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Monitoring structural transformations in crystals. 5.[1] A topotactic [2 + 2]-photodimerization reaction

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The structural changes in a crystal of 5-benzylidene-2-(4-chlorobenzyl)cyclopentanone during [2 + 2]-photodimerization were monitored by means of X-ray diffraction. It was observed that the monomers moved gradually from the position occupied in the crystal at the initial stage of the photoreaction and the dimers moved towards the position assumed at the final step. The movements of the molecules possess a rotational component. Moreover, with the progress of the phototransformation the monomers in the reacting pair gradually move closer and change their relative orientation to resemble more the product molecule. The behaviour of the molecules and also the variation of the cell constants for the studied compound were compared with data for 5-benzylidene-2-benzylcyclopentanone.

1. Introduction

In the past decade interest in photo-induced reactions in crystals has increased significantly because of the development of modern technologies and selective organic syntheses. Nevertheless, crystallographic studies of photochemical reactions were usually limited to a comparison of structures of pure substrate and pure product crystals (Anderson *et al.*, 1979; Chung *et al.*, 1991; Ehrenberg, 1968; Gnanaguru *et al.*, 1984, 1985; Guru Row *et al.*, 1983; Harada *et al.*, 1995, 1996; Jones & Theocharis, 1984; Ohhara *et al.*, 2000; Suzuki *et al.*, 1994; Theocharis & Jones, 1984, 1985; Theocharis *et al.*, 1981; Wang & Jones, 1987). In some cases the structures of mixed objects, containing both the substrate and the product, were reported (Chang *et al.*, 1987; Enkelmann *et al.*, 1993; Harada *et al.*, 1999; Kawano *et al.*, 1999; Leibovitch *et al.*, 1998; Nakanishi *et al.*, 1981; Novak *et al.*, 1993*a*,*b*; Theocharis, Desiraju & Jones, 1984). Unfortunately, in the scientific literature only a few publications deal with the monitoring of structural changes occurring in crystals during phototransformations (Bogadi *et al.*, 2002; Ohashi, 1988; Ohashi *et al.*, 1993; Turowska-Tyrk, 2001). In all the mentioned cases the structures were determined for molecules in a ground state. The recent development of time-resolved techniques also enabled studies of photo-induced crystals with molecules in an excited state (Kim *et al.*, 2002; Moffat, 2001; Techert *et al.*, 2001).

In the first part of the series (Turowska-Tyrk, 2001), the behaviour of molecules during the [2 + 2]-photodimerization in crystals of 5-benzylidene-2-benzylcyclopentanone was

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[1] Part 4: Turowska-Tyrk *et al.* (2003).

Table 1
Experimental details.

