Monitoring the Crystallographic Course of a Single-crystal → Single-crystal Photodimerization by *X*-Ray Diffractometry

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Summary Using four-circle diffractometry in a dynamic mode, the course of the topochemical photodimerization of 2-benzyl-5-benzylidenecyclopentanone has been determined.

IN certain organic crystals, the crystal packing of which may be 'engineered',[1] monomer molecules are so oriented that dimeric or polymeric species are 'preformed' within them. These dimers or polymers[2] are formed upon u.v. irradiation, often isomorphously within the monomer matrix. This fact has considerable synthetic potential and has been utilized, for example, in the generation of chiral products;[3] but its further exploitation rests upon whether the solid-state reaction is genuinely homogeneous[2,4] or whether, as has been suggested,[5] nucleation and/or precipitation of the product take place at crystalline defects. Since [2 + 2] photodimerizations serve as means for designing extended chain as well as chiral oligomers and polymers, we have selected for *X*-ray study, using four-circle diffractometry (with u.v. irradiation carried out *in situ*), 2-benzyl-5-benzylidenecyclopentanone (BBCP), the parent compound of a family of photodimerizable solids.[1] From the crystal structures of the monomer and dimer and known topochemical principles, we expect and do indeed observe ready dimerization across the centres of symmetry in crystals of (**1**) {the C(5)–C(13′) distance is 4·166 Å and the ethylenic plane-to-plane distance [C(1)–C(5)–C(4)–C(13)–C(14)] is 3·80 Å, see Figure 1}.

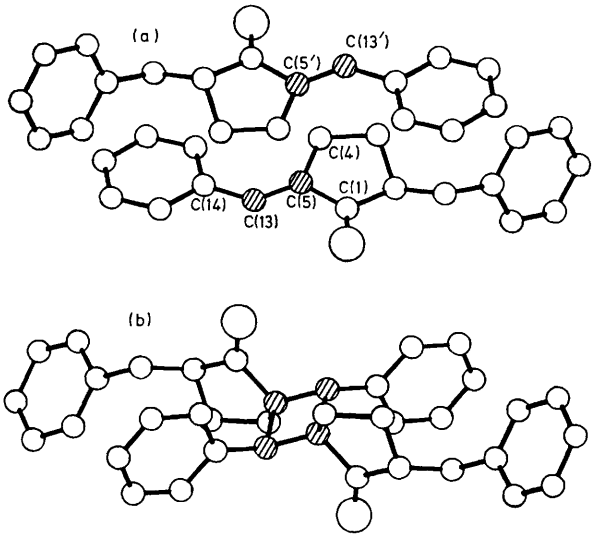

FIGURE 1. (a) The projection on (001) of the BBCP monomer structure showing two molecules across a centre of symmetry. (b) The projection on (001) of the BBCP dimer structure.

Cell parameters at any point along the conversion curve (Figure 2) were determined using some 23 reflections (and a least-squares refinement). Peak profile analysis revealed that the width of the reflections increased only moderately during the single-crystal→single-crystal transformation. Population (site-occupancy) analysis and structural refinements at particular conversions are currently being processed. What stands out unmistakably, however, is that the reaction is crystallographically homogeneous. This augurs well for future synthetic applications of organic solid-state chemistry, especially since, as presently seems likely, other photodimerizations, which suffer greater changes in unit cell dimensions (for example, 2-benzyl-5-*p*-bromobenzylidenecyclopentanone, B*p*BrBCP, Table), can be made, by judicious control of the conditions of reaction, to proceed homogeneously into a single crystal of product.

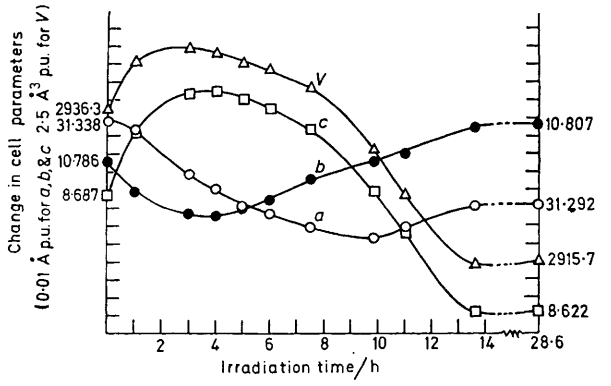

FIGURE 2. Variation of measured cell parameters with time of irradiation.

TABLE. Crystallographic data associated with the single-crystal →single-crystal dimerizations of BBCP and B*p*BrBCP (see text).

		Monomer	Dimer	% Change
BBCP	*a*/Å	31·30	31·32	0·06
	b/Å	10·78	10·81	0·28
	c/Å	8·69	8·63	−0·69
	Z	8	4	
	Space group	*Pbca*	*Pbca*	
	Unit cell volume Å³	2932	2922	
B*p*BrBCP	*a*/Å	34·25	32·96	−3·77
	b/Å	10·88	10·27	−5·61
	c/Å	8·43	8·98	+6·52
	Z	8	4	
	Space group	*Pbca*	*Pbca*	
	Unit cell volume Å³	3141	3040	

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