

Competitive isomerization and dimerization in co-crystals of 1,1,6,6-tetraphenyl-2,4-hexadiyne-1,6-diol and sorbic acid: a new look at stereochemical requirements for [2 + 2] dimerization†

Shao-Liang Zheng,* Oanh Pham, Christophe M. L. Vande Velde,‡
Milan Gembicky and Philip Coppens*

Received (in Cambridge, UK) 6th February 2008, Accepted 28th February 2008

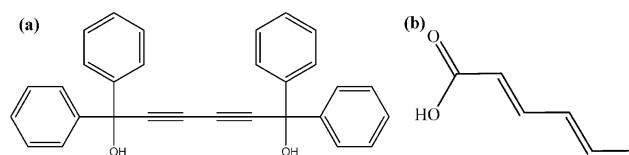
First published as an Advance Article on the web 31st March 2008

DOI: 10.1039/b802103a

Competitive [2 + 2] photodimerization and *E* → *Z* isomerization reactions occur in a co-crystal of 1,1,6,6-tetraphenyl-2,4-hexadiyne-1,6-diol upon irradiation with 325 nm light. At 90 K both reactions are observed, whereas at 280 K the dimerization reaction is very fast and inhibits isomerization as the nature of the chromophore is affected by the reaction. The temperature dependence of the stereospecificity of the dimerization reaction is related to the large sliding motion required to bring the reacting molecules into juxtaposition. The progress of the reactions has been monitored by photocrystallographic methods.

Photochemical reactions taking place in organic solids have been studied extensively. The two most common photo-reactions of olefins are geometric isomerization^{1–4} and dimerization, the latter pioneered by Schmidt and coworkers in the sixties⁵ and extensively studied since then.^{6,7} Intermolecular [2 + 2] photo-additions can be ‘template-controlled’⁸ by using diols like resorcinol,⁷ 1,1,6,6-tetraphenyl-2,4-hexadiyne-1,6-diol (‘Diol’, Scheme 1a) and derivatives^{9,10} in co-crystal systems, in which case the reactions tend to proceed as single-crystal to single-crystal reactions (SCSC), without breakdown of the crystal lattice.

In preceding work we showed that olefin-acids, as well as their coordination compounds, can be isolated in a supramolecular framework, and the corresponding SCSC *E* → *Z* and *Z* → *E* photo-isomerizations can proceed without side reactions.¹ We report here on competitive photo-reactions in co-crystals of sorbic acid (‘HSA’, Scheme 1b) and Diol, with the composition Diol-2HSA. § On exposure of a single crystal to 325 nm light the sorbic acid molecules undergo either *E* → *Z* isomerization or [2 + 2] photodimerization to form a cyclo-



Scheme 1 Diagram of (a) Diol and (b) HSA.

butane derivative, the detailed behavior depending on the temperature.

The compound crystallizes in the triclinic space group *P* $\bar{1}$ (see Table S1, ESI†). The HSA molecules are linked to the Diol by hydrogen bonding between the hydroxy groups of the Diol and carboxyl oxygen atoms of HSA [280 K: O...O 2.680(2) and 2.734(2) Å, see Table S2, ESI† and Fig. 1]. The Diol molecule occupies a crystallographic inversion center (1/2, 1/2, 1/2), while the HSA molecules are packed in parallel pairs related by an inversion center at (1, 1, 1/2). Accordingly, the double bonds are parallel to each other. As shown in Fig. 2, the distance between the potentially reactive atoms is within the range proposed for photodimerization.¹¹ This arrangement produces the centrosymmetric cyclobutane derivative on reaction.

A diffractometer-mounted crystal of Diol-2HSA was exposed to 325 nm light from a 48 mW/(0.3 cm²) He/Cd laser at 280 K. After 1 min exposure the volume of the unit cell is reduced by 2.5% (Table S1, ESI†). A three-dimensional Fourier difference map (Fig. 3a)¹² clearly shows that the photo-induced peaks correspond to the dimerization product, the C atoms being displaced by 0.89 and 1.20 Å from the original carbon plane. Least squares refinement of the data indicates that dimerization proceeds to completion (Table S1, ESI†). The C22–C23 bond length in the product is measured as 1.583(2) Å (Fig. 2a), and the terminal carbon (C26) remains in the *E*-configuration. No other significant photoinduced peaks are found in the three-dimensional Fourier difference map when irradiation is continued for up to 10 h, indicating that at 280 K no isomerization occurs upon 325 nm excitation.

