the molecular organized system based on the Naph-d_8—βCD—Ad complex at 293 K in the presence of oxygen. This result shows that molecules can efficiently be isolated, in principle, from the oxygen effect in the molecular organized system based on complexes of these molecules with cyclodextrins.

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