# A Redetermination of Diphenanthro[5,4,3-*abcd*: 5′,4′,3′-*jklm*]perylene

Isao Oonishi, Shoji Fujisawa,* Junji Aoki, and Takaaki Danno
*Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba 274*
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It has been shown that the true unit cell of diphenanthro[5,4,3-*abcd*: 5′,4′,3′-*jklm*]perylene consists of three subcells in which the atomic arrangements differ slightly from each other. The model for the ordered structure has been deduced from the consideration of weak reflections. The average structure of the subcell with $a=30.80$, $b=3.837$, $c=19.87$ Å, $\beta=112.5°$, and $Z=4$ has been redetermined. The final $R$ value is 0.103 for 1244 independent reflections. The two naphthanthrone planes in the molecule make an angle of 36°, which shows a large distortion from a planar structure.

Recently, the photoconductivities of tetrabenzo-[*a*,*cd*,*j*,*lm*]perylene (hereafter TBP) and diphenanthro-[5,4,3-*abcd*: 5′,4′,3′-*jklm*]perylene (hereafter DPP) have been observed.[1] DPP was found to have a very high photoconductivity.

In order to discuss the relation between such high photoconductivities and the intramolecular electronic states or molecular arrangement, the details of molecular geometries must be known.

The crystal structure of TBP has been determined by Kohno *et al.*[2] The $R$ value is 0.056. That of DPP has been determined by Robertson and Trotter,[3] but the R values reported by them were rather high (0.111 for $h0l$ and 0.26 for $h1l$ reflections), which suggests that the $y$ coordinates were not accurate. Therefore, we have attempted a redetermination of this material.

## Experimental

The DPP crystals used in the present investigation were obtained by condensation of naphthanthrone with copper powder, zinc chloride, and sodium chloride, by a method similar to that described by Aoki *et al.*[5] The method of preparation was different from that used by Robertson and Trotter.[4]

The crude product was dissolved in toluene and passed through a column of alumina to obtain the pure crystals. Small orange-red needles elongated along the b axis were grown by slow sublimation in a glass tube under a nitrogen atomosphere (5 mmHg).

The cross section of the crystal used for X-ray work (normal to the b axis) is $0.02\times0.2$ mm, which is smaller than that of $0.25\times0.18$ mm used by Robertson and Trotter.[3] The lattice constants of the crystal reported by Robertson and Trotter are: $a=30.73$, $b=3.855$, $c=19.87$ Å, and $\beta=113.0°$. Weissenberg photographs of the crystal used in the present investigation showed that the true a axis length is three times the above length. We observed essentially the same diffraction patterns for 10 different crystals. However, when very weak reflections are not taken into account, the unit cell corresponds to that of Robertson and Trotter (see below). This means that the true unit cell is divided into three parts, and the atomic arrangements in these subcells differ only slightly from each other. In the work by Robertson and Trotter, such weak reflections were not found, but diffuse streaks parallel to a* through Bragg reflections were found. On the contrary, such diffuse streaks are negligibly weak on our Weissenberg photographs (Plates 1 and 2). However, intense reflections corresponding to the subcell show the same features in the crystals used by both us and Robertson and Trotter. These facts suggest that there are different disorders in the two crystals, which seem to have been caused by a difference of purity.

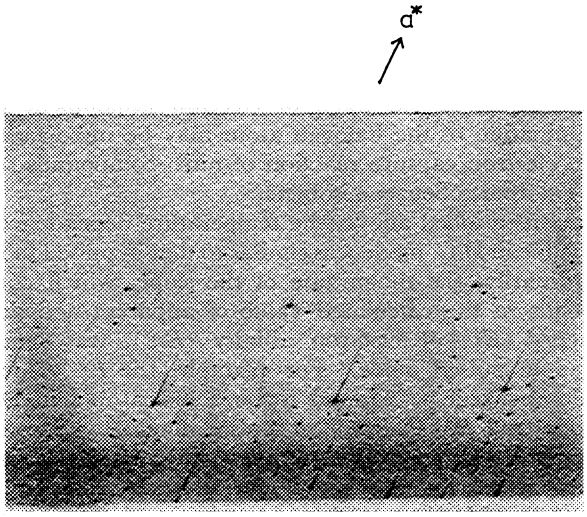

Plate 1. Weissenberg photograph of ($h$01).

