Excimer fluorescence and structures of the inclusion complexes of β-cyclodextrin with naphthalene and its derivatives

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Fluorescence of the inclusion complexes with different compositions formed by naphthalene-h_8, naphthalene-d_8, 2,7-dimethylnaphthalene (DMN), and 2-benzylnaphthalene (BN) with β-cyclodextrin (β-CD) in water was studied. Two types of fluorescence are observed, monomer (MF) and excimer (EF) fluorescence. The excimer fluorescence of the 2 : 2 complex emitted by aggregated light-dispersing crystals forming a precipitate, whereas is the MF is observed in the transparent solution. When naphthalene and β-CD are present in equimolar concentrations, EF predominates for the resulting complexes. A proposed structure of the inclusion complexes was derived from MNDO/PM3 semiempirical quantum-chemical calculations. The EF is caused by the structure of the complex, in which both naphthalene molecules are separated by a distance of 4.7 Å; they lie in parallel orientation to each other, whereby one ring is displaced from the other by one-fourth of the length of the naphthalene ring. The complexes of 2,7-DMN and 2-benzylnaphthalene with β-CD do not exhibit EF. For the 2 : 2 complex of 2,7-DMN with β-CD, this is due to the fact that the aromatic fragments are removed too far from one another. 2-Benzylnaphthalene is unable to form an inclusion complex with β-CD, in whose structure the aromatic fragments inside the cavity could be arranged in parallel planes; instead, it forms a 1 : 2 complex with β-CD.

Key words: β-cyclodextrin, naphthalene, naphthalene derivatives, inclusion complexes, structure of inclusion complexes, fluorescence, excimer fluorescence, semiempirical quantum-chemical calculations, MNDO/PM3 method.

Excimer fluorescence (EF) is due to the formation of an excited dimer of the AA* type having a relatively long lifetime (hundreds of nanoseconds) and subsequent light emission upon transformation of this dimer into two molecules A, which do not interact in the ground state. In solutions, the dimeric structure favorable for the origination of EF arises upon diffusion of molecules A. Obviously, the probability of this process increases with increase in the concentration of the molecules; for arenes, EF can be observed at concentrations of about 1 *M*.[1]

The efficiency of excimer generation is characterized by the ratio of EF intensity to the intensity of monomer fluorescence (MF) at their maxima $K = I_{\text{exc}}/I_{\text{mon}}$. We used this coefficient for quantitative estimates.

On passing to molecular-organized systems of the host—guest type, the formation of the corresponding dimeric structure and generation of EF is no longer determined by diffusion processes; instead, they are determined by the probability of formation of inclusion complexes containing two A molecules whose mutual orientation can facilitate the formation of excimers.

For naphthalene, its derivatives, and analogs, the most suitable host molecules are cyclodextrins (CD)[2] and, in particular, β-cyclodextrin (β-CD). Its molecule, shaped like a basket, consists of seven α-D-glucopyranose units linked by (1—4) glucoside bonds.[3] The internal wall in the cavity of β-CD has a hydrophobic nature and the cavity can incorporate molecules of the appropriate size upon adsorption from aqueous solutions or directly from air. A necessary condition for the formation of the inclusion complex is that the size of the guest molecule should match the size of the β-CD cavity. According to the calculations performed previously, most naphthalene derivatives as well as phenanthrene and fluorene comply with this requirement.[4]

Excimer fluorescence can be exhibited by two types of complexes containing A and CD in 2 : 1 or 2 : 2 ratio. In the former case, one γ-cyclodextrin molecule consisting of eight glucose units has a cavity large enough to form an inclusion complex with two A molecules.[5] The latter case implies association of two 1 : 1 complexes to give a 2 : 2 complex.[2,6–8] Experiments show that EF in these complexes is observed at A concentrations three orders of magnitude lower than that required for EF in homogeneous solutions.[9] However, the formation of an inclusion complex with two A molecules is not a sufficient condition for the occurrence of EF. For EF to

Published in *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 10, pp. 1716—1723, October, 2000.

1066-5285/00/4910-1699 $25.00 © 2000 Kluwer Academic/Plenum Publishers

arise, it is required that the planar A molecules be arranged parallel or nearly parallel to one another, so that interaction of an excited molecule with a nonexcited one could give a bound excited dimer. Therefore, there can be 2 : 1 or 2 : 2 complexes whose EF is suppressed due to the nonparallel orientation of arenes, although it does occur in a homogeneous solution of the A molecules.

