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THE USE OF DOPED CRYSTALS AS A MEDIUM FOR THE STUDY OF EXCITED STATE BIMOLECULAR INTERACTIONS

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A molecular crystal is an attractive medium for the study of excited state intermolecular interactions since the ground state positions of interacting molecules may be accurately determined. Besides excimer interactions in pure crystals it is possible to study (in doped crystals) exciplex interactions between host and guest molecules, and even excimer formation between two adjacent guest molecules. This approach has been utilized to observe excimer formation by several anthracene derivatives introduced as dopants in pyrene crystals. Photochemical reactions of some of these exciplexes and excimers are discussed. Excimer forming crystals are considered to be good candidates for excited state structure determination by means of pulsed x-ray diffraction.

I. INTRODUCTION

Doped molecular crystals have found widespread use as a medium for various studies in spectroscopy and photophysics. Highly resolved spectra are obtained when molecules are dissolved in some n-alkane solvents and frozen, forming a Shpol'skii matrix [1]. The ability of a guest molecule to quench the fluorescence of its host crystal has long been used to study parameters of electronic energy transfer in crystals such as exciton mobility and energy trapping [2].

In the above examples, the energy levels of the guest are essentially unperturbed (and even simplified) when incorporated into the host crystal. A different case is that of charge-transfer crystals where doping perturbs the ground state or induces a new low-lying state [3]. In this article we will consider yet another case: that where the doped crystal contains new energy levels only in the electronic excited state, and in particular bimolecular excited states. These new excited states are exciplexes (formed between adjacent host and guest molecules) and guest excimers.

We show that doped organic crystals can serve as the "solvent" medium for some studies just like fluid solutions, but with some important advantages. Using crystals as media provides information about the ground state geometries of interacting molecules. Different crystals induce different geometrical constraints which can be evaluated from x-ray diffraction studies and force field calculations. The use of different packing arrangements and varying guest concentration provides media for the study of host-guest and guest-guest interactions having different ground state geometries. A further advantage is that the crystal matrix is utilizable over a wide temperature range, including very low temperatures, over which its characteristics are generally unchanged.

Finally, we consider the possibility of direct structure determination (by x-ray diffraction) of electronically excited molecules in a crystal. In such an experiment the crystal would be simultaneously excited by an intense optical pulse and probed by a powerful x-ray pulse. One of the best candidates for such an experiment appears to be excimer forming crystals.

II. FORMATION OF EXCIPLEXES IN DOPED CRYSTALS

II.1 Survey of Exciplex-Forming Systems

We have outlined earlier [4] the conditions which cause a doped crystal to exhibit exciplex formation rather than leaving the host and guest energy levels unperturbed. Experimentally, the difference is detected from the fluorescence emitted by the doped crystal. An exciplex fluoresces to the red (lower energy) of both the host and guest emissions, as well as generally having a long decay time, usually in the range 20-200 ns. In the absence of exciplex formation, the fluorescence from the doped crystal can be identified as either host or guest fluorescence or both. (Strongly sensitized guest fluorescence is expected [2] if the lowest singlet excited state of the guest is lower than that of the host).

Exciplex formation in a doped crystal usually requires that [4]:

(i) The host and guest species comprise an electron donor-acceptor pair

(ii) The host crystal provides a geometry affording close approach and overlap between the electron clouds of neighbouring molecules

(iii) The guest be sufficiently miscible in the host crystal to form a true mixed crystal.

We have found [4,5] that condition (ii) is especially well fulfilled by excimer-forming host crystals such as pyrene and 9-cyanoanthracene. Condition (iii) has generally limited us (in accordance with principles described by Kitaigorodsky [6] to use a guest molecule of similar size, shape and symmetry to the host, and therefore concentrations have rarely exceeded 0.03 M/M (mole guest per mole host).

We have observed [4,5] a wide variety of mixed crystals exhibiting exciplex formation, which are summarized in Table 1. Typical room temperature fluorescence spectra are shown in Figure 1, and are independent of excitation wavelength in the host absorption band. At 77 K when energy transfer is inhibited in excimer forming crystals [7,8] the exciplex may only be observed if direct guest excitation is possible, or if the host crystal exhibits tail absorption identifiable with direct excitation of a host molecule adjacent to a guest [9].

