Photochemical Dimerisation in Crystalline Anthracenes

By D. P. CRAIG and P. SARTI-FANTONI

(*William Ramsay and Ralph Forster Laboratories, University College, London*)

IN a number of solid-state photodimerisation reactions the crystal structure of the monomer is a good guide to the geometrical structure of the dimer, as shown by Schmidt and co-workers.[1,2] Applied to crystalline 9-cyanoanthracene and 9-anthraldehyde the principle that the dimer structure adopted is that most nearly pre-formed in the monomer crystal leads to the expectation[1] based on the crystal structures[3,4] that *cis*-dimers will be formed instead of *trans*-photodimers as in solution.

We have irradiated thin crystals of both compounds formed from melts between silica discs and have recovered quantities of a few tenths of a gram of the photodimers. The photodimers from the solid in these two cases are *trans* in structure, contrary to expectations based on pre-formation in the monomer crystal. The infrared spectra are identical with dimers formed in solution and the dipole moments are small (0·8D for 9-CN, 0·7D for 9-CHO)* compared with the calculated 6D for *cis* 9-CN and between 3 and 5D for 9-CHO. The values are close to those for dimers from solution and indicate an overwhelming preponderance of *trans*-compound. The spectra were taken from solid dimers left after dissolving away unchanged monomer, and the conditions seem to preclude rearrangement of the initially formed dimers.

This finding is not by any means necessarily against the theory of the "topochemical" preformation of dimer structures, which can in any case apply only to regions of perfectly ordered crystallinity, but suggests that in these examples reaction occurs at defects or surfaces or in zones already disordered by dimerisation. Excitation may be carried by an exciton mechanism to such sites, where it is trapped and used in the photochemical process. Simply on grounds of steric repulsion the *cis*-dimers would be expected to be less stable than the *trans*, and topochemical influences are not strong enough in these examples to induce the formation of the less stable dimer.

These considerations are reinforced by recent studies, optical[5] and photochemical, of crystalline anthracene. We have confirmed, as have others,[6–8] that anthracene photodimerises in the pure deoxygenated crystal to give dianthracene, as was long ago claimed by Luther and Weigert.[9] This process is responsible for the "ageing" of pure single crystals of anthracene irradiated under oxygen-free conditions, as manifest by a change in the polarization ratios of fluorescence emission progressing to a point where the emitted light is unpolarized. At this stage gross crystal damage is visible under the microscope as striations along the *b*-monoclinic axis and a general loss of transparency in the irradiated zone.[5]

The rapid change in the fluorescence can be accounted for on the hypothesis that anthracene molecules have their excitation energies slightly reduced when displaced from their normal lattice orientations by proximity to sites at which dimerisation has taken place. They may then trap and emit the excitation at the expense of emission by normally oriented molecules. The emitted light would thus quickly become characteristic of defective crystal regions, even when the percentage conversion is extremely low. The absorption spectrum is not selective in this sense, being a mean of all absorbing molecules in the light beam, and no similarly large change in absorption polarization ratio is expected nor found. If instead of being emitted as fluorescence, the excitation, having been trapped in regions already damaged, may cause photodimerisation there, giving a growing zone of clustered dimers to the stage eventually of gross disruption of the monomer crystal.

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The examples in which topochemical influences are dominant may conversely be those in which excitation transfer is slower, or the disturbed molecules have *higher* excitation energies, so that photochemical change occurs in regions of perfect crystalline order.

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