The excimer fluorescence of naphthalene and some of its derivatives in homogeneous solutions has been studied in detail.[10] It was shown that only 1,8-DMN fails to produce EF; this was explained by steric restrictions to the formation of an excited dimer. The excimer fluorescence of naphthalene clusters has been studied previously.[11—14] The competition between monomeric fluorescence (MF) and EF was found for an equimolar mechanical mixture of naphthalene and dimethyl-β-CD heated in a tube. The former is entirely suppressed at 60—80 °C, while only EF is manifested; however, on heating above 90 °C, only MF is observed.[15]

Naphthalene (concentration in water of $<10^{-5}$ mol L^{-1}) and β-CD ($C = 10^{-3}-10^{-2}$ mol L^{-1}) forms a 1 : 1 inclusion complex exhibiting MF. For naphthalene concentrations of $\geq 10^{-4}$ mol L^{-1}, a 2 : 2 complex is also formed; this is accompanied by EF.[16] 1-Chloronaphthalene[6] and 2-naphthyl-1-ethanol[17] behave in a similar way, whereas 1-naphthyl-1-ethanol does not exhibit EF. The EF of cyclodextrins having substituents with a naphthalene fragment has been studied previously.[18—21]

The structures of inclusion complexes have been little studied as yet. In a recent publication,[6] it was shown that the size of the β-CD cavity is sufficient to ensure free rotation of excimerically fluorescing 1-chloronaphthalene dimer, whose volume was estimated to be 0.2 nm^3. The structures of fluorenone and xanthone complexes with cyclodextrins were determined by molecular mechanics calculations.[22]

In this work, we studied the relationship between the structures of β-CD complexes with naphthalene and some of its derivatives, which were determined by MNDO/PM3 quantum-chemical calculations, and the results of experimental measurement of fluorescence in these complexes. The purpose of this work is an attempt to predict the appearance of EF based on the structure of the inclusion complex.

Experimental

Compounds. Naphthalene (N)-h_8 and N-d_8 as well as 2,7-dimethylnaphthalene (2,7-DMN) and 2-benzylnaphthalene (2-BN), whose fluorescence had not been studied previously, were used as guests for complexation with β-CD. The compounds were purified by recrystallization; the degree of purity was checked based on the absorption and luminescence spectra. β-CD and γ-CD (Cyclolab, Hungary) were used as received. Doubly distilled water served as the solvent.

Preparation of complexes. An aqueous solution of β-CD or γ-CD (10 mL) with a concentration of $5 \cdot 10^{-3}$ mol L^{-1} was added to a quartz tube so that a thin layer of the substrate (in an amount corresponding to the specified substrate concentration in the solution) was deposited on the tube walls after evaporation of a hexane solution. The isolated tube with the resulting solution was held for 1 h on a water bath at 50 °C and then slowly cooled to ~20 °C. The solution was shaken at intervals. This treatment gave solutions containing complexes in concentrations of 10^{-4} mol L^{-1} for 2,7-DMN and 2-BN or $5 \cdot 10^{-3}$ mol L^{-1} for N-h_8 and N-d_8. To obtain N-h_8 and N-d_8 concentrations of 10^{-4} mol L^{-1} in the complex, the appropriate aqueous solutions were used and the sample of β-CD was chosen in such a way that its concentration was $5 \cdot 10^{-3}$ mol L^{-1}. Naphthalene is highly volatile; therefore, the real concentration of substrates differed from the theoretical one and was determined from the absorption spectra of solutions of the complexes.

Procedures. Absorption and fluorescence spectra were measured on a Specord M40 spectrophotometer and an Elumin-2M spectrofluorimeter. Fluorescence was excited at a frequency of 35088 cm^{-1}. The MF and EF maxima for naphthalene and its derivatives lie in the regions of 31000 and 25000 cm^{-1}, respectively.

Calculations. Semiempirical quantum-chemical calculations for substrate molecules: naphthalene, 2,7-DMN, 2-BN, and their 1 : 1 and 2 : 2 inclusion complexes with β-CD, were carried out by MNDO/PM3 (below referred to as PM3) with a standard set of parameters[23] using the PC GAMESS99 program package.[24] The HyperChem program[25] was used as a graphical interface for the preparation of input files and visualization of the results of calculations.

Structure of the monomeric β-*CD.* Previously,[4] we showed that β-CD, constructed from seven identical glucose units, has a regular structure corresponding to the C_7 group of symmetry. The β-CD structure calculated in this work had a 0.5 kcal mol^{-1} lower heat of formation ($\Delta H_f = -1468.4$ kcal mol^{-1}) than that established previously. Analysis of the structure of the O(7) heptagon constructed at the bridging oxygen atoms connecting the neighboring glucose units makes it possible to estimate the degree of symmetry of the calculated structure. In the symmetrical form of β-CD, all the angles (ϕ) should be equal to 128.57° and the figure should be strictly planar, *i.e.*, the seven τ (O—O—O—O) dihedral angles should be equal to zero and the closed curve circumscribed about the heptagon should be a circle. In addition, the symmetrical structure of β-CD has seven equivalent bond lengths and angles.

