Monitoring structural transformations in crystals. 6.[1] The [4 + 4] photodimerization of 9-methyl-anthracene

Ilona Turowska-Tyrk* and **Elżbieta Trzop**

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

Correspondence e-mail: ilona.turowska-tyrk@pwr.wroc.pl

The structural changes in a crystal of 9-methylanthracene (1) during the [4 + 4] photodimerization were monitored by means of X-ray diffraction. This is the first example in the literature of such a study of a [4 + 4] photodimerization. The results obtained were compared with data for the [2 + 2] photodimerization. The shape of the product molecules and their preferred packing can explain the crystal disintegration. This was the reason that the reaction was monitored only to 28% completion. As far as could be determined the reaction proceeds with a constant rate. The cell volume increases at the beginning of the transformation and decreases afterwards. The product molecules do not assume a fixed position in the crystal during the photo-reaction, but move in a smooth way that includes a rotational component. The movements of the reactant are much smaller. Movements of molecules characterized by a rotational component were also observed in the case of the [2 + 2] photodimerization of 5-benzylidene-2-benzylcyclopentanone and 5-benzylidene-2-(4-chlorobenzyl)-cyclopentanone. The distance between the reacting atoms of the adjacent monomer molecules of (1) decreases with the degree of reaction completion, but more slowly than in the case of the [2 + 2] photodimerizations cited above. The orientation of the neighbouring monomer molecules changes during the phototransformation so that the monomer pair resembles the dimer product.

1. Introduction

The photochemical reactions proceeding in crystals have been known for a very long time. In recent years the interest in them has increased significantly. Nevertheless, the crystallographic structural studies of the photo-reactions were usually limited to a comparison of structures of pure reactant and pure product crystals (Anderson *et al.*, 1979; Ehrenberg, 1968; Guru Row *et al.*, 1983; Harada *et al.*, 1995, 1996; Jones & Theocharis, 1984; Suzuki *et al.*, 1994; Theocharis & Jones, 1984, 1985; Theocharis *et al.*, 1981; Wang & Jones, 1987). In some cases the structures of mixed reactant–product crystals were given as evidence that the photo-reactions had proceeded (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 *et al.*, 1984; Yamamoto *et al.*, 2003*a,b*) and sometimes they were an important component of the analysis of the photochemical aspects (Hosomi *et al.*, 2000; Ohba *et al.*, 2001). Mixed-crystal structures were examined for several stages of the racemization induced by X-rays (Ohashi, 1988; Ohashi *et al.*, 1993) and the following thermal reactions: isomerization (Bogadi *et al.*, 2002), [4 + 2] dimerization (Kim,

---

[1] Part 5: Turowska-Tyrk (2003).

research papers

Hubig *et al.*, 2001; Kim, Lindeman & Koch, 2001) and polymerization (Foley *et al.*, 1999). Recently, studies of the changes in the crystal structures for many stages of the photo-induced [2 + 2] dimerization were carried out (Turowska-Tyrk, 2001, 2003).

In this part of the series we broaden our studies to include [4 + 4] photodimerization [see (I) for the equation of the reaction]. The aim of this article is to discover the structural changes proceeding during [4 + 4] photodimerization of a compound and to compare them with the data for the [2 + 2] photodimerization [see upper part of (I)]. 9-Methylanthracene (1) was chosen for study. It had been reported that it under-

goes the photoreaction in a solid state (Bart & Schmidt, 1971; Heller & Schmidt, 1971).

(I)
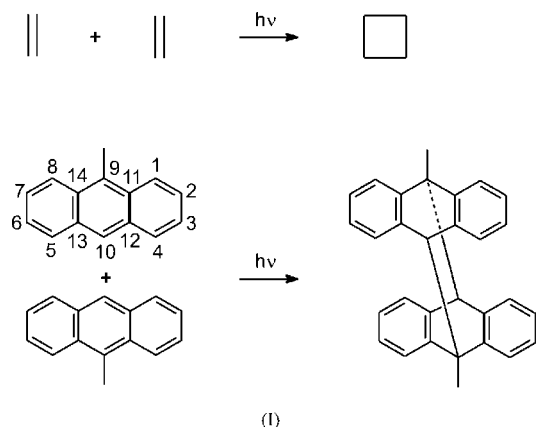
It is worth adding that in the case of the cited references the structures were analysed for crystals having molecules in a ground state. The recent development of time-resolved techniques has also enabled studies of the structures for an excited state (Kim *et al.*, 2002; Moffat, 2001; Ren *et al.*, 1999; Techert *et al.*, 2001).