When the same experiment is carried out at 90 K, a three-dimensional Fourier difference map plotted after 1 h exposure shows light-induced peaks corresponding to both dimerization and isomerization of the C24–C25 bond to the *Z*-configuration (Fig. 3b). The carbon atoms are displaced by 0.91 and 1.16 Å from the original plane through these atoms. The location of the photoinduced peak representing the terminal

Department of Chemistry, State University of New York at Buffalo, Buffalo, New York, 14260-3000, USA. E-mail: chem9994@buffalo.edu, coppens@buffalo.edu; Fax: 1-716-645-6948; Tel: 1-716-645-6800ext12217

† Electronic supplementary information (ESI) available: CCDC 676953–676960. For crystallographic data in CIF or other electronic format, Tables S1 and S2, and Fig. S1. See DOI: 10.1039/b802103a

‡ On leave from: Department of Chemistry, University of Antwerp, Universiteitsplein 1, 2610 Wilrijk, Belgium. Current address: Laboratoire de Chimie des Polymères, Université Libre de Bruxelles, CP 206/1 Boulevard du Triomphe, 1050, Brussels, Belgium.

§ A methanol solution HSA (3 mL) of (0.05 mmol) was added dropwise to a stirred methanol solution (5 mL) of Diol (0.05 mmol) at 50 °C for 30 min. Slow evaporation at room temperature produced pale yellow crystals after two weeks (yield 82%).

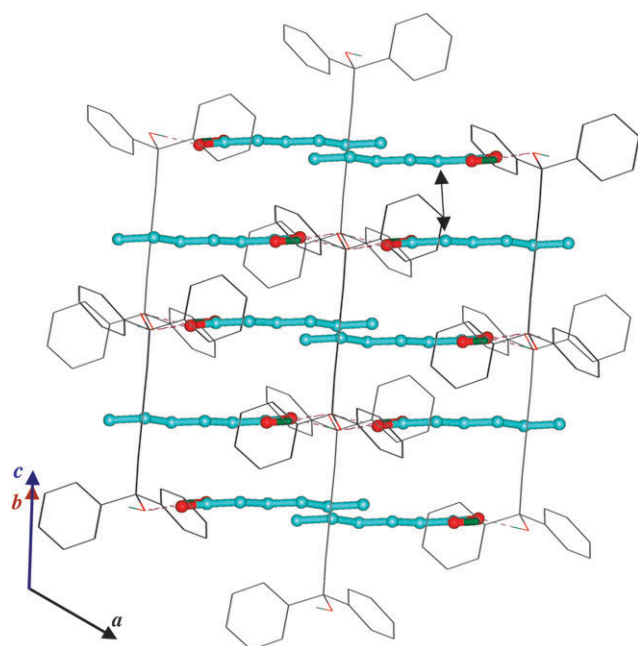


Fig. 1 Three-dimensional supramolecular architecture of Diol-2HSA viewed along the $[0, -1, 1]$ direction.

carbon atom (C26) indicates that dimerization and isomerization take place in the same molecule, as the C26 peak is at a distance of 0.74 Å from the image of the C25 atom of the unreacted molecule. The second significant difference between the 90 K and the 280 K behavior is that at the former temperature the population of the *Z-Z* dimer product is only 5.6(2)% after one hour exposure, while at the higher temperature the formation of the *E-E* dimer is very rapid and proceeds to completion. At 90 K, photoinduced carbon atom peaks corresponding to the *E-E* or *E-Z* dimer are conspicuously absent, suggesting that dimerization only occurs after isomerization of two adjacent molecules. The conversion at 90 K reaches a limit of 6.4(2)% at 8 h exposure (Table S1, ESI† and Fig. 4), accompanied by a decrease in crystal quality. At 280 K on the other hand, 1000 pulses from a nitrogen laser ($\lambda = 337$ nm) with an estimated total energy of only 150 mJ on the crystal are sufficient to produce the *E-E* dimer with a 8.0(2)% yield, the isomerization not taking place (Table S1, ESI†), and