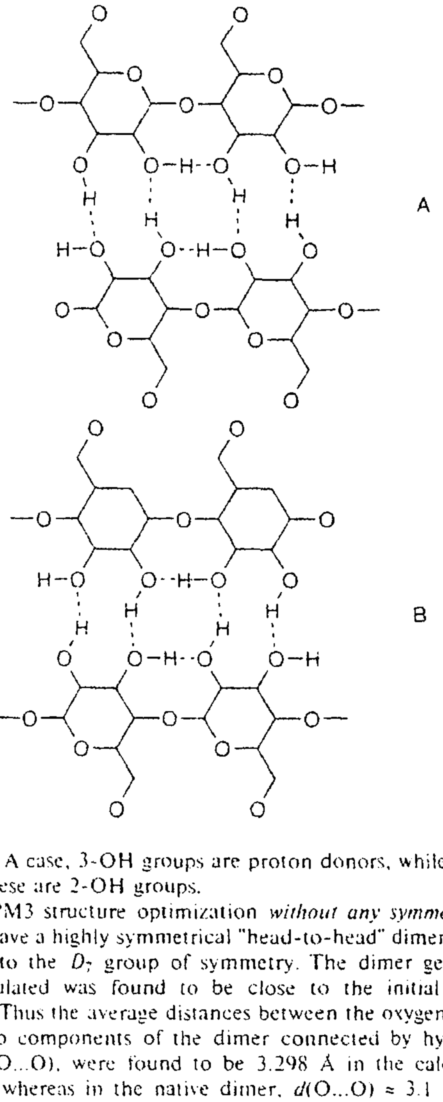
The calculated structure can be characterized by average values of the equivalent bond lengths and angles and by the ellipsicity (ε) of the circumscribed circle ($\varepsilon = R_{max}/R_{min}$, R are the radii of the circumscribed circle). The accuracy of fulfillment of the C_7 symmetry operation and, hence, the quality of optimization are determined by the standard deviations (σ) from the average bond lengths and angles: the more exact the symmetry of the molecule, the smaller the σ values and the closer ε is to unity (ε for a circle is exactly unity).

Comparison of the resulting values with published data demonstrates that the shape of the calculated β-CD structure is very close to the symmetrical structure corresponding to the global minimum:

	This work	Ref. 4	Ref. 26
ϕ/deg	128.57	128.5(6)	128.5(6)
τ/deg	0.00(4)	−0.008±4.89	128.33±2.37
ΔH/kcal mol^{-1}	1468.4	1467.9	1459.65

The structure of β-*CD dimers* was calculated as follows. The structure of a natural product, bis-(β-CD) ethyl cinnamate hydrate (BIDMOQ), was used as the initial structure for optimization.[27] In this compound, β-CD occurs as a "head-to-head" dimer. In the calculations, the hydration water and substrate molecules were removed and the missing hydrogen atoms were added in the required orientation. The patterns of formation of the CD dimer from β-cyclodextrins with right- (A) and left-oriented (B) H-bonds are shown in Scheme 1.

Scheme 1



In the A case, 3-OH groups are proton donors, while in the B case, these are 2-OH groups.

Full PM3 structure optimization *without any symmetry restrictions* gave a highly symmetrical "head-to-head" dimer corresponding to the D_7 group of symmetry. The dimer geometry thus calculated was found to be close to the initial native structure. Thus the average distances between the oxygen atoms of the two components of the dimer connected by hydrogen bonds, d(O...O), were found to be 3.298 Å in the calculated structure, whereas in the native dimer, d(O...O) ≈ 3.1 Å. The energy of dimerization calculated as the difference between the ΔH_f value of the dimer and the doubled heat of formation of β-CD was equal to −8.7 kcal mol^{-1} (Table 1).

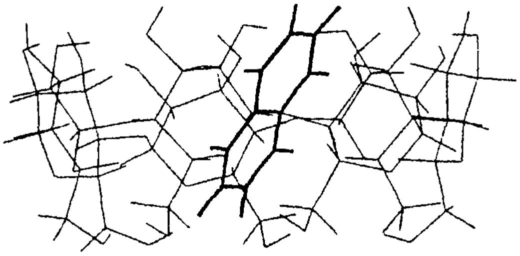


Fig. 1. Structure of the 1 : 1 β-CD—naphthalene complex determined by MNDO/PM3 calculations.

Table 1. Heats of formation (ΔH_f) of β-cyclodextrin (β-CD), β-CD dimer, naphthalene (N), 2,7-dimethylnaphthalene (DMN), 2-benzylnaphthalene (BN), 1 : 1 β-CD · N, β-CD · DMN, and β-CD · BN inclusion complexes, and 2 : 2 2β-CD · 2N and 2β-CD · 2DMN inclusion complexes and the energies of complexation (ΔE) calculated by the MNDO/PM3 method

Molecule, complex	ΔH_f	ΔE
	kcal mol^{-1}	
β-CD	−1468.4	—
2β-CD	−2945.4	−8.6[a]
β-CD · N	−1440.1	−12.1
β-CD · DMN	−1460.1	−13.2
β-CD · BN	−1421.3[b]	
	−1421.9[c]	−13.1
2β-CD · 2H	−2886.3	−30.4
2β-CD · 2DMN	−2933.1	−12.9[d]
N	40.42	
DMN	21.46	
BN	59.63	

Note. [a] The energy of dimerization of β-CD.

