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Excimers of organic molecules

N N Barashkov, T V Sakhno, R N Nurmukhametov, O A Khakhel'

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Abstract. Studies devoted to excimers in organic systems are surveyed. Processes leading to the excitation of the excimer luminescence are examined. Examples of the excimer-like glow of dimers are described. The relation between the structure of the complexes and their fluorescence properties is demonstrated. The bibliography includes 218 references.

I. Introduction

Excimers are dimers a distinctive feature of which is instability in the ground state. Their formation is observed only on photoexcitation of the system. (Here and henceforth physical dimers are considered.) After deactivation of the dimers, the latter dissociate into individual molecules. The term 'excimer' was adopted on the suggestion of Stevens and Hutton[1] and was recommended by the International Symposium on Molecular Luminescence[2] instead of the term 'excited dimer' employed previously. Dimers comprising two different chemical compounds (in particular organic molecules and inorganic species[3,4]) have been called 'exciplexes'.[2] The state of the research into these species has been described in detail in a monograph.[3]

In inorganic systems, excimers were known long before their detection in organic molecules. The atoms of certain metals and noble gases are capable of forming excimers. The optical transitions in their excimers are used for the generation of laser radiation.[5] The excimers of organic compounds were first identified in 1954.[6,7] The class of excimer-forming molecules has not been clearly outlined but it embraces almost all aromatic hydrocarbons with a planar structure and certain compounds with heteroatoms. Certain coordination compounds with organic ligands can be included among them.[8,9]

A characteristic spectroscopic feature of excimers is a luminescence band with an anomalously large Stokes shift (5000–12000 cm^{-1}). Its identification is based primarily on the following features. Its intensity relative to that of the monomer (molecular) glow in solutions increases with increase in the concentration of the chromophore. In certain media, such variation may not be observed but a common feature is the absence of visible qualitative changes in the absorption spectra of the test systems, i.e. the absence of aggregation in the ground state. Since the radiative transitions in the excimer lead to an unstable state, the excimer component is represented by a broad structureless spectral band. The overlap of the monomer and excimer components of the luminescence is as a rule appreciable. For example, for pyrene—a typical excimer-forming compound—the short-wavelength emission edge in the spectra of excimers occurs at 375 nm, while the 0–0 transition of molecular pyrene occurs at 372 nm, i.e. the excimer component almost fully overlaps the region corresponding to the luminescence of the molecular form.[10]

One of the principal characteristics of excimer-forming systems is the ratio of the excimer luminescence intensity to the intensity of the molecular fluorescence band (I_d/I_m).

The formation of excimers is observed in liquid solutions of monochromophoric molecules, in condensed and gas phases, in polymer matrices, and other media over a wide range of physicochemical conditions. The increased interest in excimer systems is due to their use for the solution of applied problems. In particular, the methods for the structural studies on polymers[11–15] and the determination of the properties of biological systems[16,17] are based on the analysis of excimer fluorescence. The spectroscopic parameters of excimers have attracted the attention of investigators also in connection with the attempts to create effective devices for the concentration of radiation.[18]

There exist also dimers which are stable in the ground state, but exhibit the spectroscopic properties of excimers. Such formations have been designated in various studies as sandwich dimers[19–21] and associated dimers.[22–26] Strictly speaking, their luminescence cannot be identified as excimer luminescence in conformity with the definition adopted[2] and they constitute an example of other forms of aggregation of excimer-forming molecules. The formation of dimers is observed in various media but the number of communications on this topic is small.

N N Barashkov¶, R N Nurmukhametov, O A Khakhel' L Ya Karpov Physicochemical Institute (¶ also Chemical Scientific-Technological Association 'Chemprogress'), ul. Obukha 10, 103064 Moscow. Fax (7-095) 975 24 50
T V Sakhno Poltava Cooperative Institute, ul. Kovala 3, 314601 Poltava, Ukraine. Fax (7-05322) 79 160

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A specific analysis of the recorded excimer-like luminescence was not carried out in all investigations, which suggests that such objects are more common (for example, in the case of many polymers).

II. Excimers in liquid solutions of monochromophoric molecules

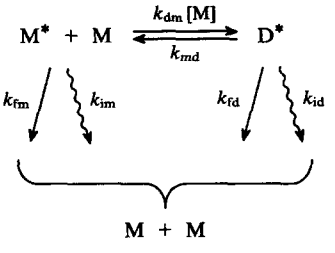
The study of processes involving the formation of the excimers of monochromophoric molecules in liquid solutions was carried out particularly vigorously in the 1960s.[27-30]

Eximer formation is determined by the mutual diffusion of molecules. The quenching of the luminescence of the monomer component obeys the Stern–Volmer relation, i.e. the ratio I_d/I_m increases linearly with increase in the dye concentration:

$$\frac{I_d}{I_m} = K[M],$$

where K is the constant of the equilibrium between the monomer and excimer centres and [M] the phosphor concentration. The equilibrium constant K is expressed in terms of the constants of the reactions presented in Scheme 1. This scheme was put forward by Forster[6,7] and was subsequently developed by Birks.[28]

Scheme 1



The constants k_{dm} and k_{md} in this scheme correspond to the rates of formation and decomposition of the excimers, k_{fm} and k_{fd} are the constants for the radiative deactivation of the monomers and excimers, and k_{im} and k_{id} are the internal conversion constants for both luminescence centres.

Analysis of the kinetics of the formation of excimers in accordance with Scheme 1 leads to the following definition of the quenching function for the luminescence of the monomer and excimer components after the exciting pulse:[28]

$$I_m(t) = A_1 \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t),$$

$$I_d(t) = A_3[\exp(-\lambda_2 t) - \exp(-\lambda_1 t)].$$

The constants for the process taken into account in Scheme 1 are expressed in terms of the parameters A_1, A_2, A_3, λ_1, and λ_2 and can be determined by various procedures.[31]

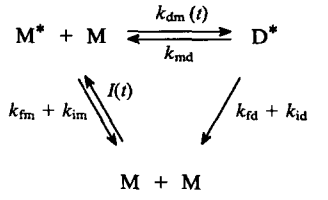
Scheme 1 has been hitherto resorted to for the interpretation of the results of experiments,[32-35] but it describes only approximately the excimer formation processes in liquid solutions. The fact that the rate of formation of excimers is assumed to be independent of time in Scheme 1 is most striking. This approximation is justified only for systems after a considerable time has elapsed since the excitation step. Since the rate of formation of excimers is controlled by the diffusion of chromophores, it follows that, in conformity with the theory of diffusion-controlled reactions,[36] it should be expressed in the form

$$k(t) = a(1 + bt^{-1/2}),$$

where $a = 4\pi DN_A R/1000$, $b = R/(\pi D)^{1/2}$, t is the time, N_A the Avogadro number, D the mutual diffusion coefficient of the chromophores, and R the effective reaction radius. The excimer kinetics in various systems have been analysed after adopting this approximation.[37-39] The time variation of the rate of formation of excimers has been called the 'transient effect'.

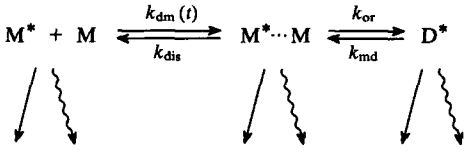
The development of experimental techniques has made it possible in recent years to obtain data for the construction of better models. In particular, a model has been proposed[40,41] (Scheme 2) in which account is taken of the possibility of the formation of excimers as a result of the reassociation of molecules [the parameter $I(t)$]. The results of calculations taking into account this parameter agree much better with experimental data than those of calculations in accordance with Scheme 1.

Scheme 2



Further improvement of Birks's scheme involved taking into account the orientation processes in the intermediate molecular complexes. Vogelsang and Hauser[42] investigated the kinetics of the quenching of the excimer and monomer luminescence using two approaches: with and without allowance for the time variation of the rate of formation of excimers. The agreement between the calculated and experimental data was better in the first case, but for the initial period both methods yielded results which differed appreciably from the experimental data. The discrepancies were explained by putting forward the following scheme (Scheme 3):[42,43] the excited and unexcited molecules approach one another, after which either excimers are formed as a consequence of the relaxation orientation (constant k_{or}) or the pre-excimer complexes dissociate (constant k_{dis}).