	6D	32D	54D	78D	96D 100min
Crystal data					
Chemical formula	$C_{19}H_{17}ClO$	$C_{19}H_{17}ClO$	$C_{19}H_{17}ClO$	$C_{19}H_{17}ClO$	$C_{19}H_{17}ClO$
M_r	296.78	296.78	296.78	296.78	296.78
Cell setting, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
a, b, c (Å)	17.128 (4), 10.563 (3), 8.790 (2)	17.089 (5), 10.564 (3), 8.812 (3)	16.951 (7), 10.590 (4), 8.803 (3)	16.781 (7), 10.627 (5), 8.735 (4)	16.686 (4), 10.688 (4), 8.664 (3)
β (°)	103.99 (2)	104.96 (3)	104.59 (4)	104.07 (4)	103.74 (3)
V (Å^3)	1543.1 (7)	1536.9 (8)	1529.3 (10)	1511.0 (12)	1500.9 (8)
Z	4	4	4	4	4
D_x (Mg m^{-3})	1.277	1.283	1.289	1.305	1.313
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	818	653	763	846	815
θ range (°)	5–20	5–18	5–17	5–18	5–19
μ (mm^{-1})	0.24	0.25	0.25	0.25	0.25
Temperature (K)	293 (2)	293 (2)	293 (2)	293 (2)	293 (2)
Crystal form, colour	Plate, colourless	Plate, colourless	Plate, colourless	Plate, colourless	Plate, colourless
Crystal size (mm)	0.68 × 0.42 × 0.15	0.68 × 0.42 × 0.15	0.68 × 0.42 × 0.15	0.68 × 0.42 × 0.15	0.68 × 0.42 × 0.15
Data collection					
Diffractometer	Kuma KM-4 CCD	Kuma KM-4 CCD	Kuma KM-4 CCD	Kuma KM-4 CCD	Kuma KM-4 CCD
Data collection method	ω scans	ω scans	ω scans	ω scans	ω scans
Absorption correction	None	None	None	None	None
No. of measured, independent and observed reflections	7593, 2973, 1881	7423, 2955, 1746	7490, 2946, 1724	7399, 2920, 1788	7326, 2905, 1873
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$R_{\rm int}$	0.042	0.052	0.061	0.052	0.056
$\theta_{\rm max}$ (°)	26.0	26.0	26.0	26.0	26.0
Range of h, k, l	$-21 \Rightarrow h \Rightarrow 17$ $-12 \Rightarrow k \Rightarrow 13$ $-8 \Rightarrow l \Rightarrow 10$	$-21 \Rightarrow h \Rightarrow 17$ $-12 \Rightarrow k \Rightarrow 13$ $-8 \Rightarrow l \Rightarrow 10$	$-20 \Rightarrow h \Rightarrow 17$ $-13 \Rightarrow k \Rightarrow 13$ $-8 \Rightarrow l \Rightarrow 10$	$-20 \Rightarrow h \Rightarrow 17$ $-13 \Rightarrow k \Rightarrow 13$ $-8 \Rightarrow l \Rightarrow 10$	$-17 \Rightarrow h \Rightarrow 20$ $-13 \Rightarrow k \Rightarrow 13$ $-10 \Rightarrow l \Rightarrow 8$
Refinement					
Refinement on	F^2	F^2	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.061, 0.147, 1.17	0.075, 0.177, 1.17	0.090, 0.221, 1.21	0.087, 0.208, 1.19	0.074, 0.199, 1.19
No. of reflections	2973	2955	2946	2920	2905
No. of parameters	275	380	380	381	275
H-atom treatment	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0579P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.053P)^2 + 0.336P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0642P)^2 + 0.6021P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0579P)^2 + 0.8067P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0835P)^2 + 0.0971P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$	0.001	0.002	0.001	0.002	0.001
$\Delta\rho_{\rm max}$, $\Delta\rho_{\rm min}$ (e Å^{-3})	0.10, −0.12	0.12, −0.11	0.12, −0.14	0.12, −0.13	0.16, −0.21
Extinction method	None	None	None	*SHELXL*	None
Extinction coefficient	–	–	–	0.042 (10)	–

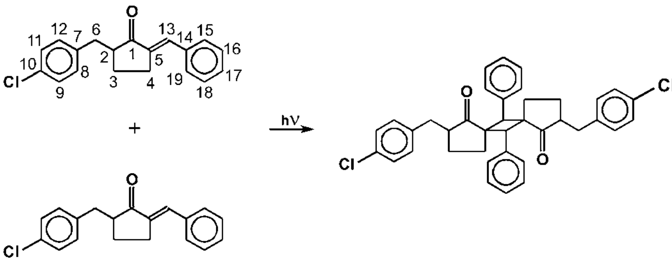
Computer programs: *KM*-4 *CCD* (Kuma Diffraction, 2000), *SHELXS*97 (Sheldrick, 1990), *SHELXL*97 (Sheldrick, 1997), *ORTEP*3 (Johnson *et al.*, 1997).

analysed. In this paper we monitor molecules in a crystal of 5-benzylidene-2-(4-chlorobenzyl)cyclopentanone, (1). The aim of this study is not only to learn the structural changes occurring in (1), but also to discover the general rules describing the changes and the behaviour of molecules during photo-induced transformations in crystals.

The topotactic reaction of (1) was discovered by Jones *et al.* (1980). Compound (1) and the product of its photoreaction were studied by Theocharis *et al.* (1981) and Jones & Theocharis (1984). It is worth adding that many systems related to benzylidenecyclopentanones are photoreactive (Honda *et al.*, 1999; Nakanishi, Jones & Thomas, 1980; Nakanishi *et al.*, 1981; Theocharis, Desiraju & Jones, 1984; Theocharis, Jones *et al.*, 1984).

