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Review Commentary

Structural transformations in organic crystals during photochemical reactions

Ilona Turowska-Tyrk*

Department of Chemistry, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

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ABSTRACT: In the 1980s and 1990s, x-ray studies of the photochemical reaction course in crystals dealt with the analysis of changes in cell constants or movements of atom groups inside molecules. This review presents the results of crystallographic studies on the monitoring of the behaviour of whole molecules in organic crystals during photochemical reactions. Papers on this subject started to appear only a few years ago. The studies showed quantitatively that reactant and product molecules do not take a fixed position in a crystal during the reaction. The product molecules move smoothly to a position assumed in the pure product crystal and the reactant molecules move from a position occupied in the pure reactant crystal. Moreover, with the reaction progress the adjacent reactant molecules gradually come closer and change their mutual orientation to resemble the product. The analysis of the photoreaction kinetics in crystals is also presented. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: photochemical reactions; crystals; reaction course; reaction order; crystal structure; structural changes; x-ray structure analysis

INTRODUCTION

Photochemical reactions taking place in organic solids and crystals have been known for a very long time. During the last decade, interest in them increased significantly, which was connected mainly with the development of modern technologies and selective organic syntheses, and also with the appearance of new techniques applied to studies of such reactions or with the improvement of the existing ones.

X-ray diffraction, Raman, infrared and NMR spectroscopy, calorimetric measurements and atomic force and optical microscopy are powerful tools used to study chemical reactions in crystals. Several examples of applying these techniques were presented by Boldyreva.[1]

X-ray structure analysis is one of the techniques often used in such studies. This is a powerful method which gives information about the geometry of molecules inside a crystal and the geometry of the crystal lattice.

In the past, x-ray structural studies of photochemical organic reactions in crystals were in most cases limited to reactant crystal structure analysis, this being the basis for the prediction and explanation of molecular product structure. Such studies were started by Schmidt and Cohen.[2] They formulated the 'topochemical postulate', which was applied by many scientists to interpret reactions in organic crystals. According to this postulate, a chemical reaction proceeds with a minimum amount of atomic and molecular movements[2] and also with minimal distortion of a reaction cavity surface.[3] However, photodimerization of some compounds proceeds non-topochemically and its product cannot be rationalized in terms of the reactant crystal structure. This phenomenon was explained by localization of the reaction at defects sites[3,4] or on a crystal surface.[5]

In some cases, structures of a pure reactant crystal and a pure product crystal (obtained by a single crystal to single crystal transformation) were compared. This allowed not only topochemical considerations but also analysis of distances between the respective atoms of the reactant and the product molecules.[6–9] Unfortunately, such analysis could not reveal the course of the reaction in detail. In a few cases, the structures of mixed organic crystals, i.e. containing both a reactant and a product, were published, but they were often treated as experimental evidence that the reaction had proceeded in crystals, and they were not analysed in detail.[10–12] Very rarely did they serve to explain the mechanism of the intramolecular[13,14] or intermolecular reactions.[15]

In the 1980s and 1990s, crystallographic studies of the photochemical reaction course dealt with monitoring changes of cell constants or monitoring movements of an atom group inside a molecule.[16–22] Papers on step-by-step studies of changes in the whole crystal structure

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*Correspondence to: I. Turowska-Tyrk, Department of Chemistry, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland.
E-mail: ilona.turowska-tyrk@pwr.wroc.pl
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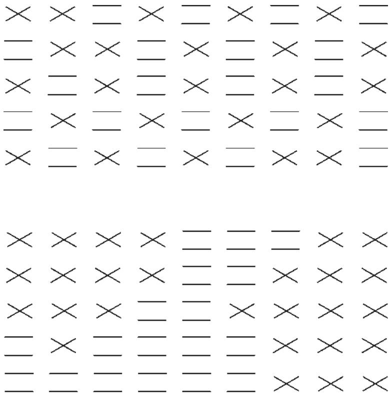


Scheme 1. Schematic representation of the homogeneous (top) and heterogeneous (bottom) reactions. In the homogeneous reactions the product molecules are distributed at random throughout the crystal and a solid solution is formed. The heterogeneous reactions can lead to crystal disintegration at a certain degree of transformation

during photochemical reactions started to appear only a few years ago. Special attention was paid to quantitative studies of movements of whole molecules in a crystal. It can be expected that such movements and changes of crystal structure accompanying them are distinct in case of intermolecular reactions. In the literature, studies of [2 + 2] photodimerization,[23–25] [4 + 4] photodimerization,[26] thermal [4 + 2] dimerization[27,28] and thermal polymerization have been reported.[29]

Such studies coincided with the increased application of area detectors in x-ray experiments. Such detectors permit very fast x-ray data collection, which is crucial when x-ray experiments must be carried out for many intermediate stages of the phototransformation. X-ray structure analysis of crystals is particularly useful in monitoring studies of a reaction course, but it always has limited use, namely, it can be applied when a chemical reaction does not bring about crystal disintegration, i.e. in studies of single crystal to single crystal transformations. Transformations of this type are an important category of photochemical reactions proceeding in crystals. Scheme 1 illustrates the difference between homogeneous and heterogeneous chemical reactions.

The main goal of this paper is to present and discuss the behaviour of molecules and structural changes in organic crystals during photochemical reactions monitored by means of x-ray structure analysis. The phenomena leading to crystal disintegration studied with the use of other methods would need a separate review.

FACTORS INFLUENCING REACTIONS IN CRYSTALS

In studies of photochemical reactions in organic crystals, a lot of attention was paid to reaction-affecting factors. There are significant differences between factors influencing reactions in the crystalline state and in solution. For instance, a compound which undergoes a reaction in a solution can be inert in a crystal. Moreover, the same compound can be inert in one crystalline (polymorphic) form and reactive in other, or it can even give different products in different polymorphs.

