

PHOTODIMERIZATION OF OLEFINS IN SOLID STATE

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ABSTRACT

Photochemical transformations of organic solids provide an exciting area of research with new synthetic possibilities. These reactions are generally governed by topochemical factors rather than the normal rules of chemical reactivity. Defects play a crucial role in some of the reactions. Some of the transformations such as the photodimerization of 4,4'-dimethoxystilbene occur in a single crystal to single crystal fashion.

INTRODUCTION

REACTIONS in organic solid state are receiving increasing attention in the last few years. Of particular interest is the area of solid state photochemical transformations where the pioneering efforts of Schmidt and co-workers¹ deserve special mention. A classic reaction studied by Schmidt and co-workers is the photodimerization of *trans*-cinnamic acid derivatives. The α -form of *trans*-cinnamic acid in which the molecules are packed with a head-to-tail relation yields the centrosymmetric truxillic acid, while the β -form where the molecular packing bears a head-to-head relation gives the mirror-symmetric truxinic acid (Chart 1); significantly, the γ -form, in which the

molecules are not favourably disposed, is light-stable. Another example of an organic reaction which occurs because of the favourable packing of molecules in the solid state is the photopolymerization of diacetylene derivatives where single crystals of monomers are converted to single crystals of polymers². In this article, we shall briefly review some of the important features of photo-dimerization of olefins in the solid state and present some of the interesting results obtained in this laboratory in recent months, especially on the photodimerisation of 4,4'-dimethoxystilbene.

TOPOCHEMISTRY AND CRYSTAL ENGINEERING

Several photochemical reactions have been reported recently where topochemical factors rather than ordinary rules of chemical reactivity govern the course of the reaction in the solid state. Many such reactions require almost no movement of molecules and proceed to completion in relatively short periods. The term 'crystal engineering' is employed to describe the design of such reactions requiring only minor reorganization of certain bonds in the molecules to form products according to topochemical principles^{3,4}. Some of the recent investigations in this area are due to

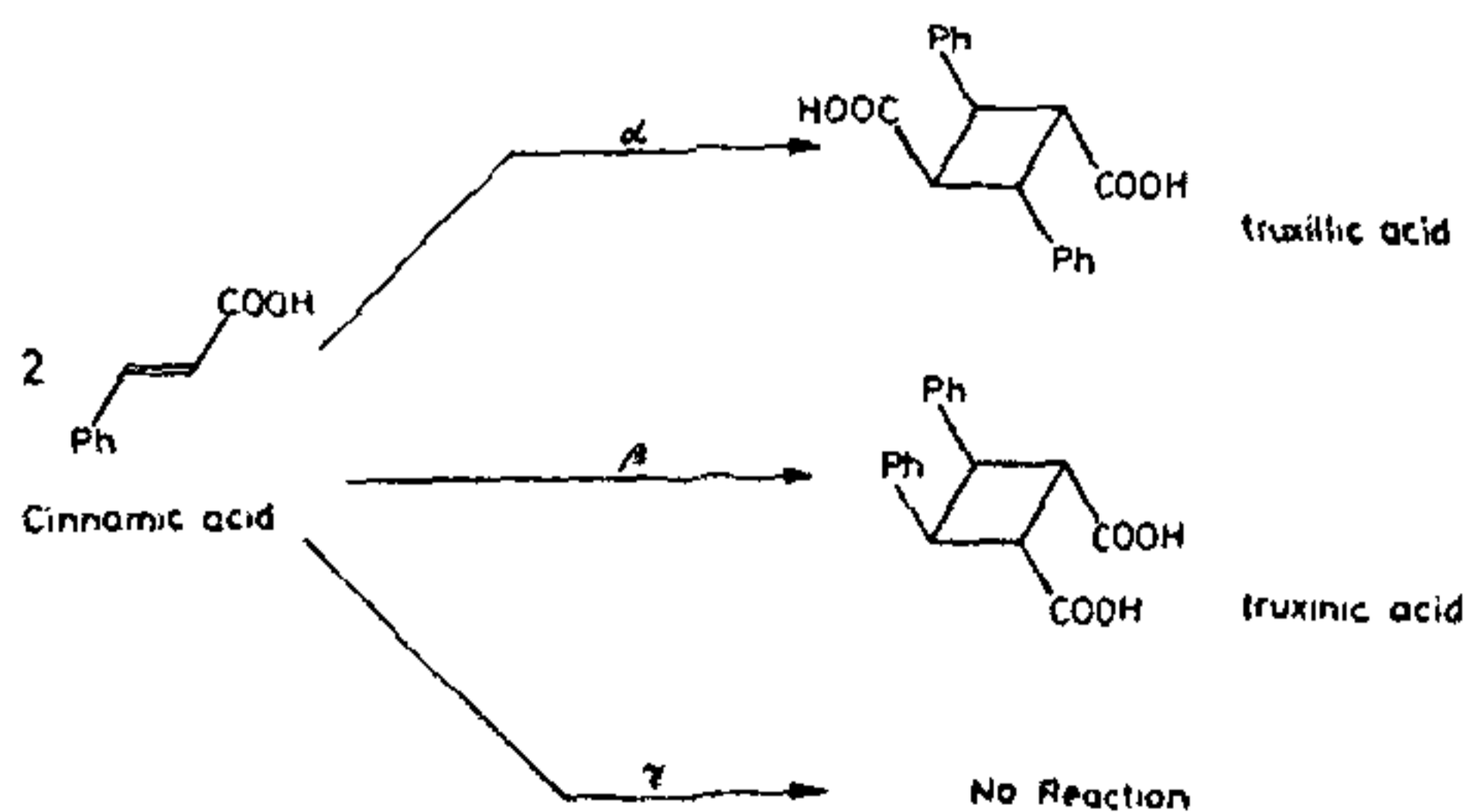


Chart 1. Dimerization of cinnamic acid in the solid state.