2. Experimental

A crystal of (1) was irradiated with UV–vis radiation in steps, after which X-ray data collection and the subsequent structure determination process were performed. The crystallization, the irradiation and the X-ray diffraction experiments were carried out in the dark. All the irradiations and X-ray experiments were performed on the same crystal. The crystal was irradiated by an Hg 100 W lamp with a BG-39 glass filter using a fibre with a maximum transmittance of *ca* 495 nm and a half-intensity width of *ca* 230 nm. The intensities of the reflections were collected by an area-detector (CCD camera) diffractometer. The general strategy of the data collections used for the area-detector diffractometers was described by Scheidt & Turowska-Tyrk (1994). The cell constants were determined on the basis of the representative part of the reflections (Kuma Diffraction, 2000). The data were corrected for Lorentz and polarization effects (Kuma Diffraction, 2000). The structures were solved with *SHELXS*97 (Sheldrick, 1990) and refined with *SHELXL*97 (Sheldrick, 1997) (full-matrix least-squares on F^2). Substrate/product disorder was a feature of all the crystal structures. The percentage of the dimer (and of the monomer) in the crystal was determined during the refinement process. For the crystals containing 32, 50, 54 and 78% of the dimer, the molecules of the substrate and of the product were treated anisotropically. For the crystals containing 6, 12, 90 and 96% of the dimer, the minor component was refined isotropically. H atoms were taken into consideration for the molecules treated anisotropically. The disorder required restraints and constraints of geometric and thermal parameters. The following possibilities from *SHELXL*97 (Sheldrick, 1997) were applied: DFIX, DANG, FLAT, AFIX, SADI and SIMU. It is necessary to add here that the $\mathrm{C}5M\cdots\mathrm{C}5D$ distance was in the range 1.02–1.14 Å and $\mathrm{C}13M\cdots\mathrm{C}13D$ in the range 1.07–1.36 Å for the stages studied of the phototransformation of (1) [see (I) for the atom-labelling scheme]. These distances are large enough to indicate that the analysed atoms are well separated and that the $\mathrm{C}5M\cdots\mathrm{C}13M^{\mathrm{i}}$ distance [(i) $2-x, -y, 2-z$] is not influenced significantly, if at all, by features of the disordered structure refinements. Selected experimental data are given in Table 1 for five of the refinements; data for the other refinements are given in the supplementary material.[2]



(I)

3. Results and discussion

Scheme (I) presents a scheme for the [2 + 2]-photodimerization of 5-benzylidene-2-(4-chlorobenzyl)cyclopentanone, (1). Fig. 1 shows two monomer molecules superimposed onto one dimer molecule in a crystal of the 50% photoreaction process, *i.e.* in a crystal containing 50% of the dimer. As for other photodimerization stages, the two substrate molecules are related by an inversion centre. The inversion centre is preserved when the molecules dimerize. As can be seen, the position and overall shape of the dimer molecule are very similar to the position and overall shape of the pair of monomers existing in the crystal. The main difference is in the middle part of the species, *i.e.* the reacting atoms and their neighbours.

The relationship between the percentage content of the dimer in the crystal and the length of the UV–vis irradiation is presented in Fig. 2. It should be emphasized here that each point in Fig. 2, and also in the following figures, refers to one structure of the actual mixed crystal exhibiting the actual substrate/product disorder. The small amount of the dimer observed in the crystal before UV–vis irradiation may be a result of the influence of daylight during the choice of the crystal for the X-ray diffraction experiments or a result of the cocrystallization of a small amount of the dimer together with the monomer. The crystal structures of the pure monomer and the pure dimer were given by Jones & Theocharis (1984) and Theocharis *et al.* (1981).

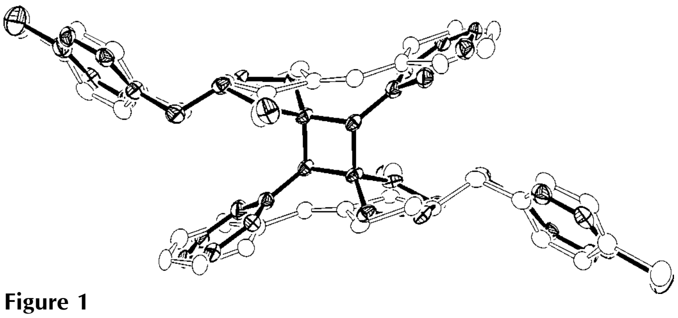


Figure 1
*ORTEP*3 (Johnson *et al.*, 1997) view of two monomer molecules (empty bonds and ellipsoids) superimposed on the dimer molecule (filled bonds and shaded ellipsoids) for the crystal at 50% of the photodimerization process. Thermal ellipsoids are drawn at the 20% probability level. H atoms have been omitted for clarity.