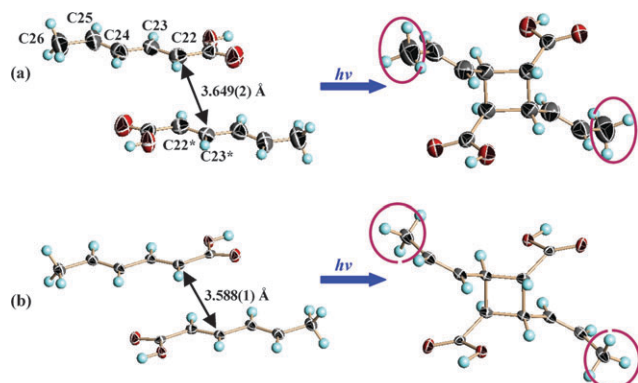


Fig. 2 Perspective views showing 50% probability displacement ellipsoids of the reaction of HSA (a) at 280 K, and (b) at 90 K.

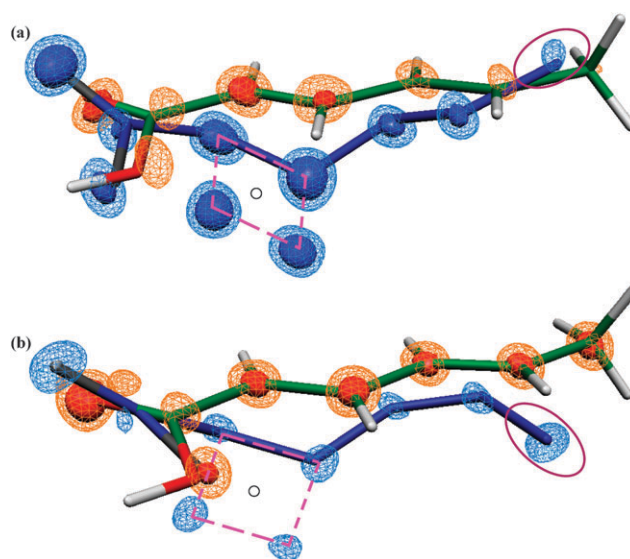


Fig. 3 The three-dimensional Fourier difference maps of the HSA (a) at 280 K after 1 min exposure (blue: 4.5; light blue: 3.0; orange: -3.0 ; red: $-4.5 \text{ e } \text{\AA}^{-3}$) and (b) at 90 K after 1 h exposure (blue: 2.0; light blue: 1.0; orange: -1.0 ; red: $-2.0 \text{ e } \text{\AA}^{-3}$). The center of symmetry is indicated by the small circle within the broken purple lines.

the reaction proceeds to 100% conversion on further irradiation (after 20 s exposure).

The occurrence of isomerization only together with dimerization indicates that the processes are interdependent at lower temperatures. Examination of the structure shows that the reacting double bonds are offset by as much as 1.48 Å in the direction parallel to the bonds, so that a large lateral shift of the molecules is required to reach a geometry conducive for formation of the essentially square cyclobutane ring. Turowska-Tyrk and Feeder and co-workers report that the $[2+2]$ SCSC dimerization of 2-benzyl-5-benzylidenecyclopentanone ('BBCP') proceeds only at room temperature but not at 100 K,^{13,14} even though we note that the $<4.2 \text{ Å}$ distance¹¹ criterion is satisfied at both temperatures. Evidently, this criterion, which has been widely quoted, is insufficient to