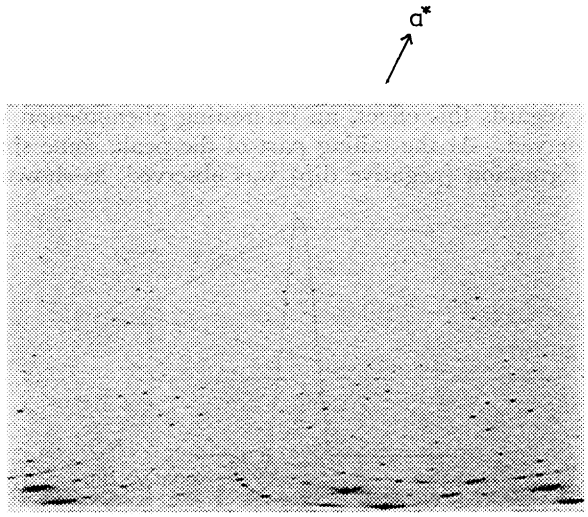

Plate 2. Equi-inclination Weissenberg photograph of ($h1l$).

*Crystal Data for Subcell.* $C_{38}H_{22}$, $M=478.60$, mp 340 °C, Space group: C2, $Z=4$; $a=30.80\pm0.04$, $b=3.837\pm0.005$, $c=19.87\pm0.03$ Å, $\beta=112.5\pm0.2°$, $v=2169.4$ Å$^3$; $D_x=1.465$, $D_m=1.45$ g cm$^{-3}$; $F(000)=1000$; $\mu$(Cu $K\alpha$)$=6.3$ cm$^{-1}$. These values agree with those given by Robertson and Trotter within the experimental errors.[3]

Sets of multiple-film equi-inclination Weissenberg photographs were taken about the b axis (0th to 3rd layers) and about the c axis (0th layer). Cu $K\alpha$ radiation was employed throughout. The intensities were estimated by means of a

Rigaku photometer MP3. Weak intensities were visually estimated with a standard film strip. They were corrected for Lorentz and polarization factors, but no absorption correction was applied. The range of relative intensities was from 1 to 50000. 1244 independent reflections fell within this range, whereas 869 others were too weak to be observed.

## The Model of Ordered Structure

When weak reflections have been taken into consideration, the extinction rules for the true unit cell are $h+k=2n$ in $hkl$ reflections; $h=6n$ when $l=2n$ and $h=2$ when $l=2n+1$ in $h0l$ reflections. The latter cannot be explained with ordinary symmetry elements.

On the other hand, the distribution of intense reflections is $h=3(2n)$ when $k=0$, $h=3(2n+1)$ when $k=1$, $h=3(2n)$ when $k=2$, and so on. Thus, the only extinction rule for the subcell is $h'+k=2n$ in $h'kl$ reflections where $h'=h/3$. Both the true unit cell and the subcell are **C**-base centered lattices. The total intensity of weak reflections (281 in number) is less than 1% of that of the intense reflections.