2. Experimental

A crystal of (1) was irradiated in steps, after each of which X-ray data were collected and the structure determined. The crystallization, the irradiation and the X-ray diffraction experiments were carried out in the dark. All the X-ray experiments were carried out on the same crystal. The crystal was irradiated by a 445 nm line (of width 10 nm) from a Xe 150 W lamp. We decided to use this line because wavelengths of higher energy caused crystal damage (cracking; Enkelmann *et al.*, 1993; Novak *et al.*, 1993*a,b*) and wavelengths of lower energy did not bring about the reaction. The intensities of the reflections were collected by means of 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). For mixed crystals, *i.e.* crystals containing the reactant and the product molecules, the atomic coordinates for the monomer were taken from the parent crystal. The first atoms of the dimer were found in a difference-Fourier synthesis and the positions of the remaining ones were calculated geometrically. The percentage of the product and of the reactant in the crystal was determined during the refinement process. The molecules of the monomer and the dimer in the mixed crystals were described anisotropically and isotropically, respectively. H atoms were taken into consideration with constraints for the monomer molecules for all the reac-
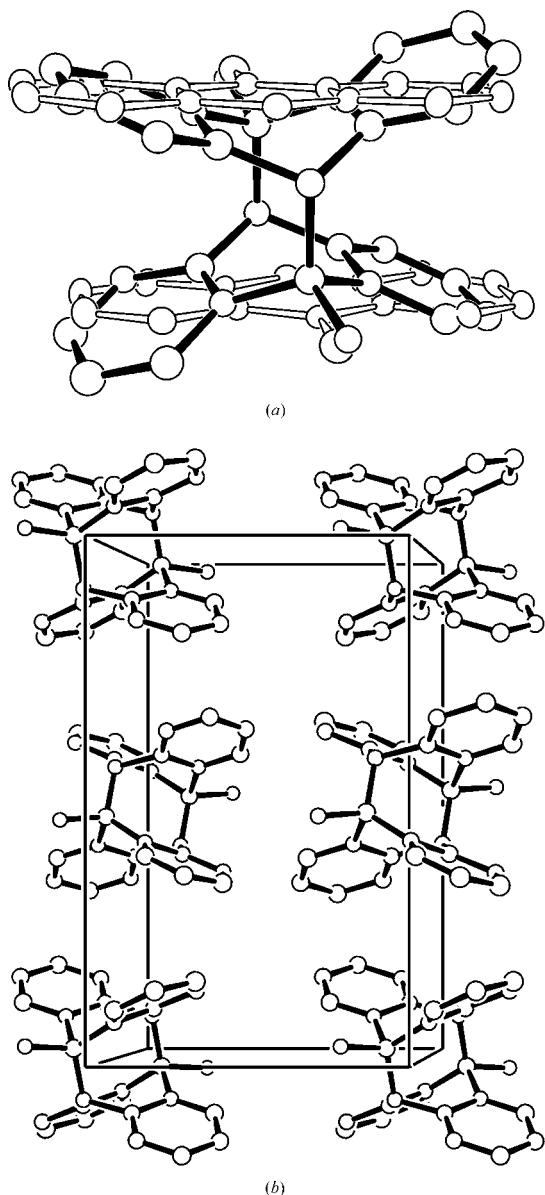
Figure 1
(*a*) *ORTEP*3 (Johnson *et al.*, 1997) view of the product molecule (filled bonds) superimposed on two reactant molecules (empty bonds) for the mixed crystal containing 24% of the product. (*b*) A fragment of the crystal lattice (dimer molecules only) is also shown. The H atoms were omitted for clarity. The displacement ellipsoids were drawn at the 10% probability level.

Table 1
Experimental details.

	8%D	15%D	24%D	100%D
Crystal data				
Chemical formula	$C_{15}H_{12}$	$C_{15}H_{12}$	$C_{15}H_{12}$	$C_{30}H_{24}$
M_r	192.25	192.25	192.25	384.49
Cell setting, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
a, b, c (Å)	8.8718 (13), 14.587 (2), 8.0776 (12)	8.8574 (16), 14.556 (3), 8.1209 (15)	8.8359 (17), 14.519 (3), 8.1512 (19)	9.7650 (13), 13.6035 (19), 8.1177 (10)
β (°)	96.489 (15)	96.58 (2)	96.74 (2)	113.308 (15)
V (Å^3)	1038.6 (3)	1040.1 (3)	1038.5 (4)	990.3 (2)
Z	4	4	4	2
D_x (Mg m^{-3})	1.229	1.228	1.230	1.289
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	500	500	500	958
θ range (°)	4–22	4–22	4–22	4–22
μ (mm^{-1})	0.07	0.07	0.07	0.07
Temperature (K)	293 (2)	293 (2)	293 (2)	293 (2)
Crystal form, colour	Plate, pale yellow	Plate, pale yellow	Plate, pale yellow	Plate, colorless
Crystal size (mm)	$0.50 \times 0.35 \times 0.20$	$0.50 \times 0.35 \times 0.20$	$0.50 \times 0.35 \times 0.20$	$0.32 \times 0.15 \times 0.12$
Data collection				
Diffractometer	Kuma KM4CCD	Kuma KM4CCD	Kuma KM4CCD	Kuma KM4CCD
Data collection method	ω scans	ω scans	ω scans	ω scans
Absorption correction	None	None	None	None
No. of measured, independent and observed reflections	3389, 1942, 1171	3414, 1942, 1044	3122, 1752, 953	3166, 1695, 1000
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.028	0.035	0.045	0.071
θ_{max} (°)	26.0	26.0	25.0	26.0
Range of h, k, l	$-10 \Rightarrow h \Rightarrow 10$	$-10 \Rightarrow h \Rightarrow 10$	$-10 \Rightarrow h \Rightarrow 10$	$-12 \Rightarrow h \Rightarrow 12$
	$-17 \Rightarrow k \Rightarrow 16$	$-17 \Rightarrow k \Rightarrow 16$	$-17 \Rightarrow k \Rightarrow 16$	$-15 \Rightarrow k \Rightarrow 13$
	$-9 \Rightarrow l \Rightarrow 5$	$-10 \Rightarrow l \Rightarrow 5$	$-9 \Rightarrow l \Rightarrow 4$	$-10 \Rightarrow l \Rightarrow 5$
Refinement				
Refinement on	F^2	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.074, 0.265, 1.15	0.095, 0.352, 1.21	0.109, 0.385, 1.34	0.078, 0.250, 1.07
No. of reflections	1942	1942	1752	1695
No. of parameters	198	198	198	185
H-atom treatment	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement	Refined independently
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1577P)^2 + 0.0018P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.2P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.2P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1425P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	<0.0001	<0.0001	<0.0001	0.001
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.32, −0.19	0.36, −0.19	0.38, −0.20	0.25, −0.22
Extinction method	*SHELXL*	*SHELXL*	*SHELXL*	*SHELXL*
Extinction coefficient	0.009 (12)	0.04 (3)	0.07 (4)	0.07 (2)