The generality of exciplex formation in doped crystals is shown both by the wide variety of systems exhibiting exciplex formation and by the fact that three distinct types of host crystal structure may be identified. 9,10-DMA is a monomer type crystal [10] and may be somewhat exceptional as a monomeric host crystal for exciplex formation. In addition, exciplex formation is observed in both pair- and stack-type excimer crystals - i.e., when a guest molecule has either one or two nearest neighbor host molecules respectively.

Table 1 also shows that there are apparently no restrictions on the relative energies of the unperturbed guest and host excited states, as the examples presented show that the lowest excited state energy of the guest may be above or below that of the host. Cases corresponding to the former are particularly noteworthy since exciplex formation in these systems represents the only known way host crystal fluorescence may be quenched by "uphill" doping, i.e., the addition of a dopant whose singlet excitation energy is higher than that of the host crystal [4].

Table 1. Summary of Exciplex-Forming Doped Crystals

HOST	GUEST	REF.	HOST CRYSTAL STRUCTURE	ENERGY LEVELS	Room	Temp	77°K	
					λmax	τnsec	λmax	τnsec
9-CNA	Perylene	[11]	S.E. [12]	c	520	120		
9-CNA	9-MeOA	[9]	S.E.	a	520	52	534	78
9-CNA	9,10-DMA	[4]	S.E.	a	515	83	535	96
9-CNA	9-MeA	[4]	S.E.	a	500	40	513	75
9,10-DMA	9-CNA	[4]	Monomer [10]	b	498	66	493	88
9,10-DMA	1,4-DCNN		Monomer	a	470		456	55
CN,MeA	9,10-DMA	[4]	S.E. [13]	a	515	70	515	70
Pyrene	9-CNA	[5]	P.E. [14]	c	470	50	483	100
Pyrene	9-ClA	[5]	P.E.	c	440	18	445	40
Pyrene	CN,MeA	[5]	P.E.	-	470	20	472	55
1,3-DClN	2-MeN	[4]	S.E. [15]	a	406			
1,4-DClN	1-MeN	[4]	S.E. [16]	a	400			
PBD	TBD		S.E. [17]	c	460	<10	455	15

λmax = wavelength of emission maximum, τ = fluorescence decay time
9-CNA = 9-cyanoanthracene; 9-MeOA = 9-methoxyanthracene;
9-MeA = 9-methylanthracene; 9,10-DMA = 9,10-dimethylanthracene;
CN,MeA = 9-cyano, 10-methylanthracene; 9-ClA = 9-chloroanthracene;
1,4-DCNN = 1,4-dicyanonaphthalene; DClN = dichloronaphthalene;
MeN = methylnaphthalene
PBD = 1-(2,6-dichlorophenyl)-4-phenyl-trans-trans-1,3-butadiene
TBD = 1-(2,6-dichlorophenyl)-4-5hienyl-trans-trans-1,3-butadiene
S.E. = stack type excimer; P.E. = pair type excimer
a - guest singlet energy is higher than both the host monomer and (if applicable) excimer energy.
b - host and guest singlet monomer levels are almost degenerate
c - guest singlet energy is lower than the host monomer but higher than the host excimer energy.

