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Ternary inclusion complexes of cyclodextrins with spin-labeled indoles and hydrocarbons. The formation of 2 : 1 : 2 complexes and partial dissociation of spin-labeled guests in the presence of a hydrocarbon liquid phase

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The interaction of ternary complexes γ- or β-cyclodextrin (CD)—spin-labeled indole (pyrrolidine (**1**) or piperidine (**2**) derivative)—hydrocarbon (benzene or cyclohexane) with the liquid phase of these hydrocarbons gives rise to a new type of complexes (s) the ESR spectra of which are indicative of a much lower rotational mobility and its weaker temperature dependence for the spin-labeled guests compared with the initial ternary complexes (w). The formation of s-complexes is accompanied by a decrease in the proportion of the initial w-complexes. This gives rise to several isosbestic points in the ESR spectra, which indicates the formation of s-complexes from w-complexes. The rotational diffusion coefficient of **2** in s-complexes decreases 6—10-fold with respect to its value for w-complexes and the libration amplitude of **1** in the s-complexes decreases to 5—6° at 295 K. Transition between the two types of complexes occurs with characteristic times of 10^3—10^5 s and is reversible: upon the removal of the hydrocarbon, the proportion of the strongly immobilized s-signal decreases, while upon its addition, it increases again. These results indicate that the strongly immobilized ESR signals belong to 2 : 1 : 2 complexes, which are formed upon the insertion of the second hydrocarbon molecule into the initial ternary 2 : 1 : 1 w-complexes. According to PM3 quantum-chemical calculations, 2 : 1 : 2 complexes are stable in energy and the geometry of hydrocarbon arrangement depends on the structure of the spin-labeled guest.

Key words: γ- and β-cyclodextrins, spin-labeled indoles, ESR spectra, inclusion complexes, stoichiometry, ternary complexes, molecular dynamics, distribution coefficients.

Previously,[1] we studied the structure and molecular dynamics of ternary inclusion complexes formed by spin-labeled indoles and hydrocarbons with cyclodextrins (CD) by solid-phase ESR. The structures of both the host molecule (β- or γ-CD) and the two guest molecules were varied in this study. Two derivatives containing pyrrolidine-*N*-oxyl (**1**) and piperidine-*N*-oxyl (**2**) radical rings were used as spin-labeled indoles and benzene and cyclohexane were used as hydrocarbons. It was found[1] that all four complexes with γ-CD and one complex with β-CD exhibit two types of ESR signals corresponding to spin-labeled guests with different rotational mobilities, whereas for two other complexes with β-CD (2β-CD—**2**—C_6H_6 and 2β-CD—**2**—C_6H_{12}), only one ESR signal corresponding to complexes with higher mobility of spin-labeled indole is recorded. The weakly immobilized ESR spectra were found[1] to belong to 2 : 1 : 1 complexes in which both guest molecules, *i.e.*, spin-labeled indole and hydrocarbon, are located in the cavity of β- or γ-CD dimers.

The purpose of this study is to elucidate the nature of complexes responsible for strongly immobilized ESR signals observed previously.[1] To this end, the influence of the hydrocarbon liquid phase on the ESR spectra of spin-labeled indoles in the β(γ)-CD—**1**(**2**)—C_6H_6(C_6H_{12}) ternary complexes was studied under steady-state and kinetic conditions and quantum-chemical calculations for the complexes of different composition and stoichiometry were carried out.

Experimental

As in previous studies,[2—4] indole derivatives, radicals with pyrrolidine (**1**) and piperidine (**2**) rings[5] were used as spin-labeled guest molecules.

The following commercial chemicals were used: β-CD (Calbiochem, Germany), γ-CD hydrate, benzene, and cyclohexane (Aldrich, Germany).

The procedures for the preparation of β(γ)-CD—**1**(**2**)—C_6H_6(C_6H_{12}) ternary complexes were described

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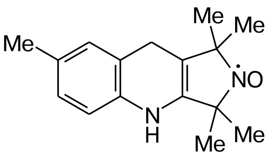

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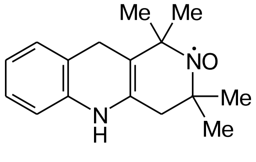

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previously.[1] The kinetics of variation of the ESR spectra in the presence of the hydrocarbon liquid phase was studied as follows: a specified amount (10 μL) of C_6H_6 or C_6H_{12} was added into a tube with a finely dispersed powder of the initial ternary complex and, after 2 min, the ESR spectra were recorded at 295 K. In subsequent experiments, the liquid hydrocarbon was removed by evaporation in an argon flow.

The ESR spectra were recorded on a Bruker ER-200D instrument in glass tubes maintained at a constant temperature to within ±0.5 °C. The temperature dependences of the ESR spectra of complexes were studied in the range of 140—340 K with a check of reversibility. The ESR spectra linear over the microwave field were recorded at a low microwave power ($P = 32$ dB, $H_1 \approx 0.0125$ G) and a small modulation amplitude, which rule out the spectrum distortion.