Computer programs used: *KM4CCD* (Kuma Diffraction, 2000), *SHELXS*97 (Sheldrick, 1990), *SHELXL*97 (Sheldrick, 1997), *ORTEP*3 (Johnson *et al.*, 1997) .

tion stages and for the dimer only for the crystal of 24, 26 and 28% reaction progress. The reactant–product superposition required the use of restraints and constraints of geometrical and thermal parameters. Their number and type depended on the refinement. The following possibilities from *SHELXL*97 (Sheldrick, 1997) were applied: DFIX, DANG, FLAT, AFIX and SIMU. Selected experimental data are given in Table 1 for four of the refinements; data for all refinements (at 0, 3, 4, 6, 8, 11, 15, 18, 24, 26, 28 and 100%D) are given in the supplementary material.[2]

3. Results and discussion

The equation of the [4 + 4] photodimerization of 9-methyl-anthracene (1) in crystals together with the atom labels is presented in (I). Also shown is a scheme for the [2 + 2] photodimerization, the photoreaction for which the structural changes proceeding in crystals were monitored and described (Turowska-Tyrk, 2001, 2003).

Fig. 1 presents the product molecule (filled bonds) superimposed on two reactant molecules (empty bonds), as found in the crystal containing 24% of the dimer. A fragment of the crystal lattice (product only) is also shown. Adjacent monomer molecules are situated head-to-tail and are related by an inversion centre. The symmetry of the dimer molecule is

research papers

also of this type. At first sight it seems that the overall shapes of the monomers and the dimer are very similar. The comparison of this figure to the analogous one for the [2 + 2] photodimerization of 5-benzylidene-2-benzylcyclopentanone and 5-benzylidene-2-(4-chloro-benzyl)cyclopentanone (Turowska-Tyrk, 2001, 2003) reveals that in the case of the [4 + 4] dimerization of (1), the overall shapes of the molecules differ more significantly. The atoms of one peripheral ring of the dimer moved beyond the borders of the monomer. This fact can be one of the explanations for the crystal cracking during irradiations. The crystal damage was the reason we carried out the reaction only to 28% completion, *i.e.* to 28% of the dimer in the crystal (see §2). Nevertheless, after the single crystals desintegrated the pure dimer was still formed (Heller & Schmidt, 1971). The [2 + 2] photodimerization proceeded to 100% of the product 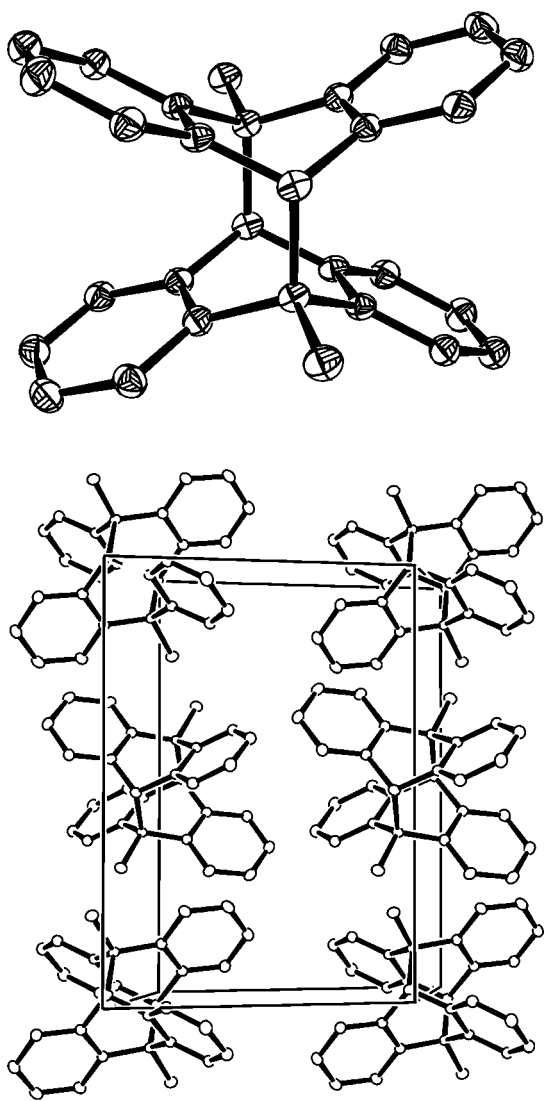without single-crystal damages in the case of 5-benzylidene-2-benzylcyclopentanone (Nakanishi *et al.*, 1981; Turowska-Tyrk, 2001) and 96% (Turowska-Tyrk, 2003) or 100% (Jones & Theocharis, 1984) in the case of 5-benzylidene-2-(4-chlorobenzyl)cyclopentanone.

In order to obtain a crystal of the pure dimer, we irradiated powder of (1) and afterwards recrystallized it. Fig. 2 presents the molecule for the crystal obtained in this way and a fragment of the crystal lattice.