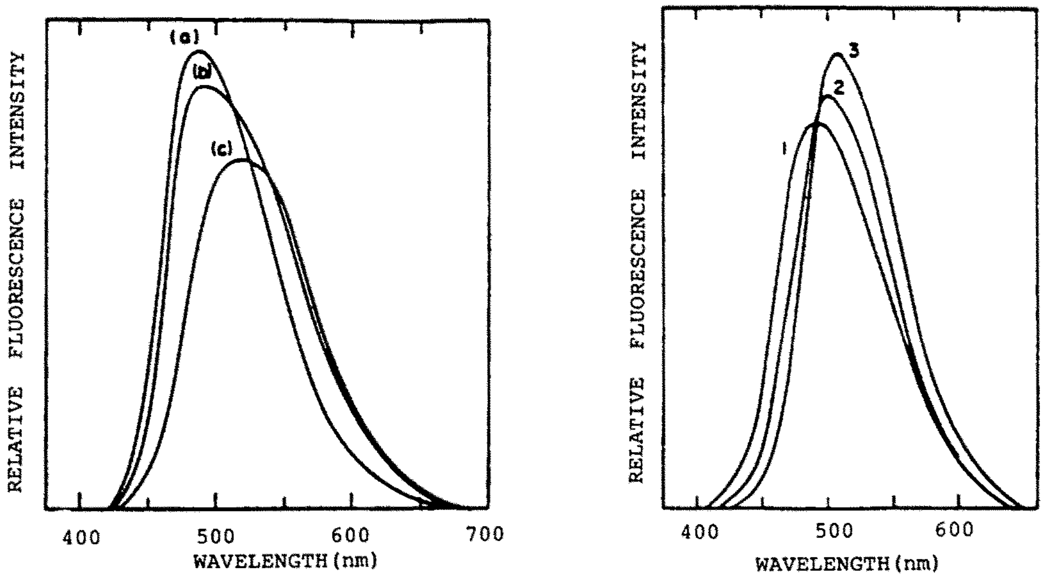


Figure 1. Left: Fluorescence spectra of pure 9-CNA (a) and 9-CNA doped with 0.003 M/M (b) and 0.03 M/M (c) 9-MeOA.
Right: Fluorescence spectra of pure 9-CNA (1) and 9-CNA doped with 0.003 M/M (2) and 0.02 M/M (3) 9,10-DMA. [Ref. 4]

II.2 Electron Donor-Acceptor Character of Exciplexes

The emission maximum of an exciplex in a non-polar solvent is given by [18]:

$$h_{max} = D_C - E_A - \Delta \qquad (1)$$

where E_D and E_A are the polarographic oxidation and reduction potentials for the electron donor and the electron acceptor species of the exciplex respectively. A value of $\Delta = 0.15 \pm 0.10$ eV, which represents Coulomb and solvation energies, fits experimental data for exciplexes in hydrocarbon solvents such as n-hexane [19]. It was found [4,5] that where redox potentials are known, eq. (1) also held for all but one of the solid state exciplexes in Table 1. The sole exception is the pyrene 9-chloroanthracene exciplex [5] where the two component molecules are about as good electron donors and electron acceptors as each other. Thus the exciplex formed by these two molecules should be stabilized by two charge resonance states (pyrene+....9-ClA$^-$) and (pyrene$^-$...9-ClA+,). Eq. (1) only considers one charge resonance state of the type (D+...A$^-$) and consequently the exciplex energy is overestimated. (A similar overestimation occurs [19] if one attempts to correlate the energy of excimers with eq. (1)). Thus, the pyrene 9-chloroanthracene exciplex has been classified [5] as a "heteroexcimer."

It seems reasonable to assume that the PBD-TBD exciplex would also be best described as a heteroexcimer rather than a donor-acceptor exciplex although redox potentials are not available to check this assignment.

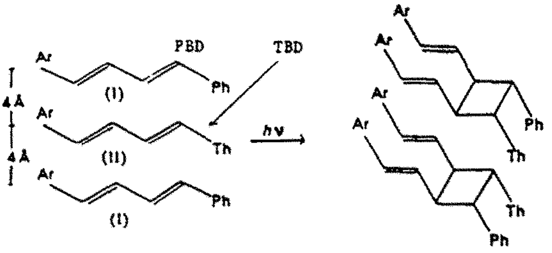
We note that a recent publication discussing exciplex formation in anthracene doped phenanthrene aggregates defines, by a similar line of reasoning, the exciplex so formed as being of mixed excimer type [20].

II.3 The Exciplex as a Solid-State Photochemical Intermediate

Of the exciplex-forming mixed crystal systems of Table 1, two were found to form photoproducts upon prolonged irradiation; namely, the 9-CNA 9-MeOA and PBD-TBD systems. In both cases the photoproduct is the heterodimer. By monitoring the fluorescence quantum yield and decay time of the 9-CNA 9-MeOA exciplex over the temperature range 5-360°K we have demonstrated [21] that the exciplex is necessarily an intermediate in the photodimerization.

The PBD-TBD system is most interseting in that the heterophotodimer is chiral, and the photoproduct from a doped single crystal shows an excess of one enantiomer [22]. This arises because PBD molecules pack [17] as stacks of molecules in a crystal of the chiral space group $P2_12_12_1$. A TBD molecule replacing a host molecule can participate in photodimerization with the host molecule either above it or below it [23], to give one of the two possible enantiomers as the product (see Fig. 2). As a result of crystal asymmetry and interaction in the excited state, reaction in one direction is preferred [23], and an excess of one enantiomer is obtained from photodimerization in a single crystal - the chirality of the dominant product presumably depends on the chirality of the crystal.