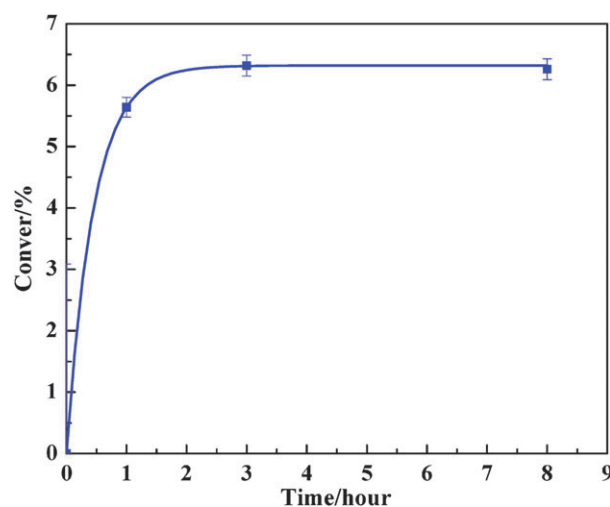
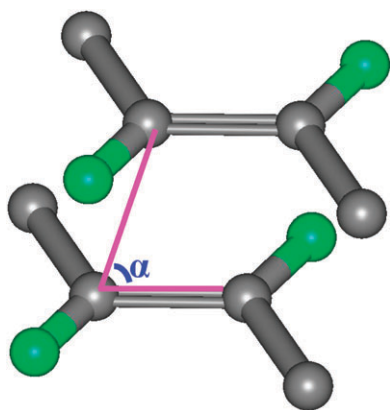


Fig. 4 Percentage photo-conversion of sorbic acid as a function of time at 90 K.



Scheme 2

assure a significant yield of the reaction at lower temperatures. The mutual offset of the double bonds quantified by the $C=C\cdots C(=C)$ angle (α in Scheme 2) is a measure of the lateral shift required, and directly related to the orbital-overlap requirement for [2 + 2] addition described by Desiraju and Kearsly,¹⁵ and summarized by Natarajan and Ramamurthy.⁷ The larger the deviation of this angle from an ideal 90° , the larger the lateral shift required for ring formation. The α angle is 65.7° in the current structure and 66.9° in the BCP crystals. Significantly, we find that for α -cinnamic acid, with an α angle of 86.0° (Fig. S1, ESI[†]),¹⁶ the dimerization does proceed at both 280 K and 90 K.¹⁷

We conclude that at 90 K, the excited state molecules do not have sufficient freedom of motion to dimerize rapidly, thus allowing isomerization to occur. We hypothesize that as the volume-demanding isomerization proceeds in the centrosymmetric crystal lattice, the disturbance of the lattice favors isomerization of a neighboring molecule. At the same time the distance between the double bonds in the adjacent molecules decreases, so that a second excitation can lead to dimerization of the pair of molecules, even at low temperature. The induced strain in the lattice is evident from the deterioration of crystal quality on prolonged irradiation, as observed for the $E \rightarrow Z$ isomerization of tiglic acid.¹ This may interfere with further progress of the reaction.

The suppression of the isomerization on rapid dimerization at 280 K may be attributed to the modification of the chromophore on dimerization such that excitation by 325 nm light is no longer possible.

In summary, single crystals of the title compound show temperature-dependent competition between isomerization and dimerization, which leads to the occurrence of both phenomena at a small yield at 90 K, but to a very rapid dimerization without isomerization at 280 K. The large molecular shift needed for dimerization to take place in the crystals of the title compound and the observed reactivity of α -cinnamic acid at 90 K point to the importance of the offset of the double bonds in the [2 + 2] dimerization process. Whereas temperature-dependence of the [2 + 2] cycloaddition reaction has been described before,^{14,18} this is to our knowledge the first example of temperature-dependent stereospecificity of an organic solid state reaction. We expect that the example presented here is by no means unique and that

competition between different reactions in complex molecular crystals is more general than currently known.

We would like to thank Prof. David F. Watson for use of his equipment in the initial photo-irradiation experiments. We are indebted to a referee for helpful comments. Research supported by Research Experience for Undergraduate Program of the National Science Foundation and NSF grant CHE0236317. CVV would like to thank the University of Antwerp for a one year grant as a postdoctoral research assistant.

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