The structure of the pure monomer crystal has been published previously (Bart & Schmidt, 1971; Cox & Sim, 1979), but we redetermined it more precisely. The results are presented in Fig. 3.

The comparison of Figs. 1 and 2 shows that although the mixed reactant–product crystal and the pure product belong to the same space group ($P2_1/c$), the dimers in the crystals are situated in a slightly different way. Additionally, the cell constants for the pure monomer and for the pure dimer are
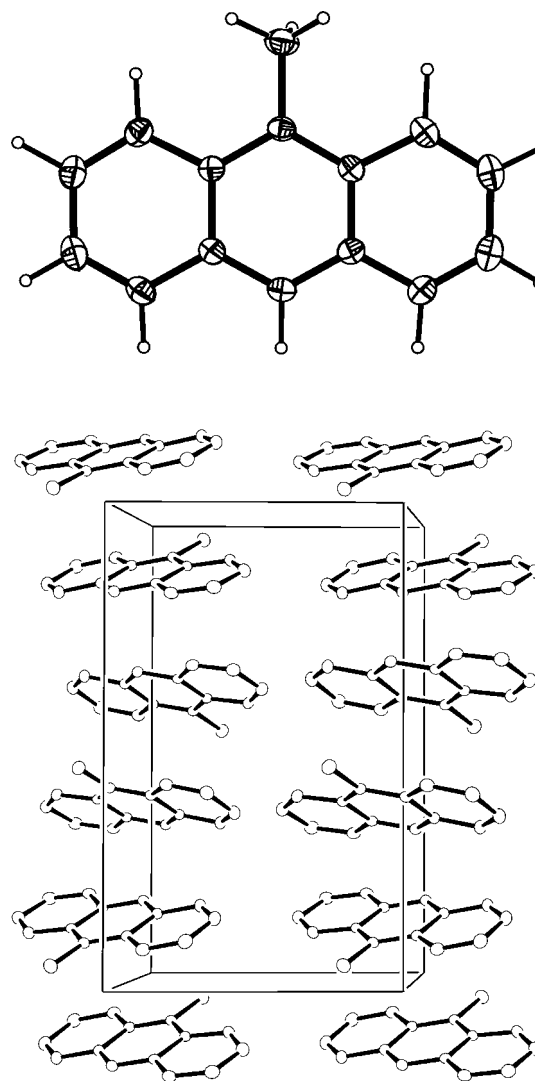

Figure 2
*ORTEP*3 (Johnson *et al.*, 1997) view of the molecule in the pure dimer crystal; a fragment of the crystal lattice is also shown. The displacement ellipsoids were drawn at the 20 and 10% probability levels, respectively. The H atoms were omitted for clarity.

Figure 3
*ORTEP*3 (Johnson *et al.*, 1997) view of the molecule in the pure monomer crystal and of a fragment of the crystal lattice. The displacement ellipsoids were drawn at the 20 and 10% probability level, respectively.

Table 2
The mutual orientation parameters.

Compound	d (Å)	α (°)	τ (°)	φ (°)	κ (°)
(1)	3.859	108.2	0	0	74.3
5-Benzylidene-2-benzyl-cyclopentanone	4.188	111.4	0	0	85.6
5-Benzylidene-2-(4-chloro-benzyl)cyclopentanone	4.027	109.7	0	0	86.7
Ideal values	<4.2	90	0	0	90

different (see Table 1). These differences can also explain the tendency of crystals of (1) to disintegrate.

The mutual orientation of monomers adjacent in the crystal is not ideal for the [4 + 4] photodimerization; the molecules are shifted relative to each other. The orientation of the molecules of the anthracene derivatives in crystals can be described in a quantitative way by the following parameters:

(i) α: C9$\cdots$C10$\cdots$C9^i and C10$\cdots$C9$\cdots$C10^i angles [(i) $2 - x, 1 - y, -z$]; see (I) for the labels of atoms. The ideal value is 90°.

(ii) φ: the angle between the middle rings of the adjacent monomer molecules. The ideal value is 0°.

(iii) τ: the torsion angles C9$\cdots$C10$\cdots$C9$^i\cdots$C10^i and C10$\cdots$C9$\cdots$C10$^i\cdots$C9^i. The ideal value is 0°.

(iv) κ: the angle between the plane of the middle ring of the parent molecule and the plane formed by C9, C10, C9^i and C10^i atoms. The ideal value is 90°.

(v) d: C9$\cdots$C10^i and C10$\cdots$C9^i distances. The ideal value is <4.2 Å (Wang & Jones, 1994; Ihmels *et al.*, 2000).

Some of these parameters, defined as above or similarly, were already proposed for the [2 + 2] photodimerization (Gnanaguru *et al.*, 1985) and the [4 + 4] photodimerization in crystals (Wang & Jones, 1994; Ihmels *et al.*, 2000). Table 2 gives the values of these parameters for the pure monomer crystal of (1) and also, for comparison, the values for 5-benzylidene-2-benzylcyclopentanone and 5-benzylidene-2-(4-chlorobenzyl)-cyclopentanone, which both undergo a single-crystal-to-single-crystal phototransformation. As can be seen, the d distance is smaller and the κ parameter has a slightly less preferable value in the case of (1). This comparison may indicate that the monomer movements necessary for reaction are not the reason for the cracking of (1), since in the case of the examined cyclopentanones the movements are not much different, but crystal disintegration was not observed.