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Thomas and co-workers. These workers have found that photopolymerization of distyrylpyrazine⁵ occurs only in the α -form in which the molecules are packed in stacks such that the potentially reactive double bonds are brought within a close proximity of 3.9 Å. Several cyclopentanone and cyclohexanone derivatives⁶ have been shown to undergo photodimerization in the solid state, some in a single crystal to single crystal fashion; this contribution of Thomas and co-workers affords considerable insight into topotactic and topochemical reactivity as well as into crystal engineering.

We have examined reversible photodimerizations of several dienes in solid state⁷, where the dimerization occurs upon irradiation of the monomer with visible light and the reverse transformation occurs upon irradiation of the dimer with ultraviolet light (Chart 2). We have found the dimerization

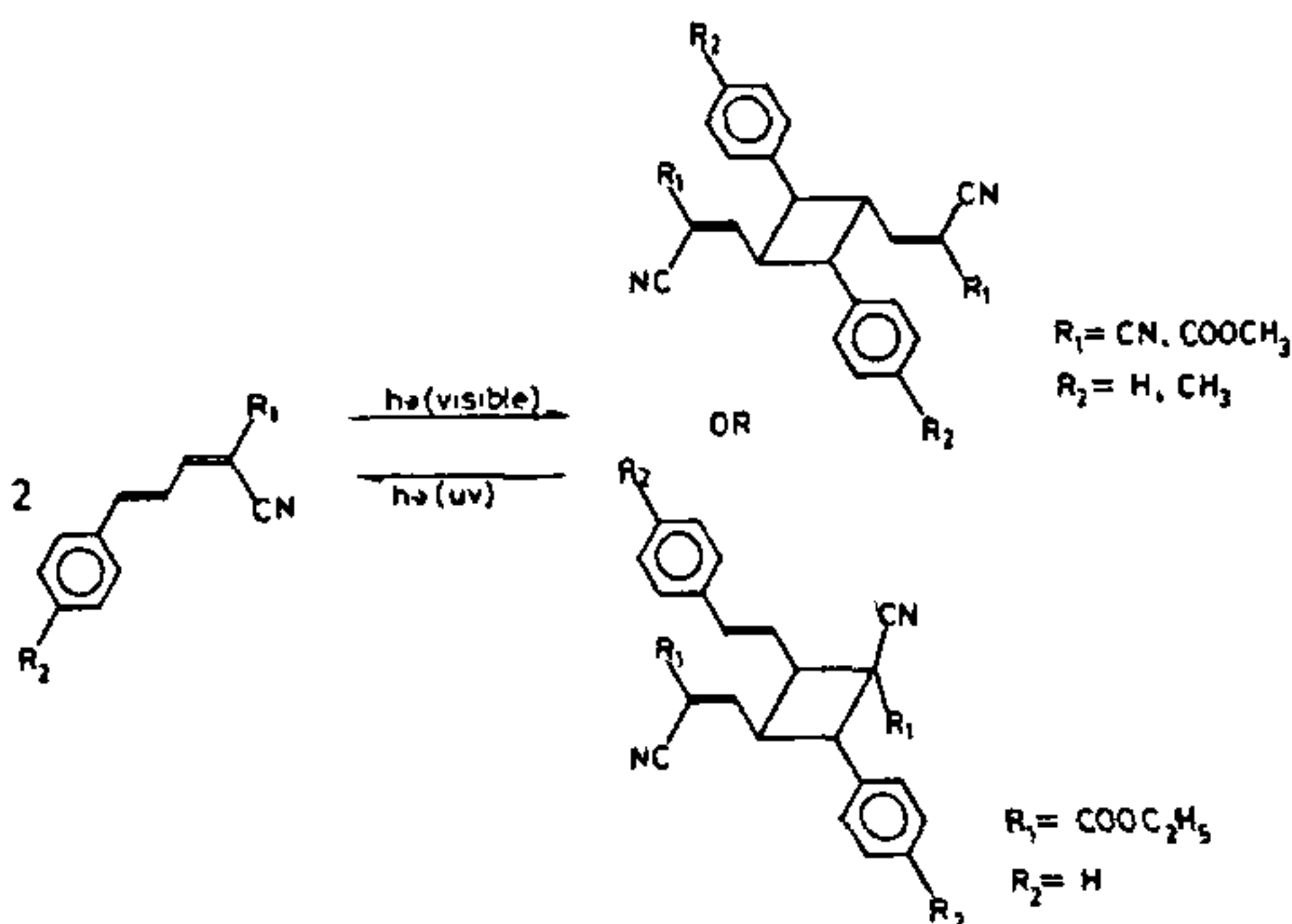


Chart 2. Reversible photodimerization of some dienes.

to be stereospecific, always yielding only one of the several possible isomers. In the crystals of these dienes, the potentially reactive double bonds are about 3.9 Å apart from each other and are so disposed with respect to one another in the crystal that they readily link up on irradiation with visible light to form the dimer (Figure 1).