Factors influencing reactions in crystals were studied most intensively in the case of the [2 + 2] photodimerization.

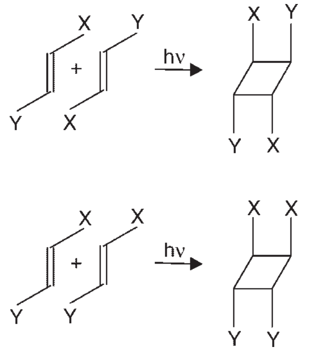
Distance between adjacent reactant molecules

For [2 + 2] photodimerization, on the basis of experimental data it is commonly assumed that the distance between directly reacting atoms should be <4.2 Å. Nevertheless, there are exceptions to this rule, e.g. for some coumarins.[30,31]

Mutual orientation of adjacent reactant molecules

For [2 + 2] photodimerization, the ideal orientation is when p(z) orbitals of the reacting double bonds are collinear.[31–33] On the other hand, there are reactions taking place with orientations very different from the above-mentioned ideal, e.g. in the case of [2 + 2] photodimerization in crystals of *trans*-cinnamamide–phthalic acid (2:1)[15] and some coumarins[30,31] and [4 + 4] photodimerization of some anthracenes.[3,4,34] Geometric criteria were created on the basis of crystal structures in the ground state. In fact, the mutual orientation of molecules in an excited state should also be taken into account.[35]

The mutual orientation of adjacent reactant molecules in a crystal determines the product (Scheme 2). If the reactant molecules are situated head-to-tail, the product is centrosymmetric, but when they are oriented head-to-head, the product has a plane of symmetry.



Scheme 2. Influence of the orientation of the adjacent monomer molecules on the structure of the product molecule

Steric factors

Steric factors can control the ease of molecular movements in crystals and consequently the reaction.[15–22,36,37] It has also been reported that in some cases hydrogen bonds were responsible for the reaction rate.[22,38]

Temperature

Temperature increase can be useful when the mutual orientation of molecules in a crystal or steric effects do not favour the reaction;[39,40] however, an excessive increase, can preclude photoreaction.

Wavelength of radiation

The type of crystal irradiation can play a decisive role as far as the reaction course and the kind of the product are concerned.[39] It has also been reported that crystal disintegration during the photoreaction could be controlled by irradiation at the long-wavelength absorption tail.[41–43] This method was successfully applied, for instance, in the case of *trans*-cinnamic acid crystals.[41] However, the opposite point of view is also known.[44]

Cooperative effects

2,5-Distyrylpyrazine (DSP) and 1,4-bis(3-pyridyl-2-vinyl)benzene (P2VB), compounds which have similar reactivity in solutions but different in isomorphous crystals, are typical examples of the influence of cooperative effects on reactions in crystals.[45] To explain the cooperative effects, let us compare them with the domino effect: a local perturbation in a crystal lattice caused by an external impulse is transmitted spontaneously throughout the crystal without any need for further external impulses.

MONITORED REACTIONS

Monitoring studies of intermolecular reactions in organic crystals were carried out mainly for photodimerization reactions. Nevertheless, even in this case changes in crystal structure accompanying the reaction, and the behaviour of reactant and product molecules in particular, were monitored for only a few compounds, namely 5-benzylidene-2-(4-chlorobenzyl)cyclopentanone[25] (**1**), 5-benzylidene-2-benzylcyclopentanone[23,24] (**2**), 4-chlorocinnamoyl-*O*,*O*′-dimethyldopamine[46] (**3**) and 9-methylanthracene[26] (**4**). Compounds **1**–**3** undergo [2 + 2] photodimerization, whereas **4** undergoes the [4 + 4] photodimerization (see Scheme 3).

It should be explained that the appearance of the molecule obtained from an x-ray structure analysis is averaged over the crystal volume. For these reasons, in the case of mixed reactant–product crystals, the product molecule superimposed on the reactant molecules will be observed, and we will deal with the case of the so-called reactant–product disorder. During crystal irradiation, the content of the product (and the reactant) changes gradually, and for different irradiation times the crystal structure will be characterized by a different reactant–product disorder. Figure 1 shows the superposition of two monomer molecules on one dimer in crystal **1**. As can be seen, it is possible to separate both kinds of molecules.

Studies monitoring structural changes in crystals during photochemical reactions require determination of crystal structures for many intermediate stages of the phototransformation.

KINETICS OF PHOTOREACTION

It is possible to calculate the percentage of dimer molecules in crystals during crystal structure determination processes. These data can give us information about the order of the studied reactions. Figure 2 shows the dependences between the dimer content in the discussed crystals and the irradiation time. The relations presented can be described by the following exponential functions:

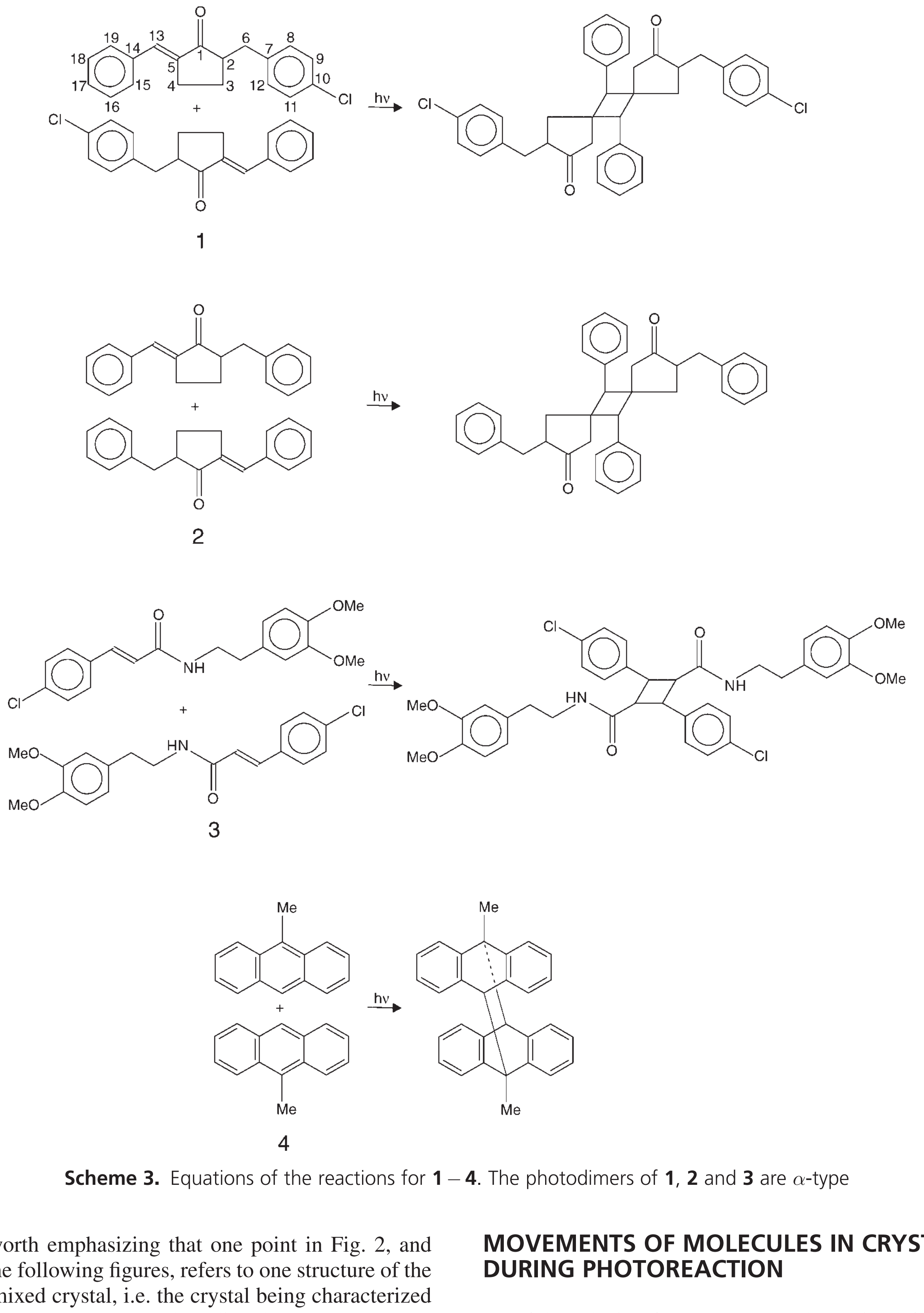
$$D = 120(16) - 114(15)\exp[-t/58(17)]$$

with correlation coefficient $r = 0.991$ and

$$D = 100 - 86(4)\exp[-t/114(11)]$$

with $r = 0.987$ for **1**[25] and **2**,[23] respectively, where D is the percentage of the dimer in the crystal, t is the irradiation time and the numbers in parentheses are standard deviations. These results indicate that the [2 + 2] photodimerization of **1** and **2** in crystals can be regarded as of pseudo-first order.

The pseudo-first order of the reaction of **2** was also determined over a wide temperature range by Honda and co-workers.[47,48] They used intensities of selected reflections to calculate the degree of reactant conversion. Figure 3 presents a semilog arithmic plot of the rate constant versus $1/T$. The rate constant exhibits its maximum value at about 200 K. The activation energy calculated from the slope of the plot in the range 117–173 K was 13.2 kJ mol^{-1}. The value of 15.2 kJ mol^{-1} was obtained for photodimerization of a styrylpyrylium salt (**5**).[49] The equation for the photoreaction is presented in Scheme 4. The observed decrease in the range 200–324 K was explained as a result of an intermolecular distance increase and a decrease in the overlap of the molecular orbitals. A rate constant reduction at higher temperatures has also been reported for photoreactions of other compounds.[50] For instance, the maximum reaction rate for the photodimerization of cinnamic acid is at ca 20 °C.[50]



Scheme 3. Equations of the reactions for **1** – **4**. The photodimers of **1**, **2** and **3** are α-type

It is worth emphasizing that one point in Fig. 2, and also in the following figures, refers to one structure of the current mixed crystal, i.e. the crystal being characterized by the current reactant–product disorder.

For **4**,[26] a linear function can be used for a description of the observed relation in the monitored range:

$$D = 1.75(5)t + 0.9(4)$$

with $r = 0.997$. This suggests a zero-order reaction.

MOVEMENTS OF MOLECULES IN CRYSTALS DURING PHOTOREACTION

Careful analysis of the structures determined for many stages of the phototransformations revealed that reactant and product molecules did not assume a fixed place in crystals. Reactant molecules gradually move away from the position occupied in the pure reactant crystal.[23–26] Figure 4(a) shows a change of the molecular orientation