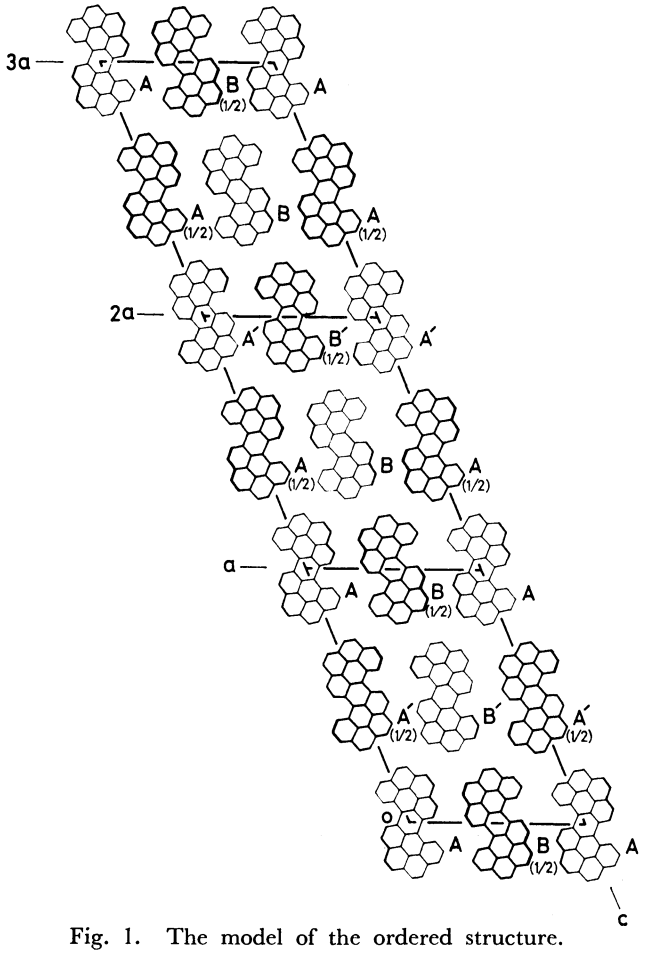


Fig. 1. The model of the ordered structure.

We have deduced the model pictured in Fig. 1 to explain the extinctions. In Fig. 1, a and c correspond to the subcell. A and B are enantiomer, and A′ and B′ are related to A and B by an approximate twofold rotation perpendicular to the ab-plane and a following translation of (3a/6, b/2), respectively. A and B′ (A′ and B) have the same shape when projected along the b axis. The molecules with the subscript of (1/2), for example A′(1/2) and B(1/2), have the height of b/2 relative to the ones without subscript.

In the true unit cell, the 4A molecules and 2B′ molecules (4B and 2A′) are in the positions of $(x, z)$, $(1/6+x, z)$, $(3/6+x, z)$, $(4/6+x, z)$, $(2/6+x, 1/2+z)$ and $(5/6+x, 1/2+z)$, respectively. Only such a relative configuration is able to explain the extinction rules described above.

The structure is built of two kinds of energetically equivalent layers parallel to the bc-plane. Along the a direction, the two kinds of layers exist laterally in the ratio of 2: 1. The former can be expressed as ABAB— and the latter as A′B′A′B′—. They are related by a reflection on the ac-plane and a following translation of (3a/6, b/2, c/2).

According to the model of Robertson and Trotter, the two kinds of layers mentioned above exist randomly in the ratio of 1: 1 along the a direction. However, they have reported that this model cannot explain the appearance of $h0l$ reflections with $l$ odd.

## Refinement of the Average Structure

The average structure is a superposition of three subcells. The overlappings of the molecules in the average structure are AAA′ and BBB′. Thus, molecules A and B are given 2/3 factors, and A′ and B′ are given 1/3 factors.

We started refinement with the parameters given by Robertson and Trotter.[3] In the least squares calculations, molecules A and B were independently refined with isotropic temperature factors. After three cycles of least squares calculations, the $R$ value converged to 19%. The three dimensional electron density map, calculated at this stage, revealed peaks with about 1/3 the height of a carbon atom, which have also been found on the two dimensional electron density given by Robertson and Trotter.[3] We assigned 1/3 factors to the peaks according to the model described above. At the same time, the factors of C(4) and C(5) atoms were changed to 2/3 (see the numbering scheme in Fig. 2). Hydrogen atoms except H(C4), H(C5), H(4′), and H(C5′) have also been found on the electron density map. However, since the shapes of the molecules A and A′ (B and B′) are very similar, only C(4), C(4′), C(5), and C(5′) atoms were separated on the electron density map.