Since there are two inequivalent reaction pathways, the possibility arises that there exists two different exciplex intermediates, i.e., one for each prochiral host-guest pair. The exciplex fluorescence of TBD doped PBD crystals at room temperature was indeed observed to be non-Gaussian in shape, with a shoulder resolvable at about 475 nm (see Fig. 3). However, this observation must be interpreted with caution since (i). A non-Gaussian or structured exciplex emission is no guarantee that more than one site is emitting, and (ii) x-ray crystallography of this mixed crystal has detected [24] disorder in the thienyl ring structure, a factor which could further complicate the exciplex spectrum.



Ph=phenyl, Th=2-thienyl

Ar=2,6-dichlorophenyl

Figure 2. Formation of Enantiomeric Products in PBD-TBD Photodimerization.

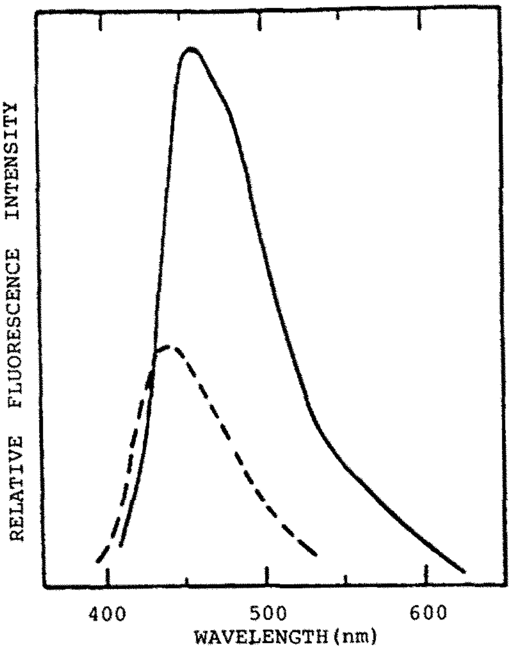


Figure 3. Emission of PBD doped with 0.05 M/M TBD at room temperature (full curve). The broken curve is the emission of a pure PBD crystal.

II.4 Numerical Simulation of Exciplex Formation in a Crystal

Force-field calculations have been employed by D.P. Craig and co-workers in an attempt to calculate the equilibrium positions of ground and excited state molecules in a host crystal. Using this method excimer formation in 9-cyanoanthracene (9-CNA) crystals has been predicted [25], as calculations clearly suggest that an excited 9-CNA molecule is energetically more stable if it moves closer to one of its neighboring molecules. No such behavior is predicted for anthracene crystals [25] in agreement with experiment. When a 9-MeOA or 9,10-DMA molecule was "placed" in a 9-CNA crystal it was found [26,27] that the ground state guest molecule is most stable midway between its two intrastack neighbors. However, calculations also were able to predict [26,27] that an excited guest is energetically more stable if it is closer to one of its neighboring host molecules - in complete agreement with the experimental finding of exciplex formation.

As mentioned above, a special case is the 9,10-DMA crystal which, although monomeric, forms exciplexes when doped with 9-CNA (or 1,4-dicyanonaphthalene). In this case, however, numerical simulations did not agree with experiment as force-field calculations did not predict [26] close interaction between 9,10-DMA (host) and 9-CNA (guest) in either the electronic ground or excited state.

III. GUEST-GUEST INTERACTIONS IN DOPED CRYSTALS

III.1 Pyrene Crystals Doped with some Anthracene Derivatives

As stated in section II.1 host/guest miscibility for most doped crystal systems is limited to rather low guest concentrations. A complete range of host/guest miscibility is found only in exceptional cases, and is only guaranteed for "mixed crystals" composed of molecules of different isotopic substitution. This strategy has been widely used to study special energy transfer effects such as percolation in $C_{10}H_8$-$C_{10}D_8$ mixed crystals [28].

High miscibility in the solid state of chemically different molecules is therefore limited to a special group of molecules. Nevertheless, some cases of high miscibility between different aromatic molecules are known. A recent publication [29] reported that 23 mole % of anthracene can be inserted into dimethylnaphthalene crystals. We have found [30] that certain anthracene derivatives dissolve in pyrene for guest concentrations up to at least 0.2 M/M. When such high guest concentrations may be employed, the probability of finding two adjacent guest molecules becomes larger. In an excimeric host crystal this can lead to the observation of guest excimer emission.

