# A Potential Photochemically driven Information Storage System

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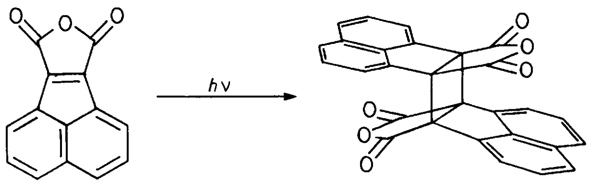
Orange acenaphthylene-1,2-dicarboxylic anhydride undergoes a solid state photochemical [2 + 2] cycloaddition upon irradiation at 390 nm to yield a white photodimer which can be cleaved back to two monomers by irradiation at 300 nm; this process can be repeated numerous times.

Solid state photoreactivity has received considerable attention recently. Part of this interest is derived from the fact that for many molecules the observed photoreactivity in the solid state is vastly different from that observed in solution. Perhaps greater interest lies in the discovery and study of new reversible solid state photochemical reactions. The exciting possibilities of using these materials in a wide range of molecular-scale devices has caught the imagination of several research groups.[1,2] Here we report the solid state and solution photoreactivity of acenaphthylene-1,2-dicarboxylic anhydride (**1**) and acenaphthylene-1,2-dicarboxylic acid (**4**). Both compounds exhibit reversible solid state photochemical dimerizations. The 1,2-disubstituted acenaphthylene derivatives studied in this report were conveniently prepared by a four-step process reported recently.[3]

Irradiation of (**1**) was expected to yield a dimeric product by analogy with acenaphthylene and maleic anhydride. However, solution phase irradiation of compound (**1**) under a variety of conditions failed to yield any photoproducts. Irradiation was carried out in dichloromethane under nitrogen, with and without a Pyrex filter, with a medium pressure mercury lamp for periods of up to 100 h.

The solid state photochemistry, however, was noticeably different. Compound (**1**) (which is bright orange) was dissolved in dichloromethane and placed in a photolysis flask. The dichloromethane was evaporated under a stream of nitrogen as the flask was turned slowly. The resulting film was irradiated in air with a 450 W medium pressure mercury lamp with a Pyrex filter for 3 h, producing nearly a quantitative yield of a white dimer (Figure 1).

While useful crystals of the dimer (**2**) could not be obtained, crystal analysis of the monomer (**1**) clearly indicated that the *trans*-isomer was the most probable product.[†] In the crystal structure of (**1**), the closest contact between the reacting double bonds of neighbouring molecules lies across a centre of symmetry, and if reaction occurs at this site, it will clearly yield the *trans*-product. The bond distance between the two reacting double bonds is 3.548(5) Å which is clearly within the normally accepted limits of solid state [2 + 2] photochemical dimerizations.[4] The solid state photochemical dimerization of maleic anhydride also yields the *trans*-dimer. As further characterization of (**2**) it was hydrolysed to the tetracarboxylic acid (**3**).



(**1**) (**2**)

**Figure 1**. (**3**) and (**4**) are the di- and tetra-carboxylic acid analogues.

The irradiation of (**4**) in a variety of solvents and conditions failed to yield any sign of [2 + 2] photochemical dimerization or any other photochemical reaction. Also irradiation of films or powders of (**4**) in several different ways for periods of up to 150 h showed no signs of any photochemical products.

The white tetracarboxylic acid dimer (**3**) was irradiated at 300 nm and turned orange almost instantaneously.[‡][§] This particular wavelength excites the dimer (**3**), but not the monomer (**4**). Then, switching the wavelength to 390 nm, the same sample was irradiated for several hours, revealing a gradual colour change of the compound from orange back to white. The orange compound was identified as (**4**).

The photochemical cleavage of (**3**) appeared to occur only on the surface. Irradiation at 300 nm for several hours with stirring yielded only a few milligrams of (**4**). The monomer is an effective energy trap and only a thin layer on the surface is undergoing the photochemical cleavage back to the monomer. Also the photochemical dimerization of the newly formed monomers back to the dimer appears to be incomplete. Switching back and forth many times between 300 and 390 nm causes a gradual build-up of the orange monomer (**4**) which eventually will not undergo photochemical dimerization.

The anhydride dimer (**2**) was also found to turn orange rapidly upon irradiation at 300 nm. However, the orange colour reverted to white in only a few minutes when the sample was irradiated with light at 390 nm which is in contrast to the tetracarboxylic acid. This process could be repeated as many times as desired. While the photochemical cleavage of the dimer to the monomer for (**2**) was instantaneous, the newly formed monomer apparently quenched any further photochemical cleavage and only a small amount of cleavage back to the monomer actually occurred.[¶] After four days of

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[†] *Crystal data* for: $C_{14}H_6O_3$, $M$ = 222.2, monoclinic, space group $C2/c$, $a$ = 13.880(3), $b$ = 9.634(2), $c$ = 15.789(3) Å, $\beta$ = 109.49(1)°, $U$ = 1990.3(7) Å$^3$, $Z$ = 8, $D_c$ = 1.48 g cm$^{-3}$, $\mu$(Mo-$K_\alpha$) = 1.1 cm$^{-1}$. Intensity data were measured on a Nicolet four circle diffractometer. The structure was solved by direct methods using the SHELXTL program and refined by full-matrix least-squares with the hydrogen atoms included in calculated positions without refinement, to give $R$ = 0.047 and $R_w$ = 0.064 for 1060 reflections with $I \geqslant 3\sigma(I)$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[‡] Irradiations at specific wavelengths were carried out with a BAUSCH and LOMB High Intensity Grating Monochromator with a 2700 groves per millimeter Ultraviolet Grating and an Achromatic Condenser Lens. The light source was a 200 W, short arc, super pressure mercury lamp with a quartz envelope.

[§] Irradiation of (**3**) (90 mg) at 300 nm for 8 h yielded 2 mg of pure (**4**). Compound (**4**) was identified by spectral analysis, having identical IR and UV data as a pure sample of (**4**).

[¶] Irradiation of (**2**) (approximately 100 mg) for four days at 300 nm yielded 1 mg of (**1**). This was identified by having the identical UV spectrum as a pure sample of (**1**). It also had the same $R_f$ value on thin layer analysis.

irradiation at 300 nm, with frequent stirring of the powder, extraction with dichloromethane yielded only enough monomer for UV identification. While the extent of cleavage of (**2**) to (**1**) was much less than in the case of (**3**), the degree of reversibility was much higher. The orange to white process only required a few minutes with a low intensity light source and appeared to be repeatable many times with no degradation of the material.‡ Both dimers (**2**) and (**3**) were found to be thermally stable at temperatures above 265 °C.

The solid state photoreactivity of (**3**) is unusual in that irradiation of (**4**) does not give any detectable amount of (**3**). However, irradiation of (**3**) can lead to small concentrations of (**4**) held in a matrix of (**3**). Under these conditions (**4**) can be photochemically dimerized back to (**3**). This process can be repeated several times but gradually the reversibility breaks down. Finally, the monomer formed cannot be dimerized upon prolonged irradiation. Presumably, the molecules of (**4**) formed initially are held in an effective matrix of (**3**) such that photodimerization is possible but eventually the monomer molecules reorientate themselves perhaps to the crystal structure of (**4**). After they have rearranged they are no longer able to photodimerize.

Further studies on these and related systems as potential information storage devices will be reported in the near future.

We acknowledge support of this work by the National Science Foundation (Grant CHE-8719728), and thank L. I. Rieke for assistance in preparing this manuscript.

*Received, 28th February 1989;* ††*Com. 9/00878K*

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†† Received in final revised form, 28th September 1989.