[b] The 1 : 1 complex of benzylnaphthalene with β-CD; the naphthalene fragment is inside the cavity.

[c] The 1 : 1 complex of benzylnaphthalene with β-CD; the benzylic fragment is inside the cavity.

[d] The energy of dimerization of the β-CD · DMN complex.

Calculations of 1 : 1 inclusion complexes of β-*CD* were carried out as follows. The molecules of substrates, *viz.*, naphthalene, 2,7-DMN, and 2-BN, were "inserted" into the β-CD cavity at the graphical interface display, the resulting structural file was converted into the input format for the GAMESS program, and full geometry optimization was performed (Fig. 1). The same result can be obtained by display coupling of two 1 : 1 complexes to form a dimer followed by geometry optimization. The energy of complexation, ΔE, was calculated as the difference

$$\Delta E = \Delta H_f(\text{compl}) - \Delta H_f(\beta\text{-CD}) - \Delta H_f(\text{subst}).$$

Since two structures of complexes are possible for 2-BN, the energies of complexation for isomeric structures are compared (see Table 1), where one of them has a benzyl fragment, while the other has a naphthalene fragment inside the cavity (Fig. 2). The comparison showed that the two types of 1 : 1 complexes for 2-BN are indistinguishable from the energy standpoint, ΔE = −12.5 kcal mol^{-1}. The energy of the formation of the inclusion complex of 2,7-DMN with β-CD was −13.2 kcal mol^{-1}.

Arene dimers. The structures of the van der Waals dimers of arenes have been repeatedly studied (see Ref. 28 and references therein). In most cases, the equilibrium structures in the ground electronic state are characterized by a T-shaped orientation of the aromatic rings in the dimer. However, the existence of EF requires parallel orientation of components.

The PM3 calculations of the van der Waals dimer (WD) of naphthalene also result in a T-shaped orientation of components with a dimerization energy of −1.4 kcal mol^{-1}; according to the Hessian calculation, this structure actually corresponds to the global minimum because it is characterized by $3N-6$ (N = 36, the number of atoms in naphthalene dimer) positive harmonic

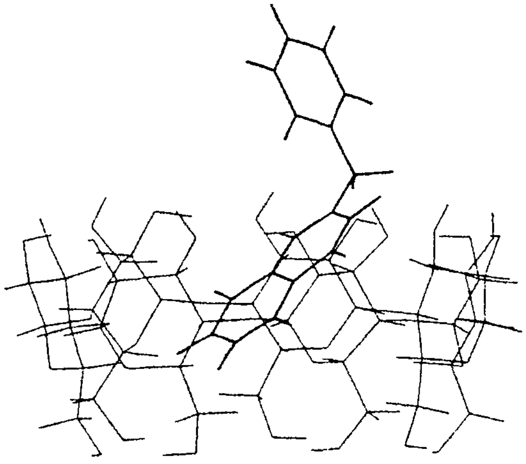


Fig. 2. Structure of the 1 : 1 β-CD—2-benzylnaphthalene complex determined by MNDO/PM3 calculations.

frequencies of vibrations. Note for comparison that the energy of the pyrrole WD with a similar orientation of components calculated by the perturbation theory amounts to −1.69 kcal mol^{-1}.[28] The structure of the naphthalene dimer with a parallel sandwich orientation of the components and with a distance of ~4.7 Å between the planes corresponds to the saddle point on the potential energy surface because it has one imaginary vibration frequency. Its dimerization energy is equal to −0.15 kcal mol^{-1}. Since this value is four times smaller than kT, it can be inferred that in this orientation of components, naphthalene molecules virtually do not interact in the ground state.

We investigated the behavior of the naphthalene WD in the cavity of the β-CD dimer by a model calculation. To this end, the T-shaped naphthalene WD was placed into the central part of the β-CD dimer cavity and the resulting structure was optimized by the PM3 method. During the geometry optimization, the naphthalene dimer acquired a nearly parallel orientation (Fig. 3). Thus, it was found that the structures of the 2,7-DMN and 2-BN dimers do not require preliminary optimization; it is sufficient to calculate the parallel orientations of these substrates in the cavity of the β-CD dimer.

Calculations of 2 : 2 inclusion complexes of β-*CD* were performed by placing two parallel N and 2,7-DMN molecules separated by a distance of ~4 Å into the cavity of the β-CD dimer followed by optimization of the complex geometry. In the resulting structures, both components are separated by a mean distance of 4.7 Å.