We have doped pyrene with anthracene derivatives containing chloro or methyl substituents in the 9- and 9,10-position [30]. The excellent miscibility of these systems is exemplified by the fact that a single crystal of 25 mole % dimethylanthracene in pyrene could be prepared. Its unit cell dimensions were determined (see Table 2) and found to exhibit only small differences from the unit cell demensions of pure pyrene.

Table 2. Unit cell dimentions of pure pyrene and pyrene doped crystals

Crystal	a(^{o}A)	b(^{o}A)	c(^{o}A)	β(deg)	V(A^3)	Ref
Pyrene	13.649	9.256	8.47	100.28	1052.9	14
$\frac{\text{Pyrene}}{\text{DMA*}}$(3:1)	13.54	9.50	8.40	97.10	1071.5	31

a, b, c and β are the monoclinic cell parameters and V is the volume of the unit cell.

*dimethylanthracene

The emission spectra of various guest molecules in pyrene were studied and the following features were observed [30]:

(i) In the low guest concentration region (below 0.05 M/M) the emission spectrum is explained by either host-guest exciplex emission (see Section II.1) or monomeric guest emission. Those emissions are also shown in Fig. 4. However, due to high guest concentrations the first peak of the emissions is reabsorbed. The corresponding decay times are shown in Table 3.

Table 3. The emission properties of some anthracene derivatives dissolved in pyrene (as host) crystals at 77^{o}K.

Guest Molecule	Guest/Host (1:100)				Guest/Host (1:5)	
	λmax (nm)	τ (nsec)	λmax (nm)	τ (nsec)	λmax (nm)	τ (nsec)
9,10 - DMA	435	18	490	50	555	225
9-Cl, 10-MA	435	16	500	40	555	90
9,10-DClA	455	25	500	40	550	60

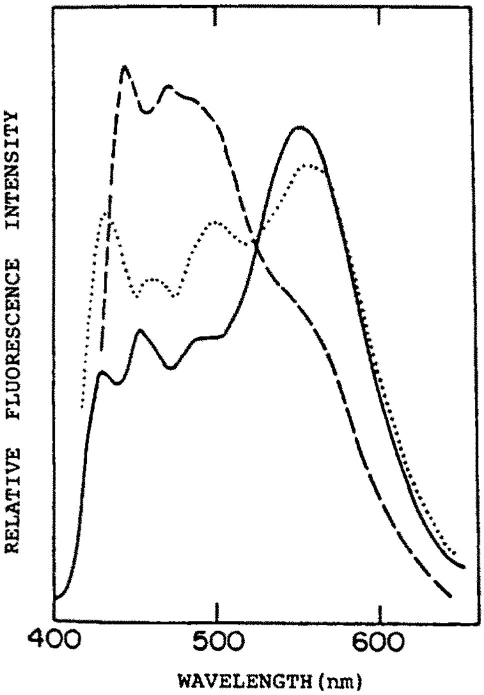
λmax = wavelength of emission maximum; τ = fluorescence decay time

9,10-DMA = 9,10-dimethylanthracene; 9-Cl, 10-MA = 9-chloro-10-methylanthracene

9,10-DClA = 9,10-dichloroanthracene.

(ii) For higher guest concentrations new broad emissions centered around 480-550 nm are observed. Those emissions are assigned to quest excimers by viture of their dependence on guest concentration, and their large Stokes shift and long lifetime.

(iii) For 9,10-disubstituted anthracene as guests, we detected three types of emissions: structured emissions showing short decay kinetics and similar to emissions from dilute pyrene solutions (see Fig. 4 and Table 3). Two structureless emissions were observed, one showing a peak at around 550 nm and the other at around 480 nm. The longer wavelength excimer is attributed to sandwich-type pairs whereas the shorter wavelength excimer to a rotated one (see Fig. 5). The degree of rotation and thus the peak may vary from pair to pair. The possibility of having more than one excimer configuration was predicted by Stevens [32] and observed experimentally [33,34]. However in the case of the disubstituted anthracenes only one excimer, the sandwich type, was detected in their corresponding pure crystalline forms. The crystalline form of the dimethylanthracene shows only structured monomer type emission.



