Structural Transformations in a Crystal during the Photochemical Reaction of 2-Benzyl-5-benzylidenecyclopentanone**

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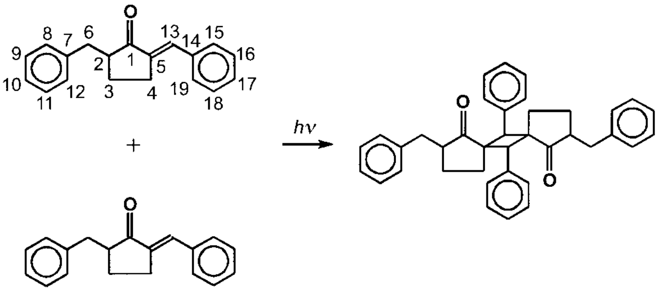
Abstract: The studies presented are the first example in which the substrate and product molecules were monitored separately over many stages during the chemical reaction progress in a crystal to understand the reaction path of the molecules in detail during the whole transformation. The BBCP, 2-benzyl-5-benzylidenecyclopentanone, single crystal was irradiated without any destruction over several steps. After each of step the X-ray structure with a different substrate/product ratio and with a disorder was determined. The study revealed that the photochemical [2+2]-cycloaddition reaction of BBCP in a crystal does not exhibit cooperative character and can be regarded as of the first-order. During the transformation the product molecules do not adopt the position of the molecules in the final pure dimer crystal, but move gradually and smoothly in this direction. The movement of the molecules was also observed for the substrate. This remarkable behaviour of the product and reactant molecules bears a rotational component. The distance between reaction centres of adjacent BBCP substrate molecules decreases fluently with the progress of the reaction, but it does not get smaller than a sum of van der Waals radii.

Keywords: dimerization · photoreaction · solid-state reactions

Introduction

Photochemical reactions in solids, particularly in crystals, have been a subject of interest for years. In the last decade this concern even increased, which was related to the development of modern materials and advanced technologies. These reactions obeyed not only topochemical,[1–12] but also non-topochemical transformations.[12–15] Nevertheless, the photoreactions in crystals were examined relatively seldom by X-ray diffraction techniques. Moreover, the X-ray structure analysis studies monitoring in detail, step by step, movements of molecules during photochemical reactions in crystals have not been published, although this is a very interesting concept. The X-ray structure analysis is a very powerful method giving information on atomic coordinates and thermal motions of atoms in crystals. Furthermore, the revolution in crystallographic experimental techniques in the Nineties, for example an introduction of area detectors and new fast data collection methods[16] for small molecules, opened new possibilities for observation structural transformations in crystals.

The [2+2]-photodimerization of BBCP, 2-benzyl-5-benzylidenecyclopentanone, was chosen as the model transformation in which a cyclobutane ring is formed from two double C=C bonds in two adjacent molecules in a crystal lattice (Scheme 1). The reaction is initiated by UV/Vis radiation and proceeds homogenously without crystal destruction that is as a single-crystal-to-single-crystal transformation, so that the X-ray structure analysis can be utilized to study this reaction. In our research the BBCP dimerization was stopped at many different stages of reaction pathway. After each step the structure of the resulting crystal containing both the substrate and the product molecules in a different ratio was determined (see Experimental Section). The crystal structure of the pure BBCP monomer and of the pure dimer was analysed earlier.[1, 2]



Scheme 1. The equation of the photochemical [2+2]-cycloaddition reaction of BBCP showing also the labelling scheme for atoms.

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[**] Monitoring Structural Transformations in Crystals, Part 1.

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Results and Discussion

The structure for one of the steps of the [2 + 2]-photodimerization of BBCP in a crystal is shown in Figure 1 and the numbering scheme for atoms is displayed in Scheme 1. Since both the substrate and the product molecules (in changing proportions) are present in the crystal during the reaction, the monomer/dimer disorder is a characteristic feature of the crystal structures.