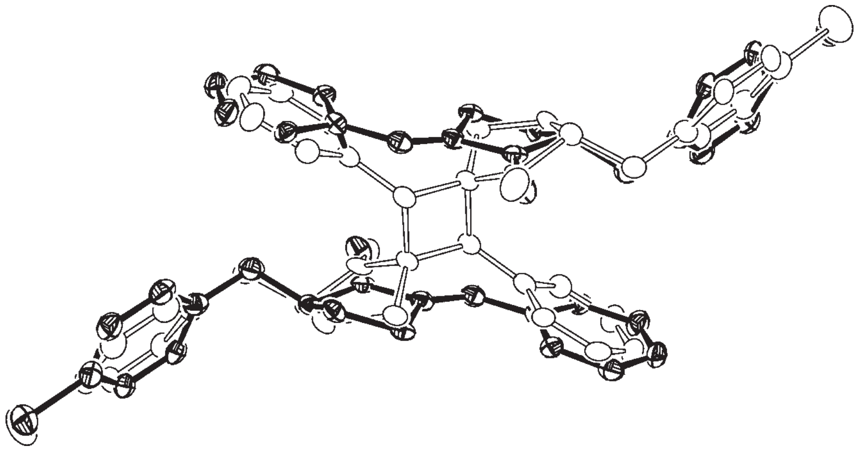


Figure 1. Product molecule superimposed on two reactant molecules in crystal **1** for 54% conversion

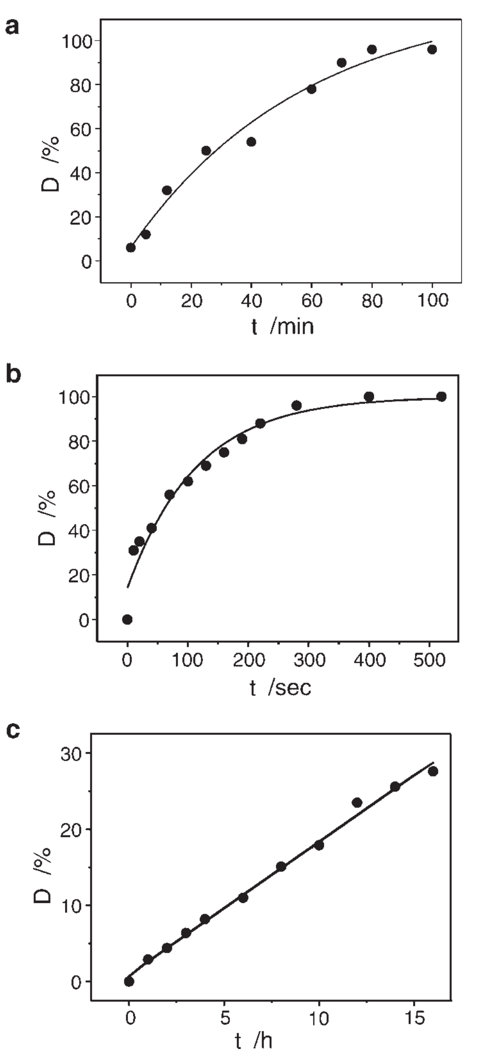


Figure 2. Dependence of the dimer percentage in the crystal on the irradiation time for (a) **1**, (b) **2** and (c) **4**. The reaction in **2** is faster than that in **1** owing to different conditions of irradiation (for **1** the radiation was transmitted through a fibre)

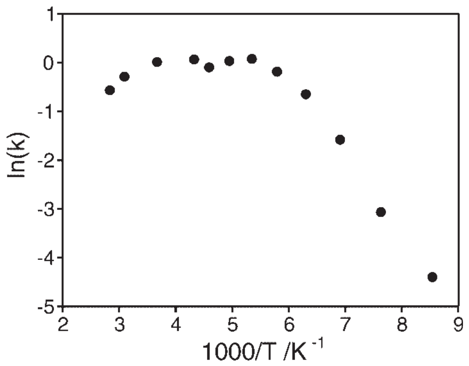
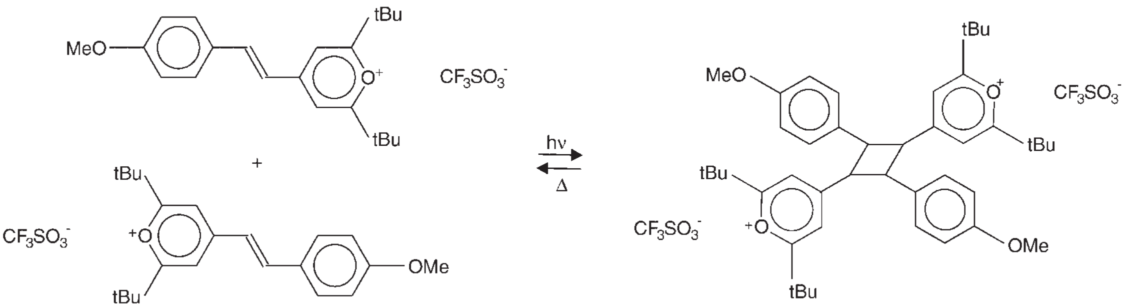


Figure 3. Dependence of the reaction rate constant on temperature for **2**. The rate constant at 273 K was set to 1

of **1**. The observed change is distinct. Product molecules behave in a similar way. They do not appear in the position occupied in the pure product crystal: they arise in a slightly different place and subsequently move smoothly towards the position assumed in the pure product crystal. The behaviour of the product molecules of **1** during the crystal phototransformation is shown in Fig. 4(b). As can be seen, the orientation change is smaller than in the case of the reactant. It should be pointed out that the final points in Fig. 4(a) and initial points in Fig. 4(b) are associated with larger standard deviations, since they refer to the minor component in the crystal.

For **2**, movements of the reactant and the product molecules are also observed.[23] They are of similar size, but not as smooth as for **1**. For **4** the change in the molecular orientation is almost unnoticeable for the reactant, but movements of the product are distinct.[26]

In the case of derivative **3**, it was said[46] that the product molecules did not make movements during the [2 + 2] photodimerization, since they had been involved in chains of hydrogen bonds. The H-bonds are presented in Scheme 5. Nevertheless, if we analyse atomic



Scheme 4. Photoreaction equation for the styrylpyrylium salt **5**. This reaction is thermally reversible

coordinates published for this compound, it can be noticed that the reactant and the product molecules also make movements during the crystal phototransformation. The behaviour of the molecules is presented in Fig. 5.