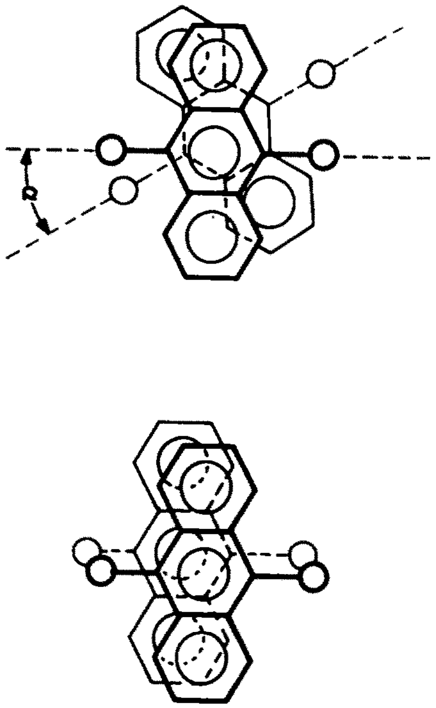


Figure 4

77 K emission spectra of pyrene doped with 0.20 M/M 9,10-dichloroanthracene (---), 9-chloro, 10-methylanthracene (....)and 9,10dimethylanthracene(—).

Figure 5

Proposed excimer configurations of the disubstituted anthracene derivatives (guest) pairs in pyrene as host crystals.

(iv) For monosubstituted anthracene guest molecules only one excimer emission was observed, but its intensity was very low at room temperature. This is attributed to photodimerization (see below). Photodimerization was not observed for these molecules at 77°K; nor was it observed at any temperature when 9,10-disubstituted anthracenes were employed as the guest.

(v) Efficient energy transfer from guest monomers to guest excimers occurs in these systems, even at very low temperatures. It is recognized (see below) that in a mixed crystal the proportion of guest molecules found as adjacent pairs may be larger than that expected for a purely statistical distribution of guest molecules in the host crystal. However, the observed ratio between guest excimer and guest monomer (or exciplex) emission was about an order of magnitude bigger than that for a purely statistical distribution of guests. Thus, at least some of the excess excimer emission intensity must be due to efficient energy transfer from the host to guest monomers and then trapping of this energy at the excimeric sites.

(vi) The guest excimeric emission observed in these mixed crystal systems is very similar to that obtained from either concentrated liquid solutions or single crystals of the same anthracene derivative. Thus, the host crystal environment has only a small influence on the structure and other characteristics of these guest excimers, and acts mainly as a heat bath.

(vii) This technique enabled the formation of excimers in a rigid solid state matrix by molecules like 9,10-dimethylanthracene which do not form excimers in their own pure crystal(10).

III.2 Photochemistry of Guest Excimers and Short-Range Order among Guest Molecules

As mentioned above, guest pairs of 9-chloroanthracene and 9-methylanthracene formed in pyrene crystals gave rise to excimer emission, and have photodimerized upon irradiation at room temperature. This is not surprising since it is well known that these molecules photodimerize [35,36] in solution and in their own pure crystals, whose structures incidentally are very similar [36] to that of pyrene. We have studied in detail [37] the photodimerization of 9-ClA incorporated at high concentrations in pyrene crystals. By measuring the yield of photodimer we were able to calculate the number of preformed adjacent 9-ClA molecules relative to the total 9-ClA concentration. The results showed that the percentage of preformed pairs was far greater than that which would be obtained from a purely statistical distribution of 9-ClA molecules among the pyrene crystal sites. This short-range ordering suggests that a guest-guest pair is energetically more favorable than a host-guest pair, in agreement with our results on guest excimer emission (see Section III, 5).

We note that short range pairwise ordering has been reported [38,39] for pyrene and perylene molecules dispersed in polymeric matrices.

IV. "TRANSIENT" DOPED CRYSTALS AND EXCITED STATE STRUCTURE DETERMINATION

One may consider as a special example of a doped crystal the case of a pure crystal containing some of its molecules in an electronic excited state. Such systems can be thought of as "transient" doped crystals since for a finite time an electronically excited molecule is found in a host crystal of ground state molecules. This esoteric nomenclature is most appropriate for cases where the excited molecules show an appreciable structural change upon electronic excitation, as from a structural point of view the excited species is readily distinguishable as a different molecular species.