Fig. 4 presents the dependence between the content of the product molecules in the crystal, D, and the time of the irradiation, t. The percentage of the product was calculated during the crystal structure refinement. It would also be useful to have points for longer irradiation times. Unfortunately, the quality of the structures for the longer times were not satisfactory. The observed relation is linear in the experimentally available region and can be described by the following equation

$$\%D = 1.75\,(5)t + 0.9\,(4)$$

with the correlation coefficient $r = 0.997$.

An exponential dependence of reaction progress on irradiation time was observed in the case of the [2 + 2] photodimerization of 5-benzylidene-2-benzylcyclopentanone and 5-benzylidene-2-(4-chlorobenzyl)cyclopentanone (Turowska-Tyrk, 2001, 2003). Nevertheless, if for the crystal of the latter compound we take into account only points to 50% reaction progress, the relation D versus t can also be described by the linear function with the correlation coefficient $r = 0.988$. In the case of 5-benzylidene-2-benzylcyclopentanone it is not reasonable to make such calculations because too few points are available.

In order to check if the [4 + 4] photodimerization of (1) stopped after the removal of the source of the radiation and the dimer content was a function of the irradiation time only, we carried out two data collections in the following way: the first, as usual, immediately after the irradiation and the second one after 24 h. The structure determinations showed that the percentage of the dimer in the crystal was exactly the same in both cases.

Fig. 5 presents the variation in cell constants and cell volume of a crystal of (1) with irradiation time. For a more accurate comparison the range of the axes was the same for Figs. 5(a)–5(c). The cell constants change in a complex way. The b parameter is constant in the first stages of the photoreaction, whereas a and c change from the start. The a and b constants decrease and c increases. The β angle does not change at the beginning of the photoreaction, but afterwards it slowly increases. The cell volume changes in an interesting way: it increases in the first several stages and decreases afterwards. A dependence of this type was also observed for the [2 + 2] photodimerization of 5-benzylidene-2-benzyl-cyclopentanone (Nakanishi *et al.*, 1980, 1981), but it should be added that in the case of 5-benzylidene-2-(4-chlorobenzyl)cyclopentanone the volume decreased from the beginning of the photoreaction (Nakanishi *et al.*, 1981; Turowska-Tyrk, 2003) and for 5-benzylidene-2-(4-bromobenzyl)cyclopentanone it was almost constant (Nakanishi *et al.*, 1981). Unfortunately, for the [4 + 4] photodimerization the
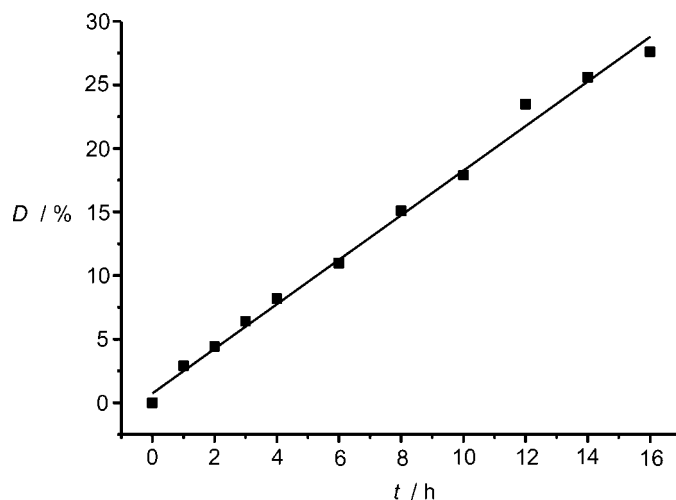

Figure 4
The relationship between the fraction of the dimer molecules in the crystal and the time of the irradiation.
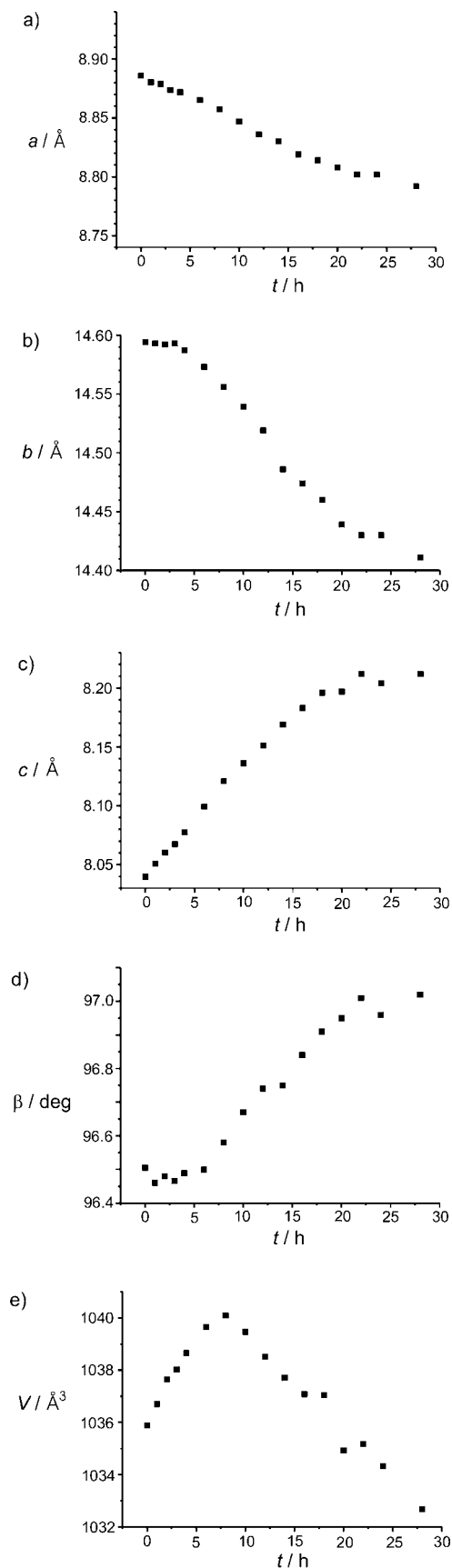
Figure 5
The variation of the cell constants and the cell volume in a crystal of (1) with the irradiation time.

relations between cell constants and the time of the irradiations are unknown.