An examination of the crystal packing in nucleic acid pyrimidine bases indicated to us that uracil, in which the olefinic double

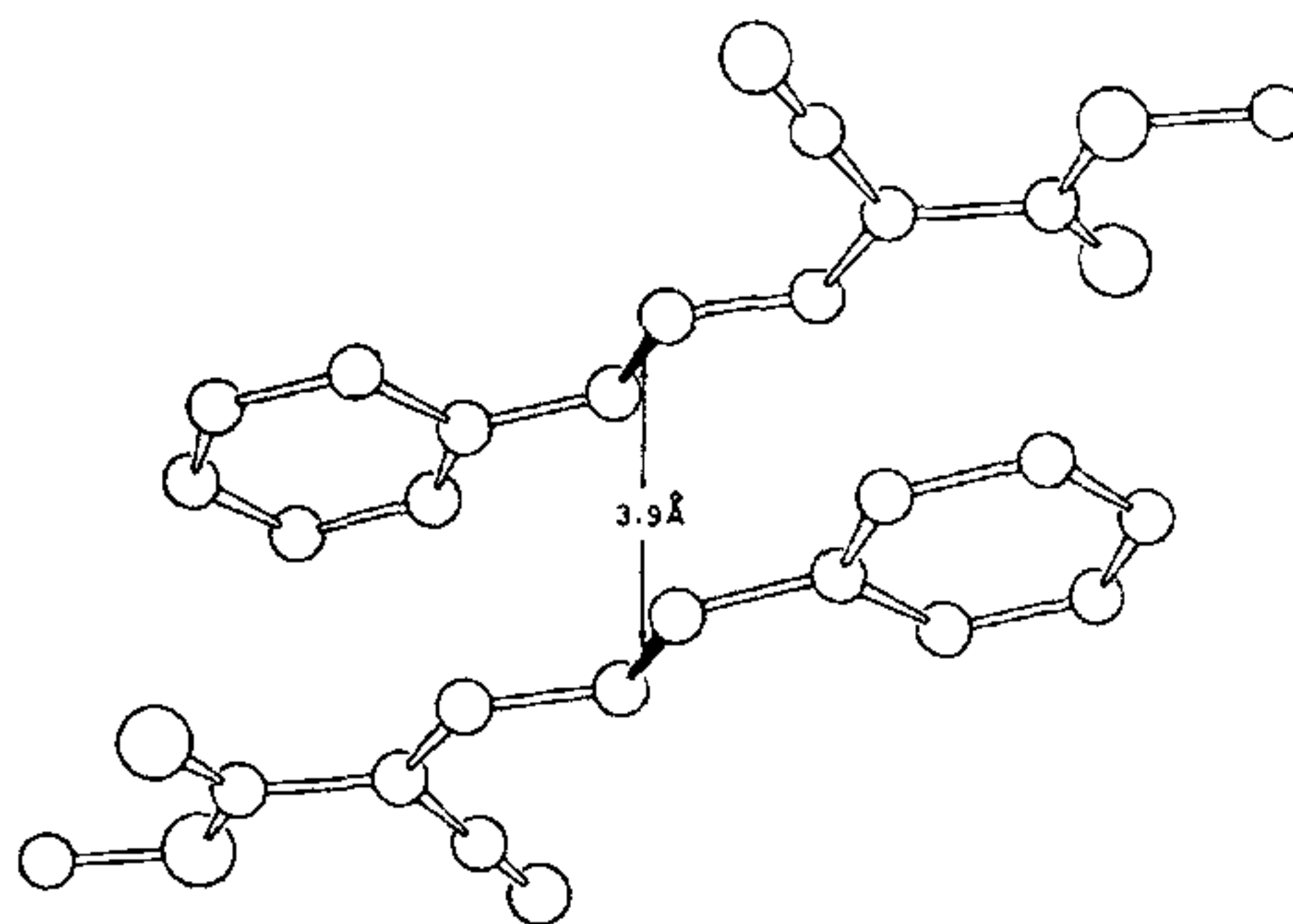


Figure 1. Two molecules of the diene, $\text{C}_6\text{H}_5\text{-CH=CH-CH=C(CN)COOCH}_3$ in the unit cell of its crystal ($Z = 2$) in proper orientation for dimerization. Potentially reactive double bonds are indicated by shaded bonds.

bonds in the adjacent molecules are about 3.2 Å apart⁸, should undergo photo dimerization in solid state. We have indeed found it to be so by experiment. Furthermore, photodimerization in the solid state yields only the *cis-syn* isomer unlike that in solution phase where four isomers are formed⁹ (Chart 3).

