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# Monitoring structural transformations in crystals. 7. 1-Chloroanthracene and its photodimer[1]

**Ilona Turowska-Tyrk* and Karolina Grześniak**

Department of Chemistry, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland
Correspondence e-mail: ilona.turowska-tyrk@pwr.wroc.pl

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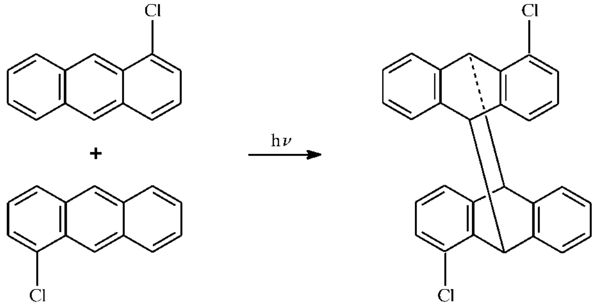
Crystals of the 1-chloroanthracene photodimer, *viz. trans*-bi(1-chloro-9,10-dihydro-9,10-anthracenediyl), $C_{28}H_{18}Cl_2$, were obtained from the solid-state [4+4]-photodimerization of the monomer, $C_{14}H_9Cl$, followed by recrystallization. The symmetry of the product molecules is defined by the orientation of the reactant molecules in the crystal. The mutual orientation parameters calculated for adjacent monomers explain the reactivity of the compound. The molecules in the crystal of the monomer and the recrystallized photodimer pack differently and the photodimer has crystallographically imposed inversion symmetry.

## Comment

Crystallographic structural studies of [4+4]-photodimerization in crystals have, in most cases, been limited to analyses of the crystal structure of the reactant (Bart & Schmidt, 1971; Heller & Schmidt, 1971; Ihmels *et al.*, 1999, 2000; Wang & Jones, 1987, 1994). The structures of the photodimers are also known, but usually the photodimerization was carried out in solution (Abboud *et al.*, 1990; Becker *et al.*, 1988; Langer & Becker, 1993*a*,*b*,*c*,*d*; Ojima *et al.*, 2000; Peters *et al.*, 2000; Sinha *et al.*, 1991; Sundell & Becker, 1994) and seldom in crystals (Chandross & Ferguson, 1966; Craig & Sarti-Fantoni, 1966; Dougherty *et al.*, 1986; Ehrenberg, 1966, 1968; Harada *et al.*, 1995, 1996; Wada & Tanaka, 1977). [4+4]-photodimerization of the single-crystal-to-single-crystal type is very rare (Craig & Sarti-Fantoni, 1966; Dougherty *et al.*, 1986; Ehrenberg, 1966, 1968; Harada *et al.*, 1995; Wada & Tanaka, 1977).

Recently, the crystal structure changes monitored step-by-step during [2+2]-photodimerization (Turowska-Tyrk, 2001, 2003), [4+4]-photodimerization (Turowska-Tyrk & Trzop, 2003), thermal isomerization (Bogadi *et al.*, 2002), [4+2]-dimerization (Kim, Hubig *et al.*, 2001; Kim, Lindeman & Kochi, 2001) and polymerization (Foley *et al.*, 1999) have been described. In this part of our series, we will analyze the structures of the reactant, (I), and product, (II), of the [4+4]-photodimerization of 1-chloroanthracene in the crystal state. The possibility of such photodimerization in the solid state was stated by Heller & Schmidt (1971). Unfortunately, the reaction cannot be conducted in the single-crystal-to-single-crystal manner. Although we undertook many trials using different wavelengths, always on the monomer low-energy absorption



(I) (II)