Scheme 3



As already mentioned, excimer formation processes lead to the appearance of physical dimers in which the electronic excitation is delocalised over both molecules.[30] However, a different approach has been developed.[44,45] According to the hypothesis put forward by the author, the appearance of the structureless emission band of the excimers (exciplexes) can be accounted for within the framework of the idea of a fractional energy transfer: as the two molecules approach one another, part of the electronic excitation energy of the first is transformed into the vibrational and rotational excitation of the second, which functions as a quenching agent. The remaining energy is emitted. In this process, the main role is attributed to the interaction of the vibrational states. It has been suggested that this theory possesses quantitative predictive power in relation to the Stokes shift of the excimer luminescence and provides criteria for the assessment of the ability of chromophores to form excimers.

III. Excimer fluorescence of crystals

Excimers are formed not only in liquid solutions but also in media with a greatly restricted mobility of the molecules. In such cases, one is dealing with the so-called excimer-forming centres and the migration of excitation energy towards them. In crystals of organic compounds, the appearance of such centres (predimer sites) is attributed to the presence of structural defects in the bulk phase,[46] the concentration of which can be raised by applying pressure (as a consequence of the sliding of dislocations, neighbouring molecules undergo a reorientation to a productive

geometry similar to the excimer geometry). The activation of these centres is usually explained by the localisation of singlet excitons on them.

The excimer fluorescence of crystals is determined by the temperature. At room temperature, the excimer state in anthracene has a higher energy than the free exciton state and at high temperatures (>400 K) the lattice stabilisation energy is reduced[47] and thermal equilibrium is established between the excimer and free exciton states with appearance of excimer fluorescence.

Typical crystals giving rise to excimer fluorescence under normal conditions are those of pyrene and the α-modification of perylene. In contrast to other polyacenes, the predimer sites in these compounds are not structural defects but regular elements of the crystal lattice—dimers arranged in parallel.[48] The excimer states in such crystals may be populated both by direct excitation and as a consequence of energy migration. The time of the transfer of excitation in pyrene is 5×10^{-5} s and the process activation energy is $\sim8.8\times10^{-21}$ J.[46] Three possible mechanisms of the migration of the excimer state have been proposed:[49] (1) dissociation of excimers into two monomers (in the ground and excited states) with subsequent energy transfer to a neighbouring pair; (2) nondissociative thermal activation of the excimers to a level having the same energy as the S_1 level of the monomer with subsequent energy transfer to a neighbouring pair; (3) the assumption of the pre-excimer geometry by the nonexcited dimeric pair as a result of thermal excitation with subsequent energy transfer from another excited pair.

In the crystals of pyrene and the α-modification of perylene, other excimer states also arise, such as the *B*-state[50] or the *V*-state[51] for pyrene and the *Y*-state[52] for perylene. Fluorescence in the frequency range between the free exciton and normal excimer bands is characteristic of these compounds. In the crystals of the α-form of perylene, normal emission is appreciably quenched below 70 K with the appearance of a new emission band of the excimer type. In the crystals of pyrene at ~120 K, there is a structural transition[48] and normal fluorescence is not quenched as the temperature is reduced. Until recently, the *V*-band was observed only in the time-resolved spectra.[50,53] Mizuno and Matsui[51] were able to obtain a metastable pyrene crystal with the structure of the high-temperature phase at temperatures below the critical temperature. The emission spectra of this and similar specimens are presented in Fig. 1. The *V*-fluorescence of the metastable crystal is recorded by the usual spectroscopic methods.

The dynamics of the excitation of the excimer luminescence in crystals with two excimer states has been investigated.[51,53] Fig. 2 presents the time-resolved spectra of a pyrene crystal in the picosecond range. The *V*-fluorescence is observed most distinctly in the early stage of the development of luminescence, which may indicate the initial relaxation of the excited dimeric pairs to the *V*-state with subsequent transition to the normal excimer state. All the transitions are activated. At high (room) temperatures, the *V*-state gives rise to a relatively indistinct potential minimum in the spectrum, so that the excited state in pyrene under the usual conditions is represented mainly by the free-exciton state and by traps of the normal type.

The situation in the crystals of α-perylene differs only by the rate of the relaxation processes. The relaxation of excitons from the free-exciton state takes place faster than in pyrene, possibly via a tunnel mechanism.[51,53] In the temperature range 4–160 K, the *Y*-state is metastable and lies above the normal excimer state.[54]

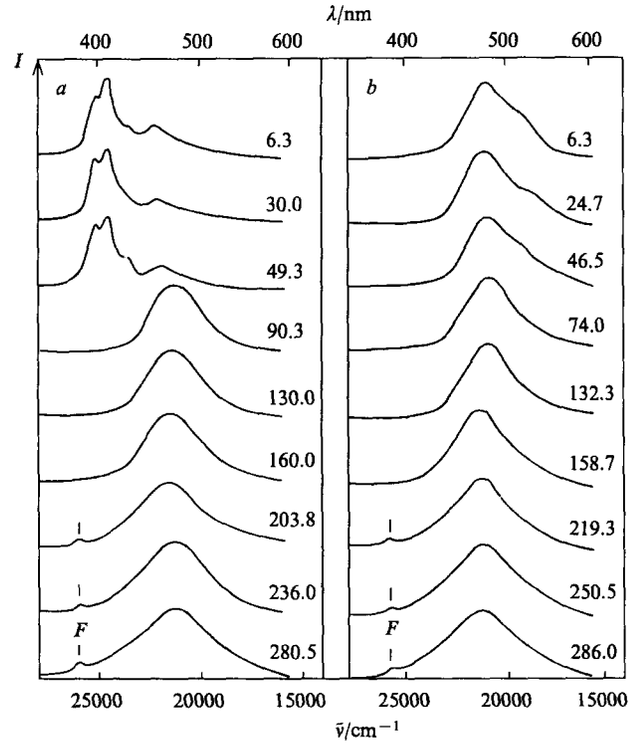


Figure 1. Temperature variation of the fluorescence spectra of crystalline pyrene:[51] (*a*) spectra of the metastable high-temperature phase; (*b*) spectra of the usual crystal; the numerals opposite the curves denote the temperature (K) at which the corresponding spectrum was obtained; *F* denotes the free exciton band.

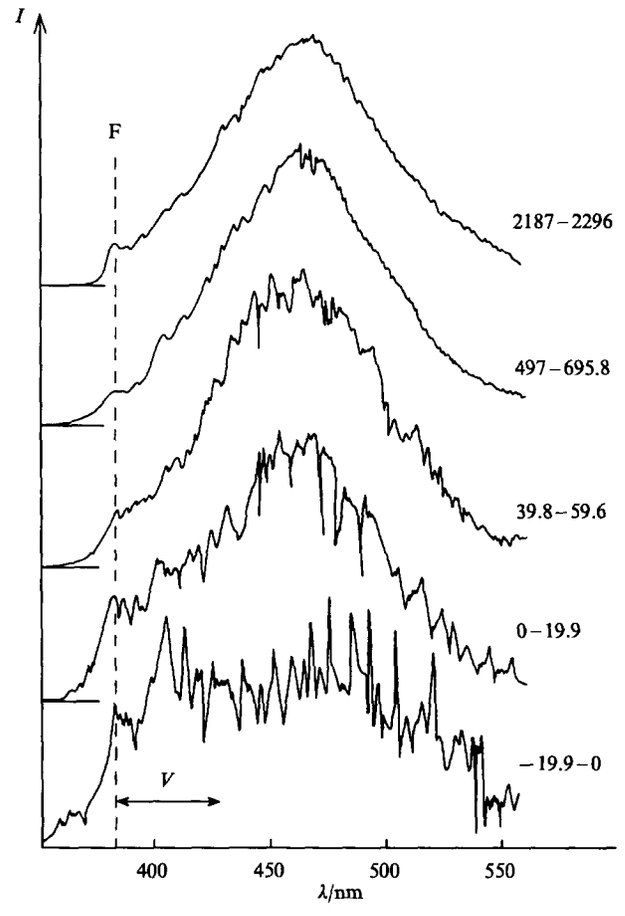


Figure 2. Time-resolved spectra of the pyrene crystal obtained at 293 K. The numbers to the right—time intervals (ps) over which the corresponding curves were integrated; the instant when the exciting laser pulse (λ = 316 nm) reaches maximum intensity is assumed to be the zero time; *F* denotes the free exciton band; *V* denotes the region corresponding to the luminescence of the *V*-centres.[51]

The energy barrier between them is[54] $\sim 310\ cm^{-1}$. It increases following the application of pressure, so that *Y*-fluorescence can be observed also at room temperature.[55]

In melts of organic substances, the specific features of the corresponding crystalline structures are apparently retained. Thus the excimer emission band in the spectra of anthracene melts[47] in the range 460–470 nm is observed only ~ 100 ps after the exciting pulse, which is evidently associated with the necessity for orientation processes on formation of excimers. On the other hand, in the pyrene melt the molecules are evidently in a predimeric state, as in the crystal, because the excimer band is recorded directly after the excitation step.[47] Admittedly, in the temperature range 450–600 K the appearance of a new emission band (390–420 nm) is observed for pyrene. It is either due to the monomolecular form (on the assumption of the thermal dissociation of dimers) or is caused by the formation of yet another kind of excimer complexes.

