Photochemical Detection of Short-range Order in a Mixed Crystal

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9-Chloroanthracene molecules, added as dopants to pyrene crystals, are found adjacent to one another in higher concentrations than that expected for randomly dispersed dopant molecules.

Studies of lightly doped mixed crystals have established that for host and dopant molecules of similar size, guest molecules are generally incorporated into the host crystal by substitutional replacement of a host molecule at certain crystal sites.[1,2] However, another question is whether guest molecules are distributed randomly throughout the crystal, or whether there is some correlation between the sites occupied by guest molecules. In general, (especially for low guest concentrations of up to say 10 mol%) it is very difficult to determine such distributions experimentally. However, spectroscopic and photochemical studies carried out in this laboratory[3,4] have led to an approach which enables us to answer some of these questions.

Various anthracene derivatives have been shown[3] to be miscible in pyrene crystals up to guest concentrations as high as 20 mol %. The pyrene host crystal structure is well known;[5] molecules are found as highly overlapped pairs. As a result the fluorescence of pure pyrene crystals is excimeric.[6] Similarly, in pyrene crystals doped with various anthracene derivatives, exciplex formation between adjacent host and guest molecules has been observed.[4] There is also some probability of finding two adjacent guest molecules; thus it is not surprising that guest excimer fluorescence has been observed[3] at high guest concentrations (a similar phenomenon has been observed recently[7] in other systems). For some systems of pyrene doped with anthracene derivatives, *e.g.* 9-chloroanthracene (9-ClA), photodimerization of guest molecules has also been observed.[3] Since it is known that the excimer is the precursor of the photodimer,[8] it follows that the yield of guest photodimers can be at most the number of pre-existing adjacent molecular pairs in the doped crystal.

Crystals of pyrene doped with 9-ClA were grown from solution by slow evaporation, and from molten pyrene–9-ClA mixtures by the Bridgman method (crystallization occurred at *ca.* 70 °C). Good quality single crystals were chosen, crushed to a powder, and irradiated for several days under an oxygen-free atmosphere. The 9-ClA content was determined (before and after irradiation) by the u.v. absorption at 390 nm, where pyrene does not absorb. The pyrene content was determined (after subtraction of 9-ClA absorption) from the absorption at 338 nm. It was observed that the pyrene

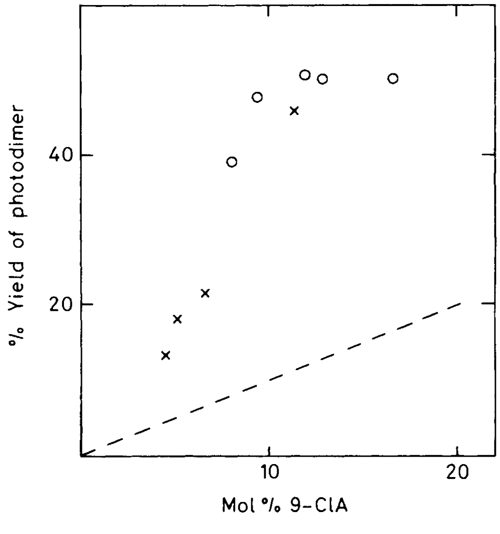

Figure 1. The yield of the 9-chloroanthracene (9-ClA) photodimer (expressed as a percentage of the total 9-ClA content) formed by irradiation of 9-ClA doped pyrene crystals *vs.* 9-ClA concentration. Crystals were grown from solution (×) or by the Bridgman method (○). The dotted line gives the results expected for a random distribution of 9-ClA molecules.

content was unchanged after irradiation, but that the 9-ClA content decreased. Chromatographic analysis revealed that the only reaction product was the 9-ClA photodimer (yields are given in Figure 1 as a function of 9-ClA concentration in the mixed crystal before irradiation). Figure 1 also shows the theoretical yield (given by the binomial distribution) that is expected for the hypothetical case of a truly random guest distribution and a quantitative yield of dimerization from all pairs of adjacent guest molecules.

The results show that the number of guest molecular pairs found experimentally is far greater than that for a random distribution.† Such short-range ordering is only expected to occur if a guest–host pair is energetically unfavourable relative to a guest–guest pair. This is not surprising in this case since the pairwise crystal structure of pyrene is quite similar to that of a stable crystal modification of 9-ClA.[9]

These results show a special case of correlation between sites occupied by guest molecules in a doped crystal. In principle, our approach could be applied to any organized binary system where dimerization or polymerization of components can occur. Indeed, in a similar way, polymerization in multilayers of ethyl and vinyl stearates has indicated[10] a random distribution of components.

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† The same dimerization yields were achieved using either weak irradiation over several days, or more rapidly, using intense irradiation. This indicates that molecular diffusion cannot be responsible for the high dimerization yields. Thus, the dimerization yield is a true measure of the number of guest molecular pairs in the doped crystal before irradiation. We also note that the excimer fluorescence of 9-ClA in pyrene host crystals is different (ref. 3) from the excimer fluorescence of pure 9-ClA crystals. Thus, the effects we observe cannot arise from segregated microcrystals of 9-ClA in the pyrene host matrix.

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