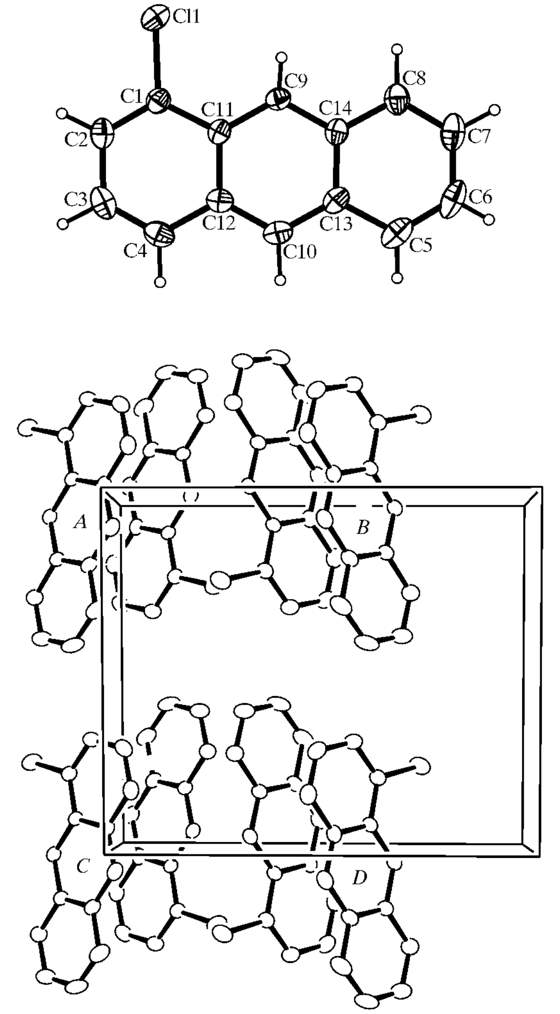


**Figure 1**
A view of the reactant molecule (I) (top) and a fragment of the crystal lattice (bottom). Displacement ellipsoids are drawn at the 25% probability level and H atoms are shown as small spheres of arbitrary radii.

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[1] Part 6: Turowska-Tyrk & Trzop (2003).

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tail (Enkelmann *et al.*, 1993; Novak *et al.*, 1993*a*,*b*), the crystals collapsed into microcrystalline material.

Figs. 1 and 2 show views of the molecules and fragments of the crystal lattices for the reactant, (I), and the product, (II), respectively. The product molecule has a characteristic shape of two united butterflies related by an inversion centre. The adjacent reactant molecules have the same orientation in the crystal. The central bonds formed between the two moieties of the dimer are elongated (Table 1), and this is also observed for photoproducts of other anthracenes. It is worth adding that there are known examples of [4+4]-photodimerization when, although the monomers were situated head-to-head in the crystal, the dimers obtained by single-crystal-to-single-crystal photoreaction had head-to-tail symmetry (Craig & Sarti-Fantoni, 1966; Ehrenberg, 1968; Kaupp, 1993). A very interesting explanation of this phenomenon was given by Kaupp (1993).

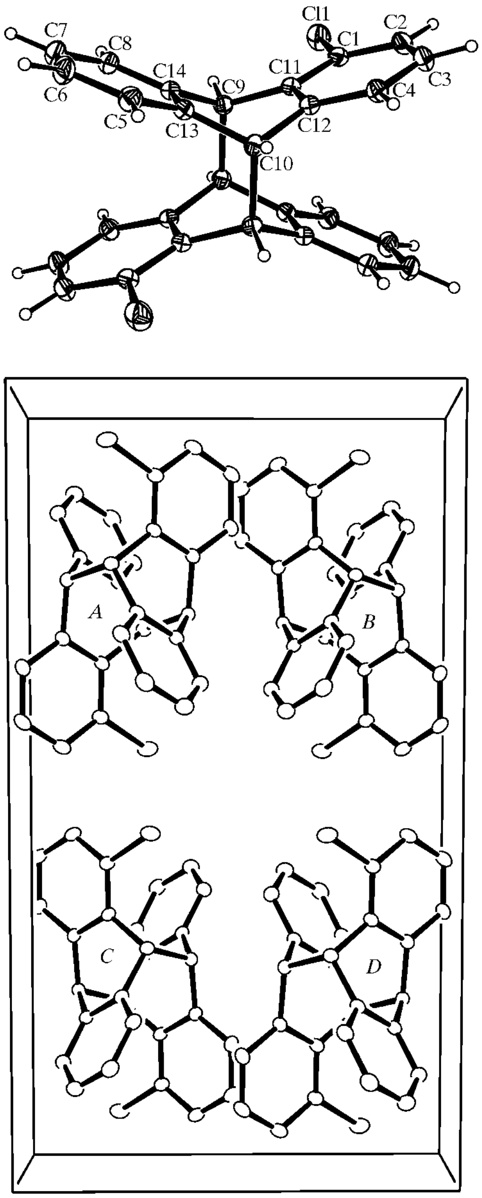

**Figure 2**
A view of the product molecule (II) (top) and a fragment of the crystal lattice (bottom). Displacement ellipsoids are drawn at the 25% probability level and H atoms are shown as small spheres of arbitrary radii.

