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Effect of Temperature and Crystal Packing on Some Excimer Emitting Crystals

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The compounds 9-chloro-anthracene and 2,4-dichloro-3'-methyl-*trans*-stilbene are dimorphic, the two crystal forms having "pair" and "stack" structures. Both forms of the above compounds show excimer emission; this emission is of higher energy and with greater temperature sensitivity in stack than in pair structures.

A number of recent studies have shown that a given chromophore pair may give rise to more than one excimer emission. Thus, the *syn*- and *anti*-[2,2]-paracyclonaphthanes give excimer emissions of different energies.¹ We have found² three excimer emissions from 9-cyanoanthracene at 77°K: at 19,800 cm⁻¹ for a pair formed by splitting the photodimer in a glass, at 18,000 cm⁻¹ for the pure crystal, and at 17,250 cm⁻¹ for a frozen concentrated chloroform solution. Similarly, Ferguson and Mau³ reported two excimer emissions from anthracene. We interpret these results to mean that external constraints may modify the structure and therefore the energy of the excimer; the constraint could be due to covalent bonds between the monomers, as in the above naphthanes,¹ or to the structure of the molecular aggregate in the other cases. One may expect, on this basis, that different crystal structures would impose different constraints which would lead to different excimer geometries.

In a study on excimer emitting anthracenes we observed that the emissions from stack structures differ from the pair structures in their spectral location and with regard to temperature sensitivity.⁴ According to our theoretical analysis of the temperature effect the shift of the maximum of emission with temperature can be expressed by:

$$\omega(T) - \omega(T = 0) \simeq \omega(T = 0)CT + \gamma KT \quad (1)$$

where

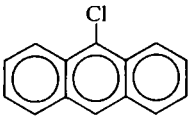
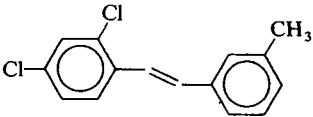
$$\gamma = \frac{1}{2} \sum_i \left(1 - \frac{\omega_{gi}^2}{\omega_{ei}^2} \right) \quad (2)$$

ω_{gi} , ω_{ei} are the intra-pair frequencies in the i th vibrational mode in the ground- and excited-states, respectively; C is a constant for a given compound. The theoretical maximum and minimum values of γ for excimers are 3 and 0, respectively; empirically we found γ to be of the order of 3 for stack structures, and of 1 for pair structures. Thus from (2) we obtain

$$\frac{\omega_g}{\omega_e}(\text{pair}) > \frac{\omega_g}{\omega_e}(\text{stack}) \quad (3)$$

Further, we found for a variety of excimers in both structures that $\omega_e \sim 100 \text{ cm}^{-1}$, so that $\omega_g(\text{pair}) > \omega_g(\text{stack})$. This means that near the equilibrium spacing the ground state potential energy surface is steeper for the pair than for the stack structures. On the other hand we found the excitation energies to be similar for the two structures. Thus the energy surfaces can be represented as in the Figure 1, and the emission from stack structures should be at higher energies than from pair structures.

We have found only two examples which we could use to check this and both are in agreement with the prediction. Our results are as follows:

Comp.	Excimer emission [$\omega_{\max} (\text{cm}^{-1})$] at 77°K	
	Stack	Pair
 (Ref. 4)	19.250	18.400
 (Ref. 5)	21.600	20.550

Both materials photodimerize in both crystal structures: the stilbene gives the topochemical products i.e. the pair structure gives the centric dimer, the stack structure the mirror one. The pair anthracenes also give the topochemical dimer, but not so the stack ones. This non-topochemical

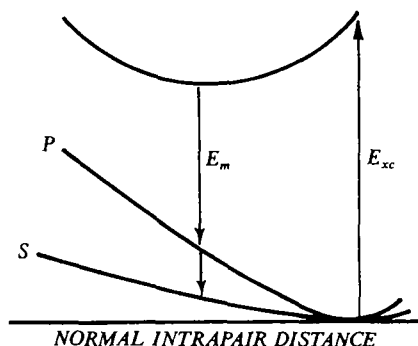


FIGURE 1 Schematic representation of potential energy surfaces in structures based on stack (S) and pairs (P).

behaviour is probably due to both non-stability of the expected *cis* photo-product and to the rapid transfer of the excitation energy to suitable structural defects in the crystal. In the stilbene, on the other hand, reaction is faster than energy transfer.

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