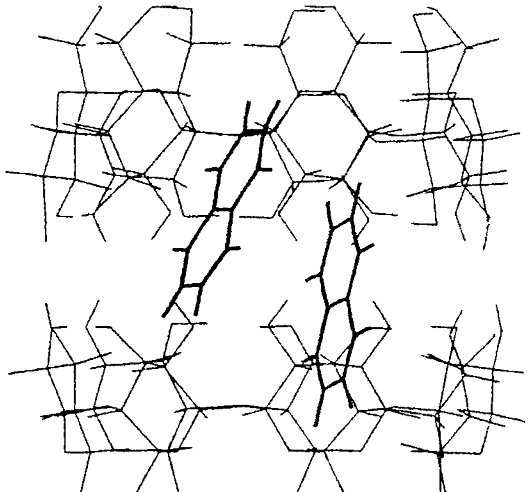


Fig. 3. Structure of the 2 : 2 β-CD—naphthalene complex determined by MNDO/PM3 calculations.

Results and Discussion

The naphthalene-h$_8$—β-CD complex. The formation of a complex from naphthalene-h$_8$ and β-CD in a saturated aqueous solution is accompanied by minor changes in the absorption spectra. In view of the arising light dispersion, the possible substantial errors in the determination of the equilibrium constant of the 1 : 1 complex can be understood.[29] However, the complex formation results in pronounced changes in the fluorescence spectra if irradiation at 35877 cm^{-1} (λ = 285 nm) is employed for excitation. The fluorescence spectra of a saturated aqueous solution of naphthalene-h$_8$ (Fig. 4, curve *1*) and its complex with β-CD (Fig. 4, curve *2*, K = 0.1) show the presence of two excimers. The optical density of these samples at the long-wavelength maximum at 36120 cm^{-1} is equal to 0.6, which corresponds to a naphthalene concentration of $9 \cdot 10^{-5}$ mol L^{-1}. These samples are not true solutions of the complexes because they contain microparticles of aggregated complexes, which are deposited with time on the cell bottom. After shaking the cell, a suspension is produced and the absorption and fluorescence spectra change. Light dispersion appears in the absorption spectra and the EF to MF ratio (see Fig. 4, curve *3*, K = 0.2) in the fluorescence spectra markedly increases. Estimates show that the change in the ratio is not caused by light dispersion. This means that EF is mainly concentrated in light-dispersing aggregated complexes whose size is fractions of microns, which is much larger than the size of the 2 : 2 complex.

When the calculated naphthalene concentration increases to $5 \cdot 10^{-3}$ mol L^{-1}, the formation of the complex with β-CD in solution (see the procedure for the preparation of complexes) results in enhanced EF of the mother liquor (see Fig. 4, curve *4*, K = 0.29), while the MF in the resulting precipitate is suppressed with respect to the EF (see Fig. 4, curve *5*, K = 4.9). Phosphorescence spectra cannot be observed for the precipitate not only at room temperature but also at 77 K due to the competing EF.[30]

Only EF is observed for naphthalene complexes prepared by grinding weighed portions of the components in molar ratios ranging from 1 : 10 to 1 : 100. This is apparently due to the high local concentrations of naphthalene because for complexes prepared in solution at a

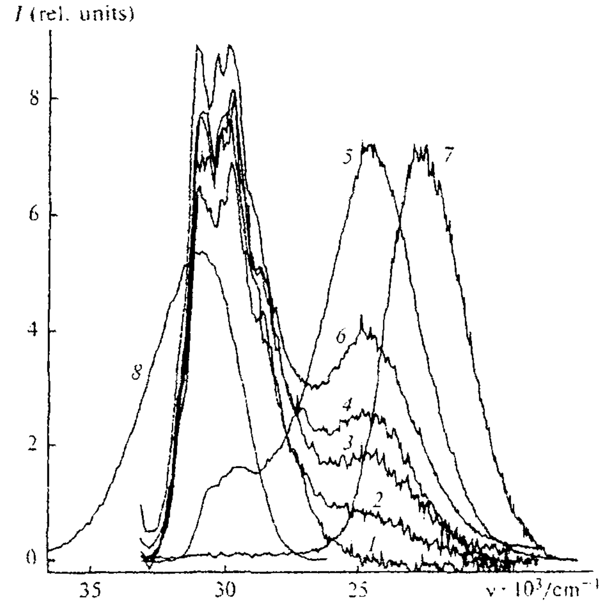


Fig. 4. Fluorescence spectra (*1—7*) and fluorescence excitation spectrum (*8*) of an aqueous solution of naphthalene and its complex with β-cyclodextrin in the region of 22000 cm^{-1} (see the text).