Our studies showed that the dimer molecules did not assume a fixed position in the crystal during the reaction, but moved smoothly. The movements included a rotational component. Fig. 6 presents the variation in the dimer orientation with the reaction progress, namely the variation in the angle between the C9D, C10D, C9D^i, C10D^i plane [(i) $2 - x, 1 - y, -z$] and xy, xz and yz planes, respectively. We considered the C9D, C10D, C9D^i, C10D^i plane because it was formed by the internal atoms which were not so influenced by the environment as the peripheral atoms of the molecule could
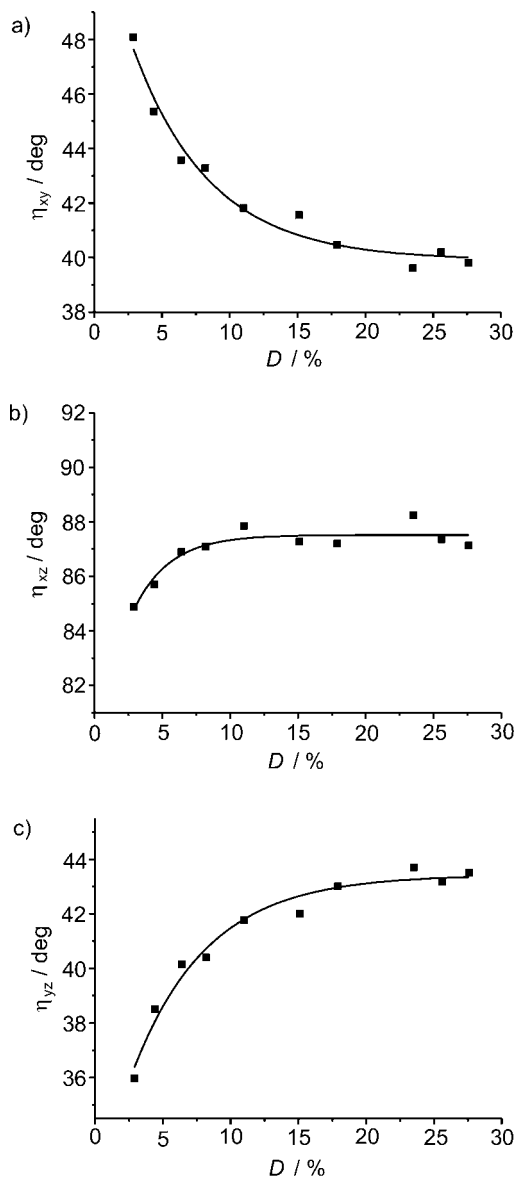

Figure 6
The variation of the angle between the C9D, C10D, C9D^i, C10D^i plane [(i) $2 - x, 1 - y, -z$] and the (a) xy, (b) xz and (c) yz planes. For better comparison the range of the axes was set to be the same. The relations were described by the following equations: $\delta_{xy} = 39.9\ (3) + 12.9\ (13)\exp[-D/5.7\ (9)]$ with $r = 0.987$; $\delta_{xz} = 43.4\ (3) - 12.0\ (12)\exp[-D/5.5\ (9)]$ with $r = 0.988$; and $\delta_{yz} = 87.52\ (18) - 8\ (3)\exp[-D/2.7\ (9)]$ with $r = 0.932$.

be. In the case of the pure dimer crystal the angles δ_{xy}, δ_{xz} and δ_{yz} mentioned are: 52.2, 77.7 and 19.8°, respectively. These values and Fig. 6 indicate in a quantitative way that the orientation of the dimer in the mixed crystals and in the pure dimer crystal differ greatly.

The movements of the monomer were monitored by the angles between the molecule plane, and xy, xz and yz planes, but they were much smaller (*ca* 0.5°) than for the dimer. Nevertheless, even for them we observed certain trends.

The movements of the dimers and the monomers having a rotational component were also observed in the case of the [2 + 2] photodimerization of 5-benzylidene-2-benzylcyclopentanone and 5-benzylidene-2-(4-chlorobenzyl)cyclopentanone (Turowska-Tyrk, 2001, 2003).