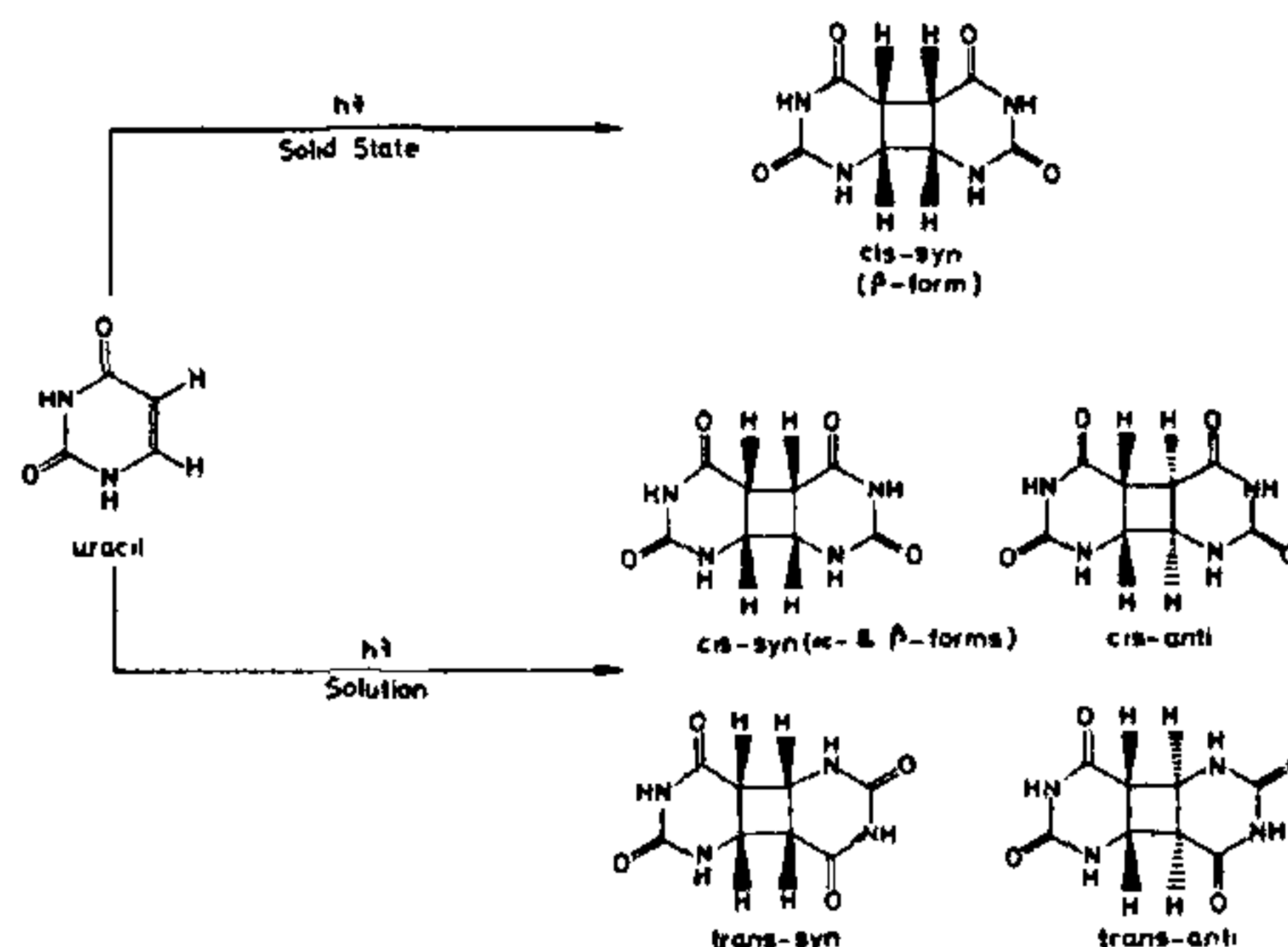


Chart 3. Dimerization of uracil.

ROLE OF DEFECTS

Not all photochemical dimerizations of organic molecules follow topochemical principles. There are examples of systems

such as the anthracene derivatives where the occurrence of phase transformations or presence of defects play a dominant role^{4,10,11}. It has been pointed out that dislocations may be involved in bringing about the photodimerization of anthracene derivatives. The dislocations bring two monomer molecules into an overlapped 'incipient dimer' configuration which is essential for the reaction to occur. We have recently found in this laboratory that 7-methoxycoumarin, unlike the parent coumarin itself, undergoes quantitative photodimerization in the solid state yielding a *syn*-head-to-tail dimer, although the potentially reactive double bonds are not favourably oriented in the crystal of the monomer¹². We have proposed that a favourable disposition of the monomer molecules may be brought about by a translation-cum-rotation involving a screw dislocation or a screw axis.

SINGLE CRYSTAL-SINGLE CRYSTAL PHOTODIMERIZATION OF 4,4'-DIMETHOXYSTILBENE

We have been interested in investigating the photo-dimerization of stilbene derivatives in the solid state, since the parent stilbene itself is photostable in the solid state. By employing electronic absorption spectroscopy, we have found that *trans*-4,4'-dimethoxystilbene undergoes transformation in the solid state on irradiation with visible light. The changes in spectra (Figure 2) suggest that this stilbene derivative may be undergoing dimerization, since the intensity of the longer wavelength band (305 nm) decreases significantly upon irradiation accompanied by an increase in intensity of the shorter wavelength band at 220 nm. X-ray powder diffraction patterns of crystals before and after irradiation for about 450 hours not only showed considerable changes in intensities of reflections, but also the appearance of some new reflections (Figure 3). Irradiation of a single crystal of this