IV. Excimers in polymers

Almost all the aromatic vinyl polymers, certain heterocyclic polymers, and their various copolymers belong to the excimer-forming class of polymers. Luminescence from both solid specimens and liquid solutions is observed. Similar properties are shown also by solid solutions of excimer-forming molecules in polymer matrices. The excimer luminescence of polymers is due to the presence in their bulk phase of two types of excimer-forming centres.

The excimer-forming centres in polymeric media can be represented both as conformations of sections of polymer chains favourable for the formation of excimers and as sections for which the energy barrier to the assumption of the excimer configuration is very small and which are capable of reorientation during the lifetime of the excited state.[11] The centres of the first type play a major role in solid polymers but they may be formed also in solutions. Neglecting the energy migration processes, the fraction of these centres can be expressed in terms of spectroscopic parameters:[31]

$$f_d = \varphi_{fd}\varphi_{fm} \Big/ \left(\frac{\varphi_{fd}}{\varphi_{fm}} + \frac{q_{fd}}{q_{fm}}\right),$$

where φ_{im} and φ_{id} are the quantum yields of the luminescence of the monomeric† and excimeric centres and $q_{fd}/q_{fm} = Q$ is the ratio of the number of quanta absorbed by the monomeric and excimeric centres. It is assumed here that $\varepsilon_d = 2\varepsilon_m$, ε_m and ε_d being the extinction coefficients of the monomeric and dimeric centres. In this case

$$\frac{I_d}{I_m} = \frac{1}{2}Q\left[(1 + 8[M]_0K)^{1/2} - 1\right],$$

where $[M]_0$ is the overall concentration of the chromophoric fragments and K is the constant of the equilibrium between the dimeric and monomeric forms.

The fraction of conformations favourable for excimer formation is defined by the expression[11]

$$f_d = \frac{W_d \exp(-\Delta E/kT)}{W_m + W_d \exp(-\Delta E/kT)},$$

where W_m and W_d are the multiplicities of the degeneracies of the monomeric and excimeric states and ΔE is the difference between their energies.

† In this section, the monomeric and dimeric centres are understood as isolated chromophores and excimer-forming pairs of chromophores respectively.

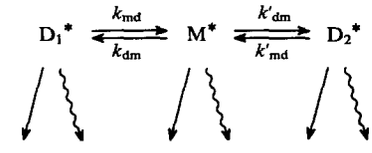
Calculations of the structures of poly-2-vinylnaphthalene, polyvinylcarbazole and polystyrene have shown that the fractions of the excimer-forming centres are of the order of 10^{-2}, 10^{-3} and 10^{-3} respectively.[11,56] In the solid polymers, the populations of the excimeric states are determined by the irradiation temperatures of the specimens.

The insignificant concentration of the excimer-forming centres in the polymers together with the observed intensity of the excimer fluorescence lead to the conclusion that the excitation energy is transferred to centres with the monomeric form of the phosphor.[11] The nonradiative migration of energy in solutions may lead to an even greater effect owing to the possibility of the rotational motions of the centres during the lifetime of the excited state of the monomer. Thus the formation of excimers in polymeric systems is a complex process involving the migration of energy and segmental rotation. Furthermore, in solutions there is also a possibility of the macroscopic diffusion of the chromophores, leading to an excimeric configuration, but in polymers these processes are less significant than in solutions of monochromic molecules. For aromatic polymers, the fluorescence of the monomers and excimers is described satisfactorily taking into account the energy migration along the chain[57–62] and in the bulk phase.[63–66] The overall schematic representation of the processes in the polymers taking into account the energy migration and the rotation of the chromophoric fragments has been examined.[59] However, the role of energy migration in polymers still has not been ultimately elucidated. There are experimental facts which cast doubt on its effectiveness. For example, polarisation measurements of the fluorescence of polystyrene films have shown[67,68] that the luminescence retains a high degree of polarisation. This agrees poorly with the hypothesis that energy transfer processes make a significant contribution.

The probability of the formation of excimers in polymeric systems is determined by the structure of the chain and its composition. Attempts have therefore been made in numerous investigations to establish the steric structure of the polymers.[69–82] The formalism of the dynamics of the rotational transitions has been developed[83] for copolymers of the type $A-B_n-A$, where A is the chromophore and B_n are neutral units. In order to establish the possible number of units in contact, computer modelling has been employed.[31,84–86] Studies have also been carried out for low-molecular-mass and bichromophoric analogues of polymers.[87–93]

Among the bichromophoric molecules, one may distinguish two types of compounds—compounds with a flexible linkage between the two chromophores and cyclophane compounds. For the former, the intramolecular excimer formation is preferred to the greatest extent if the chain between the chromophores consists of three carbon atoms.[94] However, this process takes place, albeit with a lower effectiveness, also without the maintenance of this stringent requirement.[95] The formation of intramolecular excimers in bichromophoric molecules is described by two kinetic schemes. In the first case, in the absence of the necessary degree of freedom the excimers are formed only in one steric configuration (see Scheme 1), while in the second (Scheme 4) there is a possibility of two types of complexes.[90] A similar situation is observed also for paracyclophanes,[11] anthracenophanes,[96] pyrenophanes,[97,98] etc.

Scheme 4



The effectiveness of the formation of the excimers of bichromophores in solutions is determined by the kinetics of the conformational changes in the chains linking the chromophores.[11] Depending on the method of formation of the crystals and also on the size and structure of the saturated chains, some of the cyclophanes can give rise to excimer fluorescence also in the solid state.[96]

In individual instances, excimer formation may be an intermediate stage in photochemical reactions. This applies particularly to systems incorporating anthracene chromophores.[31,99-104]

The influence of the composition of the polymer chain on the formation of excimers has been examined for vinylaryl polymers. Fig. 3 presents the dependence of I_d/I_m on the fraction of adjacent chromophores in the chain for solutions of copolymers of the two most typical representatives of this class. The nonzero value of I_d/I_m in the absence of diads in the copolymer chain indicates a finite probability of the formation of excimers between chromophores remote from one another along the chain or between chromophores of different chains. There are also polymers (for example polyacenaphthalene) in which excimers are formed between remote chromophores with a high probability.[31,74,106]

Yet another factor influencing the yield of the excimer luminescence is the molecular mass of the polymers. Typical dependences of I_d/I_m on the chain length for a solution of a copolymer with isolated chromophores and for a solution of a chromopolymer are presented in Fig. 4. Both curves tend to reach a plateau for high molecular masses. However, sometimes, as the length of the polymer chain increases, a decrease in the relative yield of the excimer luminescence is observed. Thus I_d/I_m for dilute solutions of polyindole decreased[86] with increase in chain length and tended to zero already for $N \approx 500$. This result agrees with the results of the calculation of the number of units in contact within the polymer.

Considerable interest in the kinetics of the formation of excimers and polymers has been shown in a large number of studies. The quenching of the luminescence of the monomeric and excimeric components in these media is frequently described by the sum of not two but three or more exponential functions. This shows that the processes in the system cannot be explained within the framework of Scheme 1. One (or several) of the following factors have apparently not been taken into account:[31] the different energy migration distances, the formation of excimeric states as a result of the rotation of segments, and the multiplicity

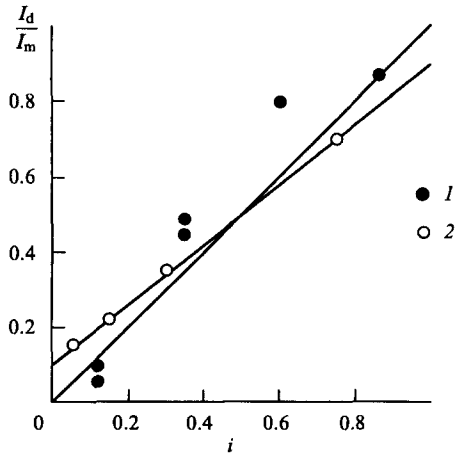


Figure 3. Dependence of I_d/I_m on the fraction of neighbouring chromophores in the chain (i): (*1*) solution of styrene-acrylonitrile in ethanol;[105] (*2*) 2-vinylnaphthalene-dimethyl-maleate in a 3:2 (by volume) tetrahydrofuran–diethyl ether mixture.[71]