After the introduction of anisotropic temperature factors for carbon atoms, six more cycles of refinement were carried out. The following weighting scheme was employed: $w=0.3$ if $F_o<F_{min}$ (4.0), $w=1.0$ for the others. The final $R$ value was 10.3% for all observed reflections. The atomic scattering factors were taken from International Tables for X-Ray Crystallography.[6] The final atomic parameters and their estimated standard deviations are given in Table 1(a) for carbon atoms and in Table 1(b) for hydrogen atoms. The positional and thermal parameters except those of the separated atoms need to be considered as the weighted average values of the overlapped atoms of molecules A and A′ (B and B′).

Table 1. Atomic parameters

(a) Positional and thermal parameters for non-hydrogen atoms ($\times 10^4$), with e.s.d.'s in parentheses ($\times 10^3$ for $y$, $\beta_{22}$, $\beta_{12}$, $\beta_{23}$).

The $\beta_{ij}$'s are defined by $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$.

| | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Molecule A | | | | | | | | | |
| C(1) | 1867(5) | 169(4) | 2078(8) | 12(2) | 72(14) | 37(5) | −4(3) | 15(5) | 1(4) |
| C(2) | 1483(5) | 220(4) | 2274(8) | 14(2) | 87(16) | 36(6) | −3(3) | 17(6) | −4(5) |
| C(3) | 1020(4) | 144(4) | 1769(7) | 10(2) | 81(14) | 30(5) | −2(3) | 11(5) | 4(4) |
| C(4) | 621(6) | 162(5) | 1985(11) | 11(3) | 43(17) | 34(7) | 1(3) | 16(7) | −3(6)[a] |
| C(4′) | 311(15) | −272(13) | −1571(17) | 23(7) | 127(54) | 13(10) | −14(10) | 38(14) | −19(13)[b] |
| C(5) | 191(6) | 87(5) | 1506(11) | 12(2) | 28(16) | 46(7) | −4(3) | 19(7) | −2(6)[a] |
| C(5′) | 99(10) | −210(10) | 1458(16) | 9(3) | 29(34) | 24(9) | −14(6) | 9(9) | −5(9)[b] |
| C(6) | 83(4) | −33(4) | 761(7) | 11(2) | 80(14) | 32(5) | 4(3) | 17(5) | 3(4) |
| C(7) | 464(4) | −31(4) | 529(7) | 8(2) | 62(12) | 29(4) | 0(2) | 14(4) | 2(4) |
| C(8) | 394(4) | −73(4) | −194(7) | 9(2) | 45(11) | 39(5) | −2(2) | 17(5) | −1(4) |
| C(9) | 790(4) | −163(4) | −416(7) | 12(2) | 68(13) | 34(5) | 0(3) | 21(5) | 3(4) |
| C(10) | 735(5) | −290(5) | −1081(8) | 11(2) | 105(18) | 39(5) | 1(3) | 18(6) | 1(5) |
| C(11) | 1121(5) | −379(5) | −1333(11) | 13(2) | 119(19) | 78(10) | 2(4) | 30(8) | 0(8) |
| C(12) | 1572(5) | −307(4) | −764(9) | 15(2) | 90(17) | 51(7) | 2(3) | 35(7) | 3(5) |
| C(13) | 1648(5) | −186(5) | −81(9) | 13(2) | 73(14) | 52(7) | 2(3) | 27(6) | 3(5) |