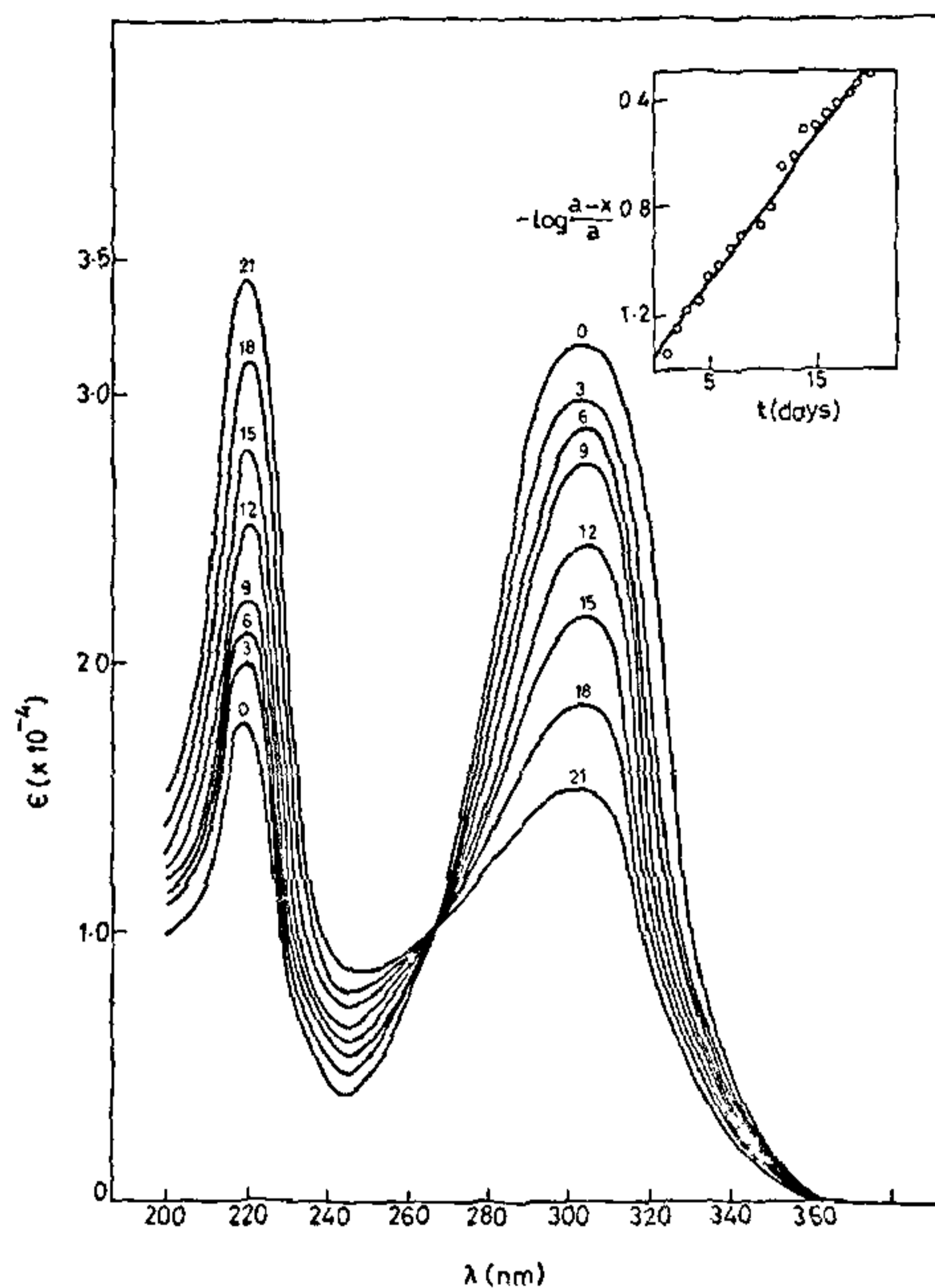


Figure 2. Changes in the electronic absorption spectrum of 4,4'-dimethoxystilbene on irradiation (360 nm). Crystals of the compound were irradiated for different periods and the spectra taken after dissolving the irradiated crystals in methanol. Numbers shown against the spectra are the number of days. (Inset: The changes apparently follow first-order rate law).