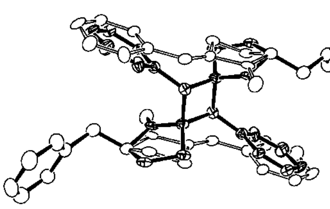

Figure 1. The ORTEP diagram of two monomer BBCP molecules (boundary ellipsoids) and one dimer molecule (filled bonds) in the crystal for 56 % of the reaction progress. Thermal ellipsoids were drawn at the 15 % probability level and hydrogen atoms were omitted for clarity.

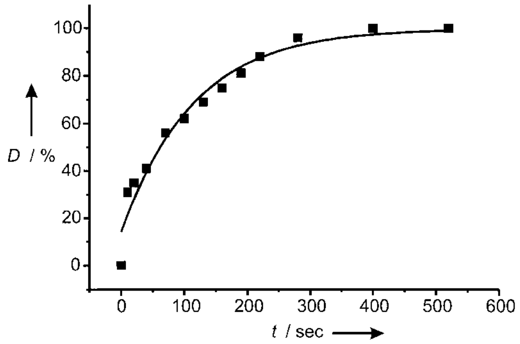

Figure 2. The dependence of the dimer percentage in the crystal, *D*, on irradiation time, *t* with $D = 100 - 86(4)\exp[-t/114(11)]$ (standard deviations in parentheses).

An analysis of the amount of dimer in the crystal studied for two different steps of the reaction progress (i.e., for 10 and 20 s of irradiation) versus total time which passed from the irradiation of the crystal revealed that the product quantity is constant and the reaction does not proceed without UV irradiation even after many (about twenty) hours. This means that the [2 + 2]-photocycloaddition of BBCP in crystals does not exhibit cooperative character as it does in the case of, for example, 2,5-distyrylpyrazine (DSP).[12–14] Such a behaviour of the BBCP crystal has one more very important aspect: its stability after irradiations enables X-ray data collections of quality proper for structure determinations (see the Experimental Section).

Figure 2 shows a dependence of the dimer amount in the BBCP crystal on the irradiation time: The reaction proceeds in a smooth and exponential way. The function of the curve is as follows:

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

where *D* is the percentage of the dimer in the crystal, *t* is the irradiation time and the numbers in the parentheses are standard deviations. The logarithmic dependence for the monomer content, *M*, on the irradiation time is linear and takes the following form:

$$\ln(M) = -0.0096(7)t + 4.5(1)$$

with the square of a correlation coefficient $r^2 = 0.975$. These results indicate that the [2 + 2]-photocycloaddition of BBCP in crystals can be regarded as of the first order.

The analysis of the changes of the atomic coordinates in the mixed crystals, that is crystals containing both the substrate and the product, reveals that during the photoreaction the dimer molecules do not adopt the position of the molecules in the pure dimer crystal (i.e., in the crystal containing only the product), but move gradually and smoothly towards such a position. Figure 3 displays changes of *z* coordinate of C5D and C13D atoms in the cyclobutane ring and of C14D – C17D in the dimer phenyl group (see Scheme 1 for atoms labels). For clarity the range of the "*z*-coordinate" axis is the same for all a) – f) plots. It can be observed that peripheral atoms of the molecule, that is C16D, C17D (and also C18D, not presented in Figure 3) move more than atoms of the middle part, that is C5D, C13D, C14D and C15D. Moreover, C13D and C5D shift in opposite directions. Atoms of the rest part, that is of the