In the case of α-(acetylamino)cinnamic acid dihydrate crystal,[7] it was observed that the positions of the photodimer molecule in the mixed crystal of 12% reaction progress and in the pure dimer crystal were slightly different. The distance between the respective atoms in both crystals was in the range 0.09–0.45 Å. Scheme 6 presents an equation for the photoreaction.

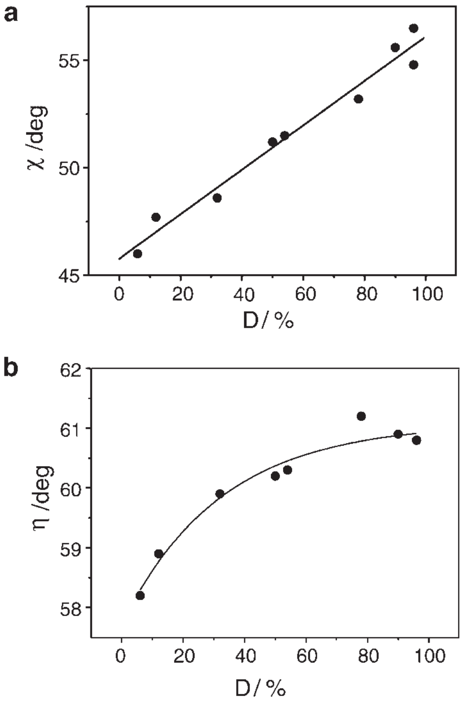
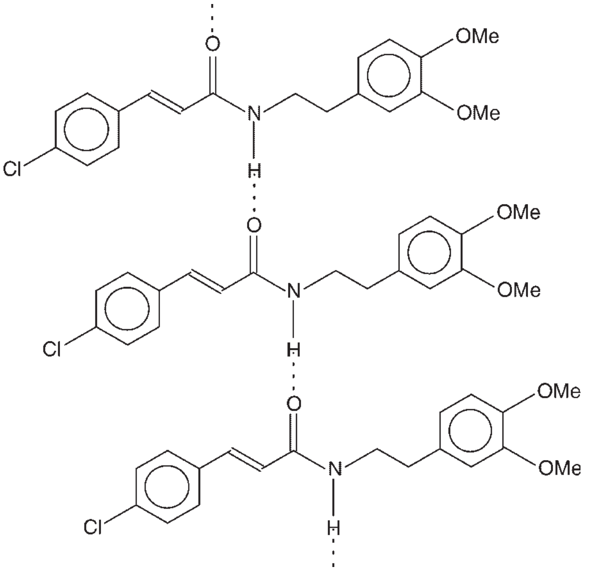


Figure 4. Variation in the angle formed by (a) the O1—C1—C5—C13 and (b) the cyclobutane and *xy* planes with the photodimer content for **1**. See Scheme 3 for the atom numbering. The relations can be described by the following equations: (a) $\chi = 45.8(4) + 0.103(7)D$ with correlation coefficient $r = 0.986$[24] and (b) $\eta = 61.1(2) - 3.4(3)\exp[-D/32.3(7)]$ with $r = 0.982$.[25] The numbers in parentheses represent the standard deviations in the last digits. The O1—C1—C5—C13 molecular fragment and the cyclobutane ring were chosen for monitoring purposes, because they are rigid and not as deformable as border parts of the molecule might be

A very interesting phenomenon was discovered for the adjacent reactant molecules in the monitored crystals. With photoreaction progress the molecules gradually come closer to each other.[23–26] Their behaviour for **1**, **2** and **4** is presented in Fig. 6. It can be explained in the following way: the product molecules, being smaller than a pair of the reactant molecular, exert stress on the reactant molecules and force them to come closer. The more of the product there is, the stronger the effect is. One more characteristic can be derived from Fig. 6. The slopes of the lines are slightly different for the examined compounds and can be correlated with the distance between the adjacent reactant molecules: the greater the distance, the greater is the slope. This is understandable, as the lattice characterized by larger intermolecular contacts can be stressed more easily.

Values of the distance between reacting monomer atoms in several intermediate crystals have also been given for *trans*-cinnamic acid[51] and styrylpyrylium



Scheme 5. Chain of N—H···O hydrogen bonds in the reactant crystal of **3**. The monomer molecules forming a cyclobutane ring belong to two different chains. The H-bonds are not destroyed during the photoreaction

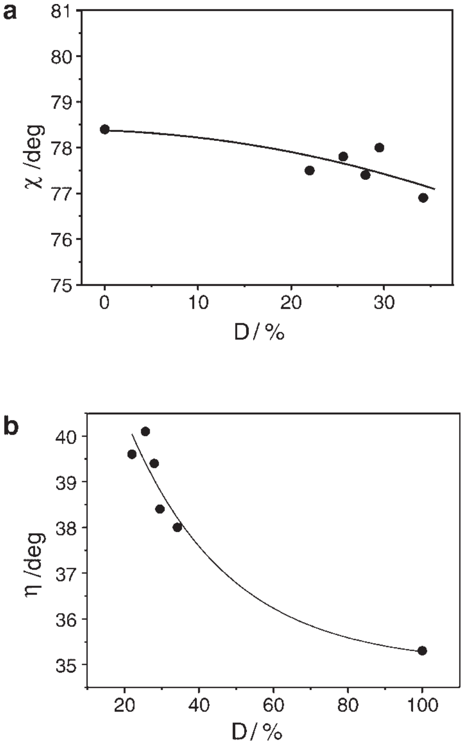


Figure 5. Variation in the angle formed by (a) O1—C1—C5—C13 and (b) the cyclobutane and *xz* planes for **3** with photoreaction progress. See Scheme 3 for the atom numbering. The relations in (a) and (b) can be described by $\chi = 78.4(4) - 0.01(6)D - 0.001(2)D^2$ with $r = 0.79$ and $\eta = 35.0(9) + 11(5)\ \exp[-D/27(16)]$ with $r = 0.965$, respectively. The numbers in parentheses represent standard deviations in the last digits