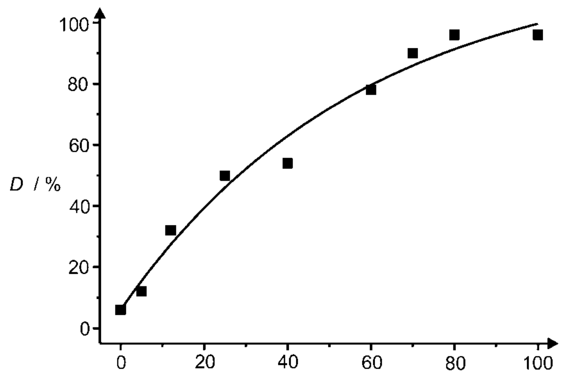


Figure 2
The dependence of the percentage of the dimer in the crystal on the time of UV–vis irradiation. The observed relation can be described by the exponential equation $D = 120\,(16) - 114\,(15)\exp[-t/58\,(17)]$ with the correlation coefficient $r = 0.991$. The numbers in parentheses represent the standard uncertainty in the last digits.

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[2] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK0133). Services for accessing these data are described at the back of the journal.

In order to check if the [2 + 2]-photodimerization stops in a crystal of (1) after removal of the UV–vis radiation source, we made two data collections: the first, as usual, immediately after the irradiation and the second after *ca* 24 h. The crystal structure analysis revealed the same dimer content in the crystal for both data collections. Such stability of the crystal of (1) after the UV–vis irradiation was very useful since it enabled high-quality X-ray data collections for the structure determinations.

Fig. 3 shows the variation in cell constants and cell volume with a change in the dimer content in the crystal. It should be emphasized here that a change in the parameters is presented *versus* a change in the dimer content in the crystal, not *versus* only the time of UV–vis irradiation. As can be seen, the cell volume decreases gradually during the photodimerization process. It is interesting that the decrease is observed from the beginning of the phototransformation. In the case of 5-benzylidene-2-benzylcyclopentanone, the cell volume first increased and then decreased gradually (Nakanishi, Jones, Thomas, Hursthouse *et al.*, 1980; Nakanishi *et al.*, 1981). In the case of the 5-benzylidene-2-(4-bromobenzyl)cyclopentanone crystal, the cell volume was virtually constant during the