We analysed the influence of the dimer molecules on the monomers during the crystal phototransformation. Fig. 7(*a*) presents the variation in the distance between the directly reacting atoms of two monomer molecules, C9$M\cdots$C10M^{i} [(i) $2 - x, 1 - y, -z$], with the photoreaction progress. The line 1 is for compound (1) and lines 2 and 3 are for the [2 + 2] photodimerization of 5-benzylidene-2-(4-chlorobenzyl)cyclopentanone (Turowska-Tyrk, 2003) and 5-benzylidene-2-benzylcyclopentanone (Turowska-Tyrk, 2001), respectively. As can be seen from Fig. 7(*a*) the lines are not parallel. Relation 1 can be described by the following equation

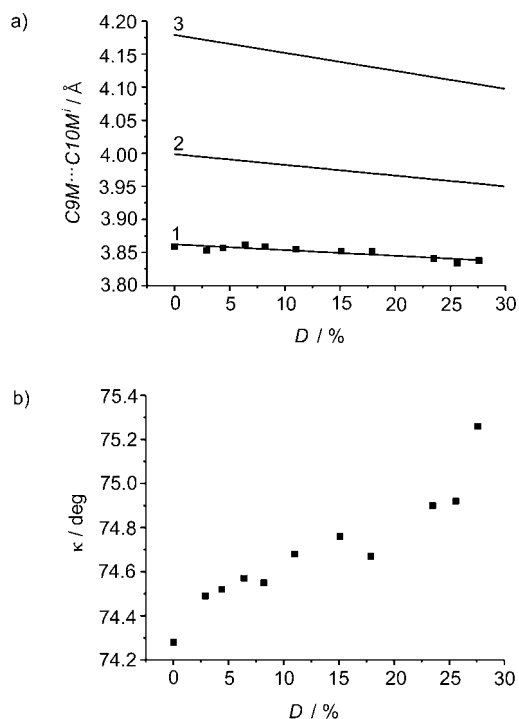$$d = 3.862\,(2) - 0.00086\,(15)D,\ r = 0.89,$$

a)

b)

Figure 7
(*a*) The variation in the distance between the reacting atoms of two adjacent monomer molecules, C9$M\cdots$C10M^{i} [(i) $2 - x, 1 - y, -z$], with the dimer content for (1) – line 1. The lines 2 and 3 are for the [2 + 2] photodimerization of 5-benzylidene-2-(4-chlorobenzyl)cyclopentanone and 5-benzylidene-2-benzylcyclopentanone, respectively. (*b*) The variation in the κ mutual orientation parameter with the dimer content for (1).

where d is the distance between the reacting atoms of the adjacent monomer molecules and D is the dimer content in the crystal.

The relations 2 and 3 were described as follows (Turowska-Tyrk, 2001, 2003)

$$d = 4.00\,(2) - 0.0018\,(3)D,\ r = 0.922$$

and

$$d = 4.18\,(2) - 0.0030\,(3)D,\ r = 0.968,$$

respectively.

The slope for the first line is different from the slopes for the second and third lines at the 3σ probability level, *i.e.* with the probability 99.7%. The above three equations indicate that the power of the influence of the dimer molecules on the monomers or/and the sensitivity of the monomer molecules decrease in the following order: 3, 2, 1. The intermolecular distances between the reacting adjacent monomers decrease in the same order.

The variation in the intermolecular distance between the reacting atoms is not the only symptom of the influence of the product molecules on the reactants. Fig. 7(*b*) presents the dependence of κ, the mutual orientation parameter of the monomer molecules, on the dimer content in the crystal. The following relation can be observed: the greater the per cent dimer, the closer the κ angle is to the ideal value, *i.e.* 90° observed for the dimer molecule. The change, which is smaller, was found for the a orientation parameter. Similar effects were also observed in the case of 5-benzylidene-2-(4-chlorobenzyl)cyclopentanone (Turowska-Tyrk, 2003).

4. Conclusions

We monitored the structural changes in a crystal of 9-methylanthracene (1) during the [4 + 4] photodimerization by means of X-ray diffraction. This is the first example of such a study for a [4 + 4] photodimerization. We compared the results with the data for the [2 + 2] photodimerization. The following similarities were observed:

(i) the molecules did not take a fixed position in the crystal, but moved in a smooth way as the reaction progressed; the movements included a rotational component;

(ii) the distance between the reacting atoms of the adjacent monomer molecules decreased as the reaction progressed;

(iii) the mutual orientation of the monomers changed towards the one more resembling the dimer.

The following differences were observed:

(i) studies of the [4 + 4] photodimerization of (1) were possible only up to 28% progress because of the crystal cracking; the crystal disintegration of (1) was explained by means of the shape of the reactant and the product molecules and their preferred packing;

(ii) the distance between the reacting atoms of the adjacent monomer molecules changes more slowly with the reaction progress than in the case of the [2 + 2] photodimerization of 5-benzylidene-2-benzylcyclopentanone and 5-benzylidene-2-(4-chlorobenzyl)cyclopentanone.

research papers

References

Anderson, B. F., Ferguson, J., Morita, M. & Robertson, G. B. (1979). *J. Am. Chem. Soc.* **101**, 1832–1840.

Bart, J. C. J. & Schmidt, G. M. J. (1971). *Isr. J. Chem.* **9**, 429–448.

Bogadi, R. S., Levendis, D. C. & Coville, N. J. (2002). *J. Am. Chem. Soc.* **124**, 1104–1110.

Cox, P. J. & Sim, G. A. (1979). *Acta Cryst.* B**35**, 404–410.

Ehrenberg, M. (1968). *Acta Cryst.* B**24**, 1123–1125.

Enkelmann, V., Wegner, G., Novak, K. & Wagener, K. B. (1993). *J. Am. Chem. Soc.* **115**, 10390–10391.

Foley, J. L., Li, L., Sandman, D. J., Vela, M. J., Foxman, B. M., Albro, R. & Ekhardt, C. J. (1999). *J. Am. Chem. Soc.* **121**, 7262–7263.