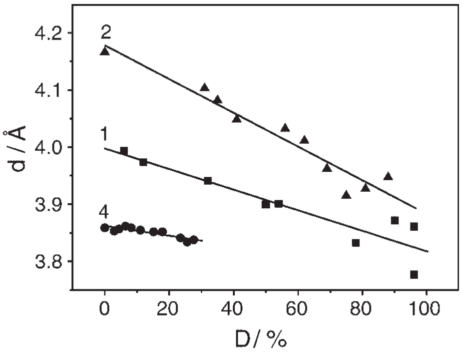


Figure 6. Variation in the distance between the atoms directly taking part in the photoreaction with the dimer content. Lines 1, 2 and 4 are for **1**, **2** and **4**, respectively. The regression equations are as follows: $d = 4.00(2) - 0.018(3)D$ with $r = 0.922$, $d = 4.18(2) - 0.0030(3)D$ with $r = 0.968$ and $d = 3.862(2) - 0.00086(15)D$ with $r = 0.89$ for **1**,[25] **2**[23] and **4**,[26] respectively. The numbers in parentheses represent the standard deviations in the last digits

triflate **5**.[52] For *trans*-cinnamic acid they are 3.59, 3.48, 3.49 and 3.52 Å for 0, 28, 40 and 67% conversion, respectively, and for styrylpyrylium triflate (**5**) 3.42, 3.42 and 3.07 Å for 0, 13 and 67% conversion, respectively. Unfortunately, it is not possible to find relationships similar to those in Fig. 6. Moreover, the 3.07 Å distance seems to be underestimated in comparison with the sum of the van der Waals radii, 3.40 Å.[53]

The change in the distance between the adjacent monomer molecules with photoreaction progress has also been mentioned for **3**.[46] Figure 7 presents such a relationship derived from the published atomic coordinates. Unexpectedly, the slope of the line is larger than in the case of **2**.

It is of interest to establish whether the power of the relationships presented in Fig. 6 is dependent on temperature. Figure 8 shows the respective data for low (100 K) and room temperature for **2**. As can be seen, the two lines are almost parallel, which indicates that the discussed effect is temperature independent.[24]

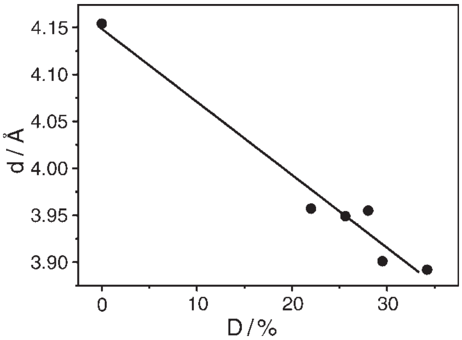
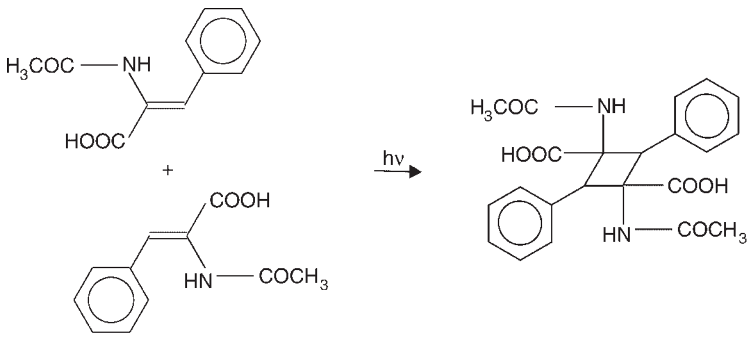


Figure 7. Change in the distance between the monomer atoms directly taking part in the photoreaction with reaction progress for **3**. The relation can be described by $d = 4.15(2) - 0.0078(7)D$ with $r = 0.984$



Scheme 6. Photoreaction equation for α-(acetylamino)cinnamic acid

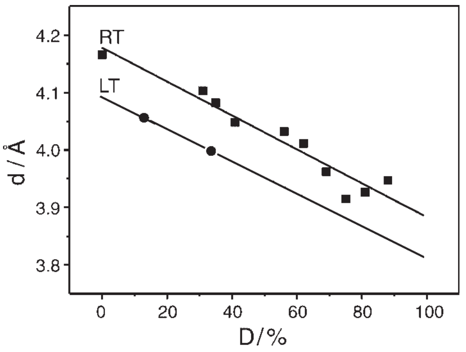


Figure 8. Variation in the distance between the directly reacting monomer atoms with photoreaction progress for **2**. The top and bottom lines are for the room-and low-temperature structures, respectively

The reactant molecules of the studied compounds also exhibit another interesting feature. With photoreaction progress, the adjacent monomer molecules change their mutual orientation to look like the product. This dependence has been described in the case of **1**,[25] but it can be observed also for **2** and **3** if we analyse the atomic coordinates for these compounds. The discussed effect is presented in Fig. 9.