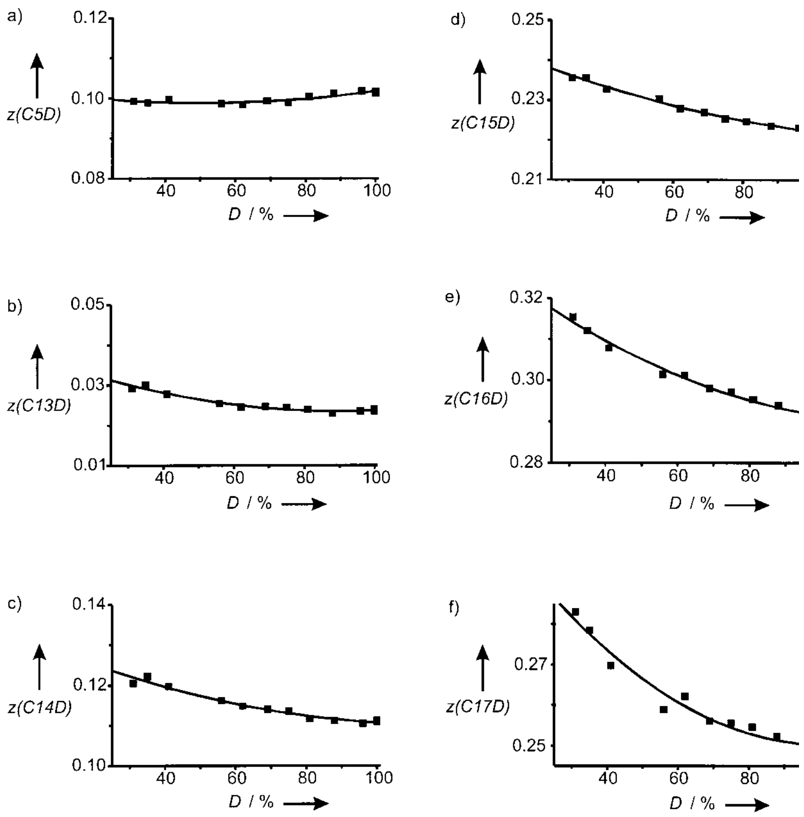

Figure 3. The change of *z* atomic coordinate of C5D, C13D and C14D – C17D dimer atoms with the dimer content in the crystal. All regression equations are of the second-order and squares of correlation coefficients are in the range of 0.95 – 0.99 for b) – f) plots and 0.84 for a).

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benzyl-cyclopentanone fragment—not presented in Figure 3, travel in the same direction as C5D. Furthermore, atoms of the border part of this fragment, that is of the benzyl, move more than those of the cyclopentanone ring. The smallest atom shift along the *z* direction is observed for C5D and C13D (0.02 and −0.07 Å, respectively); the biggest is observed for C10D, C11D in the benzyl fragment (both 0.36 Å) and for C17D in the phenyl ring (−0.32 Å). The movements, but less pronounced and characteristic, are also observed for *x* and *y* coordinates of the atoms of the dimer.

When a change of the *c* constant with a variation of the dimer content in the crystal is taken into account, all the above considerations are still valid. Although the change of the cell constants during the BBCP photoreaction has already been published,[1, 17] those studies were only related to irradiation time but without any details on the substrate/product content in a crystal.