Results and Discussion

The temperature dependences of the initial ESR spectra of some complexes containing strongly and weakly immobilized components are shown in Fig. 1. The distance between the outer extrema ($2A_{zz}'$, see Fig. 1) was used as the spectral parameter of the rotational mobility for both signals. It is seen that at low temperatures s- and w-signals overlap but at higher temperatures (at about 250—340 K), two signals with different $2A_{zz}'$ are observed, the $2A_{zz}'$ values being much higher for s-signals than for w-signals.

The temperature dependences of $2A_{zz}'$ for s- and w-signals in the range where these spectra are well resolved for some γ- and β-CD complexes are presented in Fig. 2. It is seen that not only the absolute values of $2A_{zz}'$ but also their temperature dependences of these parameters for s- and w-signals are substantially different: for w-signals, $2A_{zz}'$ depends appreciably on the temperature, whereas for s-signals this parameter almost does not change in the temperature range of 230—300 K.

In order to identify the nature of s-complexes, we studied the effect of incubation of the initial solid-phase ternary complexes with the liquid phase of the corresponding hydrocarbon (benzene or cyclohexane). Hydrocarbon was added directly into the tube with the sample (see Experimental) and ESR spectra were recorded in different time intervals; the first spectrum was recorded 2 min after the addition. The incubation with the hydro-

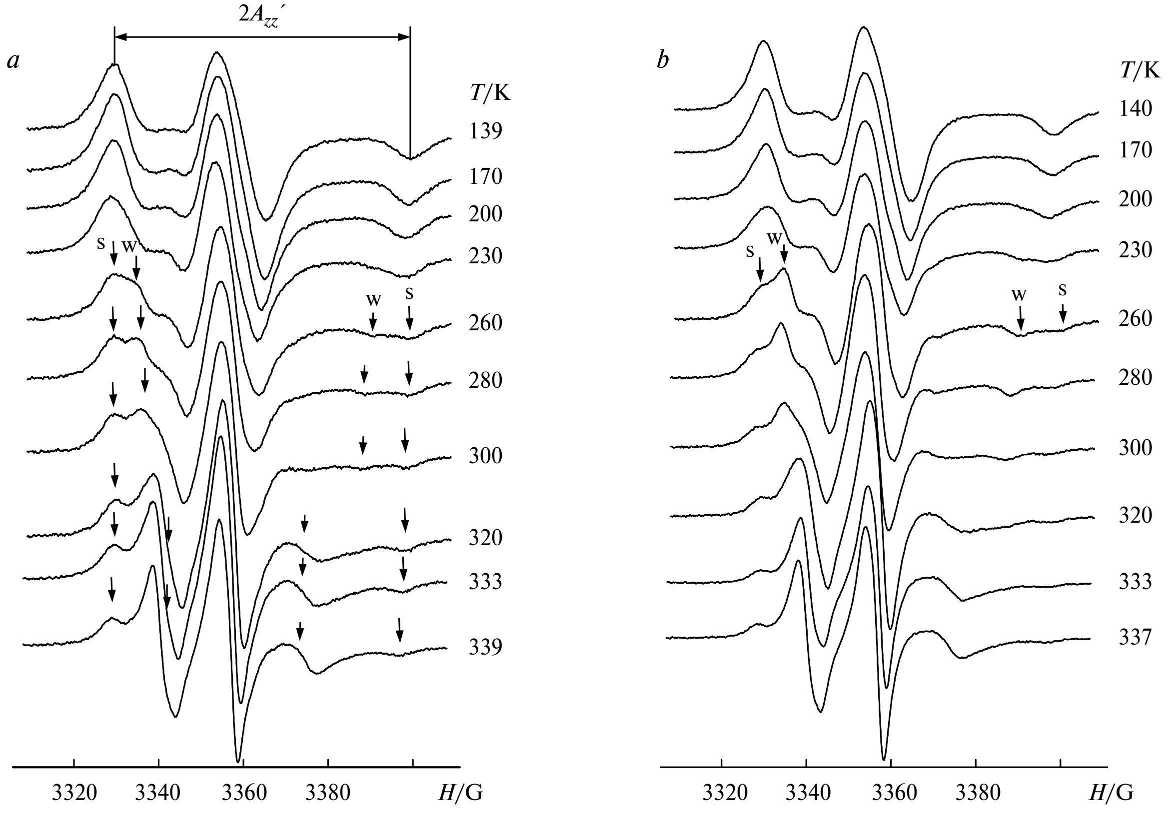

Fig. 1. Temperature dependences of the ESR spectra of the γ-CD—**2**—C_6H_6 (*a*) and γ-CD—**2**—C_6H_{12} (*b*) complexes. The letters "w" and "s" refer to weakly and strongly immobilized signals (see the text). At temperatures of 260, 280, and 300 K, the arrows mark the positions of the outer extrema for both signals; at temperatures of 320, 333, and 339 K, the inner arrows indicate the positions of the centers of the $m = \pm 1$ HFC components of w-signals.