In the case of **1**–**4**, the adjacent reactant molecules are related by an inversion centre. This means that the reacting C=C bonds are mutually parallel. The inversion centre is also preserved in the product molecule. Thus the C=C bonds moved parallel in order to form the cyclobutane ring. A more complex situation takes place in the case of co-crystals of *trans*-cinnamamide with phthalic acid (2:1).[15] The molecular formula of the three-component assembly is presented in Scheme 7. During the [2 + 2] dimerization one of the adjacent *trans*-cinnamamide molecules changes its conformation by pedal-like movements (Scheme 7). Such behaviour of the reactant

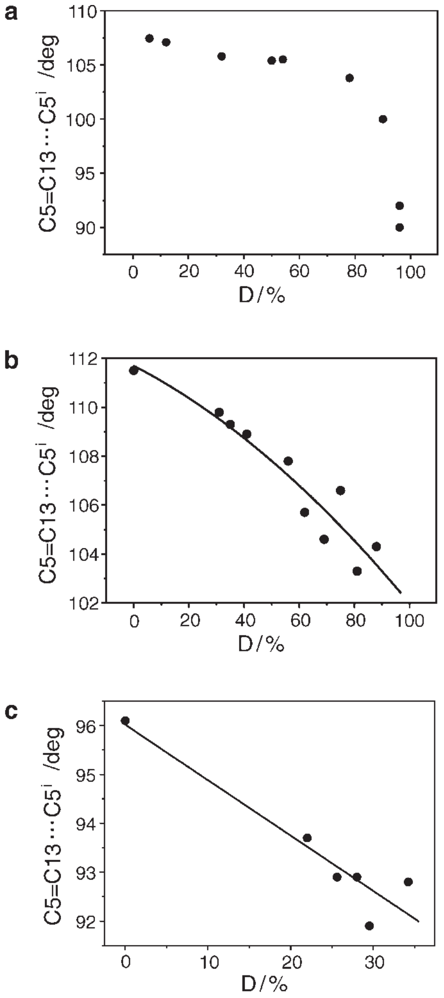
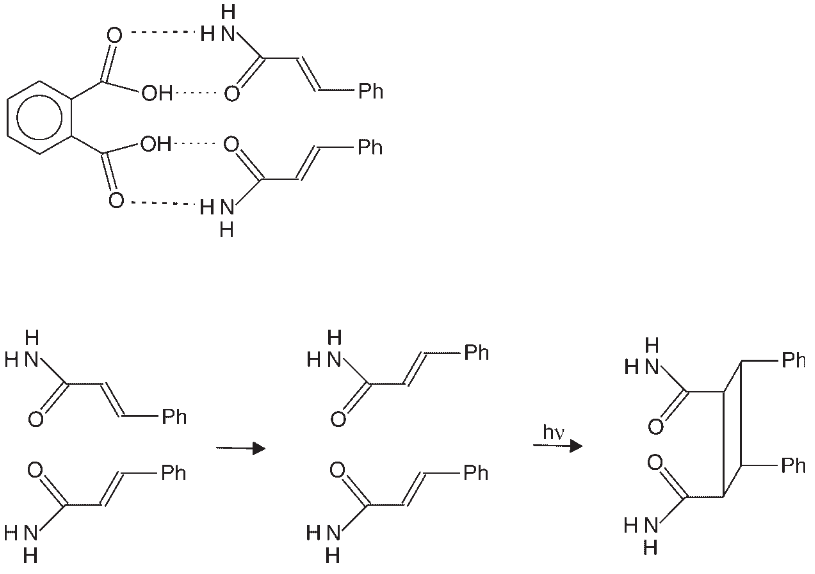


Figure 9. Change of $C5{=}C13\cdots C5^{i}$ angle with photoreaction progress for compounds (a) **1**, (b) **2** and (c) **3**. See Scheme 3 for the atom numbering; $C5^{i}$ means the C5 atom from the adjacent reactant molecule. The regression equations are $\alpha = 111.7(9) - 0.06(4)D - 0.0004(4)D^2$ with $r = 0.947$ and $\alpha = 96.0(5) - 0.11(2)D$ with $r = 0.945$ for **2** and **3**, respectively



Scheme 7. Molecular formula and the [2 + 2] photodimerization equation for *trans*-cinnamamide–phthalic acid (2:1) crystal

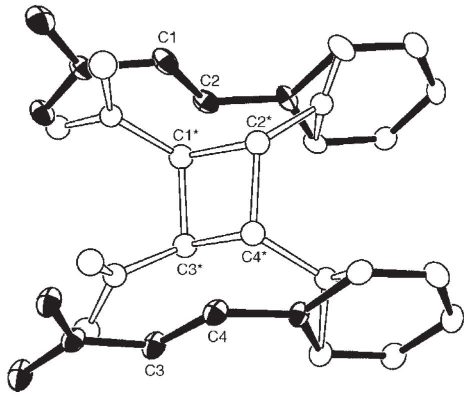


Figure 10. Two *trans*-cinnamamide molecules superimposed on one photodimer molecule. C1, C2, C3 and C4 represent the monomer reacting atoms and asterisks for the corresponding photodimer atoms

molecule was deduced on the basis of the x-ray structure of the partly (13.2%) reacted crystal. Figure 10 presents the mixed reactant–product structure. The C=C bonds are in a criss-crossed arrangement. [The twist angle is 97.1(4)° and the centre-to-centre distance is 4.252(3) Å for the pure reactant crystal.] The symmetry of the photodimer indicates the necessity of the pedal-like rotation around C1=C2 bond and the approximately parallel movement of C3=C4 to form the cyclobutane ring. The pedal-like movements have also been analysed.[54]

Recently, the time-resolved x-ray diffraction technique was applied to studies of the [2 + 2] photodimerization of *p*-formyl-*trans*-cinnamic acid.[55] The studies showed that for times shorter than 100 ps a pair-like transient state in a crystal was formed.