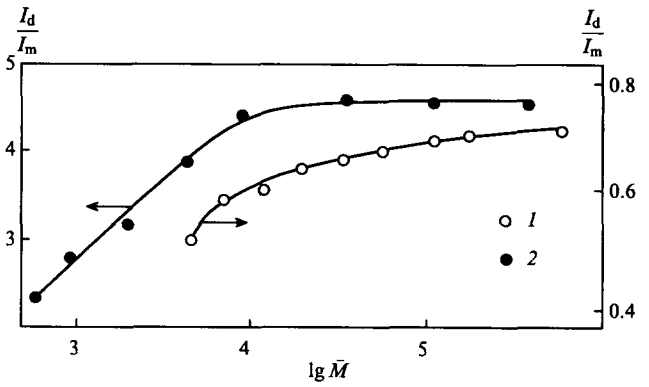
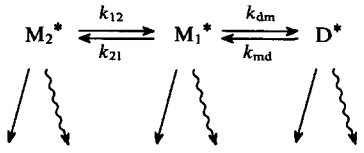


Figure 4. Dependence of I_d/I_m in solution on the molecular mass: (*1*) copolymer of the type $(A-B_n)_N$ (where A = chromophore, B_n = neutral unit, and n = 100) in tetrahydrofuran;[107] (*2*) styrene homopolymer in 1,2-dichloroethane.[11]

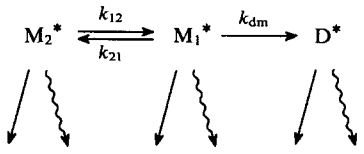
of types of excimeric and monomeric states. Thus models postulating the existence of two different monomeric states have been put forward (Schemes 5–8; M_1 and M_2 designate different conformers).[106,108,109]

In Schemes 5–7, excimers may be formed only from the conformers M_1 as a result of the mutual rotation of the segments. Scheme 8 presupposes their formation also from the conformers M_2 as a result of macroscopic chain motions.

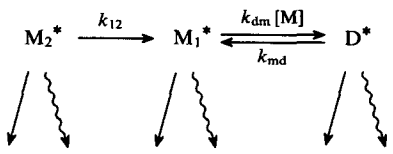
Scheme 5



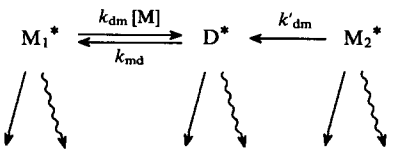
Scheme 6



Scheme 7

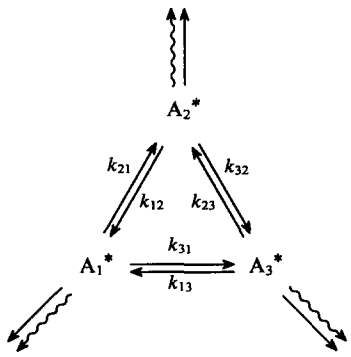


Scheme 8



The formation of several types of excimeric states has been postulated.[110,111] In order to account for the kinetics of the quenching of the luminescence in styrene copolymers, a model with three different monomeric and two excimeric centres, not taking into account the energy migration, was put forward.[112] The general Scheme 9, including three equivalent interconvertible spectral centres A_n, has been analysed.[108]

Scheme 9



However, the models presented in Schemes 5–9 are applicable only to the interpretation of experiments in which the quenching of the luminescence is described by a triexponential function.

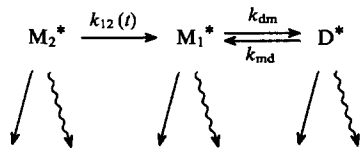
Systems in which the quenching of the fluorescence is described more aptly by a tetraexponential relation have been investigated.[111,113,114] The appearance of the fourth component in the expression for $I(t)$ can be attributed to the formation of the fourth luminescence centre, designated as a relaxing monomer or the third excimer. However, the approaches involving allowance for a larger number of luminescence centres for the description of multiexponentially decaying systems have not come to be used widely. Another approach is probably more productive. Thus it has been suggested[59] that the multiexponential decay of fluorescence be regarded as the sum of several dominant energy migration pathways, each of which is represented by the combination of all the possible versions of this process. In this case, the characteristic times of the dominant processes are not related directly to the times of specific physical transformations. Because of this, it has been stated that the excimer kinetics in aromatic polymers must not be described by any kind of phenomenological model on the basis of the number of allowed exponential functions. This approach agrees with the results of studies on the diffusion of energy in nonordered donor–acceptor systems, which indicate the nonexponential nature of the decay of their fluorescence.

A kinetic model based on the initial postulate that chromophores are not constant-energy centres as a consequence of the high dispersion of their relative positions has been developed[65,66] for polyvinylcarbazole films. The excitation energy of the high-energy chromophores migrates to low-lying states with the transfer frequency

$$\nu(T,t) = \nu_0 \exp\left[-\left(\frac{T_0}{T}\right)^2\right] + \nu_1^{\alpha} t^{\alpha-1},$$

where ν_0 is the frequency of the transfer of excitation in a hypothetical regular constant-energy polymer, ν_1 the discrete step in the variation of the excitation transfer frequency, α a dimensionless parameter assuming values from 0 to 1, T_0 the experimental temperature, and t the time. The dependence of I_d/I_m for the model on λ_{exc}, observed in the region of the long-wavelength edge of the absorption band of polyvinylcarbazole, constitutes experimental confirmation of the proposed model.[65] Scheme 10, which explains the tetraexponential decay of the excimer fluorescence in liquid solutions of polyvinylcarbazole, has also been examined in accordance with this model.[115] If $\alpha = 1/2$, the expression for the transfer frequency formally agrees with the expression for the excimer formation constant, which occurs in the kinetic equations for solutions of monochromic molecules. This approach has been extended to polymer systems.[59,116–120]

Scheme 10



The excimer kinetics have been studied in detail in polyvinylcarbazoles.[121] Studies on polymers of different tacticity by time-resolved spectroscopic methods have in the main confirmed the postulates put forward by Fredriekson and Frank.[59] The existence of two excimeric states has been demonstrated (the formation, together with the usual excimers, of excimeric complexes of yet another kind is observed fairly frequently).[73,76,116,122] The transformations of the high-energy excimeric complexes into normal complexes as a result of the excitation of fluorescence is of interest in this instance.

V. Excimer-forming molecular dimers

So far as we are aware, special studies on dimers of excimer-forming molecules which are stable already in the ground state have not been carried out with the exception of a series of early investigations.[19–21] The spectroscopic manifestations in absorption and emission attributed to such dimers are not subject to clear-cut rules as in the case of excimers. Furthermore, the same compounds have dissimilar optical characteristics under different conditions which can be explained by the nonuniformity of the aggregates formed.

The fact that excimer-forming molecules can be associated in the ground state is not unexpected because attraction forces between the molecules always exist.[123] For example, the interaction energy is $\sim 3.1 \times 10^4$ J mol^{-1} in naphthalene dimers[124] and $\sim 5.9 \times 10^4$ J mol^{-1} in pyrene dimers.[125] Calculations carried out also in other investigations[126] yielded a positive heat of formation of the unexcited excimer-forming dimers. However, quantum-chemical calculations for excited and unexcited dimers have yielded data for the interaction energies of only isolated pairs — a state which is remote from the real conditions. In organic solvents, the potential barrier stabilising the dimeric state vanishes owing to the interaction of the molecules with the solvent,[127] so that the interpretation of the ground and excited states of the pair of chromophores in the form presented in Fig. 5 is in general correct in a qualitative description of the potential energy levels of the excimer-forming system. Dimers stable in the ground state were not detected in special studies of solutions of pyrene in isooctane (10^{-3} M).[10] Presumably the dynamics of the processes in other organic solvents at moderate concentrations of the chromophore is also described satisfactorily by Schemes 1–3. However, even in good solvents one cannot neglect the interaction of the dissolved molecules. As an example, one may quote the result of a study[128] where an anomalously high yield of the excimer fluorescence of dilute solutions of pyrene (10^{-6} M) in ethylene liquefied under pressure and in other solvents was observed. This indicates the existence of a certain degree of long-range order between the chromophores in solution, although naturally one is not dealing in this instance with dimers.