The mutual orientation of adjacent monomer molecules in a crystal is one of the factors influencing [4+4]-photodimerization (Bart & Schmidt, 1971; Heller & Schmidt, 1971; Ihmels *et al.*, 1999, 2000; Wang & Jones, 1987, 1994). This orientation can be described by the following five parameters (Ihmels *et al.*, 2000; Turowska-Tyrk & Trzop, 2003; Wang & Jones, 1994): $\alpha$, the C9$\cdots$C10$\cdots$C9$^{i}$ and C10$\cdots$C9$\cdots$C10$^{i}$ angles, $\tau$, the C9$\cdots$C10$\cdots$C9$^{i}\cdots$C10$^{i}$ and C10$\cdots$C9$\cdots$C10$^{i}\cdots$C9$^{i}$ torsion angles, $\varphi$, the dihedral angle between the central rings of adjacent monomers, $\kappa$, the angle between the central ring of the parent monomer molecule and the plane formed by atoms C9, C10, C9$^{i}$ and C10$^{i}$, and $d_i$, the C9$\cdots$C10$^{i}$ and C10$\cdots$C9$^{i}$ distances [symmetry code: (i) $-x$, $-y$, $-z$]; the ideal values for these are 90, 0, 0 and 90°, and less than 4.2 Å, respectively. The parameters are 98.21 (8), 0, 0 and 67.86 (8)° and 3.760 (3) Å, respectively, for (I), and 108.2, 0, 0 and 74.3° and 3.859 Å, respectively, for 9-methylanthracene (Turowska-Tyrk & Trzop, 2003). These values explain the reactivity of both compounds.

There are also differences between (I) and 9-methylanthracene. The reactant and recrystallized product crystals of the former belong to different space groups, namely $P2_1/c$ and $C2/c$, respectively. The *a* cell constant is doubled in the product. Moreover, comparison of Figs. 1 and 2 shows that, although the orientation of the upper molecules (*A* and *B* pairs) is similar, the orientation of the lower molecules (*C* and *D* pairs) is very different for the reactant and the product. This might be the reason why the photoreaction is accompanied by crystal disintegration, making the monitoring of structural changes by means of X-ray structure analysis impossible. We succeeded in carrying out such monitoring in the case of 9-methylanthracene, although only to about 30% reaction progress (Turowska-Tyrk & Trzop, 2003). In the case of 9-methylanthracene, the space group was the same ($P2_1/c$) and the cell constants and crystal packing more similar for the reactant and the recrystallized photoproduct crystals.

## Experimental

Crystals of the 1-chloroathracene monomer, (I), were obtained by crystallization from a mixture of acetone and cyclohexane (1:1). Crystals of the photodimer, (II), were obtained by irradiation of the reactant powder with the 430 nm line from a 150 W Xe lamp, followed by recrystallization from a mixture of chloroform and toluene (1:1).

### Compound (I)

*Crystal data*

$C_{14}H_9Cl$
$M_r = 212.66$
Monoclinic, $P2_1/c$
$a = 10.3280\ (9)$ Å
$b = 12.0802\ (11)$ Å
$c = 8.4369\ (7)$ Å
$\beta = 100.673\ (8)°$
$V = 1034.41\ (16)$ Å$^3$
$Z = 4$
$D_x = 1.366$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 1959 reflections
$\theta = 5$–$26°$
$\mu = 0.33$ mm$^{-1}$
$T = 293\ (2)$ K
Prism, yellow
0.40 × 0.30 × 0.20 mm

### *Data collection*

Kuma KM-4 CCD area-detector diffractometer
$\omega$ scans
4935 measured reflections
1991 independent reflections
1641 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.025$
$\theta_{\rm max} = 26.0^\circ$
$h = -12 \rightarrow 12$
$k = -14 \rightarrow 14$
$l = -5 \rightarrow 10$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.161$
$S = 1.07$
1991 reflections
172 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0851P)^2 + 0.3292P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.37$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.30$ e Å$^{-3}$

## Compound (II)

### *Crystal data*

$C_{28}H_{18}Cl_2$
$M_r = 425.32$
Monoclinic, $C2/c$
$a = 20.232$ (2) Å
$b = 11.0746$ (13) Å
$c = 9.0872$ (11) Å
$\beta = 101.475$ (10)°
$V = 1995.4$ (4) Å$^3$
$Z = 4$

$D_x = 1.416$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 1164 reflections
$\theta = 5$–$22^\circ$
$\mu = 0.34$ mm$^{-1}$
$T = 293$ (2) K
Plate, colourless
0.30 × 0.20 × 0.08 mm

### *Data collection*

Kuma KM-4 CCD area-detector diffractometer
$\omega$ scans
4922 measured reflections
1945 independent reflections
1545 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.030$
$\theta_{\rm max} = 26.0^\circ$
$h = -21 \rightarrow 24$
$k = -13 \rightarrow 13$
$l = -11 \rightarrow 8$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.119$
$S = 1.08$
1945 reflections
172 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 0.9967P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.22$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.26$ e Å$^{-3}$

**Table 1**
Selected interatomic distances (Å) for (II).

| | | | |
|---|---|---|---|
| C9—C11 | 1.508 (3) | C10—C13 | 1.508 (3) |
| C9—C14 | 1.516 (3) | C11—C12 | 1.398 (3) |
| C9—C10$^{\rm i}$ | 1.615 (3) | C13—C14 | 1.394 (3) |
| C10—C12 | 1.506 (3) | | |

Symmetry code: (i) $\frac{1}{2} - x, \frac{3}{2} - y, -z$.

