X-Ray Observations of Orientations of Photodimer in Single Crystals of Anthracene

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By use of *X*-ray diffraction, the photodimer, obtained when single crystals of anthracene are irradiated with Pyrex-filtered u.v. light, has been examined and the geometric relationship of the dimer to the original anthracene crystal has been established. Although the crystal structure of the dimer is apparently not modified by the presence of the surrounding anthracene crystal, the orientation of the dimer crystals is distinctly not random and appears to be dictated by the periodicity of the surrounding unreacted anthracene. Parallel matching repeat distances between the monomer and dimer are compared. Each dimer crystal forms in one of several (at least six) orientations permitted by the anthracene crystal, each orientation being associated with a specific well-developed face of the anthracene crystal.

It is well known that single crystals of anthracene photo-dimerize under appropriate conditions,[1-4] as in the present work, where single crystals of anthracene, when irradiated with u.v. light, give rise to the dimer, di-*p*-anthracene, which crystallizes inside the anthracene crystal with its normal structure. The present work explores the geometric relationship of the dimer to the original anthracene crystal.

EXPERIMENTAL

A description of the dimerization, including preparation, irradiation, and identification of the product from *X*-ray photographs has been published previously.[1] Table **1** presents the crystallographic data for both anthracene (A) [5,6] and di-*p*-anthracene (DPA).[7] On composite photographs of crystals which were half yellow [1] (early stage of dimerization) and half white (later stage of dimerization), high-angle anthracene reflections were compared and no change in the lattice dimensions of the anthracene was detected. As the reaction proceeded a general, but very slight, diminution in the intensity of the anthracene reflections was observed on the composite *X*-ray photographs. This observation indicates that most of the dimerized crystal, perhaps 95%, was still anthracene.

The complex *X*-ray pattern is a superposition of the anthracene crystal diffraction pattern and the patterns of crystals of dimer related to the anthracene crystal in several different geometric ways. The intensity of the Bragg reflections of the dimer is of the order of the intensity of the anthracene thermal scattering pattern. A few anthracene crystals were *X*-ray photographed before and after u.v. irradiation to identify the dimer pattern. The following *X*-ray photographs were taken (not all on the same crystal and each set was repeated on at least two crystals): rotation photographs along *a* and *b* axes, stationary-crystal photo-

Table 1

Physical constants of anthracene (A) and di-*p*-anthracene (DPA)

	Anthracene *	Di-*p*-anthracene †
Formula	$C_{14}H_{10}$	$C_{28}H_{20}$
System	Monoclinic	Orthorhombic
Space-group	$P2_1/a$	*Pbca*
Z	2	4
Unit-cell dimensions (Å):		
a	8·562	8·127
b	6·038	12·08
c	11·184	18·85
β°	124° 42′	
U/Å^3	475·35	1850·58
Vol. per dimer unit (Å^3)	475·35	462·6 ‡
M.p. (°C)	216·5	244
Habit	Colourless plates; tabular parallel to {001}, {201}, and {110} faces present, sometimes $\{11\bar{1}\}$	Colourless plates; tabular parallel to {001}, {010}, and {110} faces present
D_m/g cm^{-3}	1·25	1·26
D_c/g cm^{-3}	1·24	1·28
Molecular symmetry	$\bar{1}$	$\bar{1}$

* At 290 K. Taken from refs. 5 and 6. † Taken from ref. 7. ‡ Decrease 2·7%.

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[6] P. Groth, 'Chemische Krystallographie,' vol. 5, Engelmann, Leipzig, 1919, p. 437.

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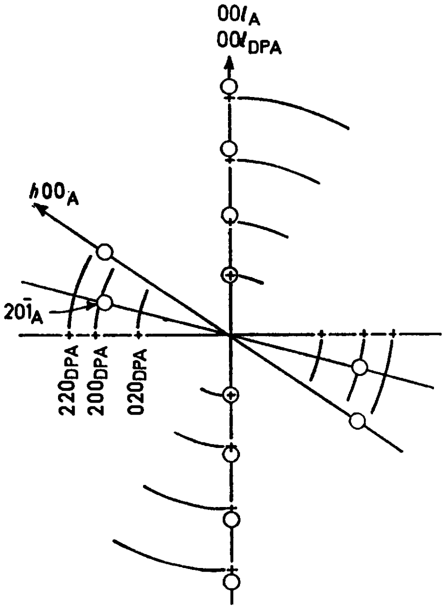
graphs at 10° intervals through 180° along both *a* and *b* axes, 10° oscillation photographs such that the crystal rotated 5° on both sides of the corresponding stationary-crystal photograph, and *h*0*l*, *h*1*l*, 0*kl*, 1*kl* Weissenberg photographs. An attempt was made to detect transient one- or two-dimensional intermediate stages,[8,9] but no evidence of this was found on the diffraction photographs.