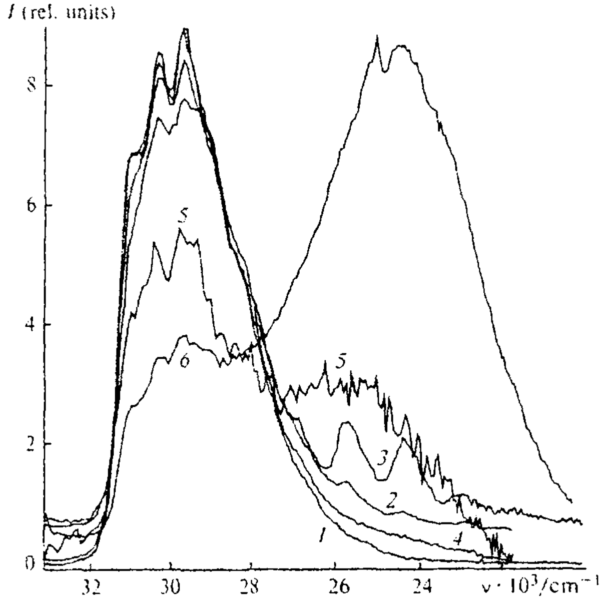


Fig. 5. Fluorescence spectra (*1—6*) of an aqueous solution of 2,7-dimethylnaphthalene and its complexes with β- and γ-cyclodextrins (see the text). Spectra *2*, *3*, *5*, and *6* are shifted along the ordinate axis for clearness.

naphthalene concentration of 10^{-4} mol L^{-1} and a β-CD concentration of $2 \cdot 10^{-3}$—10^{-2} mol L^{-1}, MF predominates (see Fig. 4, curves *2* and *3*).

The naphthalene-d$_8$—β-CD complex. The complex formed upon the addition of β-CD to a saturated aqueous solution of naphthalene-d$_8$ (D_{36120} = 1) is characterized by K = 0.57 (see Fig. 4, curve *6*). For comparison, the complex of naphthalene-h$_8$ in a lower (by 70%) concentration has K = 0.1. If the formation of excimers in the complexes of naphthalene-h$_8$ and naphthalene-d$_8$ with β-CD is supposed to occur with equal efficiencies, the dependence of K on the arene concentration substantially deviates from the theoretical dependence known for homogeneous solutions in which the K value should be inversely proportional to the concentration.[31]

The 2,7-DMN—β-CD complex. The use of a substituted naphthalene should change the structures of 1 : 1 and 2 : 2 complexes, which can have an influence on their fluorescence. Indeed, the fluorescence spectrum of the complex of 2,7-DMN with β-CD does not exhibit EF (Fig. 5, curve *1*) due to the fact that the dimeric structure of the arene in the 2 : 2 complex does not bring about an interaction needed for the appearance of excimers. The calculation of the structure of the 2 : 2 complex (see below) confirms this explanation.

It should be noted that in homogeneous solutions, 2,7-dimethylnaphthalene, unlike 1,8-dimethylnaphthalene, does exhibit EF.[1]

Shaking of a sample containing the complex affords a slightly turbid suspension; only when the instrument amplification for the recording of fluorescence is increased by an order of magnitude, does the fluorescence spectrum display several weak narrow bands in the region where EF is normally observed, instead of the expected broad band (see Fig. 5, curve *2*). The assumption that these bands are due to impurities is not confirmed because neither the aqueous solution of β-CD nor homogeneous solutions of 2,7-DMN in ethanol or hexane exhibit luminescence in this region. However, similar bands were observed for a freshly prepared saturated aqueous solution of 2,7-DMN (see Fig. 5, curve *3*); during storage of the solution, the bands gradually disappear and their nature has not been elucidated.

After the sample has been stored for several days, a structureless band appeared in the spectrum of a suspension prepared from the precipitate (see Fig. 5, curve *4*); this could be assigned to EF. Probably, the formation of the dimeric structure inducing the EF is a long process because the opening through which the guest molecule enters the β-CD cavity is not sufficiently wide. However, this band coincides with the band observed in the fluorescence spectrum of the product of the dark reaction of 2,7-DMN in water (see Fig. 5, curve *5*), while the fluorescence excitation spectrum in this region does not coincide with the excitation spectrum observed in the MF region.

Thus, no EF of 2,7-DMN in the complex with β-CD can be observed, which is a consequence of the complex structure. However, EF is clearly recorded for the complex of 2,7-DMN with γ-CD at a calculated concentration in the solution of $1 \cdot 10^{-3}$ mol L^{-1}. As for the naphthalene complex, MF in the precipitate is suppressed with respect to EF (see Fig. 5, curve *6*).