Gnanaguru, K., Ramasubbu, N., Venkatesan, K. & Ramamurthy, V. (1985). *J. Org. Chem.* **50**, 2337–2346.

Guru Row, T. N., Ramachandra Swamy, H., Ravi Acharya, K., Ramamurthy, V., Venkatesan, K. & Rao, C. N. R. (1983). *Tetrahedron Lett.* **24**, 3263–3266.

Harada, J., Ogawa, K. & Tomoda, S. (1995). *Chem. Lett.* pp. 751–752.

Harada, J., Ogawa, K. & Tomoda, S. (1996). *Mol. Cryst. Liq. Cryst.* **277**, 119–123.

Harada, J., Uekusa, H. & Ohashi, Y. (1999). *J. Am. Chem. Soc.* **121**, 5809–5810.

Heller, E. & Schmidt, G. M. J. (1971). *Isr. J. Chem.* **9**, 449–462.

Hosomi, H., Ohba, S., Tanaka, K. & Toda, F. (2000). *J. Am. Chem. Soc.* **122**, 1818–1819.

Ihmels, H., Leusser, D., Pfeiffer, M. & Stalke, D. (2000). *Tetrahedron*, **56**, 6867–6875.

Johnson, C. K., Burnett, M. N. & Farrugia, L. J. (1997). *ORTEP*3. Windows Version. University of Glasgow, Scotland.

Jones, W. & Theocharis, C. R. (1984). *J. Cryst. Spectrosc. Res.* **14**, 447–455.

Kawano, M., Sano, T., Abe, J. & Ohashi, Y. (1999). *J. Am. Chem. Soc.* **121**, 8106–8107.

Kim, C. D., Pillet, S., Wu, G., Fullagar, W. K. & Coppens, P. (2002). *Acta Cryst.* A**58**, 133–137.

Kim, J. H., Hubig, S. M., Lindeman, S. V. & Kochi, J. K. (2001). *J. Am. Chem. Soc.* **123**, 87–95.

Kim, J. H., Lindeman, S. V. & Kochi, J. K. (2001). *J. Am. Chem. Soc.* **123**, 4951–4959.

Kuma Diffraction (2000). *KM*4*CCD* Software, Version 166. Kuma Diffraction, Wrocław, Poland.

Leibovitch, M., Olovsson, G., Scheffer, J. & Trotter, J. (1998). *J. Am. Chem. Soc.* **120**, 12755–12769.

Moffat, K. (2001). *Chem. Rev.* **101**, 1569–1582.

Nakanishi, H., Jones, W., Thomas, J. M., Hursthouse M. B. & Motevalli, J. M. (1980). *J. Chem. Soc. Chem. Commun.* pp. 611–612.

Nakanishi, H., Jones, W., Thomas, J. M., Hursthouse, M. B. & Motevalli, J. M. (1981). *J. Phys. Chem.* **85**, 3636–3642.

Novak, K., Enkelmann, V., Wegner, G. & Wagener, K. B. (1993*a*). *Angew. Chem.* **105**, 1678.

Novak, K., Enkelmann, V., Wegner, G. & Wagener, K. B. (1993*b*). *Angew. Chem. Int. Ed.* **32**, 1614–1616.

Ohashi, Y. (1988). *Acc. Chem. Res.* **21**, 268–274.

Ohashi, Y., Uchida, A. & Sekine, A. (1993). *Reactivity in Molecular Crystals*, edited by Y. Ohashi, pp. 115–153. Tokyo: VCH.

Ohba, S., Hosomi, H. & Ito, Y. (2001). *J. Am. Chem. Soc.* **123**, 6349–6352.

Ren, Z., Bourgeois, D., Helliwell, J. R., Moffat, K., Srajer, V. & Stoddard, B. L. (1999). *J. Synchrotron. Rad.* **6**, 891–917.

Scheidt, W. R. & Turowska-Tyrk, I. (1994). *Inorg. Chem.* **33**, 1314–1318.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELX*97. University of Göttingen, Germany.

Suzuki, T., Fukushima, T., Yamashita, Y. & Miyashi, T. (1994). *J. Am. Chem. Soc.* **116**, 2793–2803.

Techert, S., Schotte, F. & Wulff, M. (2001). *Phys. Rev. Lett.* **86**, 2030–2033.

Theocharis, C. R., Desiraju, G. R. & Jones, W. (1984). *J. Am. Chem. Soc.* **106**, 3606–3609.

Theocharis, C. R. & Jones, W. (1984). *J. Chem. Soc. Chem. Commun.* pp. 369–370.

Theocharis, C. R. & Jones, W. (1985). *J. Chem. Soc. Faraday Trans. 1*, **81**, 857–874.

Theocharis, C. R., Nakanishi, H. & Jones, W. (1981). *Acta Cryst.* B**37**, 756–758.

Turowska-Tyrk, I. (2001). *Chem. Eur. J.* **7**, 3401–3405.

Turowska-Tyrk, I. (2003). *Acta Cryst.* B**59**, 670–675.

Wang, W. N. & Jones, W. (1987). *Tetrahedron*, **43**, 1273–1279.

Wang, W. N. & Jones, W. (1994). *Mol. Cryst. Liq. Cryst.* **242**, 227–240.

Yamamoto, S., Matsuda, K. & Masahiro, I. (2003*a*). *Angew. Chem.* **115**, 1674–1677.

Yamamoto, S., Matsuda, K. & Masahiro, I. (2003*b*). *Angew. Chem. Int. Ed.* **42**, 1636–1639.