CHANGES IN UNIT CELL CONSTANTS

The structural changes proceeding in crystals during photoreactions are accompanied by changes in unit cell constants. Cell constants belong to the most often analysed parameters in monitoring studies of chemical reactions in crystals.[16–18,20–22]

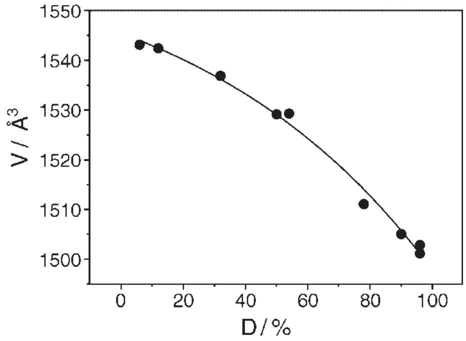
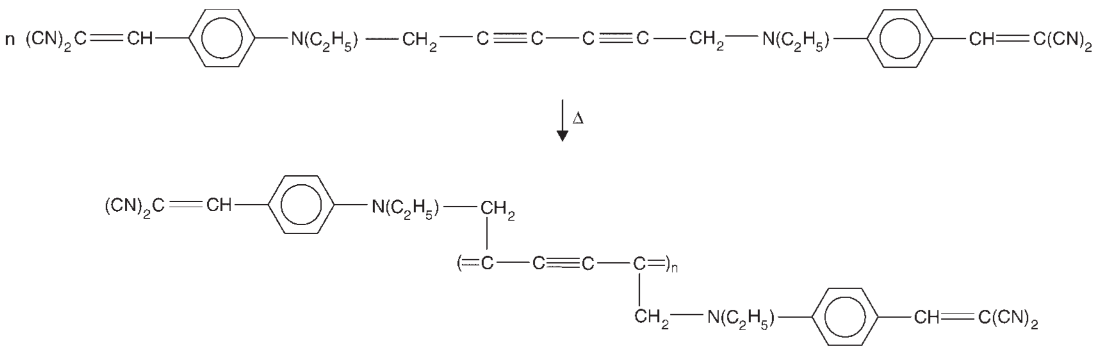


Figure 11. Change in the unit cell volume for **1** with the dimer content

Since the volume of the dimer molecule is smaller than that of the monomer pair, it can be expected that the unit cell volume will decrease with photodimerization progress. Such a dependence exists for **1**,[25] which is shown in Fig. 11. Nevertheless, for **2** it was reported that the unit cell volume increased slightly at the beginning of the photoreaction and subsequently it gradually decreased.[10] In the case of the bromo derivative of **2**, 5-benzylidene-2-(4-bromobenzyl)cyclopentanone, the cell volume is almost constant during the reaction.[10] The increase at the beginning of the reaction and the following decrease were also observed in the case of **4**.[26] The changes in the unit cell volume caused by the photoreaction are not large: about 3, 1 and 4% for **1**, **2** and **3**, respectively.

Very surprising values of the unit cell volume were reported for the styrylpyrylium derivative **5**, namely 2393.8, 2385 and 2435.5 Å^3 for a crystal containing 0, 13 and 67% of the dimer, respectively.[42]

The individual unit cell constants change in a complex way: some of them increase and others decrease to various extents. The observed decrease may be related to the fact that in a given direction van der Waals interactions are transformed into chemical bonds. A very interesting variation in unit cell constants can be revealed from data reported for the polymerization of a diacetylene derivative.[29] The reaction equation is presented in Scheme 8. In contrast to the photodimerization of **1**–**4**, the α and β angles between crystallographic axes change substantially as presented in Fig. 12.



Scheme 8. Polymerization equation for the diacetylene derivative

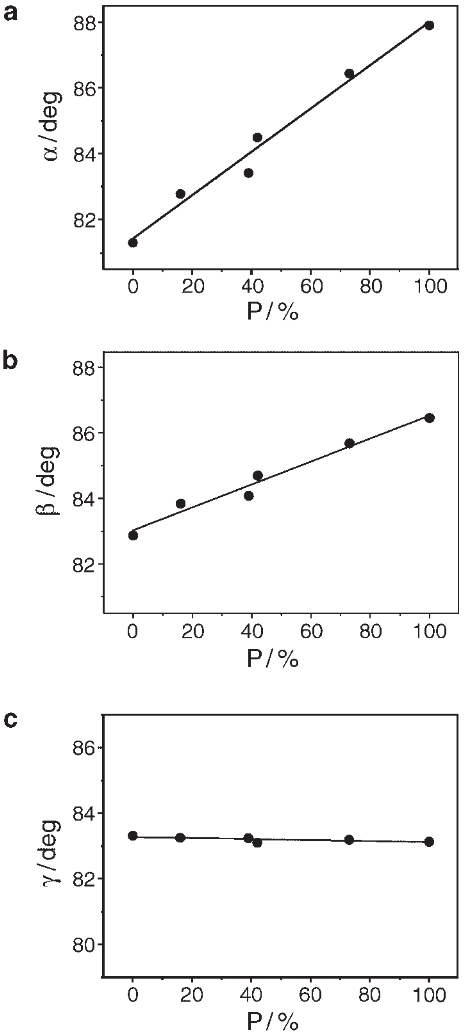


Figure 12. Changes in the (a) α, (b) β and (c) γ angles with polyacetylene content (see Scheme 8 for the formula)[30]

CONCLUSIONS

This paper has surveyed the behaviour of reactant and product molecules during photochemical single crystal to single crystal reactions. The course of the reactions of this type can be examined by x-ray structure analysis. This method provides information on the geometry of molecules and their mutual orientation in crystals. The studies show in a quantitative way that reactant and product molecules do not assume a fixed position in a crystal, but move gradually and smoothly along with the photoreaction progress. The product molecules move to the position occupied in the pure product crystal and the reactant molecules move from the position assumed in the pure reactant crystal. Moreover, as the reaction progresses, the adjacent monomer molecules gradually come closer and change their mutual orientation to resemble the dimer. This paper has also considered kinetic studies of the photochemical reactions in crystals.

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