

## Organic Solid Photochromism via a Photoreduction Mechanism. Photochromism of Viologen Crystals

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Crystals of viologens such as (1) and (2) exhibit reversible photocolour development, attributed to radical cation formation, by u.v. irradiation in air.

Viologens such as *N,N'*-dibenzyl-4,4'-bipyridinium dichloride undergo rapid reversible photoreduction in a solid poly(*N*-vinyl-2-pyrrolidone) matrix even in the presence of air.<sup>1</sup> This phenomenon is caused by electron transfer to the viologen cation from the counter anion.<sup>2,3</sup>

Work on the effect of the chemical structure on photocolour development in viologens in the solid state has revealed that some crystalline viologens undergo reversible photocolour development even in the presence of air, whereas most crystalline viologens failed to show this phenomenon. This phenomenon (photochromism) has been observed in simple

crystals without any added reductants or matrices and therefore indicates photo-catalysed electron transfer to the viologen cation  $V^{2+}$  from the paired counter anion  $X^-$ , as in equation 1. Viologens (1) and (2) show this unusual phenomenon in the crystalline state.

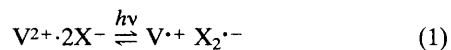
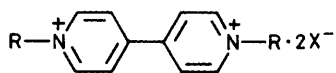
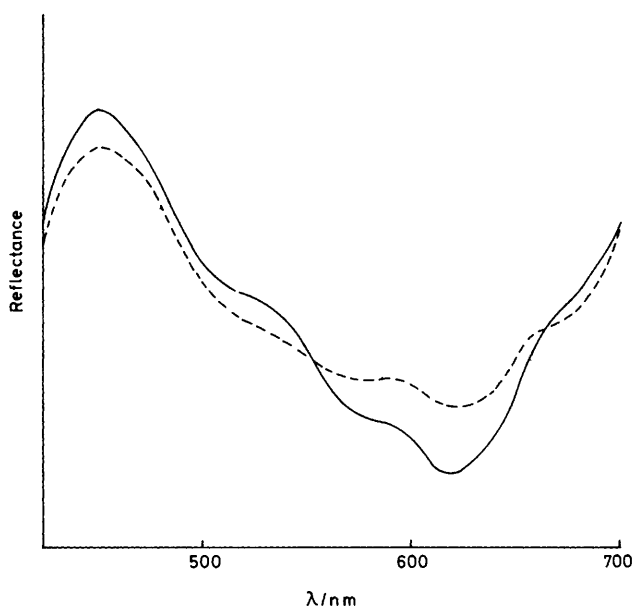


Figure 1 shows the absorption spectra of finely divided crystals of (1) and (2) exposed to u.v. light, as determined by the reflection method, and are similar to those of the known



- (1); R =  $[\text{CH}_2]_3\text{SO}_3^-$   
 (2); R =  $\text{CH}_2\text{Ph}$ ; X =  $p\text{-MeC}_6\text{H}_4\text{SO}_3^-$



**Figure 1.** Visible absorption spectra of viologen crystals exposed to u.v. light. (1) —; (2) - - -. Irradiations were carried out for 60 s, 10 cm from a 75 W Hg lamp (Toshiba SHL-100UV2). The ordinate has no meaning other than to show the shapes of absorption curves (Hitachi 200—10 spectrophotometer).

viologen radical cations.<sup>4</sup> The absorption spectra show no evidence of aggregation of radical cations. The colour developed in crystal (1) by u.v. light is stable and, when left to stand in air in the absence of u.v. light, the blue colour developed persists longer than a year. The colour is lost rapidly on heating above 100 °C. In contrast, the blue colour of crystal (2) developed in u.v. light fades rapidly (within 5 min at

**Table 1.** Relationship between chemical structure of viologen crystal and photochromic behaviour.<sup>a</sup>

R	X <sup>-</sup>	Colour <sup>b</sup> developed by light	Stability <sup>c</sup> of developed colour
$[\text{CH}_2]_3\text{SO}_3^-$		Blue (620 nm)	>1 year
$\text{CH}_2\text{Ph}$	$p\text{-MeC}_6\text{H}_4\text{SO}_3^-$	Blue (620 nm)	<5 min
$\text{CH}_2\text{Ph}$	$\text{Cl}^-$	N <sup>d</sup>	—
$\text{CH}_2\text{Ph}$	$\text{Br}^-$	N	—
$\text{CH}_2\text{Ph}$	$\text{BF}_4^-$	Pale blue	<60 s
$\text{C}_3\text{H}_7$	$\text{Br}^-$	N	—
$\text{C}_3\text{H}_7$	$\text{EtSO}_3^-$	N	—
$\text{CH}_2\text{Ph}$	$\text{PhSO}_3^-$	N	—

<sup>a</sup> Purified by recrystallization and subsequent vacuum drying. <sup>b</sup> 60 s Irradiation either with u.v. light from a 75 W mercury lamp or with direct sun light in the air. <sup>c</sup> Stored in the dark under ambient conditions. <sup>d</sup> N = No colour development.

20 °C in air). Both colour developments take place within 1 min even in sun light.

Table 1 summarizes the relationship between the chemical structure of common viologen crystals and their photochromic behaviour. From Table 1 it can be seen that the reversible photocolour development is affected by the structure of the viologen, and conventional viologens such as those with halide ions do not show any photocolour development in the air. This phenomenon appears to be related not only to the chemical structure of the viologen, but also to the crystal structure, both these factors contributing to the thermodynamic stability of the cation radical produced in the viologen crystal by light.

Received, 1st October 1984; Com. 1375

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