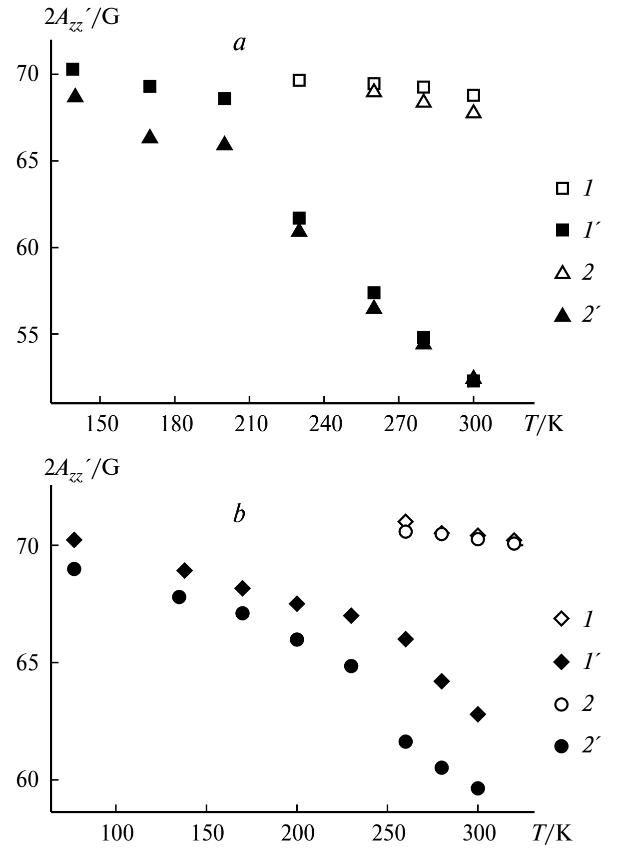

Fig. 2. Temperature dependences of the $2A_{zz}'$ parameter for the s- (*1*, *2*) and w-complexes (*1*′, *2*′) of γ-CD; (*a*) γ-CD—**2**—C_6H_6 (*1*, *1*′), γ-CD—**2**—C_6H_{12} (*2*, *2*′); (*b*) γ-CD—**1**—C_6H_6 (*1*, *1*′), γ-CD—**1**—C_6H_{12} (*2*, *2*′).

carbon results in two effects. First, with an increase in the incubation time, the w-signal amplitude decreases, while the amplitude of the more immobilized s-signal increases in parallel (Fig. 3). Second, a new ESR signal appears resulting from spin-labeled indole (**1** or **2**) with a lineshape corresponding to the fast rotation region (Fig. 4). This signal appears only in the presence of C_6H_6; no such signal is observed upon the incubation with C_6H_{12} within the sensitivity of the ESR spectrometer.

An increase in the s-signal intensity and a decrease in the w-signal intensity take place in the presence of both hydrocarbons for all complexes where these signals are initially observed. It can also be seen from Fig. 3 that the set of ESR spectra corresponding to different recording times has isosbestic points. The presence of these points means that s-complexes are formed from w-complexes. It is noteworthy that the w → s transition is reversible: upon the removal of the liquid hydrocarbon, the fraction of s-complexes decreases, while that of w-complexes increases.

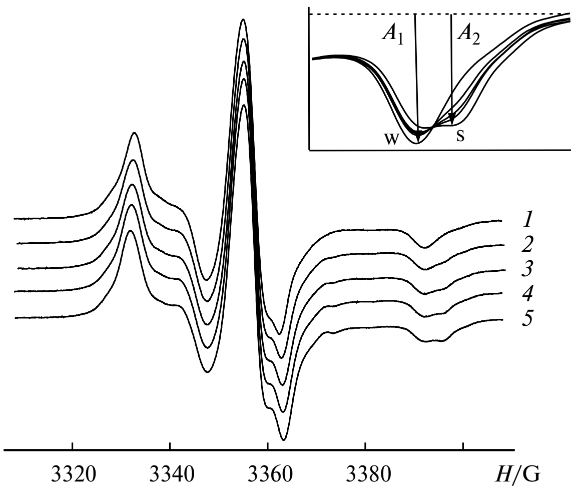

Fig. 3. ESR spectra of the γ-CD—**1**—C_6H_{12} complex in the solid phase in the absence of C_6H_{12} (*1*) and after incubation with C_6H_{12} for $1.2 \cdot 10^2$ (*2*), $3.6 \cdot 10^3$ (*3*), $1.24 \cdot 10^4$ (*4*), and $9.8 \cdot 10^4$ s (*5*). The inset shows the $m = -1$ components of the w- and s-signals with the amplitudes A_1 and A_2; the inset spectra were recorded with a larger number of accumultions and using the Savitzky—Golay smoothening method.