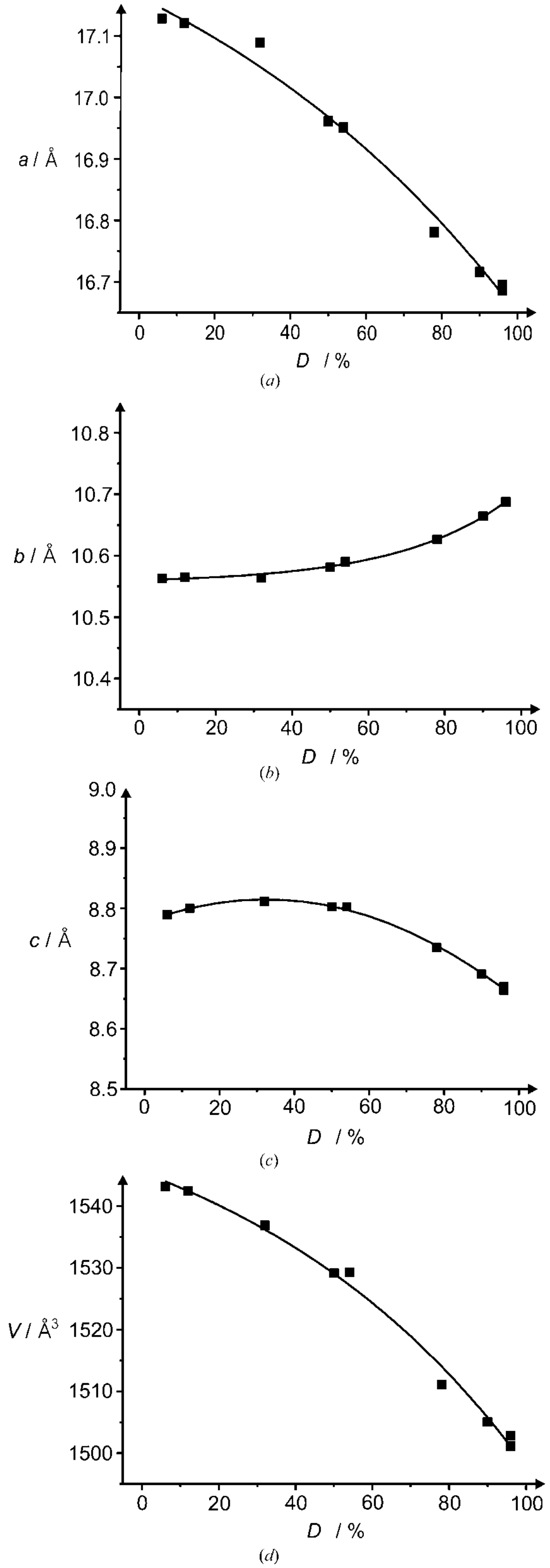

Figure 3
The dependence of (*a*)–(*c*) the cell constants and (*d*) the cell volume on the photoreaction process. The observed relations can be described by the equations (*a*) a = 17.5 (2) − 0.3 (2)exp[D/101 (38)], r = 0.994, (*b*) b = 10.555 (3) + 0.005 (1)exp[D/29 (2)], r = 0.998, (*c*) c = 8.777 (3) + 0.0024 (2)D − 3.7 (1) × $10^{-6}D^2$, r = 0.999, (*d*) V = 1564 (9) − 18 (8)exp[D/78 (19)], r = 0.996. The numbers in parentheses represent the standard deviations in the last digits.

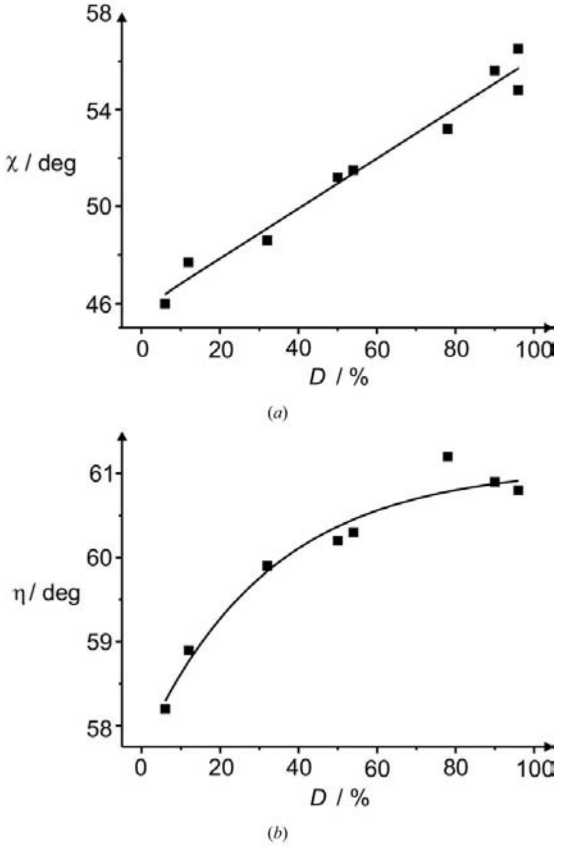

Figure 4
The variation in the angle formed by (*a*) the O1M—C1M—C5M—C13M and xy planes (the χ angle), and (*b*) the C5D—C13D—C5$D^{\rm i}$—C13$D^{\rm i}$ [(i) $2-x, -y, 2-z$] and xy planes (the η angle) with the photodimerization process. Relation (*a*) can be described by the equation χ = 45.8 (4) + 0.103 (7)D with r = 0.986; (*b*) can be described by the relation η = 61.1 (2) − 3.4 (3)exp[−D/32.3 (7)] with r = 0.982. The numbers in parentheses represent the standard deviations in the last digits.

photodimerization process (Nakanishi *et al.*, 1981). The dependences given in the above-mentioned references were related only to the length of UV–vis irradiation not to the dimer percentage content.

Analysis of the crystal structures being determined for several stages of the photodimerization of (1) revealed very interesting behaviour for the substrate and the product molecules. The molecules change their orientation slightly during the photoreaction process. Fig. 4(*a*) shows the variation in the angle formed by the O1*M*—C1*M*—C5*M*—C13*M* and *xy* planes (the χ angle) with a variaion in the dimer content of the crystal. Similar relations were also observed for the *xz* and *yz* planes. We analysed the O1*M*—C1*M*—C5*M*—C13*M* plane because it is almost planar and is formed by atoms of the middle part of the molecule, which is not as deformable as the torsion angles in the border parts might be (Kitaigorodsky, 1973; Krygowski & Turowska-Tyrk, 1987). In the case of the dimer we monitored the angle between the cyclobutane ring and the *xy* plane (the η angle) (Fig. 4*b*). Changes of this type were also observed for the [2 + 2]-photodimerization of 5-benzylidene-2-benzylcyclopentanone (Turowska-Tyrk, 2001).