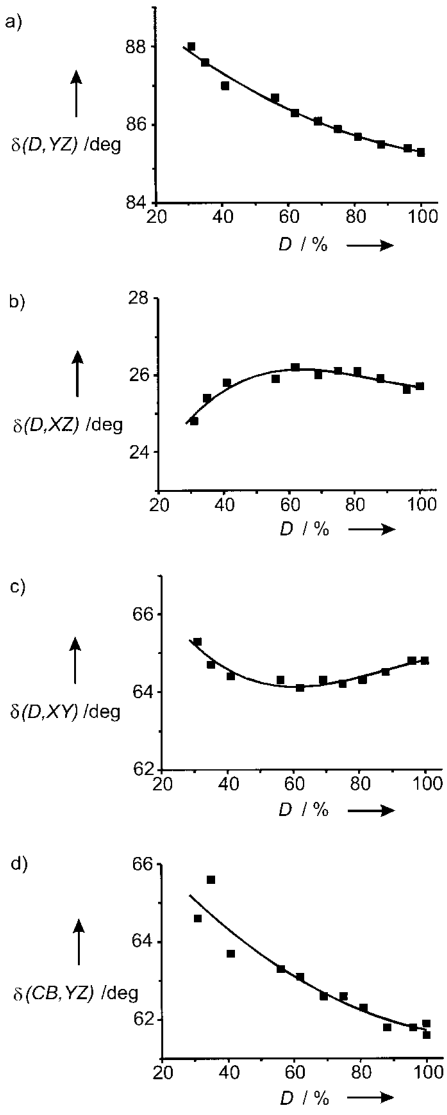

Figure 4. The change of the angle between the best dimer molecule plane and a) *YZ*, b) *XZ*, c) *XY* planes, and d) the change of the angle between the cyclobutane and *YZ* planes during the reaction path that is with the dimer content in the crystal. The regression equations and squares of correlation coefficients are as follows: a) $\delta(D,YZ) = 3.2(7)\cdot 10^{-4}D^2 - 0.08(1)D + 90.0(3)$, $r^2 = 0.986$, b) third-order dependence, $r^2 = 0.90$, c) third-order dependence, $r^2 = 0.90$, d) $\delta(CB,YZ) = 4(2)\cdot 10^{-4}D^2 - 0.10(3)D + 68(1)$, $r^2 = 0.91$. δ: dihedral angle, numbers in parentheses give standard deviations.

The behaviour of the product molecules described indicates that their movement during the reaction exhibits a rotational component. This rotation on the reaction path is illustrated in Figure 4. As it can be seen the angle between the best plane of the product molecule and the (100) plane (that is *YZ*) decreases in a smooth and statistically significant way. Similar relations are shown for (010) and (001) (i.e., *XZ* and *XY*, respectively) planes. The dependence for the angle between the cyclobutane ring and (100) plane is also presented. For clarity the range of the δ axis is the same in all cases.

The substrate molecules in the crystal reveal a very similar behaviour as the product molecules. The monomers also move gradually on the reaction path and their movements also bear a rotational component. The angles between the best monomer plane and the (100), (010) and (001) planes are presented in Figure 5.

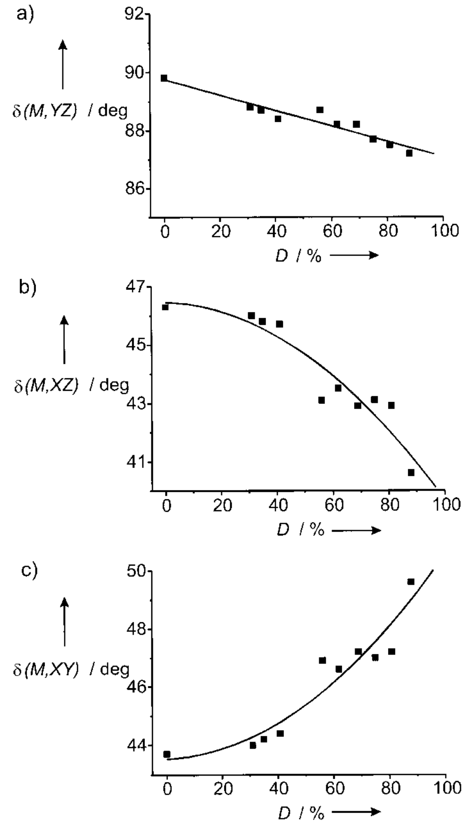

Figure 5. The change of the angle between the best monomer molecule plane and a) *YZ*, b) *XZ* and c) *XY* planes during the reaction path that is with the dimer content in the crystal. The point for the pure monomer crystal was calculated on the ground of data taken from ref. [1]. The regression equations and squares of correlation coefficients are as follows: a) $\delta(M,YZ) = -0.026(3)D + 89.7(2)$, $r^2 = 0.91$, b) $\delta(M,XZ) = -6(3)\cdot 10^{-4}D^2 + 46.5(7)$, $r^2 = 0.89$, c) $\delta(M,XY) = 7(3)\cdot 10^{-4}D^2 + 43.5(6)$, $r^2 = 0.90$. δ: dihedral angle, numbers in brackets give standard deviations.