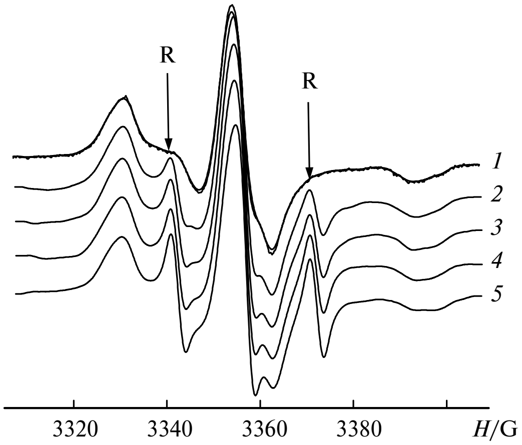

Fig. 4. ESR spectra of γ-CD—**1**—C_6H_6 in the presence of the C_6H_6 liquid phase (*1*) and after incubation with C_6H_6 for $1.5 \cdot 10^2$ (*2*), $3.6 \cdot 10^3$ (*3*), $10.8 \cdot 10^3$ (*4*), and $97.2 \cdot 10^3$ s (*5*). The arrow marks the $m = \pm 1$ signal components of radical **1** dissociated from the complex into the C_6H_6 phase.

The time variation of the fraction of s-complexes can be approximately described using the ratio $A_2/(A_1 + A_2)$, where A_1 and A_2 are the $m = -1$ component amplitudes for w- and s-complexes, respectively (see Fig. 3). These variations are shown in Fig. 5 for γ-CD complexes having different compositions. Although these dependences are represented only by several points, it is seen that the kinetics of the w → s transition cannot be described by one exponent; it includes fast and slow regions with characteristic times differing by about two orders of magnitude. This kinetics is similar for all four γ-CD complexes; however, the fraction of s-complexes obtained after long-term incubation with hydrocarbons (near the equilibrium) depends somewhat on the composition: for the complexes

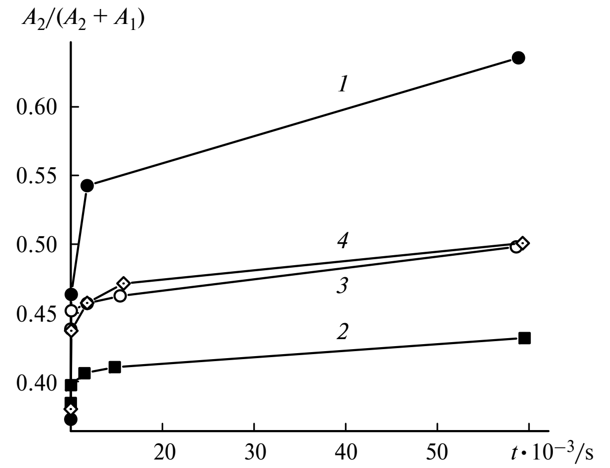

Fig. 5. Time dependences of the fraction of strongly immobilized signals (s) for 2γ-CD—**2**—$2C_6H_6$ (*1*), 2γ-CD—**2**—$2C_6H_{12}$ (*2*), 2γ-CD—**1**—$2C_6H_6$ (*3*), and 2γ-CD—**1**—$2C_6H_{12}$ (*4*) complexes.

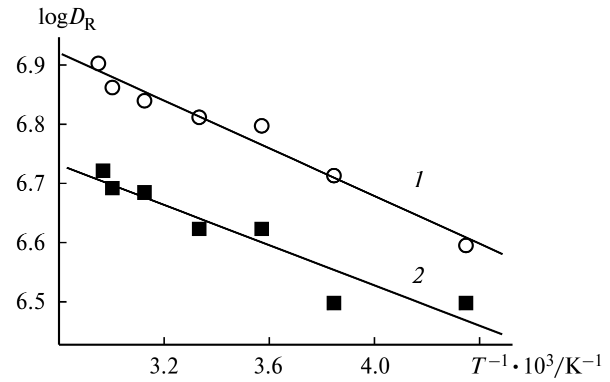

Fig. 6. Temperature dependences of the rotational diffusion coefficients for radical **2** in the 2γ-CD—**2**—$2C_6H_6$ (*1*) and 2γ-CD—**2**—$2C_6H_{12}$ (*2*) complexes in the Arrhenius coordinates.

with **2** in the presence of C_6H_6, it is almost 1.5 times higher than in the presence of C_6H_{12}, whereas for complexes with **1**, the fraction of s-complexes almost does not depend on the nature of the hydrocarbon (see Fig. 5).