Another picture has been observed in solvents such as water. In aqueous solutions of pyrene, the aggregation of the latter is attributed to its hydrophobic nature. In this case, the maximum of the structureless excimer fluorescence band undergoes a hypsochromic shift by 10–20 nm.[129] The luminescence excitation spectra of the dimeric and monomeric components differ considerably under these conditions. The hydrophobic nature of the chromophores leads to their aggregation in aqueous solutions also in the case of several water-soluble polymers, which is manifested in the absorption spectra.[130–134] The constant of the equilibrium between the monomeric and dimeric centres depends

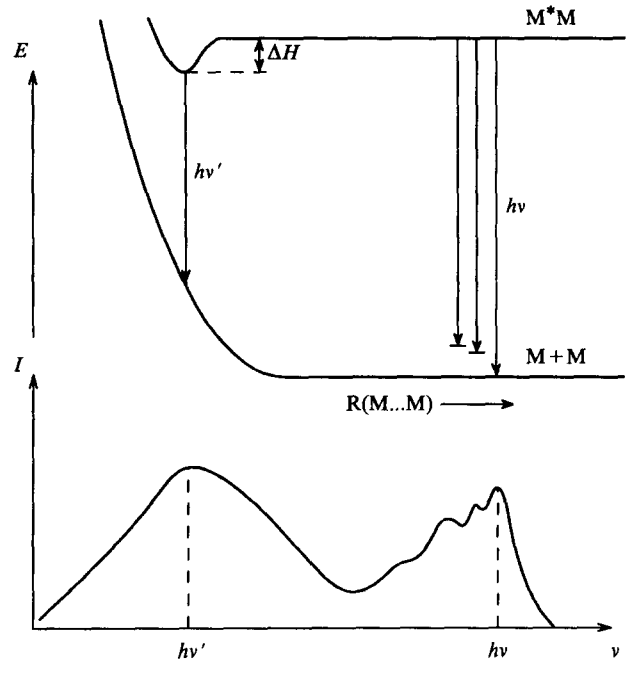


Figure 5. Potential energy (E) diagram for the monomer–excimer system: R(M ... M) = intermolecular distance; ν and ν' = frequencies of radiative transitions in the monomer and excimer respectively; ΔH = heat of formation of the excimers; the upper curve corresponds to the interaction of the molecules in the excimer and the lower to the interaction of the unexcited molecules; the Franck–Condon transitions in the excimer lead to a dissociative ground state which is responsible for the appreciable Stokes shift and the lack of structure in the luminescence.[1]

on temperature. The emission from the phenanthrene dimers has been recorded[135] in the slow fluorescence spectra of solutions in perfluorohexane only at 200 K. On raising the temperature to room temperature, the unexcited dimers dissociated.

There are data indicating the establishment of thermal equilibrium between the excimeric and dimeric centres. Perylene, added to films of the Langmuir–Blodgett type, has been investigated.[136] At room temperature, only the monomeric and dimeric components were recorded in the fluorescence spectra. As the temperature was reduced to 110 K, a new structureless fluorescence band appeared in the long-wavelength region of the spectrum and was attributed to the appearance of excimeric centres.

A pyrene crystal consists of pairs of molecules interacting in the ground state even at room temperature. With decrease in temperature to helium temperature, interaction in the dimers intensifies. Because of this, a new component appears in the absorption spectra of the pyrene crystal in the form of an inflection in the region of 395 nm, which has undergone a bathochromic shift of ~20 nm relative to the molecular absorption band.[49] The existence of pre-excimeric states of this type has been detected also in the absorption spectra of fused anthracene.[137]

Two types of dimers, formed as a result of different processes, have been identified on the basis of the absorption spectra of pyrene single crystals in Shpol'skii's matrices[138] at $T = 4.2-77$ K. The first process, with an activation energy of ~6 cm^{-1}, predominated in the temperature range 4.2–30 K. The formation of excited complexes from aggregates corresponding to the regular crystal structure was postulated in this instance. The second process, with an activation energy of ~70 cm^{-1} and manifested above 30 K, was explained by the presence of defects in the microcrystals, i.e. by the photoexcitation of the dimers, the structure of which differs from the regular crystal structure.

In the emission spectra, the luminescence of the dimers can sometimes be difficult to distinguish from the excimer fluorescence, so that studies on absorption spectra are more reliable for the identification of the dimers. The appearance of an absorption band in the long-wavelength section of the spectrum of the monomolecular form of the phosphor indicates the formation of dimers. As a rule, the new component is indistinct. Fig. 6 presents the absorption spectra of metastable dimers of anthracene and its derivatives obtained by the photochemical decomposition of the chemical dimers in a solid matrix at low temperatures. The luminescence of such species is fully excimer-like, while in the absorption spectrum only a slight bathochromic shift is recorded. Therefore, if both monomeric and dimeric centres absorb radiation in the system, then the fraction of dimers formed can be recorded from the intensity of the absorption band of the molecular S_1 transition.[24, 129, 134, 139] Fig. 7 shows how the optical density in the dimer–monomer system, induced by the displacement of the equilibrium, is redistributed as a function of the solvent composition.

The absorption spectra of the dimers (Fig. 6) demonstrate the general features characteristic of aggregates of this type:[19] the intensity maxima of all the bands due to the dimers have lower energies than the corresponding maxima in the spectra of the monomers (the intensity maximum is represented by the 0–1 transition in the spectra of the dimers and by the 0–0 transition in those of the monomers); an appreciable broadening of the bands in the spectra of the dimers relative to those of the molecules is observed; the total oscillator strength of the transition in the dimer is lower than twice the oscillator strength of the corresponding transition in the monomer.

The greatest number of communications refer to the formation of excimer-like molecular dimers in Langmuir–Blodgett films of different kinds[136, 140–144] or in films obtained by depositing the chromophore onto a solid base[139, 145, 146] and also in fluorescent polymers[130–134, 147, 148] and in solid solutions of the molecules in organic[149] and inorganic[150–152] glasses. Depending on the conditions in the formation of the specimens, the chromophores in such systems can apparently exist in the form of dimers, which may or may not be manifested spectroscopically. If they are not, the excitation of the excimer fluorescence is explained by the migration of energy to the excimer-forming centres.[153–159]

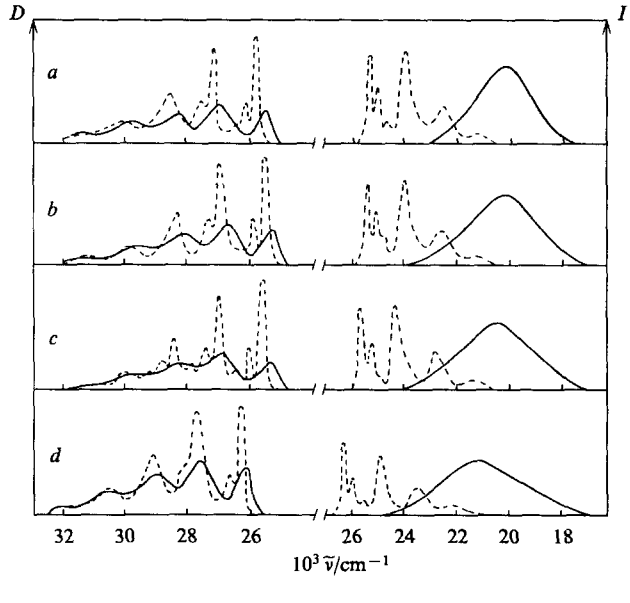


Figure 6. Absorption and emission spectra of the sandwich dimers in methylcyclohexane[19] at 77 K; the spectra of the monomer obtained after unfreezing and refreezing the specimens are indicated by dashed lines: (*a*) 9-methylanthracene; (*b*) 9-bromoanthracene; (*c*) 9-chloroanthracene; (*d*) anthracene.

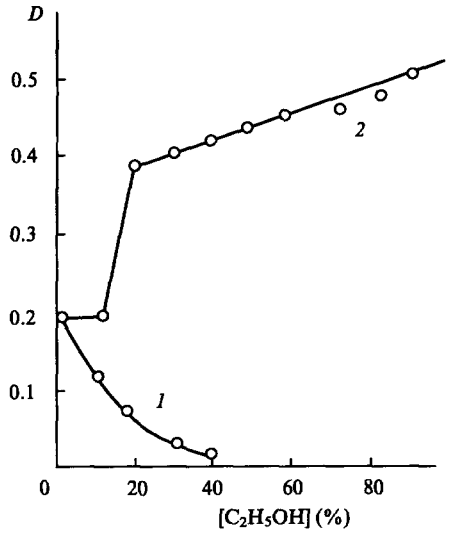
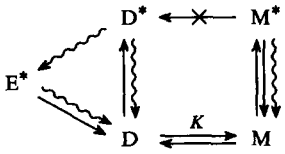


Figure 7. Optical densities of solutions of pyrene in a water–ethanol mixture[129] (phosphor concentration 14×10^{-6} M). Wavelength (nm): (*1*) 360 (S_1 transition in the monomer); (*2*) 319 (S_2 transition in the monomer).