Another remarkable feature of the monomer molecules performance on the reaction path is reduction of a distance between reacting atoms C5 and C13′. Figure 6 demonstrates the change of this distance during the transformation. The

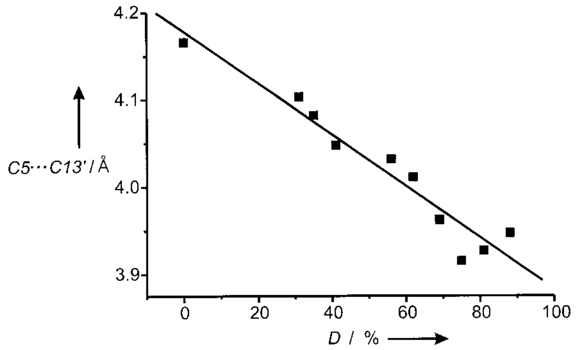

Figure 6. The change of the C5···C13′ distance between two reacting monomer molecules during the reaction path. C13′ means the C13 atom transformed by symmetry. The distance for the pure monomer crystal was taken from ref. [1].

dependence is linear and the regression Equation is as follows:

$$\mathrm{dist(C5\cdots C13')} = -0.0030(3)D + 4.18(2)$$

with the square of a correlation coefficient $r^2 = 0.937$. It should be emphasized that the distance analysed does not decrease below the sum of the van der Waals radii.[18]

Reversal of chemical reactions in crystals is an essential feature of materials used in advanced technologies.[19] A homogenous, that is single-crystal-to-single-crystal, thermal reverse transformation takes place in the case of (*E*)-2,6-di-*tert*-butyl-4-[2-(4-methoxyphenyl)ethenyl]-pyrylium trifluormethansulfonate.[3, 19] The X-ray structure analysis processed for BBCP showed that the dimerization is not reversible in 373 K after 20 h (melting points for the pure monomer and the pure dimer crystals are 124.5–125.5 °C and 236–238 °C, respectively[1]).

Conclusion

The remarkable behavior of the substrate and product molecules during the photochemical dimerization of BBCP in a crystal was monitored by the X-ray structure analysis. The dimer molecules move gradually and fluently to the position occupied in the pure dimer crystal. Both product and substrate movements possess a rotational component. The monomer reaction centres approach each other with the transformation progress. The reaction examined in a crystal does not feature cooperative character and can be regarded as of the first order. The described results were obtained for the single-crystal-to-single-crystal transformation. In the case of the reaction with a crystal destruction, the transformation path may be different.

Experimental Section

General information: All irradiations and X-ray experiments were performed on the same crystal. The crystal was irradiated in several steps by an Hg 100 W lamp with a 039FG11-50 glass filter which had a maximum of transmittance at about 495 nm and a half-intensity width about 230 nm. After each step of irradiation intensities of reflections were collected by an area detector (CCD camera) diffractometer and a crystal structure was determined. The general strategy of data collections used for area-detector diffractometers was described elsewhere.[16] Due to time demands of the experiment (it was possible that some cooperative effects could play a role), extremely fast data collections were performed. For first three irradiations of the crystal, that is for 10, 20 and 40 s irradiations, the whole of one data collection took only about 70 minutes. This time was increased for the crystal after next irradiations to about three hours. The cell constants were determined on the ground of most collected reflections.[20] The data were corrected for the Lorentz and polarization effects.[20] The structures were solved with the SHELXS-86[21] program and refined with SHELXL-97 (full-matrix least squares on F^2).[22] The substrate/product disorder was a feature of all mixed crystal structures. The percentage of the dimer (and of the monomer) in the crystal was determined during the refinement process. Due to a small number of observed reflections for one hour data collections, the substrate and product molecules were refined only isotropically in these cases. For three hours data collections molecules of both types were treated anisotropically, except of the crystal containing 88 and 96 % of the dimer when the monomer was treated as isotropic. For all cases hydrogen atoms of both molecules were taken into consideration, but with some constraints (excluding the 88 % and 96 % dimer crystal when only H atoms for the dimer were considered). The disorder was the reason for using many restraints and constraints of geometrical and thermal parameters, but their number and type depended on the refinement demands. The following possibilities from SHELXL-97[22] were applied: DFIX, FLAT, EADP, EXYZ, AFIX for all the mixed crystals and additionally ISOR for the 62 % and SIMU for the 88 % dimer crystal. For almost all cases the benzyl fragment of the substrate and product molecules was treated as overlapped. The ORTEP[23] view of two reactant monomer molecules and one product dimer molecule showing a typical disorder is presented in Figure 1. Selected experimental data for the crystal are given in Table 1; crystal description: colourless, crystal size = 0.40 × 0.28 × 0.14 mm^3, crystal system = orthorhombic, space group = *Pbca*, $Z = 8$, $F(000) = 1120$, $2\theta_{max} = 52°$, $\lambda(\mathrm{Mo_{K\alpha}}) = 0.71073$ Å, $\mu = 0.07$ mm^{-1}, $T = 293$ K. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-154255–154265 for 31–100 % D crystals. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Table 1. Experimental data.[a]