We raise this point since we have suggested a few years ago [40] that a direct structural determination of electronically excited molecules using x-ray diffraction should be possible due to the availability of high intensity, short pulse x-ray and optical sources. Further, we believe that among the most promising candidates for such structural determinations would be excimers, since their appreciable geometrical changes upon excitation should ensure a sufficient difference in x-ray diffraction between excited and ground state molecules.

X-ray diffraction, though being a powerful technique is not very sensitive. For a feasible determination of excited state structure by x-ray diffraction, some requirements have to be fulfilled; among them is the build-up of a relatively high (perhaps 0.5%) of electronically excited species, in order to distinguish the x-ray diffraction from that of the unexcited crystal. In pure molecular crystals such a concentration cannot usually be maintained even for short times, since efficient energy migration leads to rapid mutual annihilation of excited states.

One approach to partially overcome such a problem might be to use a mixed crystal in which the guest molecule (whose excited state structure will be determined) is situated substitutionally at a crystallographic position, and which can be selectively excited into either its singlet or triplet excited state. In general this will only be possible if the guest excitation energy is lower than that of the host.

Another alternative is to use excimers. This seems to be the most promising candidate due to the expected large geometrical change upon excitation(41), as well as the fact that electronic energy migration in excimer-forming crystals can be eliminated by cooling to low temperatures [7,8]. The main mechanism which will then control the concentration of excimers will be long range excimer-excimer annihilation [30]. We have shown that in such an annihilation one excimer acts as a donor and the other as an acceptor, resulting in the annihilation of one excimer(30). Such a high density of excited states was also shown to give rise to an anomalous slowing down of the decay kinetics due to a photon-excimer reabsorption process [42]. However, this last mechanism does not alter the instantaneous concentration of excited states.

It has also been shown that for some excimers both the excimer and fluorescence (43) and excimer absorptions (30) are polarized in the plane defined by the aromatic rings forming the excimer. Based on this and the previously mentioned data, we have suggested to engineer a crystalline system which is expected to sustain even a higher excimer concentration than anticipated for regular pure excimers forming crystals(44). Figure 6 shows a schematic drawing of such a suggested crystal. The excimer forming pairs are chemically attached to a non-aromatic large molecule. The nearest neighboring excimer forming pairs are aligned orthogonally and the translationally equivalent ones are separated by about 40°A.

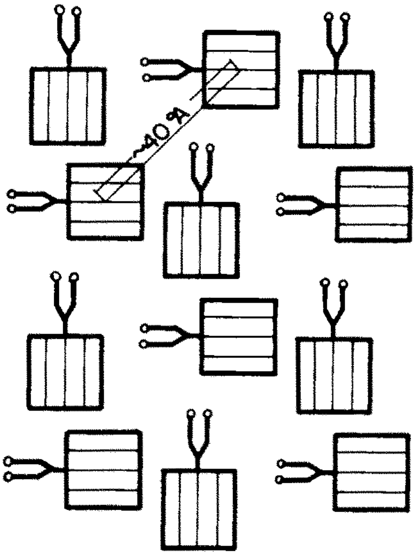


Figure 6. Schematic drawing of an imaginary excimer forming crystal for excited state structure determination by means of pulsed x-ray diffractions.

To summarize, this kind of transient mixed crystal system as described here is suggested to be one of the most suitable systems for the time resolved x-ray determination of excited state structure.

V. EXPERIMENTAL

The host crystals and dopant molecules were purified by column chromatography and zone refining. Fluorescence spectra were measured using either a modified Aminco-Bowman spectrofluorometer or by means of a high resolution set-up consisting of: 900 W. Xe lamp, a 0.5m Bausch & Lomb monochromator (1200 grooves/mm) for excitation, and detection by means of a Spex 0.75m monochromator (1200 grooves/mm), an EMI photomultiplier and a PAR HR-8 lock-in-amplifier. Samples were cooled by means of an Air-Product cryostat down to liquid helium temperature. Fluorescence decay times were determined using excitation from a Molectron UV-400 nitrogen laser or a Molectron DL-200 tunable dye laser. Detection was by means of a fast photomultiplier and a transient digitizer (Tetronix 7912) or a fast oscilloscope (Tetronix 7704A).

VI. CONCLUSION

We have shown that a wide variety of spectroscopic, photochemical and structural studies of bimolecular excited state complexes may be performed using a suitable doped crystal. This technique has led us to several interesting new discoveries including energy trapping in "uphill" doped crystals, formation of guest excimers and detection of short-range order among guest molecules.

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