The attempts at a systematic treatment of the observed wide variety of the fluorescence properties of the dimers have demonstrated the following features. Radiation is absorbed by dimers which differ in their interaction energies in the ground state in different systems. Energy transfer processes from isolated chromophores also play a definite role. The type of interaction between the molecules in the ground state of the dimer is close to the type in the excited state,[20] so that the transitions between the levels yield a spectrum which resembles that of molecular fluorescence. If during the excitation period the dimer can relax to the excimer geometry, its spectrum resembles that of the excimer. A structured spectrum of the luminescence due to the dimer has been published.[135] The case of strong interaction has been described for anthracene dimers,[96] the maximum of the excimer-like fluorescence showing a bathochromic shift by ~100 nm relative to the spectrum illustrated in Fig. 6.

Pyrene and naphthalene, adsorbed in the form of dimers (stable in the ground state) on the surface of silica gel, have been investigated.[139,145] Dimerisation was recorded on the basis of the luminescence excitation spectra. The proposed process dynamics is illustrated in Scheme 11.[139]

Scheme 11



It is suggested that the fluorescence arises in the excimeric state, although the dimeric centres absorb. The symbols M* and D* in the scheme denote the monomers and dimers excited respectively from the ground states M and D, E* is the excimer formed as a result of small steric relaxations of the excited dimer, and K is the constant of the equilibrium between the monomeric and dimeric centres in the ground state. It is suggested that, during the lifetime of the excited state of the monomer, there is no energy transfer to the dimeric form. In this case, the dependence of I_d/I_m on the concentration of the chromophores is expressed thus:

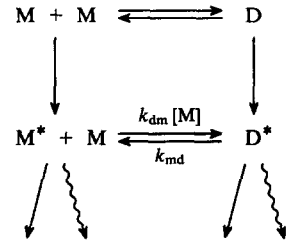
$$\frac{I_d}{I_m} = A\left[(1 + 8K[M_0])^{1/2} - 1\right],$$

where $A = \varepsilon_d \varphi_{ed} \varphi_e / 4K\varepsilon_m \varphi_m$ (φ_m and φ_e are the quantum yields of the fluorescence of the monomer and excimer respectively and φ_{ed} is the quantum efficiency of the formation of the excited dimers). The excited dimers relax to the excimeric state very rapidly[145] and the fluorescence arises after less than 1 ns.

These experiments may be compared with studies on the van der Waals fluorene dimers formed in molecular beams on expansion at an ultrasonic velocity.[160,161] The potential energy curves for such systems and the energy transitions are illustrated in Fig. 8. The radiative transitions lead to the dissociated state, although radiation is absorbed by the dimeric form. Similar data are available for benzene[162] and naphthalene derivatives.[163] Excimer-like fluorescence has been recorded under analogous conditions also on excitation of the trimers of 1-cyano-4-methylnaphthalene and its higher-order clusters. The excitation of the stable associated species of 1-cyanonaphthalene with triethylamine[164] and of fluorene with methyl-substituted dienes[165] also led to the appearance of an exciplex-like glow. Comparison of the spectroscopic parameter of the dimers and excimers has shown that the latter are characterised by a greater Stokes shift of the luminescence and a longer lifetime of the excited state (150 and 62 ns for the excimers and dimers of 1-cyano-4-methylnaphthalene respectively).[163]

The excimer-formation processes in liquid-crystal systems began to be studied comparatively recently.[166–168] The formation of excimers in such systems has been unambiguously confirmed by time-resolved spectroscopy.[167] At high chromophore concentrations, one cannot rule out the formation of excimers via the migration of energy to the excimer-forming centres.[168] Subsequent studies on these systems demonstrated the possibility of molecular association in the ground state. In order to explain the experimental results, Scheme 12, including the formation of dimers stable in the ground state, was put forward:[169]

Scheme 12



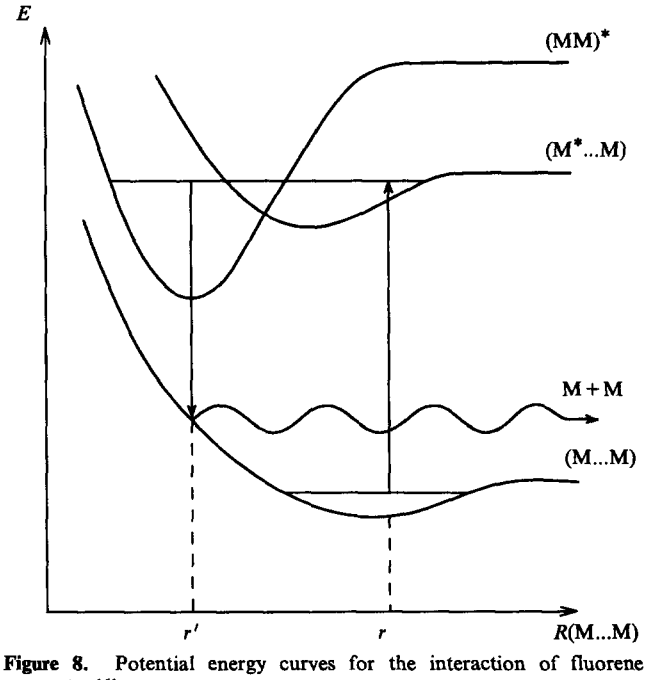


Figure 8. Potential energy curves for the interaction of fluorene molecules.[161]

According to this scheme, the decay of the fluorescence of the monomeric and dimeric components is described by a biexponential relation. In all probability, a more complex model of the excitation of the excimer-like luminescence is also possible in liquid-crystal mixtures. The fluorescence of the dimers stable in the ground state has been recorded[170] in time-resolved spectra. A triexponential function best described the decay of the luminescence of the excimer-like component.

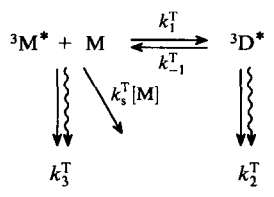
The fluorescence properties of the excimer-forming dimeric systems have been described most fully by Yamanaka et al.[152] Solid solutions of pyrene in an inorganic glass exhibit a structured band in the time-resolved spectra due to the fluorescence of the dimers (the *D* band in Fig. 9) with maxima at 381, 399, and 418 nm. At the same time the luminescence of the sandwich (E_2 band) and high-energy (E_1 band) excimers is observed in the spectrum. Isolated molecules emit the *M* band, which is manifested after the decay of the *D* fluorescence.

VI. Excimer phosphorescence and slow excimer fluorescence

The interaction of two excimer-forming molecules, one of which is in the excited triplet state, leads to the appearance of excited triplet dimers. Their phosphorescence was observed in almost all media where the singlet excimers were found to be formed: in liquid solutions, crystals, and polymers.

In liquid solutions, the existence of excimer phosphorescence was established on the basis of the following experimental facts:[171,172] the excitation spectrum of this type of phosphorescence is identical with the absorption spectrum of the corresponding monomer; the yield of the excimer phosphorescence increases with increasing solute concentrations; the excimer phosphorescence bands are observed only in liquid solutions and are absent from the spectra of frozen specimens; the phosphorescence of the excimers, like that of the monomers, is quenched by oxygen when the hermetic seal in the cell is broken. Analysis of the kinetics of the formation of the triplet complexes in conformity with Scheme 13 showed that the rate of the process is much lower than the rate of diffusion. It has been suggested that dimers are formed via a stage of intermediate complexes even before the acquisition of the excimer configuration.

Scheme 13



The constants k_1^T and k_{-1}^T in the scheme correspond to the rates of formation and dissociation of the complexes, the constants k_3^T and k_2^T correspond to the rates of the radiative and nonradiative deactivation of the monomers and dimers respectively, and k_s^T is the self-quenching rate constant.

The reliability of data concerning the existence of triplet excimers in liquid solutions has been questioned. Nickel and Prieto[124] reproduced the experiments from a large number of studies (see the list of references in their communication) where the breakdown of triplet phosphorescence had been reported. The reproduced experiments yielded a negative result and it was concluded that the observed luminescence is more likely to be the impurity glow of the solvents. The results lead to the conclusion that the triplet excimers of aromatic hydrocarbons are unstable, although the existence of weakly bound intramolecular triplet excimers in certain diarylalkanes has been admitted.