	31 % D	35 % D	41 % D	56 % D	62 % D	69 % D	75 % D	81 % D	88 % D	96 % D	100 % D
a [Å]	31.251(7)	31.239(8)	31.250(10)	31.252(6)	31.244(7)	31.243(5)	31.249(5)	31.249(6)	31.268(5)	31.273(5)	31.286(4)
b [Å]	10.764(3)	10.762(3)	10.756(3)	10.768(2)	10.765(2)	10.7714(18)	10.7741(18)	10.7809(19)	10.7922(18)	10.7985(16)	10.8063(15)
c [Å]	8.7378(17)	8.7345(19)	8.719(2)	8.7208(14)	8.7165(14)	8.7012(12)	8.6874(12)	8.6750(12)	8.6576(11)	8.6382(10)	8.6260(9)
V [Å^3]	2939.3(12)	2936.5(13)	2930.7(14)	2934.7(9)	2931.7(10)	2928.2(8)	2924.9(8)	2922.5(9)	2921.5(8)	2917.1(7)	2916.3(6)
ρ_{calcd} [Mg m^{-3}]	1.186	1.187	1.189	1.187	1.189	1.190	1.191	1.192	1.193	1.195	1.195
measured reflections	6738	6689	6680	6999	6875	6967	6957	6974	6941	6949	6878
measured indep. reflections	2834	2833	2820	2834	2828	2826	2822	2819	2820	2815	2810
obs. indep. reflections	589	604	574	1105	1232	1178	1203	1241	1272	1292	1326
R_{int} (measured reflections)	0.056	0.055	0.053	0.049	0.053	0.046	0.046	0.044	0.044	0.043	0.043
refined parameters	130	130	130	228	225	225	225	225	219	239	182
R_1 (obs. reflections)	0.084	0.084	0.088	0.085	0.132	0.088	0.083	0.080	0.074	0.071	0.066
$wR2$ (obs. reflections)	0.252	0.246	0.264	0.258	0.274	0.264	0.241	0.241	0.233	0.220	0.188
R_1 (all data)	0.276	0.273	0.276	0.185	0.226	0.186	0.173	0.166	0.154	0.151	0.140
$wR2$ (all data)	0.291	0.282	0.307	0.286	0.295	0.302	0.266	0.266	0.255	0.247	0.211
ρ_{max} [e Å^{-3}]	0.24	0.21	0.18	0.16	0.20	0.33	0.17	0.17	0.15	0.29	0.16
ρ_{min} [e Å^{-3}]	−0.22	−0.19	−0.19	−0.13	−0.15	−0.22	−0.14	−0.14	−0.14	−0.17	−0.13

[a] For the mixed crystal containing n % of the dimer molecules the "n % D" abbreviation is used.

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