

Solid State Dimerisation of β -Nitrostyrene: a Disordered Photoreactive Crystal

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The unusual solid state dimerisation of β -nitrostyrene to yield two isomeric cyclobutanes is accounted for by its disordered, photoreactive crystal structure which permits a *trans* \rightarrow *cis* isomerisation.

Most solid state 2 + 2 cycloaddition reactions of alkenic compounds are strictly controlled by the topochemistry either of the bulk or of defect regions in the crystal.¹⁻³ The result, in both cases, is the formation of a single photodimer. When bulk topochemistry controls the reaction, the stereochemistry of the cyclobutane dimer may be anticipated geometrically (*trans*-cinnamic acid, 2-benzyl-5-benzylidencyclopentanone, 2,5-dibenzylidencyclopentanone, α -benzylidene- γ -butyrolactone, 2,5-distyrylpyrazine). When defect topochemistry controls the reaction the outcome of the reaction is generally not predictable but even so, only a single product is obtained (9-cyanoanthracene, 4-formylcinnamic acid, 7-methoxycoumarin).⁴ In this connection, the photodimerisation of crystalline β -nitrostyrene (**1**) is of interest since *two* products (**2a**) and (**2b**), are produced in comparable amounts. This reaction has been investigated previously,^{5,6} but no explanation has been advanced for this intriguing result. Accordingly, a study of β -nitrostyrene and some of its derivatives was initiated.

The structures of the dimers (**2a**) and (**2b**) were deduced spectroscopically by Shechter and co-workers, who studied the solid state reaction of (**1**).⁶ We found that these dimers are produced in a 3 : 1 ratio when crystalline (**1**) is irradiated with sunlight at 5°C. The stereochemistry of the dimers was confirmed by us with X-ray crystallography. It was found that the centrosymmetric (**2a**) molecules lie on inversion centres in the crystal ($P2_1/n$, $Z = 2$, $R = 0.048$, 1135 reflections) while the (**2b**) molecules are chiral ($P2_12_12_1$, $Z = 4$, $R = 0.046$, 800 reflections). The crystal structure of (**1**) was determined next since this is crucial to any explanation for the formation of these dimers. The structure was solved routinely but the refinement showed that the alkenic bridge is disordered, with positional occupancies of 74 : 26 for the alternative molecular orientations. This disordered model refined quite satisfactorily.[†]

Figure 1 shows the orientation of nearest neighbours in crystalline (**1**). Neighbouring molecules with the same orientation (74 or 26%) are inversion related and the double bond centre-to-centre distance is 3.82 Å. This corresponds to the α -configuration of Schmidt^{1,7} and the formation of the centrosymmetric dimer (**2a**) is easily understood. The formation of the second 'anomalous' dimer (**2b**) may be rationalised by assuming that a photochemical *trans* \rightarrow *cis* isomerisation precedes the 2 + 2 cycloaddition. The disordered crystal structure contains enough empty space for such a change in molecular shape and topochemical reaction of neighbouring *trans* and *cis* molecules would result in the appropriate

stereochemistry for dimer (**2b**). Such a photochemical *trans* \rightarrow *cis* equilibration has been reported for nitrostyrenes in solution.⁸ There is no reason to believe that it is precluded in the solid, provided spatial factors are favourable.

There is evidence that the formation of dimers such as (**2b**) requires both a photoreactive α -structure and a capability for solid state *trans* \rightarrow *cis* isomerisation such as is conferred by the type of crystallographic disorder seen here. The crystal structure of 3,4-dimethoxy- β -nitrostyrene (**3**) was determined ($Pcab$, $Z = 8$, $R = 0.040$, 1191 reflections). This structure is of the α -type but ordered. Neighbouring molecules are at a centre-to-centre separation of 3.62 Å and the solid is photoreactive yielding only a single dimer, the topochemically expected (**4**), although (**3**) is isomerised photochemically in solution to the *cis*-form. Similarly, 2,4-dichloro- β -nitrostyrene, (**5**) adopts a ' β -type' 4 Å structure in accordance with the 'chloro-rule'⁹ ($Fdd2$, $Z = 16$, $R = 0.076$, 505 reflections). This structure is ordered too and neighbouring molecules are at the short axis separation of 3.833 Å. Alkene (**5**) is accordingly photoreactive to yield the mirror-symmetry dimer (**6**). Dimers (**4**) and (**6**) were characterised by n.m.r. and mass spectra [major peaks (**4**): $C_{10}H_{11}NO_4$ $M/2^{++}$; (**5**) $C_{16}H_9Cl_3$ ($M - HN_2O_4$)⁺]. The behaviour of (**3**) and (**5**) is very reminiscent of the corresponding *trans*-cinnamic acids. However, 4-methyl- β -nitrostyrene (**7**) adopts an 'unreactive' γ -struc-