Such conclusions aroused the active opposition of a number of investigators, which has given rise to a controversy.[173] On the other hand, the presence of triplet excimers in crystals and

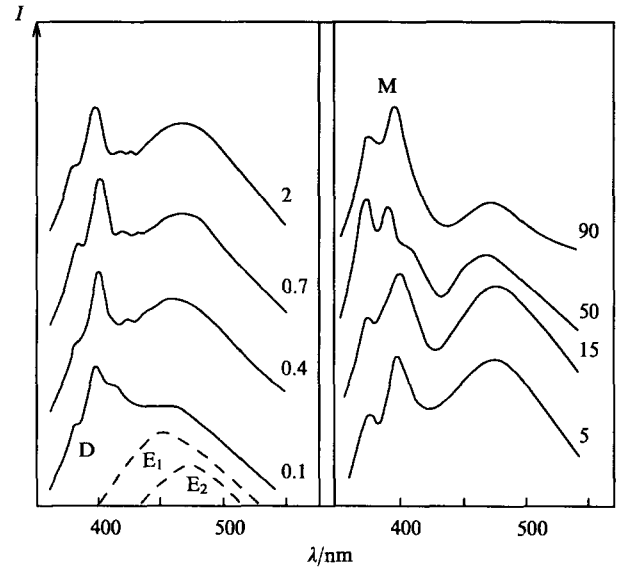
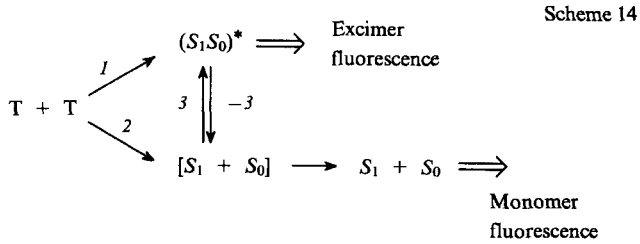


Figure 9. Time-resolved fluorescence spectra of solid solutions of pyrene in a silicate glass[152] (4×10^{-2} M); the numerals opposite the curves represent time (ns).

polymeric media is apparently not open to doubt. Two types of excimers have been detected in pyrene crystals[174-176] and excimer phosphorescence has been observed at low temperatures also in the crystals of halo-derivatives of benzene,[174,177,178] phenanthrene, and naphthalene.[179] Triplet excimers are formed in carbazole-containing[29,180-182] and naphthyl-containing[183-187] polymers.

Apart from the formation of triplet excimers, intersystem crossing processes initiate a slow excimer fluorescence. In the general case, its appearance is a consequence of processes leading to a slow *P* type fluorescence.[27] Different versions of the excimer formation processes on interaction of two triplet molecules in solutions are illustrated in Scheme 14.

Scheme 14



Three pathways leading to the excitation of excimer fluorescence of this type are possible: (1) simultaneous formation of singlet excimers and pairs of monomers (reactions *2* and *1*); (2) formation of singlet excimers with their subsequent dissociation to the monomeric form (reactions *1* and *3*); (3) exclusive formation of monomeric centres with subsequent formation of singlet excimers as a result of the reassociation of the molecules in the ground and excited singlet states (reactions *2* and *3*). Singlet excimers are formed after triplet–triplet annihilation via a stage involving intermediate complexes. The slow excimer fluorescence may be recorded if the rapid excimer fluorescence does not arise.[100,188,189]

The slow excimer fluorescence, induced by the migration of triplet excitons, is also observed both in liquid solutions of polymers and in solid polymer matrix at low temperatures. This confirms data indicating an increase in the intensity of the slow singlet fluorescence relative to phosphorescence with increase in the molecular mass of the homopolymer.[182,187]

VII. The structure of excimeric complexes

Excimers have a structure with a coplanar (sandwich) disposition of the molecular planes and an intermolecular distance of 3–3.5 Å. This conclusion was reached already at an early stage of the research into excimers, which agrees with data on the structures of crystals of the type of pyrene, α-perylene, 1,12-benzoperylene, etc.[19,48,96] The luminescence of such crystals is of the excimer type. This is also confirmed by the results of numerous experiments with flexible bichromophores in liquid solutions: the formation of intramolecular excimers is observed only when the molecule is capable of assuming the sandwich form. This type of structure has been confirmed also by the analyses of the polarised excimer fluorescence,[190] quantum-chemical calculations,[35,126,191–196] and the results of photochemical experiments.[3,11,19,20] However, the structure of the chromophores themselves or the influence of external factors frequently prevent the assumption of this geometry.

The introduction of bulky substituents, crystal structure defects, the morphological characteristics of chromophore-containing polymers, etc. frequently lead to the appearance of several types of excimeric configurations in real systems: in certain cases, it is possible to distinguish spectroscopically, together with excimers of the normal (sandwich) type, also one or several other types of excimers, which can be identified in terms of the polarisation characteristics of the glow, the position of the fluorescence band maximum, and the lifetime of the excited state of the complex. The wavelengths of the luminescence maxima of different types of excimers of certain compounds are listed in Table 1.

Excimers exhibiting luminescence in the region between the molecular band and the band due to normal excimers exist for virtually all classical excimer-forming chromophores (pyrene, naphthalene, anthracene, and carbazole). This type of luminescence is attributed to aggregates, which, in contrast to the normal ones, are characterised by an incomplete overlap of the orbitals of the aromatic nuclei. Such states are designated as high-energy states, second excimers, or dimer-like excimers. Nevertheless, their stabilisation requires a significant degree of overlap of the aromatic rings; for example, a degree of overlap of 25% is insufficient for naphthalene.[204] For more bulky chromophores, the degree of overlap of the electron shells may be smaller compared with compounds with a short conjugation chain.[11] An incomplete sandwich structure may arise also for a not fully parallel relative arrangement of the chromophores in the polymer chain.[86]

Spectroscopic data do not permit the determination of the details of the spatial disposition of the molecules in the excimeric complex, but in the case of polymeric systems the geometry of the excimeric centres may be found from conformational calculations for the chains.[72,78,101,199,203,205,206] The polarisation characteristics of the luminescence of excimers for different helicoidal configurations of the polymer chain have been obtained by computational methods and from the analysis of the fluorescence.[203,207–210] The different structures of the excimers in polymers have been attributed to the positions of the interacting molecules in the chain: the structures of the complexes are different when they are formed between neighbouring and remote sections of the polymer. If the polymer chain contains two types of nonequivalently linked chromophores, the formation of three types of excimeric complexes is noted.[199]

Isolated ('free') isomers are characterised by a finite number of relatively stable states, the population of which is determined by the influence of external factors. Calculations have shown that, for an intermolecular distance of ~3 Å, the excimers of naphthalene, anthracene, and pyrene can assume only two steric configurations. The interaction energy depends on the angle between the long molecular axes in the sandwich dimer and, together with the principal minimum (at 0°), has local minima at 55°[35] or 40°–50°[126] for pyrene, at 75° for naphthalene,[193,194] and at 65° for anthracene.[195]

The ability of molecules to form different excimeric configurations is associated with the contributions of different states to the wave function for the system. The stability of excimeric complexes is determined by the exciton-resonance interaction and the forces arising as a result of charge transfer.[30] In this sense, excimers are regarded as a special case of exciplexes. With increase in the length of conjugation in the benzene–naphthalene–anthracene–pyrene, etc. series, the energy gap between the molecular levels diminishes, which leads to an increase in the role of the exciton–resonance interaction. For example, the interaction due to charge transfer predominates in the benzene complexes,[162] whereas pyrene excimers are described almost entirely by the exciton-resonance component of the wave function.[35,211] Since the charge-resonance interaction is more isotropic, the benzene excimers may be formed in different configurations, although the sandwich configuration is nevertheless the most stable.[162]

In this connection, one should note that there are virtually no literature data on high-lying excited states of the excimers. As a rule, they do not play a significant role in the kinetic process examined in the previous sections. They aroused interest precisely in connection with the study of the two-photon ionisation of benzene. The stabilisation energy of its excimers in the second excited state exceeds by an order of magnitude this parameter for the S_1-excited complexes (1.8×10^4 and 5.9×10^2 J mol^{-1} respectively).[162]

For compounds with a pyrene fragment (i.e. with a long aromatic system), two configurations of excimers, differing by the displaced positions of the molecules in the sandwich complexes relative to one another (by half the length of the benzene ring along the long axes), can be clearly distinguished. Excimers of one of these type are formed in crystals, being retained also in liquid solutions.[28] The centrosymmetric structure of the excimer determines its zero ground state overall dipole moment and hence the forbidden optical transitions. This is reflected in the different fluorescence decay times: ~150 ns for the centrosymmetric model and 60–70 ns for the structure with incomplete overlap of the π-systems of the aromatic rings.[90] The same type of system occurs also in α-perylene crystals. Calculations have shown[191] that an isolated perylene excimer has an energy minimum for the complete overlap of the rings, but dimers of this type do not occur in crystals.