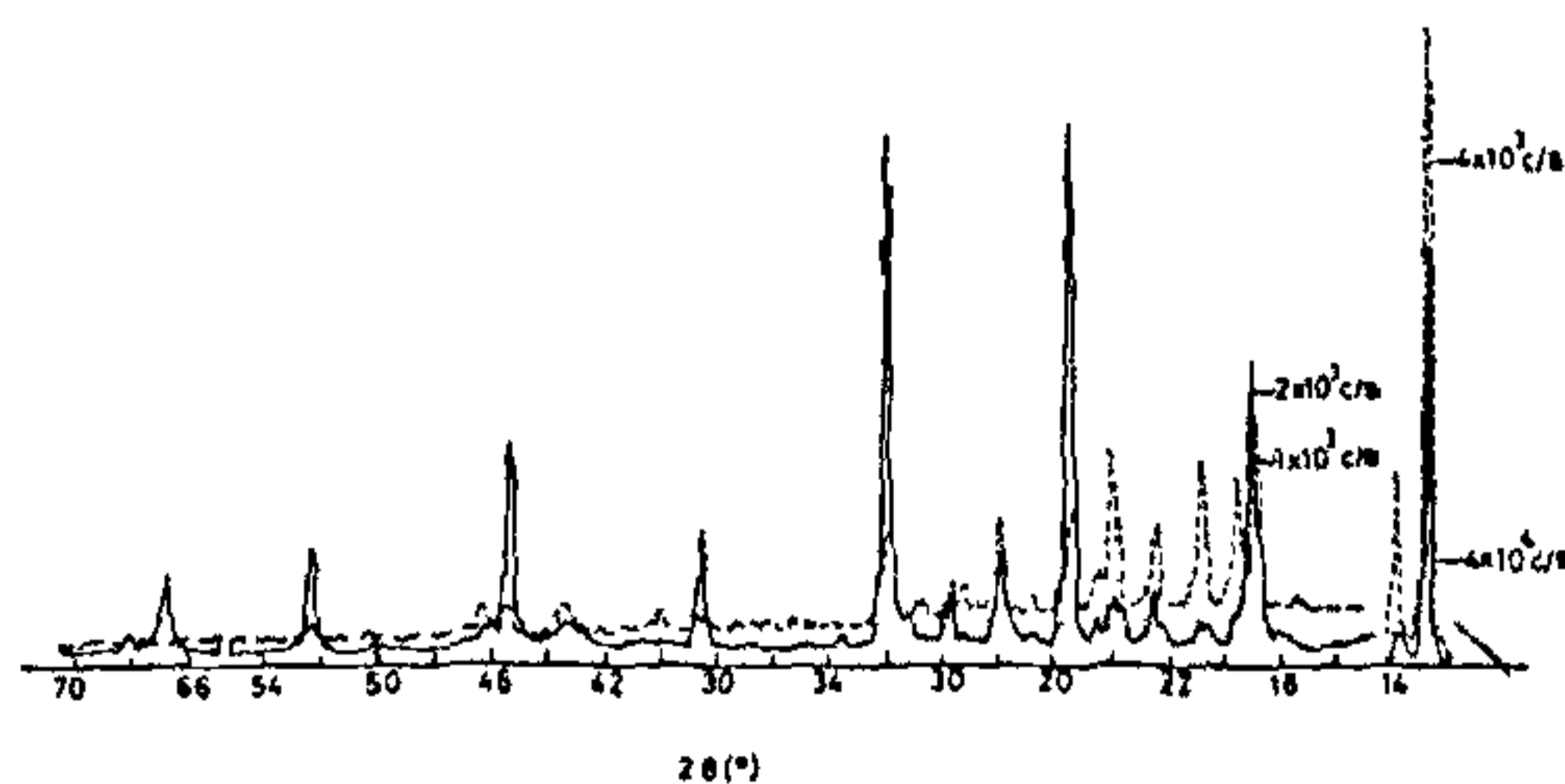


Figure 3. Changes in the X-ray powder diffraction pattern of 4,4'-dimethoxystilbene on irradiation (360 nm, 450 hr): full line, before irradiation; dotted line, after irradiation.

compound indicated that the dimerization is likely to occur in a single crystal to single crystal fashion, the cell parameters of the monomer and dimer being nearly equal. In

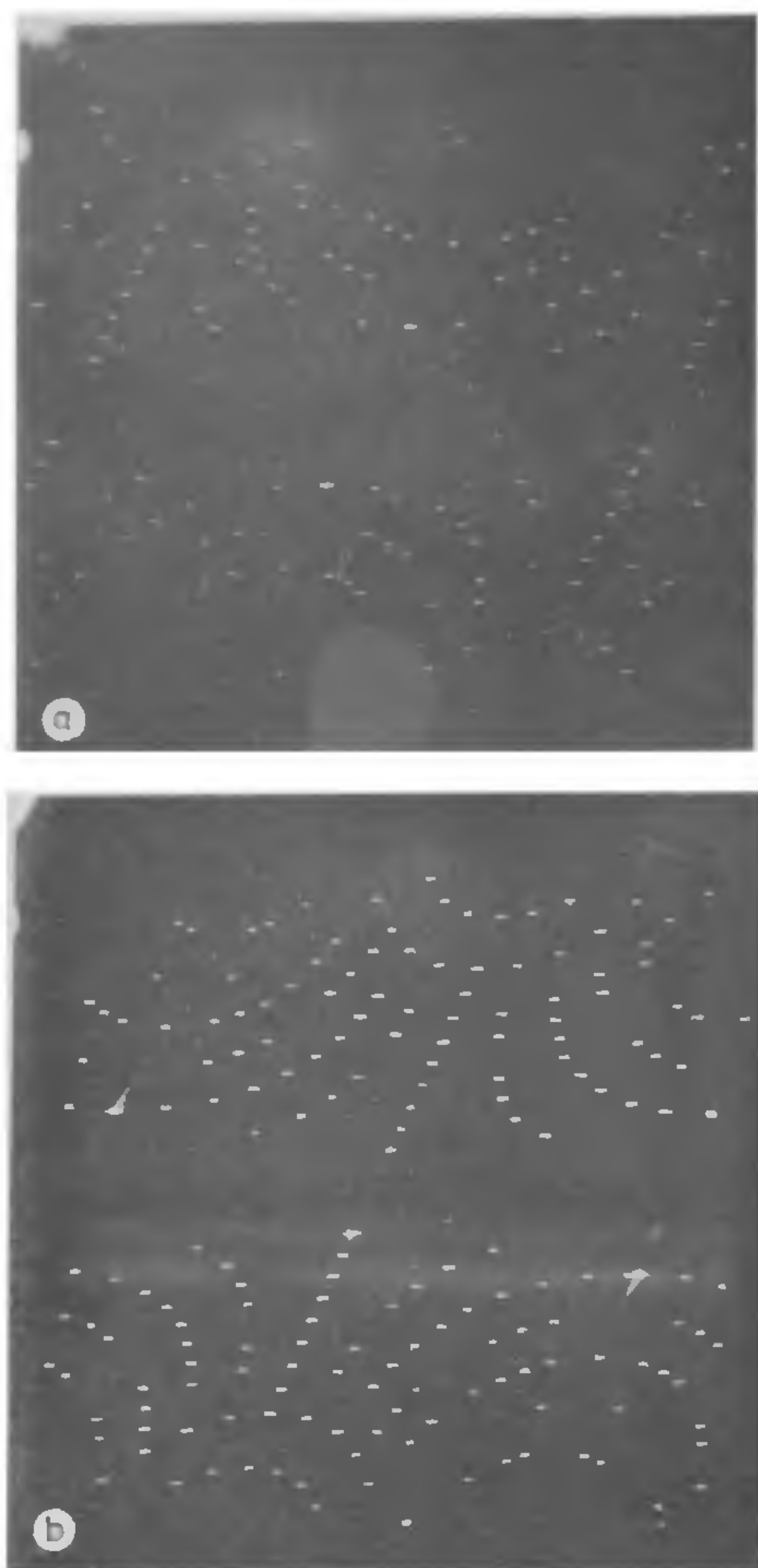


Figure 4. Weissenberg photograph of a single crystal of 4,4'-dimethoxystilbene (a) before and (b) after irradiation (360 nm, 450 hrs).

Figure 4 we show zero layer Weissenberg photographs of a single crystal before and after irradiation (450 hr), to illustrate the nature of changes in the unit cell and in Figure 5 we have shown oscillation photographs of these crystals. We readily see that there is a change in the crystal axes, the *a* axis becoming the *b* axis and *vice versa*.

