Tetrahedron Letters,Vol.24,No.31,pp 3263-3266,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

REVERSIBLE PHOTODIMERIZATION OF PHENYLBUTADIENES IN THE SOLID STATE[+]

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__Abstract:__ Based on x-ray crystallographic studies, it is shown that crystal chemical factors govern the reversible photodimerization of phenylbutadienes in the solid state.

Photodimerization of olefins in the solid state has been investigated fairly extensively in recent years[1]. Topochemical factors, rather than ordinary rules of chemical reactivity, generally govern the course of such solid state reactions[2,3]. The most well-known example of topochemical reactions is the 2 + 2 photodimerization of trans-cinnamic acid derivatives yielding centrosymmetric truxillic acid or mirror-symmetric truxinic acid depending on whether the monomer pairs are performed in a head-to-tail or head-to-head fashion. Strategies adopted to ensure an appropriate orientation of the dimerizable units which would enable the reaction to occur with only a minor reorganization of the bonds has been referred to as crystal engineering.

We have been interested in the dimerization of phenylbutadiene derivatives of the type $C_6H_5CH{=}CH{-}CH{=}CR_1R_2$ in the solid state, particularly in view of the possible occurrence of reversible photochromism. Thus, all the butadiene derivatives with $R_1 = R_2 = CN$ or COOH as well as $R_1 = CN$ and $R_2 = COOR$ (R = Me, Et, _n_-Pr, _i_-pr, _n_-Bu, _i_-Bu and _s_-Bu)

[+]Contribution No. 212 from the Solid State & Structural Chemistry Unit, Indian Institute of Science.

undergo facile dimerization in the solid state on irradiation with visible light giving high yields of the dimer. The dimerization is stereospecific and of the 12 possible, sterically different, cyclobutyl dimers that can be formed from a trans-trans monomer, only one (generally centrosymmetric) dimer is formed. The dimers on irradiation with ultraviolet light give back the monomers though not quantitatively. The dimers of three of the phenylbutadienes with R_1 = CN and R_2 = COOR (R = Me, *i*-Pr and *i*-Bu) exhibited nearly reversible photochromism with a minimum of side reactions.

We have carried out a crystallographic study of cinnamylidinecyanoacetate, $C_6H_5CH{=}CH{-}CH{=}CR_1R_2$ with R_1 = CN and R_2 = COOMe, showing photochromism. The monomer crystallizing in the $P\bar{1}$ space group (Z=2) has the unit cell dimensions, a = 7.239Å, b = 7.762Å, c = 11.273Å, α = 104.4°, β = 94.76° and γ = 111.43°. The structure was solved ($R \approx 9\%$) making use of 1124 reflections employing Cruickshank's weighting scheme for refinement. The packing of the monomer molecules given in Fig. 1 clearly shows how pairs of planar molecules are arranged in a centrosymmetric fashion with a favourable orientation of the potentially reactive double bonds. The distance between the double bonds (3.5Å) is within the allowed range of distances for dimerization to occur. Topochemical photodimerization therefore occurs readily giving rise to a symmetric dimer.

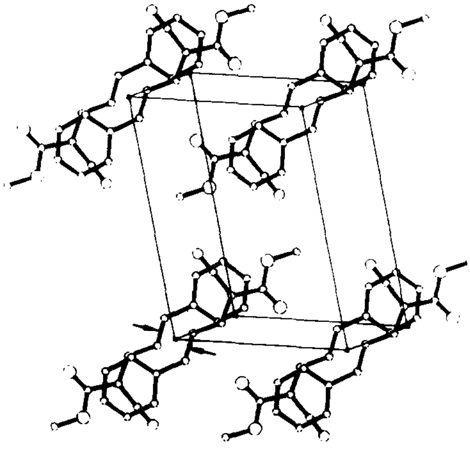

Fig. 1.

Molecular packing in the crystal of cinnamylidinecyanoacetate monomer viewed down the a-axis. The potentially reactive double bonds (shown by arrows) are 3.5Å apart.

The dimer of cinnamylidinecyanoacetate also crystallizes in the $P\bar{1}$ space group (Z=1) and has the unit cell dimensions, a = 7.968Å, b = 8.075Å, c = 9.563Å, α = 104.9°, β= 111.7° and γ = 77.4°. The structure of the dimer was solved ($R \approx 9\%$) making use of 1220 reflections. The structure and stereochemistry of the dimer are shown in Fig. 2 wherein we have also superimposed two monomer diene molecules. It is clear that only a

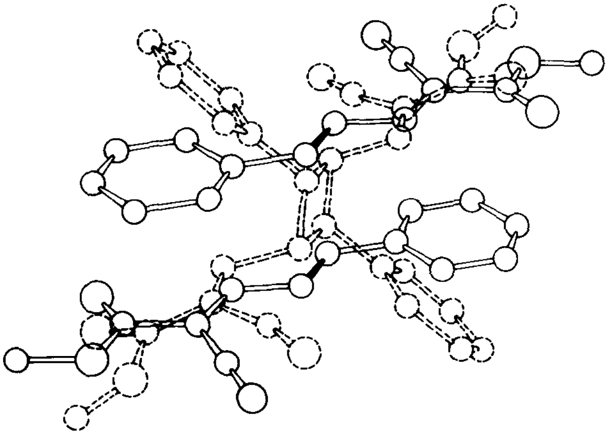

Fig. 2

Dimer of cinnamylidinecyanoacetate. Two molecules of the monomer are superimposed to show the minor reorganization in atom positions of the diene molecules occurring the 2+2 dimerization in solid state.

minor reorganization in atomic positions of the diene molecules occurs during the 2+2 photodimerization; the crystal of the monomer indeed has "incipient dimers". The dimer once formed, can readily break up (on UV irradiation) to give back two monomers. The photochromic system investigated here provides yet another example of crystal engineering where topochemical factors govern the course of reactions.

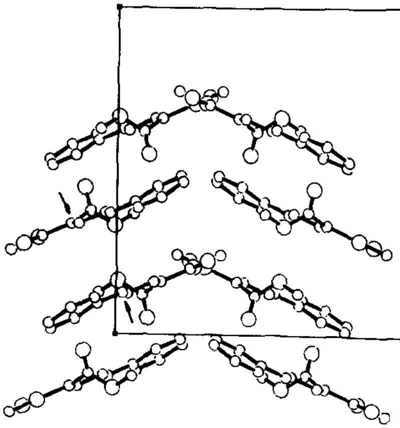

Fig. 3

Molecular packing in the crystal of dimethyl cinnamylidinemalonate viewed down the a-axis. The potentially reactive double bonds are indicated by arrows.

Unlike the phenylbutadiene derivatives discussed hitherto, dimethyl cinnamylidinemalonate, $C_6H_5CH=CH-CH=C(COOMe)_2$ does not undergo dimerization in the solid state. It however polymerizes due to surface melting because of its low melting point (66°C). This diester crystallizes in the space group Pccn (Z=8) with the unit cell dimensions, a = 11.821Å, b = 15.168Å and c = 14.774Å. The structure was solved (R $\approx$9%) making use of 1635 reflections. Molecular packing viewed down the c-axis showed the double bonds to be most unfavourably oriented for any reaction to occur. The packing viewed down the a-axis (Fig. 3) show that the potentially reactive double bonds are skewed with respect to each other and the nearest distance between them is 5.5Å.

Acknowledgement. The authors thank the National Institutes of Health for support of this research (Grant 01-136-N).

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(Received in UK 11 May 1983)