The short decay time of the V and Y components relative to the normal glow in pyrene and α-perylene makes it possible to attribute these types of fluorescence to the formation of weakly bound complexes. It is assumed that such states arise as a consequence of the incomplete relaxation of the molecules in the dimers.[50,54,191] According to Sumi,[52] the nature of these centres can be related to the association of pairs of molecules more remote from one another in the crystal than in the case of the dimeric pairs discussed above.

The relation between the thermodynamic parameters and structure of excimers has been examined.[90] It was shown that the entropy–enthalpy ($\Delta S - \Delta H$) relations are different for different excimeric configurations (Fig. 10). Another conclusion is that the entropy gain may be responsible for the formation of weakly bound complexes with a small or even positive value of ΔH. This accounts for the existence of weakly bound triplet excimers.

The structures of triplet excimers have been calculated, but contradictory results were obtained.[126,192,195,212] According to the data of Padma and coworkers,[126,192] the structure of the naphthalene and anthracene triplet excimers differs from the sandwich structure. For pyrene, the structures of the complexes of both multiplicities were obtained for virtually identical asymmetric configurations. The structure of the triplet state of all the molecules considered is virtually identical with the structure of the corresponding unexcited dimers. This has been explained by the fact that the stability of the triplet structure of excimers is determined by van der Waals forces, as in the unexcited dimers.

Table 1. The fluorescence maxima of the excimers

Chromophore	Experimental conditions	λ_{max}^{fl}/nm	Ref.
Benzene (phenyl)	Liquid state	320	197
	Solution of polystyrene–acrylonitrile copolymer in methanol	325	105
	Solution of polystyrene in 1,2-dichloroethane	332	82
	Solution of low-molecular-mass polystyrene analogues (2,4-diphenylpentane, 2,4,6-triphenylpentane, 2,4,6,8-tetraphenylnonane) in methylene chloride	330	198
	Solutions in dichloromethane		
	of hexaphenoxycyclotriphosphazene	~340	199
	hexacresoxytriphosphazene	~330	199
	polybisphenoxyphosphazene (T = 160–300 K)	305–310	199
	polybis-*p*-cresoxyphosphazene (T = 160–300 K)	320–330	199
Naphthalene (naphthyl)	Solution in cyclohexane	390	200
	Aqueous solution of the 2-vinylnaphthalene–maleic acid copolymer		
	normal excimer	400	71
	high-energy excimer	<400	71
	Adsorbed on SiO_2	390	145
	Solid solution in silicate glass (high-energy excimer)	375	150
Anthracene (anthryl)	Single crystal (T > 400 K)	~475	47
	Sandwich dimer in methylcyclohexane (T = 77 K)	475	19
	Poly-9-vinylanthracene film deposited electrochemically on a SnO_2 electrode	500	201
	Solution of anthracenophane in methanol in the presence of $NaClO_4$	510	96
	Anthracenophane in the crystal phase	570	96
	Solution of 9-methylanthracene in benzene	580	96
		~560	200
Pyrene (pyrenyl)	Aqueous solution	460	129
	Adsorbed on SiO_2	470	139
	Solution in cyclohexane	482	200
	Langmuir–Blodgett films		
	normal excimer	470	157
	high-energy excimer	420	157
	Single crystal	460	47
	Melt (T = 428–578 K)	460–450	47
	low-energy excimer (T = 448 K)	~500	47
	Solution in silicate glass		
	normal excimer	475	152
	high-energy excimer	450	152
	structured band due to dimers	380–420	152
	Solution of methyl 4-(1-pyrenyl)butyrate		
	in toluene	480	202
	in methyl benzoate	485	202
	in polystyrene	445	202
	in poly(methyl methacrylate)	440	202
	Solution of a pyrenyl-substituted polypeptide in tetrahydrofuran (T = 210–290 K)	440–480	203
Phenanthrene	Solution in perfluorohexane (T = 200 K) structured band due to dimers	330–450	135
	Adsorbed on Al_2O_3	400	153
Carbazolyl	Polyvinylcarbazole		
	normal excimer	420	121
	high-energy excimer	380	121
Perylene	Solution in benzene	588	200
	Single crystal	625	52
	Langmuir–Blodgett films		
	excimer	600	144
	band due to dimer	546	144

The differences between the singlet and the corresponding triplet complexes are determined largely by the different contributions of the exciton–resonance interaction.

The geometrical differences between excimers of different multiplicities have been demonstrated experimentally in relation to the following examples. Chandross and Dempster[20] obtained naphthalene sandwich dimers in a methylcyclohexane glass at 77 K. The fluorescence of such dimers was excimer-like whereas the phosphorescence was of the structural type corresponding to the naphthalene monomer. In another study,[213] where solutions of binaphthalene compounds were investigated, only the fluorescence due to the monomer and the triplet excimer glow were actually recorded; the association of the singlet complexes was hindered, whereas the triplet ones might have been formed with an asymmetric configuration.

Calculations of the geometries of the unexcited naphthalene, anthracene, and pyrene dimers showed that[126] the centrosymmetric sandwich conformation does not give rise to a stable ground state. The benzene dimers, which are stable in the ground state, are assumed to be capable of assuming the T-type, sandwich,[214,215] and V-type (house of cards)[216] forms. These states are separated by small potential barriers, so that the geometry of the benzene dimers is very sensitive to external influences.[217]

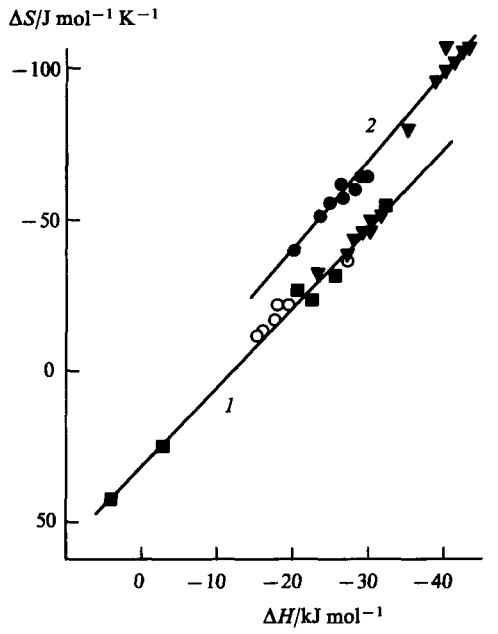


Figure 10. Dependence of ΔS on ΔH for intramolecular excimers of certain dipyrenylalkanes in various solvents.[90] The data plotted along straight line *1* correspond to centrosymmetric complexes with full overlap, while those plotted along line *2* correspond to complexes with displaced molecules (partial overlap).

VIII. Conclusion

In the present review we have attempted to concentrate attention on questions which arose during the last 10–15 years and which have not been adequately analysed in the scientific literature. This concerns primarily the conditions under which various excimer species arise. Unfortunately the available information does not permit a deeper elucidation of this problem. Without accurate calculations of the geometries of the complexes, it is impossible to achieve significant results in studies on the assignment of the spectroscopic manifestations of the excimeric centres to their structure. Such calculations have still not been carried out. Nevertheless steps taken in this direction would make it possible to obtain a more precise method in the field of studies, which have already become traditional (studies on the kinetics and the structure of the medium), using excimer-forming fluorescent probes.

Another problem which has become urgent is due to the unsuccessful definition of excimers adopted in the literature.[2] In particular, one may point to the lack of clear-cut criteria for the assignment of fluorescence to the excimeric or dimeric type. Nevertheless, this is not a fundamental problem. In the literature, there are examples of the study of dimers and excimers from a general standpoint (i.e. when no account is taken of the difference between them).[46,218] However, the simplified consideration of excimers from the standpoint of the somewhat idealised Scheme 1 frequently hinders the understanding of the essential features of the phenomenon. Attention was already drawn to this at an earlier stage. For example, two definitions of excimers have been formulated:[124] kinetic and spectroscopic. The former reflects the dynamic aspect of the formation of the excited complexes, while the latter definition postulates the similarity of the fluorescence characteristics of the excimeric and dimeric centres. The data presented in this review show that the second approach is also limited in character. For example, the low-temperature fluorescence of crystalline pyrene (Fig. 1) is excimeric despite the resolved vibrational structure if its consideration is based on the fact that the excitation is initially localised in a free-exciton state (i.e. in the monomer). In our view, the term excimers should be given to appropriately excited associated species stabilised by resonance interaction, regardless of the nature of the ground state.

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