The h0l Weissenberg Photograph.—For this layer all six of the dimer orientations have important axes parallel to the monomer monoclinic *b* axis and also both the $00l_{\mathrm{A}}$ and the $20\bar{1}_{\mathrm{A}}$ sets of reflections are displayed in the photograph. The later two sets of reflections are reflected from the two most developed faces of anthracene, and their importance will be seen as the argument is developed. Originally the anthracene crystal was mounted about the monoclinic b_{A} axis since $2b_{\mathrm{A}} = b_{\mathrm{DPA}}$ (Table 1) suggested that the b_{A} and b_{DPA} axes might be aligned.



Some reflections which appear on the *h*0*l* reciprocal net of the dimerized crystal

The Figure shows some reflections which appear on the *h*0*l* reciprocal net of the dimerized crystal. The anthracene reflections are indicated by open circles. The relatively sharp di-*p*-anthracene reflections of configurations *A*, *B*, and *C* are represented by plus signs. The fibrous reflections of configurations *D*, *E*, and *F* are represented by circular arcs.

The anthracene reflections were first indexed. The $00l_{\mathrm{A}}$, $h00_{\mathrm{A}}$, and $20\bar{1}_{\mathrm{A}}$ anthracene reflections are represented in the Figure, but other appropriate anthracene reflections which appeared on the *X*-ray photographs are omitted. The remaining diffraction pattern had *d* spacings consistent with those of the dimer but could not be compatibly indexed to a single orientation. They could easily be grouped into two sets: those with fibrous spread <*ca.* 4°, *i.e.* relatively sharp reflections, and those with fibrous spread >15°.

The sharp reflections cannot be indexed to a single orientation. However, prominent sharp $00l_{\mathrm{DPA}}$ reflections were easily indexed from a combination of *d* spacings and relative intensity. Perpendicular to the sharp $00l_{\mathrm{DPA}}$ reflections were three sharp dimer reflections collinear with the $40\bar{3}_{\mathrm{A}}$ anthracene reflection. Using the hypothesis that these dimer reflections were compatible with the $00l_{\mathrm{DPA}}$, hence of the form $hk0_{\mathrm{DPA}}$, they were indexed (from *d* spacings) as 200_{DPA}, 020_{DPA}, and 220_{DPA}. The fact that reflections of mixed indices, with the appropriate relative intensity, appear in the expected positions on the photograph establishes the existence of three dimer configurations called *A*, *B*, and *C*. A search of the 0*kl* Weissenberg photograph revealed, as expected, corresponding reflections with *d* spacings compatible with the 020_{DPA}, 200_{DPA}, and 120_{DPA} dimer reflections. These reflections were collinear with the $0k0_{\mathrm{A}}$ anthracene reflections. In order that all the dimer configurations be described by the right-handed co-ordinate systems, these reflections are formally indexed as 020_{DPA}, $\bar{2}00_{\mathrm{DPA}}$, and $\bar{1}20_{\mathrm{DPA}}$. Table 2 lists the planes of anthracene with the corresponding parallel planes of dimer configurations *A*, *B*, and *C*. The transformation[10] was then made from reciprocal (Table 2) to direct space (Table 3).