| C(14) | 2114(5) | −116(5) | 485(9) | 10(2) | 88(16) | 57(7) | −1(3) | 26(6) | 2(6) |
| C(15) | 2190(4) | 0(4) | 1145(8) | 9(2) | 93(16) | 44(6) | −1(3) | 14(6) | −2(5) |
| C(16) | 1798(4) | 65(4) | 1367(8) | 10(2) | 76(14) | 44(6) | −4(3) | 16(6) | −2(5) |
| C(17) | 1259(4) | −110(4) | 133(8) | 10(2) | 65(13) | 42(6) | −2(2) | 22(5) | −1(4) |
| C(18) | 1334(4) | −6(4) | 848(7) | 10(2) | 56(12) | 35(5) | 0(2) | 14(5) | 3(4) |
| C(19) | 938(4) | 32(4) | 1063(7) | 9(2) | 64(13) | 29(4) | −1(2) | 13(4) | −1(4) |
| Molecule B | | | | | | | | | |
| C(1) | 1580(5) | 632(4) | 4226(8) | 13(2) | 83(14) | 44(6) | −3(3) | 28(6) | −2(5) |
| C(2) | 1134(5) | 683(4) | 3739(7) | 14(2) | 96(15) | 25(4) | −1(3) | 23(5) | 3(4) |
| C(3) | 735(5) | 603(5) | 3893(8) | 11(2) | 97(15) | 35(5) | 1(3) | 17(5) | 0(5) |
| C(4) | 268(8) | 607(7) | 3354(12) | 18(4) | 107(26) | 36(8) | 7(5) | 25(9) | 16(8)[a] |
| C(4′) | 643(12) | 199(10) | 6970(14) | 11(5) | 84(36) | 0(7) | −4(6) | 3(9) | 12(8)[b] |
| C(5) | −132(7) | 491(7) | 3526(12) | 13(2) | 103(26) | 59(9) | 5(4) | 22(8) | −3(8)[a] |
| C(5′) | −207(12) | 258(12) | 3496(20) | 15(5) | 49(41) | 53(13) | 3(7) | 33(13) | 7(13)[b] |
| C(6) | −72(4) | 425(4) | 4262(7) | 12(2) | 65(12) | 28(4) | 3(2) | 16(5) | 3(4) |
| C(7) | 391(4) | 433(4) | 4783(7) | 9(2) | 44(10) | 30(4) | 0(2) | 15(4) | −3(4) |
| C(8) | 465(4) | 387(4) | 5525(7) | 9(2) | 72(14) | 33(5) | −2(2) | 12(5) | 4(4) |
| C(9) | 944(4) | 302(4) | 6069(8) | 12(2) | 71(13) | 35(5) | 0(3) | 16(5) | −1(4) |
| C(10) | 1030(5) | 174(5) | 6750(8) | 13(2) | 105(18) | 40(6) | 0(3) | 20(6) | −2(5) |
| C(11) | 1479(6) | 93(6) | 7278(10) | 18(3) | 117(18) | 51(7) | 2(4) | 17(7) | 6(7) |
| C(12) | 1865(5) | 159(5) | 7054(9) | 13(2) | 94(17) | 47(6) | 7(3) | 16(6) | 0(5) |
| C(13) | 1794(5) | 274(4) | 6366(9) | 12(2) | 77(14) | 45(6) | 4(3) | 18(6) | −1(5) |
| C(14) | 2174(5) | 345(5) | 6145(10) | 11(2) | 100(17) | 56(8) | 5(3) | 16(7) | 1(6) |
| C(15) | 2118(5) | 464(4) | 5456(9) | 11(2) | 80(15) | 50(7) | 0(3) | 20(6) | −1(5) |
| C(16) | 1653(4) | 527(4) | 4935(8) | 11(2) | 58(13) | 41(5) | 0(2) | 22(5) | −3(4) |
| C(17) | 1333(4) | 350(4) | 5823(8) | 9(2) | 63(13) | 44(6) | 1(2) | 13(5) | 0(5) |
| C(18) | 1260(4) | 460(4) | 5132(7) | 10(2) | 55(11) | 32(5) | 1(2) | 16(5) | −3(4) |
| C(19) | 799(4) | 498(4) | 4594(7) | 11(2) | 57(12) | 34(5) | 2(2) | 21(5) | 1(4) |

a) Population 2/3. b) Population 1/3.