Low-angle reflections with $\theta$ below 5.8° were not measured. H-atom parameters were freely refined.

For both compounds, data collection: *KM*-4 *CCD Software* (Kuma, 2000); cell refinement: *KM*-4 *CCD Software*; data reduction: *KM*-4 *CCD Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Johnson *et al.*, 1997); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1681). Services for accessing these data are described at the back of the journal.

## References

Abboud, K. A., Simonsen, S. H. & Roberts, R. M. (1990). *Acta Cryst.* C**46**, 2494–2496.
Bart, J. C. J. & Schmidt, G. M. J. (1971). *Isr. J. Chem.* **9**, 429–448.
Becker, H.-D., Skelton, B. W., Turner, A. B. & White, A. (1988). *Aust. J. Chem.* **41**, 1977–1982.
Bogadi, R. S., Levendis, D. C. & Coville, N. J. (2002). *J. Am. Chem. Soc.* **124**, 1104–1110.
Chandross, E. A. & Ferguson, J. (1966). *J. Chem. Phys.* **45**, 3564–3567.
Craig, D. P. & Sarti-Fantoni, P. (1966). *J. Chem. Soc. Chem. Commun.* pp. 742–743.
Dougherty, D. A., Choi, C. S., Kaupp, G., Buda, A. B., Rudziński, J. M. & Osawa, E. (1986). *J. Chem. Soc. Perkin Trans.* 2, pp. 1063–1070.
Ehrenberg, M. (1966). *Acta Cryst.* **20**, 182–186.
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. & Eckhardt, C. J. (1999). *J. Am. Chem. Soc.* **121**, 7262–7263.
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.
Heller, E. & Schmidt, G. M. J. (1971). *Isr. J. Chem.* **9**, 449–462.
Ihmels, H., Leusser, D., Pfeiffer, M. & Stalke, D. (1999). *J. Org. Chem.* **64**, 5715–5718.
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.
Kaupp, K. (1993). *GIT Fachz. Lab.* **37**, 581–586.
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 (2000). *KM-4 CCD Software*. Version 166. Kuma Diffraction, Wrocław, Poland.
Langer, V. & Becker, H.-D. (1993*a*). *Z. Kristallogr.* **207**, 259–261.
Langer, V. & Becker, H.-D. (1993*b*). *Z. Kristallogr.* **207**, 262–264.
Langer, V. & Becker, H.-D. (1993*c*). *Z. Kristallogr.* **208**, 104–107.
Langer, V. & Becker, H.-D. (1993*d*). *Z. Kristallogr.* **208**, 108–110.
Novak, K., Enkelmann, V., Wegner, G. & Wagener, K. B. (1993*a*). *Angew. Chem.* **105**, 1678–1680.
Novak, K., Enkelmann, V., Wegner, G. & Wagener, K. B. (1993*b*). *Angew. Chem. Int. Ed. Engl.* **32**, 1614–1616.
Ojima, T., Akutsu, H., Yamada, J. & Nakatsuji, S. (2000). *Chem. Lett.* pp. 918–919.
Peters, K., Peters, E.-M., Grimme, J. & Quast, H. (2000). *Z. Kristallogr. New Cryst. Struct.* **215**, 307–308.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Sinha, H. K., Lough, A. J. & Yates, K. (1991). *J. Org. Chem.* **56**, 3727–3728.
Sundell, S. & Becker, H.-D. (1994). *Z. Kristallogr.* **209**, 995–996.
Turowska-Tyrk, I. (2001). *Chem. Eur. J.* **7**, 3401–3405.
Turowska-Tyrk, I. (2003). *Acta Cryst.* B**59**, 670–675.
Turowska-Tyrk, I. & Trzop, E. (2003). *Acta Cryst.* B**59**, 779–786.
Wada, A. & Tanaka, J. (1977). *Acta Cryst.* B**33**, 355–360.
Wang, W.-N. & Jones, W. (1987). *Tetrahedron*, **43**, 1273–1279.
Wang, W. N. & Jones, W. (1994). *Mol. Cryst. Liq. Cryst.* **242**, 227–240.