The whole set of results, *i.e.*, the appearance (an increase) of the strongly immobilized s-signal upon the addition of low-viscosity hydrocarbons, the parallel decrease in the fraction of the initial w-complex, the presence of isosbestic points, and reversibility of the w → s transition can apparently be attributed only to the fact that in the presence of the liquid phase, a second hydrocarbon molecule is incorporated into the existing 2 : 1 : 1 ternary complex, *i.e.*, a 2 : 1 : 2 complex is formed. Indeed, incorporation of the second hydrocarbon molecule into γ- or β-CD dimers should decrease the free volume inside the dimer and, hence, reduce the rotational mobility of spin-labeled indole. In addition, the 2 : 1 : 2 s-complex is formed from 2 : 1 : 1 w-complex, which gives rise to isosbestic points. Finally, there exists a dynamic equilibrium between these complexes, which shifts toward the s-complex with excess hydrocarbon and toward the w-complex upon the removal of the hydrocarbon.

In the previous study,[1] the libration amplitudes were determined for radicals **1** incorporated into w-complexes using the parameters $2A_{zz}'$, and for radicals **2**, the rotational diffusion coefficients (D_R) were determined in the Brownian rotational diffusion model using the parameters $S = 1 - A_{zz}'/A_{zz}$ (A_{zz}' and A_{zz} are the distances between the outer extrema of the ESR spectrum at a given temperature and at 77 K, respectively). We carried out similar estimates for complexes responsible for the s-signals. It was found however that for **1**, the A_{zz}' values for s-complexes exceed the A_{zz} values at 77 K, evidently, because the w-complexes make a considerable contribution to the latter value. Therefore, we roughly estimated the libration amplitude proceeding from the temperature dependence of A_{zz}' in the region where s-signals are separated from w-signals. In this region, the $2A_{zz}'$ values change by 0.2—0.3 G. By using relations published previously,[1] it was found that the average libration amplitudes (Δθ) for different s-complexes do not exceed 5—6° even at 333 K, *i.e.*, the insertion of the second hydrocarbon molecule results in almost complete immobilization of radicals **1**.

The D_R values for radical **2** at different temperatures in the 230—340 K range were determined for 2γ-CD—**2**—$2C_6H_6$ and 2γ-CD—**2**—$2C_6H_{12}$ complexes using the S values found from A_{zz} measured at 77 K and the $S(D_R)$ calibration dependence calculated previously.[1] The resulting temperature dependences are fitted satisfactorily with straigt lines in the Arrhenius coordinates (Fig. 6). The activation energies and pre-exponential factors for rotation are presented in Table 1.

It is seen from Fig. 6 and Table 1 that the D_R values for s-complexes are 6—10 times lower than those for the corresponding w-complexes[1] and the activation energy for rotation is somewhat lower for s-complexes than for w-complexes. As for 2 : 1 : 1 complexes, the spin label reorientation mechanism and the physical meaning of the activation energy for reorientation in these complexes are not entirely clear. Presumably, the label reorientation (the formation of free volume) requires cooperative motion of all guest molecules. The probability of this motion for 2 : 1 : 2 complexes is lower than for 2 : 1 : 1 complexes.

Table 1. Arrhenius parameters of the rotational mobility: preexponents (A) and activation energies (ε_a) for the rotation of spin-labeled indole **2** in the 2γ-CD—**2**—$2C_6H_6$ and 2γ-CD—**2**—$2C_6H_{12}$ complexes corresponding to highly retarded ESR signals

Complex	log$A$	ε_a/kcal mol^{-1}
2γ-CD—**2**—$2C_6H_6$	7.48±0.05	0.92±0.08
2γ-CD—**2**—$2C_6H_{12}$	7.2±0.1	0.78±0.10

The D_R values for the s-complex with C_6H_6 are 30—60% higher than those for the s-complex with C_6H_{12}. As for 2 : 1 : 1 complexes (see Ref. 1), the greater mobility of **2** in 2γ-CD—**2**—$2C_6H_6$ than in 2γ-CD—**2**—$2C_6H_{12}$ can be attributed to the smaller molar volume of C_6H_6 and, hence, to greater free volume for the reorientation of **2** in the γ-CD dimer cavity.

Finally, the higher mobility of **2** compared to **1** is partly due to the intramolecular mobility in the piperidine ring. In addition, as shown by calculations (see below), the complexes with **2** differ in geometry from the complexes with **1** by the fact that in the former, the distances from the spin-labeled guest to the hydrocarbon molecule are somewhat longer than in the complexes with **1**. This gives rise to a greater free volume available for reorientation of molecules **2**.

To verify this interpretation, we carried out semi-empirical PM3 quantum-chemical calculations for 2 : 1 : 2 complexes. As previously,[1] the calculations were done using a standard set of parameters and different initial positions of the second hydrocarbon molecule in the cavities of the γ- and β-CD dimers. The complexation energies or heats of formation (kcal mol^{-1}) were characterized using the following relations:

$$\Delta E_A = \Delta E_{\text{comp}} - \Delta E_{\text{2CD—SL}} - 2\Delta E_{\text{HC}},$$

$$\Delta E_B = \Delta E_{\text{comp}} - \Delta E_{\text{2CD}} - \Delta E_{\text{SL}} - 2\Delta E_{\text{HC}},$$

$$\Delta E_C = \Delta E_{\text{comp}} - 2\Delta E_{\text{CD}} - \Delta E_{\text{SL}} - 2\Delta E_{\text{HC}}.$$

Here ΔE_{comp}, ΔE_{CD}, ΔE_{SL}, ΔE_{HC}, ΔE_{2CD}, and $\Delta E_{\text{2CD—SL}}$ are the calculated heats of formation of the 2 : 1 : 2 complex, CD, spin-labeled indole, hydrocarbon, CD dimer, and the CD dimer—**1**(**2**) binary complex, respectively. Thus, the ΔE_A, ΔE_B, and ΔE_C values characterize the formation energies of the same complex obtained from different initial states.