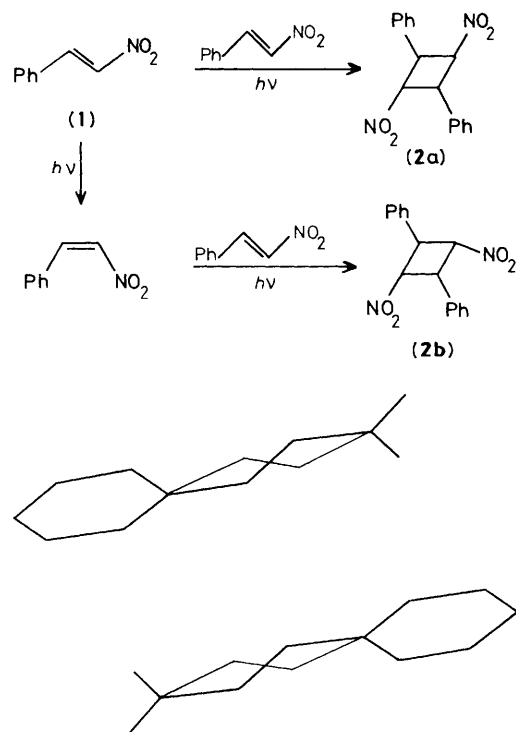
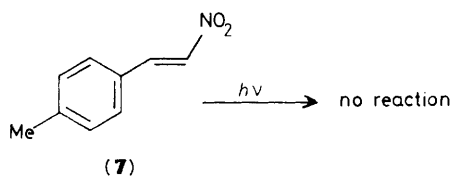
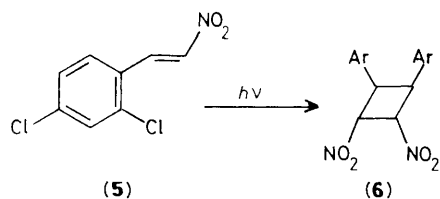
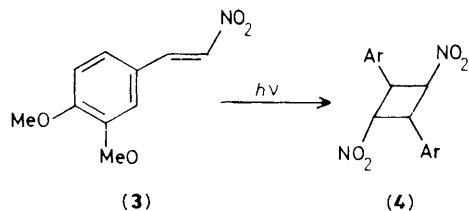


Figure 1. Arrangement of inversion-related molecules of *trans*- β -nitrostyrene, $Ph-CH=CH-NO_2$, in the crystal. Both the disordered orientations of the alkenic bridge are shown. The double bond centre-to-centre separation is 3.82 Å, rendering the crystal photoreactive.

[†] Crystal data for (**1**): $C_8H_7NO_2$, $M = 149.15$, monoclinic, $P2_1/c$, $a = 8.0970(6)$, $b = 5.7682(5)$, $c = 18.647(2)$, Å, $\beta = 117.71(5)^\circ$, $U = 771.0(1)$ Å³, $Z = 4$, $F(000) = 312$, $D_x = 1.28$ Mg m⁻³, $\lambda(Mo-K_\alpha) = 0.57$ cm⁻¹, $T = 133$ K, Enraf-Nonius CAD-4 diffractometer, structure solution SHELXS-86, refinement SHELX-76, $R = 0.053$, $R_w = 0.066$, 783 independent reflections with $I \geq 3(\sigma)$, hydrogens in calculated positions, one set of disordered alkenic carbons isotropic, all other atoms anisotropic, maximum and minimum final difference electron density 0.14 and -0.14 e Å⁻³. 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.



ture^{1,7} with a short axis of 4.816 Å (*Pnma*, $Z = 4$, $R = 0.074$, 402 reflections). Most interestingly, this structure is disordered in nearly the same manner as (1) with the presence of a bisecting crystallographic mirror plane necessitating that the two orientations of the alkenic bridge be equally populated. However, (7) was found to be photostable. These observations indicate that topochemical arguments are paramount in this family of compounds but that the further presence of disorder may permit alternative reaction pathways.

It is possible that analogies may be drawn between solution chemistry which is based on molecular structure and solid state

chemistry which is based on crystal structure.¹⁰ Rudimentary homologous series for crystal structures such as benzene, naphthalene, and anthracene have been recognised.^{11–13} Polymorphism has a molecular analogy in structural isomerism with the topochemical principle bridging crystals and molecules.¹ Similarly, non-centrosymmetry in crystals is paralleled by molecular chirality. To continue the analogy, disorder in a reactive crystal finds a molecular extension in alternative reaction pathways.

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