The 2-benzylnaphthalene—β-CD complex. The fluorescence spectrum of the 2-benzylnaphthalene complex with β-CD is similar to the spectrum shown in Fig. 5 (curve *1*), *i.e.*, no EF is observed for this complex even at high concentrations of 2-BN. The calculation of the complex structure presented below shows that the size of the molecule is such that either the benzyl or naphthalene moiety can fit into the β-CD cavity, whereas the other moiety protrudes above the upper edge of the cavity (see Fig. 2). Therefore, dimerization of the complex in which two β-CD molecules are linked according to the "head-to-head" pattern and contain two substrate molecules is unlikely. The formation of the 2 : 1 β-CD—BN complex in which one host molecule has a benzylic fragment in the cavity, while the other one contains a naphthalene fragment appears more likely.

The structure of inclusion complexes of naphthalene and its derivatives with β-CD. The structure of the 2 : 2 naphthalene complex with β-CD presents interest due to the fact that the constant of association of the binary complex to the 2 : 2 dimer is very high ($4 \cdot 10^3$ L mol^{-1}), whereas the constant of formation of the binary complex of β-CD with naphthalene is 685 L mol^{-1} (see Ref. 16). In addition, according to the data of luminescence spectra, a complex of this type appears to form when inclusion compounds are prepared by grinding the solid components (see above).

We performed calculations for the 2 : 2 complex constructed as a "head-to-head" dimer of β-CD with one naphthalene molecule in the cavity of each β-CD molecule (see Fig. 3). According to the calculation, the energy of the 2 : 2 β-CD—naphthalene complex is exceptionally high and amounts to −30.4 kcal mol^{-1} with respect to the components. The subtraction of the energies of two naphthalene molecules shows that their insertion into the cavity of the dimer should be accompanied by energy expenditure equal to −16.8 kcal mol^{-1}, which is smaller than twice the energy of formation of the complex of β-CD with naphthalene (−24.2 kcal mol^{-1}). The energy of association of two 1 : 1 complexes into a 2 : 2 complex is estimated to be −6.1 kcal mol^{-1}, which is somewhat smaller than the energy of dimerization of β-CD molecules without inclusions (−8.7 kcal mol^{-1}, see Table 1). Thus, according to calculations, association of binary complexes into a 2 : 2 aggregate is energetically favorable. This is consistent with the experimental complexation constants presented above.

In the structure of the complex, the planes of the two naphthalene molecules are nearly parallel to each other and are displaced from each other by one-fourth of the length of the naphthalene ring. Thus, the aromatic systems of the components overlap fairly extensively. The average distance between the planes is 4.7 Å.

If the van der Waals radii of the C and H atoms are assumed to be 1.7 and 1.15 Å,[32] then the maximum length of the naphthalene molecule is 8.75 Å, the width is 7.26 Å, and the "thickness" is 3.4 Å. The volume of a naphthalene molecule is 0.22 nm^3 and the volume occupied by a WD cannot be smaller than 0.44 nm^3. Hence, the value equal to 0.2 nm^3 for the volume of the naphthalene dimer in the cavity of the β-CD dimer was underestimated by Hamai [6] by a factor of at least 2, which may be due to the low accuracy of the method of measurements he used.

The volume of the naphthalene dimer located in the cavity of the 2 : 2 complex, which was found in this study to be 0.42 nm^3, is ~0.1 nm^3 smaller than the calculated volume occupied by the free naphthalene dimer with planar orientation of components. Thus, the naphthalene dimer located in the β-CD cavity proves to be more compact than the free dimer. Since the overlap of one-fourth of the aromatic fragments is sufficient for the generation of EF, the orientation of the naphthalene molecules found in calculations, which implies overlap of not less than three-fourths of the π-systems, is able to ensure coupling of the components after excitation of one of the molecules to give an AA* dimer.

A different structure was found for the 2 : 2 complex of β-CD with 2,7-DMN. The planes of the two 2,7-DMN molecules virtually do not overlap in this complex because this is prevented by the methyl groups. Experimental data are consistent with the calculated structure of the complex; no EF is observed in this case.

The complex of 2-BN does not exhibit EF either. This is explained by the size of the 2-BN molecule. Irrespective of whether the naphthalene or benzyl moiety is inserted into the β-CD cavity, the other part of the molecule remains outside and can apparently enter the cavity of a second β-CD molecule to form the β-CD · 2-BN complex (2 : 1), which tends to exhibit MF, as observed in experiments.