Table 2 presents the ΔE_A, ΔE_B, and ΔE_C values for the structures most stable in energy (the maximum $\Delta E_i < 0$) obtained for all γ-CD complexes. It can be seen that the formation of energetically stable complexes with 2 : 1 : 2 stoichiometry is indeed possible. The calculations also showed that 2 : 1 : 2 complexes of various compositions have rather similar arrangements of guest molecules. Examples of these structures for complexes with **1** and **2** are shown in Fig. 7. In one of these, the hydrocarbon molecules are located near both narrow bases ("tails") of the "head-to-head" dimer, and the C_6H_6 plane or the averaged C_6H_{12} plane are tilted relative to the bases and are approximately parallel to the planes of the indole groups of spin labels **1** or **2**. In the other structure, one hydrocarbon molecule is located near the narrow dimer base to which the NO bond is oriented, while the other hydrocarbon molecule is arranged near and parallel to the indole ring. For the γ-CD complexes with **2** and both hydrocarbons, the first type structure is more stable (see Fig. 7, *a*). The most stable structure for the complex of **1** with C_6H_6 is also similar to the first type, whereas for the complex of **1** with C_6H_{12}, the second type structure is more stable (see Fig. 7, *b*). As seen in Fig. 7, in both structures, the hydrocarbon molecules create steric hindrance to the rotation of spin-labeled indole, which is consistent with the

Table 2. Energies of formation of 2 : 1 : 2 γ-CD complexes

Complex	$-\Delta E_A$	$-\Delta E_B$	$-\Delta E_C$
	kcal mol^{-1}		
2γ-CD—**1**—$2C_6H_6$	18.0	30.1	49.9
2γ-CD—**1**—$2C_6H_{12}$	17.7	29.8	49.6
2γ-CD—**2**—$2C_6H_6$	15.7	31.1	50.9
2γ-CD—**2**—$2C_6H_{12}$	16.8	32.2	52.0

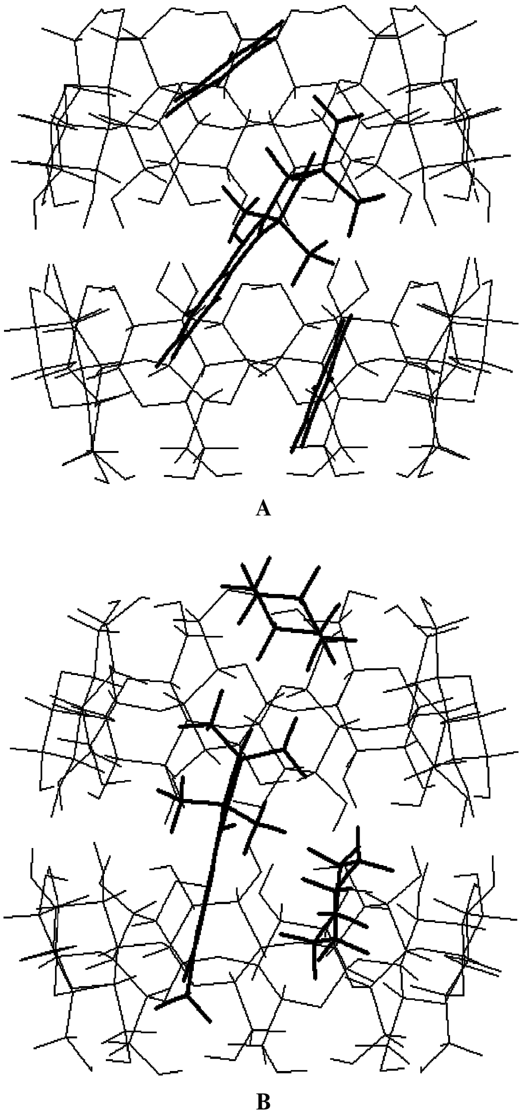

Fig. 7. PM3-calculated structures of 2 : 1 : 2 complexes for γ-CD—**2**—C_6H_6 (**A**) and γ-CD—**1**—C_6H_{12} (**B**).

experimentally observed immobilization of spin label motion in 2 : 1 : 2 complexes. Nevertheless, as can be seen from Fig. 6, radical **2** has a substantial rotational mobility in both complexes with C_6H_6 and C_6H_{12}. This mobility is possible through cooperative motion of the guest and host molecules, which gives rise to free volume. It is also facilitated by intramolecular dynamics of the piperidine ring.