TABLE 2

Planes of anthracene and the corresponding parallel planes of di-*p*-anthracene configurations *A*, *B*, and *C*

	Di-*p*-anthracene		
Anthracene	*A*	*B*	*C*
$(001)_{\mathrm{A}}$	$(001)_{\mathrm{DPA}}$	$(001)_{\mathrm{DPA}}$	$(001)_{\mathrm{DPA}}$
$(010)_{\mathrm{A}}$	$(010)_{\mathrm{DPA}}$	$(\bar{1}00)_{\mathrm{DPA}}$	$(\bar{1}20)_{\mathrm{DPA}}$
$(40\bar{3})_{\mathrm{A}}$	$(100)_{\mathrm{DPA}}$	$(010)_{\mathrm{DPA}}$	$(110)_{\mathrm{DPA}}$

TABLE 3

Matching repeat distances (Å) and angles (°) of three configurations *A*, *B*, and *C* of DPA fitted to anthracene as calculated from relatively sharp DPA reflections

Confign.	Anthracene	DPA	% Change*
A	$[100]_{\mathrm{A}}$ 8·56	$[100]_{\mathrm{DPA}}$ 8·13	−5
	$2[010]_{\mathrm{A}}$ 12·08	$[010]_{\mathrm{DPA}}$ 12·08	0
	$[304]_{\mathrm{A}}$ 36·89	$2[001]_{\mathrm{DPA}}$ 37·70	+2
	$\angle[100]_{\mathrm{A}\wedge}[304]_{\mathrm{A}}$ 89·3°	$\angle[100]_{\mathrm{DPA}\wedge}[001]_{\mathrm{DPA}}$ 90°	
B	$4[010]_{\mathrm{A}}$ 24·16	$3[\bar{1}00]_{\mathrm{DPA}}$ 24·39	+1
	$3[100]_{\mathrm{A}}$ 25·68	$2[010]_{\mathrm{DPA}}$ 24·16	−6
	$[304]_{\mathrm{A}}$ 36·89	$2[001]_{\mathrm{DPA}}$ 37·70	+2
	$\angle[100]_{\mathrm{A}\wedge}[304]_{\mathrm{A}}$ 89·3°	$\angle[\bar{1}00]_{\mathrm{DPA}\wedge}[001]_{\mathrm{DPA}}$ 90°	
C	$4[1\bar{1}0]_{\mathrm{A}}$ 41·91	$5[100]_{\mathrm{DPA}}$ 40·66	−3
	$4[120]_{\mathrm{A}}$ 59·41	$5[010]_{\mathrm{DPA}}$ 60·40	+2
	$[304]_{\mathrm{A}}$ 36·89	$2[001]_{\mathrm{DPA}}$ 37·70	+2
	$\angle[1\bar{1}0]_{\mathrm{A}\wedge}[120]_{\mathrm{A}}$ 89·9°	$\angle[100]_{\mathrm{DPA}\wedge}[010]_{\mathrm{DPA}}$ 90°	

* Calculated according to the formula 100(anthracene repeat distance — di-*p*-anthracene repeat distance)/anthracene repeat distance.

The $00l_{\mathrm{DPA}}$ fibrous reflections are centred approximately collinear with the $20\bar{9}_{\mathrm{A}}$ reflection. Again if the *h*0*l* Weissenberg photograph is examined 90° from the fibrous $00l_{\mathrm{DPA}}$ reflections, then fibrous reflections 200_{DPA}, 020_{DPA}, and 220_{DPA} can be indexed. These three fibrous reflections are approximately centred collinear to the $20\bar{1}_{\mathrm{A}}$ reflections of anthracene (Figure). The three reflections 200_{DPA}, 020_{DPA}, and 220_{DPA}, together with $00l_{\mathrm{DPA}}$ suggest three additional

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[9] K. Lonsdale, E. Nave, and J. F. Stephens, *Phil. Trans.*, **1966**, *A*, **261**, 1.

[10] M. J. Buerger, 'Crystal Structure Analysis,' Wiley, New York, 1960, p. 407.

TABLE 4

Planes of anthracene and the corresponding parallel planes of DPA configurations *D*, *E*, and *F*

Anthracene	DPA *D*	DPA *E*	DPA *F*
$(20\bar{1})_{\mathrm{A}}$	$(100)_{\mathrm{DPA}}$	$(010)_{\mathrm{DPA}}$	$(110)_{\mathrm{DPA}}$
$(20\bar{9})_{\mathrm{A}}$	$(001)_{\mathrm{DPA}}$	$(001)_{\mathrm{DPA}}$	$(001)_{\mathrm{DPA}}$
$(010)_{\mathrm{A}}$	$(010)_{\mathrm{DPA}}$	$(\bar{1}00)_{\mathrm{DPA}}$	$(\bar{1}20)_{\mathrm{DPA}}$