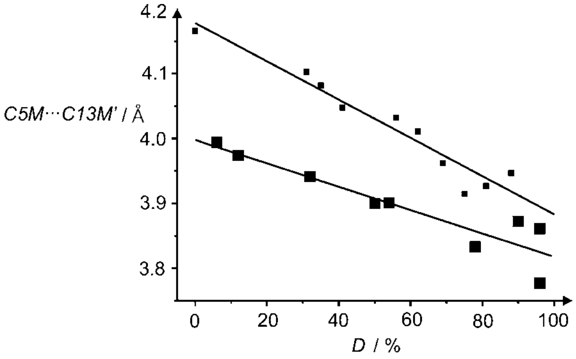

Figure 5
The variation in distance between the reaction centres of the adjacent monomer molecules with the variation in dimer content. The dependence of (1) (the bottom line) can be described as follows: $(C5M\cdots C13M^{i}) = 4.00\,(2) - 0.0018\,(3)D$ with $r = 0.922$. The numbers in parentheses represent the standard deviations in the last digits.

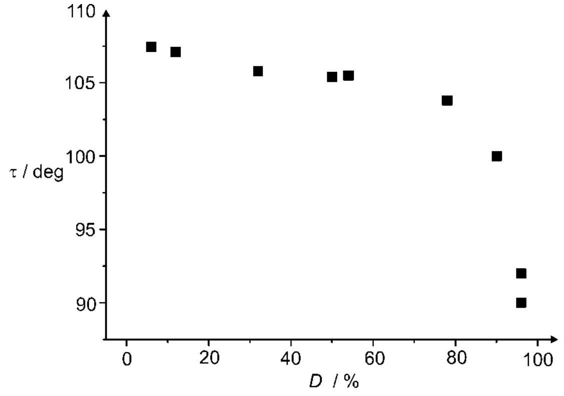

Figure 6
The variation in C13*M*—C5*M*···C13*M*^{i} angle (τ) with the phototransformation process.

The next aspect that we monitored deals with the influence of the product molecules on the substrate molecules. Fig. 5 shows the variation in the distance between two adjacent monomers with the crystal phototransformation process. The bottom line concerns a crystal of (1) and the upper line is for 5-benzylidene-2-benzylcyclopentanone and is taken from Turowska-Tyrk (2001). As can be seen, the more product present in the crystal the smaller the distance between the substrate molecules. Nevertheless, the monomer molecules do not move closer than the sum of the van der Waals radii (Bondi, 1964). The observed relation can be explained in the following way: the product molecules, being smaller than a pair of substrate molecules, cause stresses in the crystal that result in the monomers moving closer. It is interesting that the lines in Fig. 5 are not parallel. The greater slope for the 5-benzylidene-2-benzylcyclopentanone crystal indicates the stronger influence of the dimer molecules and/or the greater sensitivity of the monomers.

The variation of the distance between the reaction centres of the substrate molecules is not the only symptom of the influence of the product on the substrate. The remarkable dependence is shown in Fig. 6. The figure presents the variation in the C13*M*—C5*M*···C13*M*^{i} angle (the τ angle), formed by the adjacent monomer molecules, with an increase in product content. The same relation is also observed for the C5*M*^{i}···C13*M*—C5*M* angle. As can be seen, the angle changes from the initial values of *ca* 107 to 90° for the final stages of the crystal phototransformation, which indicates that the two C=C bonds move towards each other to form the cyclobutane ring.

4. Conclusions

We monitored the structural changes in a crystal of 5-benzylidene-2-(4-chlorobenzyl)cyclopentanone (1) during [2 + 2]-photodimerizaton by means of X-ray diffraction. It was observed that the monomer molecules moved gradually from the position adopted in the crystal at the initial stage of the phototransformation and the dimers moved towards the position occupied at the final stage. The movements of the molecules possess a rotational component. Moreover, during the phototransformation the monomers change their mutual orientation and in the final stages adopt an orientation resembling the dimer. In addition, the monomers gradually come closer to each other. The behaviour of the molecules in a crystal of (1) and also the variation in cell constants were compared with the data for 5-benzylidene-2-benzylcyclopentanone.

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