It is seen from Table 2 that the formation energies of the γ-CD complexes with C_6H_6 and C_6H_{12} do not differ much both for complexes with **1** and **2**. It is of interest to compare these results with the fractions of s-complexes present after long incubation times with hydrocarbons (see Fig. 5). Since the fraction of s-complex is proportional to the concentration of the hydrocarbon, it is more correct to normalize the $A_2/(A_1 + A_2)$ values (see Fig. 5) for such comparison to the molar concentrations of C_6H_6 and C_6H_{12} and, in addition, to take into account the differences between the solvation of both hydrocarbons in their liquid phases. The ratio of these concentrations is ~1.22. The difference between the solvation energies can apparently be neglected, because the boiling points (80 and 81 °C, respectively) and the evaporation heats (7.35 and 7.34 kcal mol^{-1}) of these hydrocarbons are very similar. The normalized ratios of the fractions of s-complexes with C_6H_6 and C_6H_{12} are 1.2±0.2 and 0.82±0.2 for the complexes with **1** and **2**, respectively. Thus, the correlation of the calculated complexation energies (see Table 2) with the experimental relative fractions of s-complexes, taking into account the experimental errors and PM3 approximations, can be regarded as satisfactory.

As already stated, the incubation with a liquid hydrocarbon (benzene) gives rise to a new ESR signal from the spin-labeled indole (**1** or **2**) with line shapes corresponding to fast rotation (see Fig. 4). A comparison of these signals with the ESR spectra of the corresponding radicals in C_6H_6 shows that they have identical isotropic HFC values. A precision comparison of the rotation correlation times is difficult due to partial overlap of the new signal with w- and s-signals. Therefore, in order to verify the identity of the new signal with the signal from the radical in benzene, we subtracted the latter signal from the overall spectrum of the complex. The appearance of a signal of the opposite polarity served as the criterion for ending the subtraction. It was found that this signal appears simultaneously for the $m = \pm 1$ components. This means that the shape of the "fast" signal is identical to that of the signal from the benzene solution. Thus, in the presence of liquid benzene, spin-labeled indole is redistributed from the solid-phase complex to the C_6H_6 liquid phase. The fact that unlike C_6H_6, in the C_6H_{12} liquid phase, no signals of free radicals can be observed for the complexes of both spin-labeled indoles with γ-CD and C_6H_{12} is apparently due to the substantially lower solubility of spin-labeled indoles in C_6H_{12} compared to C_6H_6. To check this interpretation, we measured the solubilities of compound **2** in C_6H_6 and C_6H_{12}. It was found that the solubility in C_6H_6 is more than an order of magnitude higher than in C_6H_{12}, *i.e.*, the transfer from the complex in C_6H_{12} is energetically unfavorable for this reason.

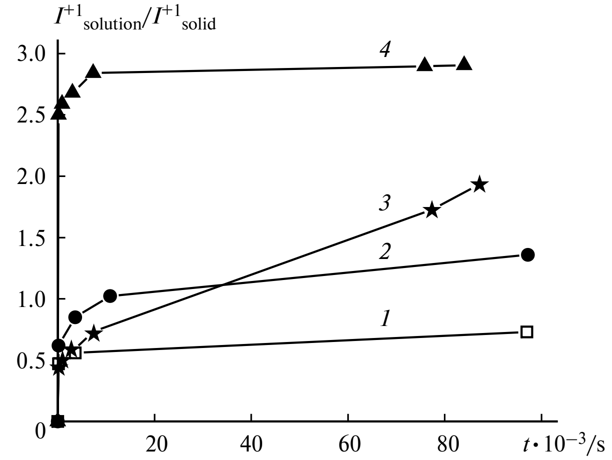

Fig. 8. Time dependences of the ratio of the amplitudes of $m = +1$ signal components from the label in solution and the immobilized overall signal from the 2 : 1 : 1 and 2 : 1 : 2 complexes: γ-CD—**2**—C_6H_6 (*1*), γ-CD—**1**—C_6H_6 (*2*), β-CD—**2**—C_6H_6 (*3*), and β-CD—**1**—C_6H_6 (*4*).