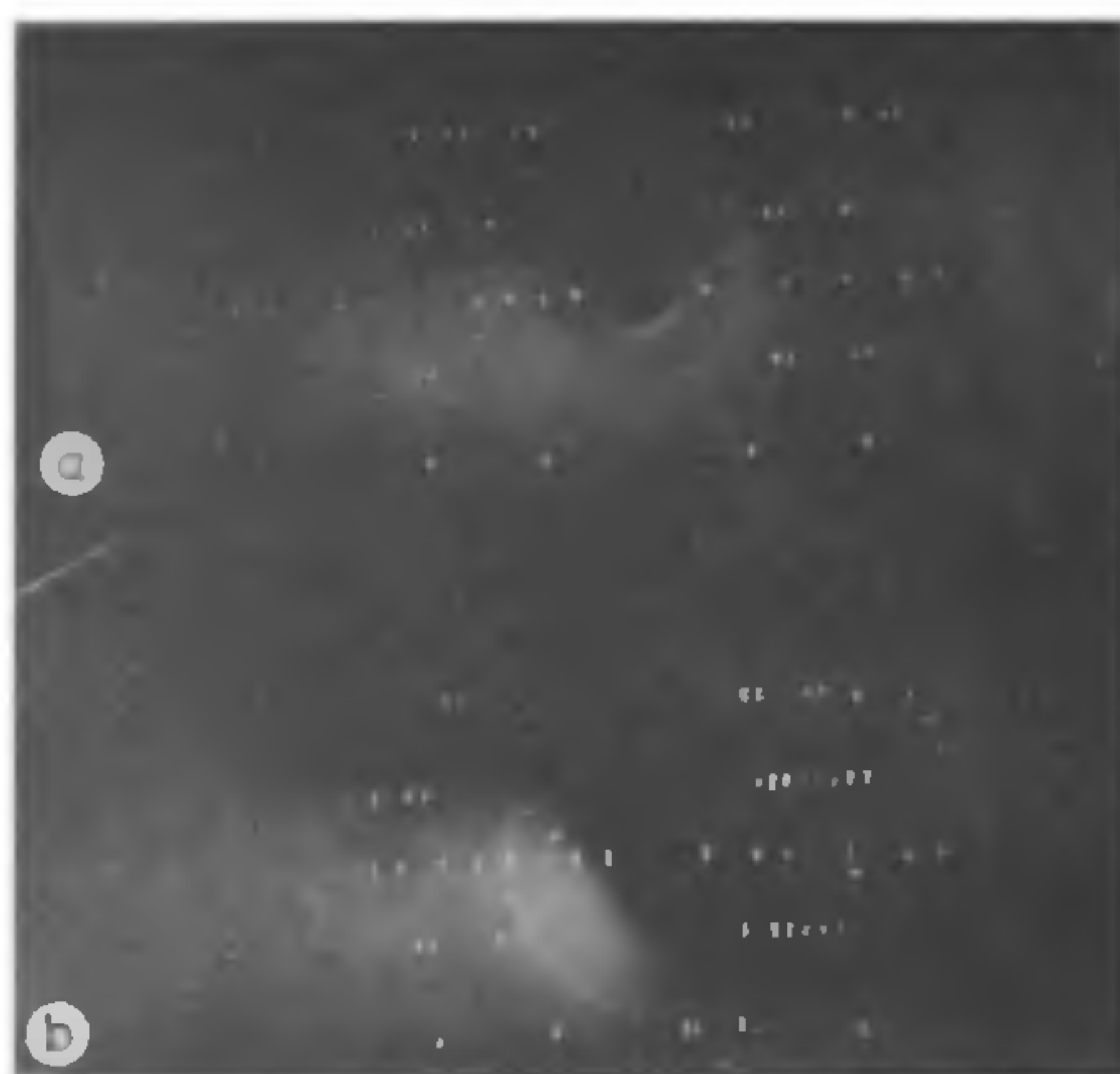


Figure 5. Oscillation photograph of a single crystal of 4,4'-dimethoxystilbene (a) before and (b) after irradiation (360 nm, 450 hr).

The lattice dimensions of the crystal before and after irradiation are shown in table 1.

The nature of the transformation in 4,4'-dimethoxystilbene, including the small changes in lattice dimensions, is similar to that observed by Nakanishi *et al*¹³ in the case of 2-benzyl-5-benzylidenecyclopentanone. It appears that photodimerization of 4,4'-dimethoxystilbene is yet another example of a topochemical and a topotactic reaction for which the product matrix is essentially of single crystal character. We have solved the crystal structure of the 4,4'-dimethoxystilbene monomer and in Figure 6

TABLE 1
Crystallographic data of 4,4'-dimethoxystilbene and its dimer.

	Monomer	Dimer
Space Group	P _{bca}	P _{cab}
<i>a</i> (Å)	6.10	7.24
<i>b</i> (Å)	7.24	6.10
<i>c</i> (Å)	27.06	27.48
Z	4	2
V (Å ³)	1195	1213