(b) Positional parameters for hydrogen atoms ($\times 10^3$)

Mean isotropic temperature factor for hydrogen atoms is 4.0 Å$^2$.

| Molecule A | $x$ | $y$ | $z$ | Molecule B | $x$ | $y$ | $z$ |
|---|---|---|---|---|---|---|---|
| H(C1) | 224 | 225 | 247 | H(C1) | 192 | −325 | 404 |
| H(C2) | 153 | 323 | 256 | H(C2) | 109 | −275 | 316 |
| H(C4) | 67 | 288 | 242[a] | H(C4) | 23 | 703 | 283[a] |
| H(C4′) | 26 | −356 | −209[b] | H(C4′) | 65 | 88 | 739[b] |
| H(C5) | −15 | 94 | 168[a] | H(C5) | −46 | 439 | 313[a] |
| H(C5′) | −41 | −244 | −189[b] | H(C5′) | −2 | 193 | 672[b] |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H(C10) | 41 | −325 | −176 | H(C10) | 76 | 140 | 686 |
| H(C11) | 107 | −490 | −196 | H(C11) | 153 | −20 | 783 |
| H(C12) | 191 | −344 | −92 | H(C12) | 220 | 125 | 747 |
| H(C14) | 238 | −144 | 26 | H(C14) | 248 | 288 | 654 |
| H(C15) | 253 | 37 | 149 | H(C15) | 246 | 519 | 526 |

a) Population 2/3. b) Population 1/3.

The observed and calculated structure factors are listed in Table 2.**

## Description and Discussion

Figure 2 shows the average structure projected along the b axis and at the same time the bond lengths and angles in the molecules. When the atoms C(4) and C(5) are changed to the atoms C(4′) and C(5′), the molecules A and B change to the molecules A′ and B′, respectively. Since A and A′ (B and B′) have not been separated, as explained above, we cannot discuss the details of the bond lengths and angles, but only the shapes of molecules A and B.

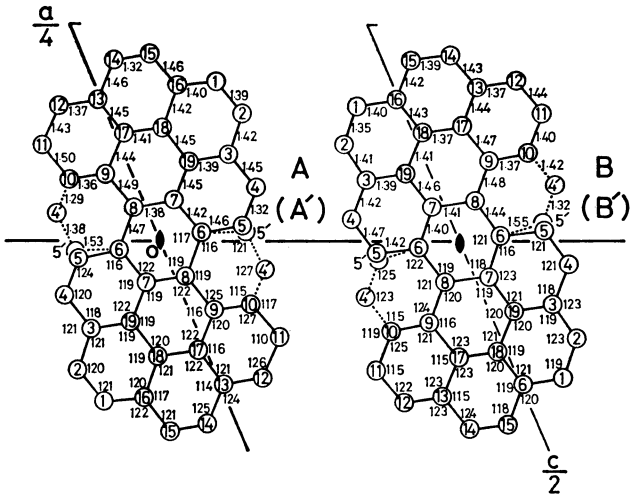


Fig. 2. The projection of the average structure along the b axis, and the bond lengths and bond angles.

Figure 3 shows the diagrams of DPP and TBP. In the molecule A, the downward naphthanthrone is twisted in a clockwise direction and the upper one is twisted in a counterclockwise direction around the arrow in Fig. 3. Figure 4 shows the perspective drawing of the molecule A, looking down along the arrow in Fig. 3 which runs through the two carbon atoms of the central ring. The molecules A and B are significantly distorted from a planar structure due to repulsions between the hydrogen atoms at the positions denoted with * in Fig. 3. Such distortion forces the central ring to adopt a twisted boat form. The molecules A and B are left- and right-handed propeller-shaped respectively. There exist short contacts at the positions marked * in Fig. 3. The

** Table 2 has been deposited with the office of Chemical Society of Japan, 1-5 Kanda-Surugadai, Chiyoda-ku, Tokyo 101 (Document No. 7826).

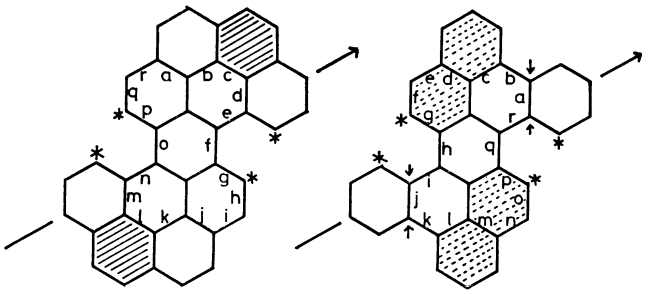


Fig. 3. The diagrams of DPP and TBP.

