

stable state involves some sort of rearrangement such as a *cis-trans* or keto-enol isomerization, a heterolytic cleavage, etc. Depending on the system, photochromism may occur in the solid, in solution or in a rigid medium such as a plastic¹⁵. We discuss here some high-pressure studies on a series of bianthrone¹⁶. (See top of *Figure 12*.) These include bianthrone (BA), 2,2'-dimethyl bianthrone (2,2'-DMBA), 2,2'-dibromobianthrone (2,2'-DBRBA) and 4,4'-dimethyl bianthrone (4,4'-DMBA). Most bianthrone undergo a photochromic rearrangement as illustrated in the centre of *Figure 12*¹⁷ but the 4,4'-derivative, because of steric effects, undergoes the rearrangement shown at the bottom. We refer to the normal state as A and the photochromic state as B.

Bianthrone exhibit photochromism at temperatures below $\sim -50^{\circ}\text{C}$ in liquid solution or in a plastic. At sufficiently elevated temperature they transform thermochromically in the liquid but not in the plastic. The crystal is neither photochromic nor thermochromic, but will transform under strong shearing action. All of these processes are reversible over a period of time.

The effects of pressure on the electronic energy levels of the four bianthrone derivatives dissolved in polymethyl methacrylate (PMMA) have been studied¹⁶. BA has also been studied in polystyrene (PS). All effects discussed are reversible. In *Figure 13* we exhibit the spectra of 4,4'-DMBA in its normal state and after several hours irradiation in the A peak. The

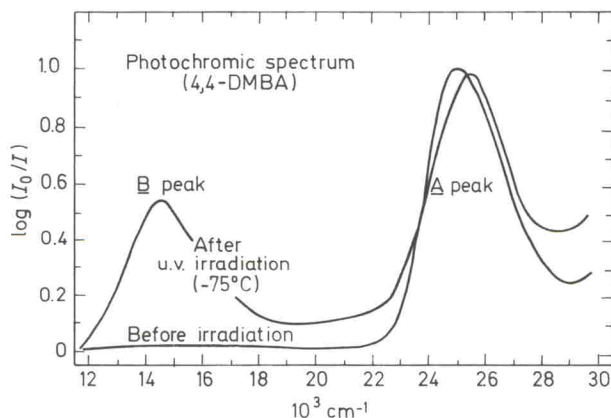


Figure 13. Spectra of unirradiated and irradiated 4,4'-DMBA in PMMA

photochromic peak (B) is obvious. In *Figure 14* we show the spectra of bianthrone (BA) at a series of pressures. The peak (B) grows with increasing pressure. Repeated spectra at the same pressure gave the same fractional conversion, so this is not an artifact of irradiation while taking the spectrum. It can also be shown that it is not a result of heating by compression. The extinction coefficients of the two peaks are roughly the same, so the relative peak areas are a reasonable measure of the fractional conversion. The fraction converted is shown as a function of pressure in *Figure 15* for BA.

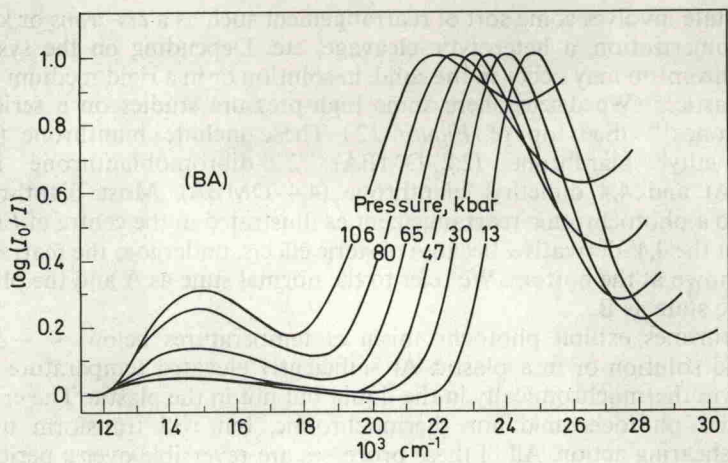


Figure 14. Spectra of BA in PMMA at various pressures

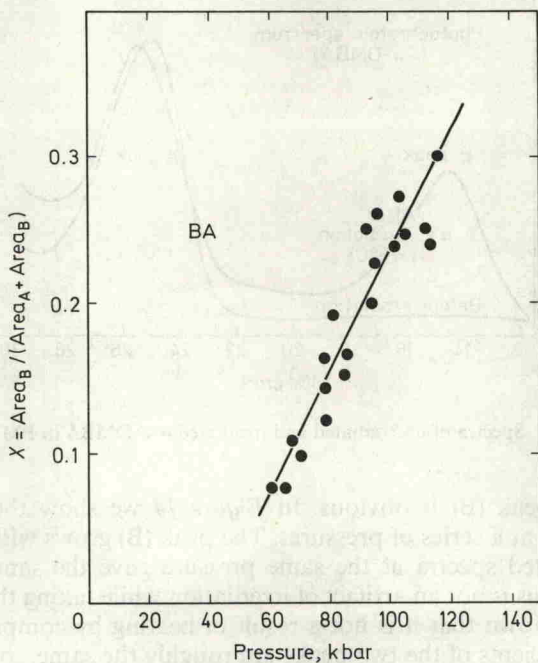


Figure 15. Conversion from A to B form against pressure: BA in PMMA