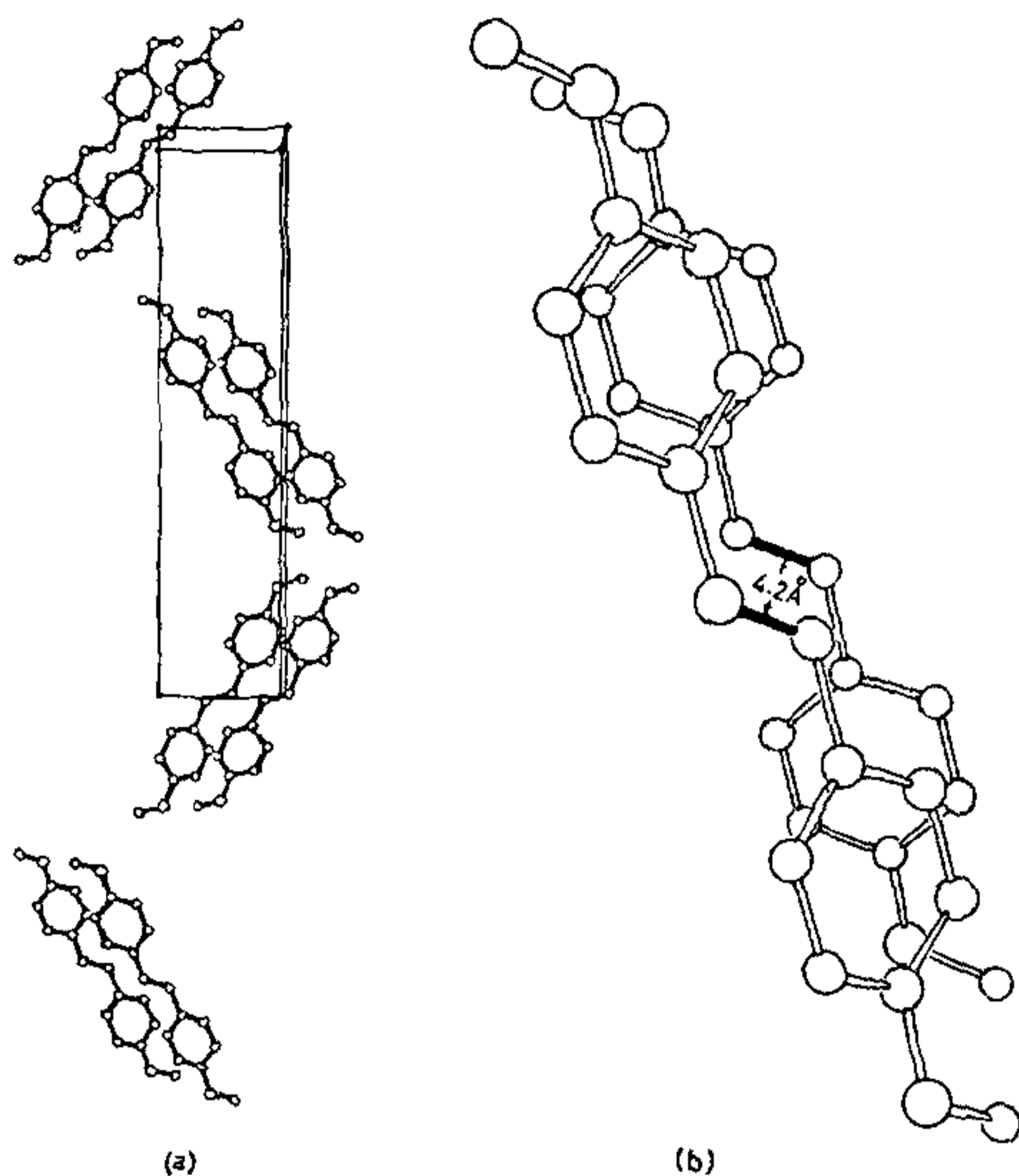


Figure 6. (a) Packing diagram of 4,4'-dimethoxystilbene ($Z = 4$). (b) Two molecules of 4,4'-dimethoxystilbene in proper orientation for dimerization to occur. (Potentially reactive bonds have been shaded).

we have given the packing diagram which clearly shows that the potentially reactive double bonds are properly oriented to form the centrosymmetric dimer upon irradiation. The distance between the two double bonds is $\sim 4.2 \text{ \AA}$ which is just the upper limit for dimerization to occur. We have not been able to solve the crystal structure of the dimer employing the single crystal irradiated for 450 hr because of the coexistence of both the monomer and the dimer. Major changes in intensity on irradiation were found to occur in 600, 800, 040, 060, 240 and 420 reflections, generally those involved in the change in axes.

We have isolated small amounts of the dimer by column chromatography of the irradiated solid, and the ^1H nmr shows that the centrosymmetric dimer is mainly formed. Two doublets centred at $\delta 4.214$ ($J_{\text{cis}} = 21$ cps and $J_{\text{trans}} = 8$ cps) are assigned to the four cyclobutyl protons; a singlet at

$\delta 3.494$ is assigned to the twelve methoxy protons and a multiplet between $\delta 6.664$ and 7.285 to the sixteen aromatic protons. Although we have not completely solved the mechanism of the photodimerization of *trans*-4, 4'-dimethoxystilbene, the results that we have obtained so far clearly indicate how seemingly straightforward photodimerization in solid state can pose difficulties. We considered the possibility of *trans-cis* isomerization of the stilbene *via* the dimer (as in the case of dibenzoyl ethylene¹⁴), but have found no evidence for the presence of any *cis*-isomer in the irradiated crystal.

CONCLUDING REMARKS

The brief discussion of photodimerization of olefins presented above would suffice to illustrate the interesting features of solid state transformations in organic systems. We have a long way to go before exploiting solid state photochemical reactions in organic synthetic strategies. Organic solid state reactions have, however, provided some new interesting possibilities for stereospecific synthesis. An important development in this area is that of asymmetric synthesis¹⁵. Synthesis of chiral molecules has been accomplished starting from achiral ones crystallizing in chiral space groups. Thus, asymmetric induction has been achieved in the photopolymerization of unsymmetrically substituted dienes¹⁶, wherein the chirality of the crystal is transferred to the product molecule during the reaction. Another possibility is to cage achiral reactant molecules into a chiral host to obtain a chiral product; an example of such an asymmetric synthesis in inclusion compounds is the photopolymerization of 1, 3-pentadiene in deoxycholic acid¹⁷.

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