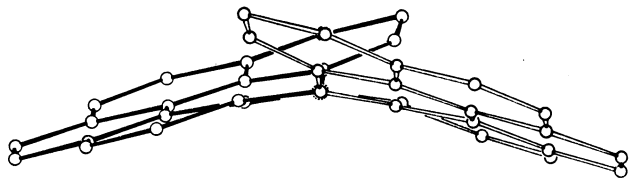

Fig. 4. A perspective drawing of DPP.

distances of C(5)···C(10) are 3.01 Å in the molecule A, and 2.87 Å in the molecule B. They correspond to the mean value of 2.953 Å reported by Robertson and Trotter, and are comparable to 2.971 and 2.944 Å in TBP.

The molecule DPP consists of two naphthanthrone skeletons. The deviations of the atoms from the mean planes through naphthanthrone moieties range from −0.11 to 0.34 Å in the molecule A, and from −0.31 to 0.12 Å in the molecule B. The two planes in the molecule A (B) make an angle of 36° (36°), which are larger than 30.5° in the molecule TBP described below.

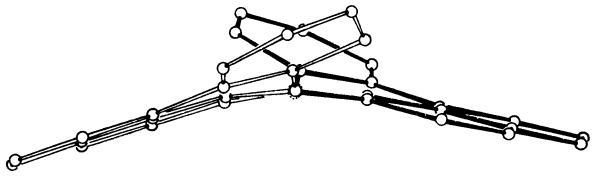

Fig. 5. A perspective drawing of TBP.

To compare DPP with TBP, the right-handed propeller-shaped TBP is drawn in Fig. 5, according to the parameters given by Kohno *et al.*[2] It is taken looking down along the large arrow in Fig. 3. The molecule TBP consists of two benzanthrone skeletons. The two naphthalene moieties, shaded with the dotted lines in Fig. 3, are planar within±0.05 Å, and the two planes make an angle of 30.5°. On the other hand,

the atoms in the [*a*]- and [*j*]-benzene rings significantly deviate from the planes. The largest deviations are 0.670 and 0.624 Å, respectively. Thus, the benzanthrone moieties in TBP are largely bent in the parts indicated with the small arrows in Fig. 3. Twisting of the central ring is partially relaxed due to such bending, compared to the twisting in DPP.

However, in the naphthanthrone moieties of DPP such a large bending is prevented by an additional benzene ring, shaded with the solid lines in Fig. 3. The strain distributes over the whole molecule.

Thus, the distortions of DPP and TBP are clearly different, and the overlappings of molecules in the DPP and TBP crystals are different as well. These differences seem to be the reason why the photoconductivity of DPP is larger than that of TBP.

In order to give a detailed discussion of the mechanism of photoconduction, we need to gather more data of photoconductivity and crystal structure for polycyclic aromatic hydrocarbons where there are repulsions between hydrogen atoms.

All these calculations were carried out on a HITAC 8700/8800 at the Computer Center of University of Tokyo with a local version of the Universal Crystallographic Computation Program System, UNICS (1967).

## References

1) Y. Kamura, H. Inokuchi, J. Aoki, and S. Fujisawa, *Chem. Phys. Lett.*, **46**, 356 (1977).
2) Y. Kohno, M. Konno, Y. Saito, and H. Inokuchi, *Acta Crystallogr., Sect. B*, **31**, 2076 (1975).
3) T. M. Robertson and J. Trotter, *J. Chem. Soc.*, **1959**, 2614.
4) E. Clar, W. Kelley, J. M. Robertson, and M. G. Rossmann, *J. Chem. Soc.*, **1956**, 3878.
5) J. Aoki, M. Takekawa, S. Fujisawa, and S. Iwashima, *Bull. Chem. Soc. Jpn.*, **50**, 1017 (1977).
6) "International Tables for X-Ray Crystallography," Vol. III, Birmingham, Kynoch Press (1962).