The influence of side reactions on the fluorescence. The results presented above were obtained using freshly prepared samples. On storage in aqueous solutions, naph-

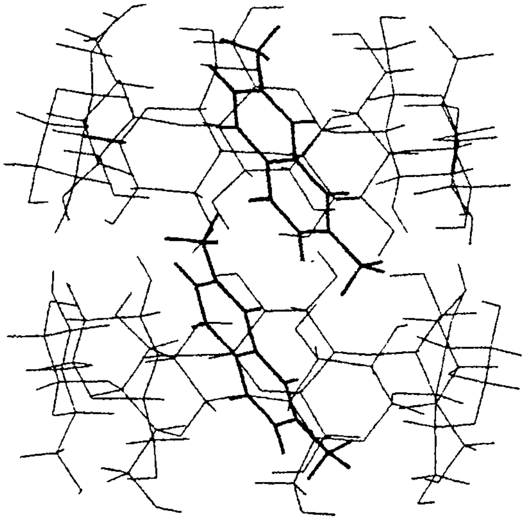


Fig. 6. Structure of the 2 : 2 β-CD—2,7-dimethylnaphthalene complex determined by MNDO/PM3 calculations.

thalene and its derivatives are converted into other stable compounds exhibiting structureless fluorescence in the same spectral region in which the EF of naphthalene is observed. This transformation of naphthalene was observed 5 days after its saturated solution in water had been prepared. In other cases, this required a month or longer periods. Neither heating to 50 °C for 5 h nor irradiation with the nonfiltered light from a DRSh-500 lamp accelerated the process. This phenomenon was also observed in diethyl ether but not in hexane. The isolated product was insoluble in hexane but was readily soluble in water and ethanol.

Apparently, this product resulted from a dark reaction involving oxygen; the different periods it takes for the product to appear are due to the different degrees of tightness ensured by the ground joints through which atmospheric oxygen gets into the solution. To verify this assumption, we prepared an oxygen-free sample of a saturated aqueous solution of naphthalene-h$_8$. The MF of the arene measured after 3.5 months was equal to that observed immediately after preparation.

Identification of the products formed from naphthalene and its derivatives was beyond the scope of our study but we still studied the spectral transformations because they were among the reasons for the nonreproducibility of the results of measurements of the EF of the complexes.

Figure 4 (curves *7* and *8*) presents the fluorescence spectra and the fluorescence excitation spectra of the final product of the transformation of naphthalene in water. During the formation of this product, the maximum of the fluorescence spectrum undergoes a bathochromic shift in the 24500—22600 cm^{-1} range.

The final product is also formed in an aqueous solution of the naphthalene complex with β-CD, which first induces an increase in the fluorescence efficiency in the region of 25000 cm^{-1}. This increase may also be related to an increase in the EF intensity because the processes of formation of 2 : 2 complexes can require substantial periods of time. The measurements related to complexes are normally performed at least 24 h after the required components have been mixed. The product of the dark reaction may form over periods of time of the same order, which hampers quantitative measurements of the EF.

The concentration of arene in water is equilibrated with that in the CD complex; the equilibrium can be disturbed upon the formation of a stable product from the arene. Indeed, upon prolonged storage of an aqueous solution of the naphthalene complex with β-CD, the naphthalene passes entirely into the product, as indicated by the changes in the absorption and fluorescence spectra. Similar reactions take place in aqueous solutions of the complexes of naphthalene derivatives with β-CD. Thus, to preserve the complexes intact, one should take measures to prevent dark reactions of arenes, for example, removing oxygen from the solution.

Processes of aggregation and their influence on the fluorescence of complexes. Our results demonstrate that the aggregation of complexes changes substantially their fluorescence, in particular, the EF to MF ratio. However, β-CD itself can also form aggregates in aqueous solutions; the characteristic time of aggregation is several days, which was confirmed by our measurements of the absorption spectra of an aqueous solution of β-CD. Especially pronounced changes in the absorption of the solution take place in the first 24 h and are related to the formation and precipitation of light-dispersing aggregates.

The preparation of samples according to one of the procedures implies the use of an aqueous solution of β-CD; hence, the degree to which β-CD is aggregated can influence the structure of the complexes formed and their fluorescence. This should be taken into account for obtaining reproducible results of spectral measurements.

During measurements, it was found that β-CD cannot be stored close to naphthalene because of the appearance of structureless fluorescence (which is retained after keeping β-CD at 50 °C for 4 h) in the region typical of the MF of naphthalene. Apparently, naphthalene from the gas phase forms an inclusion complex with β-CD.

The formation of inclusion complexes of naphthalene and its derivatives with β-cyclodextrin either enhances the EF with respect to that in homogeneous solutions (N-h$_8$ and N-d$_8$) or, in some other cases, prevents EF (2,7-DMN, 2-BN). This is related to the structure of 2 : 2 complexes, which is substantially different for naphthalene and its derivatives, as confirmed by relevant quantum-chemical calculations. The formation of products of a dark reaction was detected in aqueous solutions of naphthalene and its derivatives; the products display structureless fluorescence in the same region in which the EF of these arenes is observed, which can bring about errors in the investigation of EF.

The authors are grateful to the Russian Foundation for Basic Research for financing the access to the Cambridge Structural Database.

This work was supported by the Russian Foundation for Basic Research (Project No. 97-03-32604a).

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Received February 28, 2000