TABLE 5

Matching repeat distances (Å) and angles (°) of configurations *D*, *E*, and *F* of DPA fitted to anthracene as calculated from the mid-point of elongated (fibrous) DPA reflections

Confign.	Anthracene	DPA	% Change*
D	$2[0\bar{1}0]_{\mathrm{A}}$ 12·08	$[010]_{\mathrm{DPA}}$ 12·08	0
	$[102]_{\mathrm{A}}$ 18·86	$[001]_{\mathrm{DPA}}$ 18·85	0
	$[\bar{9}0\bar{2}]_{\mathrm{A}}$ 67·00	$8[100]_{\mathrm{DPA}}$ 65·04	−3
	$\angle[102]_{\mathrm{A}}\wedge[\bar{9}0\bar{2}]_{\mathrm{A}}$ 86·5°	$\angle[001]_{\mathrm{DPA}}\wedge[100]_{\mathrm{DPA}}$ 90°	
E	$4[0\bar{1}0]_{\mathrm{A}}$ 24·16	$3[\bar{1}00]_{\mathrm{DPA}}$ 24·39	+2
	$[102]_{\mathrm{A}}$ 18·86	$[001]_{\mathrm{DPA}}$ 18·85	0
	$[\bar{9}0\bar{2}]_{\mathrm{A}}$ 67·00	$6[010]_{\mathrm{DPA}}$ 72·48	+8
	$\angle[102]_{\mathrm{A}}\wedge[\bar{9}0\bar{2}]_{\mathrm{A}}$ 86·5°	$\angle[001]_{\mathrm{DPA}}\wedge[010]_{\mathrm{DPA}}$ 90°	
F	$5[0\bar{1}0]_{\mathrm{A}}$ 30·20	$2[\bar{1}10]_{\mathrm{DPA}}$ 29·12	−4
	$[102]_{\mathrm{A}}$ 18·86	$[001]_{\mathrm{DPA}}$ 18·85	0
	$[\bar{9}0\bar{2}]_{\mathrm{A}}$ 67·00	$3[210]_{\mathrm{DPA}}$ 60·75	−9
	$\angle[010]_{\mathrm{A}}\wedge[\bar{9}0\bar{2}]_{\mathrm{A}}$ 90°	$\angle[\bar{1}10]_{\mathrm{DPA}}\wedge[210]_{\mathrm{DPA}}$ 87·3°	
	$\angle[102]_{\mathrm{A}}\wedge[\bar{9}0\bar{2}]_{\mathrm{A}}$ 86·5°	$\angle[001]_{\mathrm{DPA}}\wedge[210]_{\mathrm{DPA}}$ 90°	

* See Table 3.

configurations. Reflections of mixed indices with the appropriate relative intensity again appear in the expected position on the photographs; these three fibrous dimer configurations are called *D*, *E*, and *F*. Table 4 represents corresponding planes and Table 5 represents the real-space transformations of configurations *D*, *E*, and *F*.

DISCUSSION

Consider the association of the sharp reflections with the $(001)_{\mathrm{A}}$ anthracene face and the association of the fibrous reflections with the $(20\bar{1})_{\mathrm{A}}$ face. The percentage change in comparing lattice constants (Tables 3 and 5) is not enough to account for this drastic difference. However compare the shortest repeat distances approximately perpendicular to the well-developed anthracene face. Perpendicular to the $(001)_{\mathrm{A}}$ face, $[304]_{\mathrm{A}}$ has a repeat distance of 36·89 Å with a corresponding dimer repeat distance of 37·70 Å. Perpendicular to the $(20\bar{1})_{\mathrm{A}}$ face, $[902]_{\mathrm{A}}$ has a repeat distance of 67·00 Å with corresponding dimer repeat distances of 65·04, 72·48, and 60·75 Å. The $[902]_{\mathrm{A}}$ repeat distance appears to be too long to lock in the associated dimer configuration. The fibrous spread [9] of a reflection is a direct measure of the mosaic nature of the diffracting material.

Twinning in the product has been observed in solid-state reactions.[11] Dimer configuration *B* (or *E*) could be considered a twin of *A* (or *D*) across $(\bar{2}30)_{\mathrm{DPA}}$ because $3[100]_{\mathrm{DPA}} = 2[010]_{\mathrm{DPA}}$.

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