The partition coefficient of the spin-labeled indole between the complex in the solid phase and the hydrocarbon solution (K) was determined by comparing the ESR signals of the complex and spin-labeled indole in a solution with reference samples. In addition, the distribution of the spin-labeled indole between the complex in the solid phase and the hydrocarbon solution can be characterized by the ratio of the amplitudes of the $m = +1$ components of the "fast" ESR signal and the sum of the retarded w- and s-signals (Fig. 8). This value characterizes the free energy of transfer of the spin-labeled guest from the complex to the hydrocarbon phase. These ratios were determined for various complexes of γ- and β-CD with **1** and **2** and with C_6H_6 as the second guest (Table 3, Fig. 8). The dissociation energy of spin-labeled indole from the ternary complex in vacuum (ΔE_d) can be determined by quantum-chemical calculations. For complexes with 2 : 1 : 1 and 2 : 1 : 2 stoichiometric ratios, these values (ΔE_d and ΔE_d*, respectively) can be found using the following relations:

$$\Delta E_d = \Delta E_{comp} - \Delta E_{SL} - \Delta E_{2CD-HC},$$

$$\Delta E_d{}^* = \Delta E_{comp}{}^* - \Delta E_{2CD-2HC} - \Delta E_{SL},$$

where ΔE_{comp} and $\Delta E_{comp}{}^*$ are the formation heats of 2 : 1 : 1 and 2 : 1 : 2 complexes, respectively. If the spin-labeled guest is exchanged with C_6H_6, one gets

$$\Delta E_d{}' = \Delta E_{comp} - \Delta E_{SL} - \Delta E_{2CD-HC} + \Delta E_{HC}.$$

These values are also presented in Table 3. Quantitative comparison of experimental partition coefficients (or

Table 3. Dissociation energies of the spin-labeled guest from the 2 : 1 : 1 complex without the exchange (ΔE_d) and with the exchange for benzene ($\Delta E_d'$) and from the 2 : 1 : 2 complex without exchange with benzene (ΔE_d*), and partition coefficient of spin-labeled indole between a hydrocarbon solution and the solid-phase complexes (K)

Complex	$-\Delta E_d$	$-\Delta E_d'$	$-\Delta E_d^*$	K
	kcal mol^{-1}			
2β-CD—**2**—C_6H_6	8.9	2.75	8.75	0.022
2γ-CD—**1**—C_6H_6	11.8	5.1	16.0	0.0086
2γ-CD—**2**—C_6H_6	18.7	12.0	17.0	0.0075

free energies of transfer) and the quantum-chemical data (ΔE_d) is impossible, because the free energies of transfer are thermodynamic values, *i.e.*, they are ensemble averages that include enthalpy and entropy terms, and, second, represent differences between the free energies of the spin label in the complex and in liquid benzene; however, the latter value was not taken into account in the calculations. Nevertheless, the partition coefficients and the relative ΔE_d values for complexes with C_6H_6 can be compared qualitatively, because for all of these complexes, the final state of the spin label is the same (a solution in C_6H_6). It is seen from Table 3 that the partition coefficients of the spin-labeled indoles between the complex and C_6H_6 are higher in the case of β-CD than γ-CD and are somewhat higher for **1** than for **2**. The dissociation energies of spin-labeled indoles from 2 : 1 : 1 and 2 : 1 : 2 ternary complexes increase in the same order (see Table 3), *i.e.*, the experimental and theoretical data are in qualitative agreement.

It is also of interest to compare the formation kinetics of the s-complexes with the dissociation kinetics of spin-labeled indoles (*i.e.*, time dependence of the $A_2/(A_1 + A_2)$ ratio, see Fig. 5) and the intensity ratio for the "fast" and immobilized signals (see Fig. 8). It is seen from Figs 5 and 8 that the characteristic times are approximately equal for both processes, despite the fact that they differ substantially in energy. This result suggests that diffusion of C_6H_6 molecules within solid microparticles (microcrystals) containing paramagnetic ternary complexes is the rate-limiting step of both processes. These complexes are obtained with the use of a large excess of CD and hydrocarbon.[1] Since the ESR lineshapes of the complexes are indicative of a high magnetic dilution (the absence of dipole—dipole interaction between the spin-labeled guests), the sample can be considered as the solid phase of the CD—hydrocarbon binary complexes doped with ternary complexes containing spin-labeled indoles.

Note that in the presence of a liquid hydrocarbon phase, the $2A_{zz}'$ value for the w-complexes does not change. This means that the rotational mobility of the spin-labeled guests in the w-complexes does not change either, and hence, the local structure of a microparticle around the ternary complexes also seems to remain unchanged in the presence of the liquid hydrocarbon macrophase.

* * *

Thus, all the experimental data and the results of quantum-chemical calculations obtained in this study lead to the conclusion that in ternary system β(or γ)-CD—spin-labeled indole (**1** or **2**)—hydrocarbon (benzene or cyclohexane) in the presence of a liquid hydrocarbon phase, in addition to 2 : 1 : 1 complexes, 2 : 1 : 2 complexes are formed with one molecule of spin-labeled indole and two hydrocarbon molecules that are incorporated into the CD dimers. The rotational mobility of spin-labeled indoles in the latter complexes is substantially immobilized upon the inclusion of the second hydrocarbon molecule. The concentration of 2 : 1 : 2 complexes increases in the presence of the liquid hydrocarbon and decreases upon its removal. These results indicate that rather large supramolecular ensembles based on CD can be self-assembled; these ensembles including functional guest molecules could serve to perform more complicated photophysical or chemical functions.

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