521. *Crystal-structure Studies of Polynuclear Hydrocarbons. Part IV. The* β-*Modification of Dinaphtho*(7′ : 1′-1 : 13)(1″ : 7″-6 : 8)*peropyrene.*

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Crystallographic data for a second (β) modification of the dinaphthoperopyrene are given. The space group is centrosymmetric, $P2_1/c$, but the spectra decrease rapidly in intensity. The apparently high temperature factor is probably due to irregularities in packing, and it is unlikely that a very accurate structure could be determined.

DURING the investigation of the structure of the dinaphthoperopyrene two crystalline modifications were obtained, and the structure of the dark-red α-modification was completely elucidated.[1] The pale-red β-modification occurs in the sublimate as aggregates of very small crystals. We were able to isolate only one small single crystal of this modification in the form of a slender plate with {100} developed, and weighing about 0·01 mg.

Rotation and oscillation photographs were taken about the a, b, and c axes of this one crystal, and moving-film photographs of ($h0l$), ($h1l$), and ($hk0$). The unit cell is monoclinic with $a = 16{\cdot}01 \pm 0{\cdot}08$, $b = 7{\cdot}48 \pm 0{\cdot}02$, $c = 21{\cdot}51 \pm 0{\cdot}05$ Å, $\beta = 118{\cdot}6° \pm 0{\cdot}5°$, and volume 2263 Å^3. The m. p., 343°, appeared to be slightly higher than that of the α-modification (340°). The density, determined by flotation in aqueous potassium iodide, was 1·41. For this measurement a larger polycrystalline aggregate was used and the result is not very accurate, but it agrees reasonably well with the value of 1·39 calculated

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[1] Part III, preceding paper.

for four molecules of $C_{38}H_{18}$ per unit cell. For $\lambda = 1{\cdot}542$ Å the linear absorption coefficient μ is 7·35 cm.$^{-1}$. The absent spectra are ($h0l$) when l is odd, and ($0k0$) when k is odd, which determine the space group unambiguously as $C_{2h}{}^5$–$P2_1/c$.

A full survey of the ($h0l$) and ($h1l$) intensities was made by normal beam and equi-inclination Weissenberg methods. These records revealed that there is a very rapid decrease in the intensities of the high-order reflections, an effect which is almost exactly analogous to that observed in diperinaphthyleneanthracene[2] and in circumanthracene.[3] The small size of the crystal made any more exact evaluation of the temperature factor difficult, but it is certainly abnormally high. The effect can scarcely be due to large thermal vibrations of the atoms or to molecular librations in a crystal with such a high melting point. It is most likely due to small irregularities in packing so that atoms in successive molecules are occasionally displaced from their mean positions, an effect which would be indistinguishable from displacement due to thermal motion. This slight disorder in the crystal is of a different type from that which has been established in the α-modification,[1] in which the temperature factor is normal and the spectra can be observed to the limit of copper radiation.

It was at first suspected that the different behaviour of the β-modification might be due to the presence of impurity. The density determination checks the molecular weight to within 2%, but a further test was made by examination of the absorption spectra. A small quantity of each type of crystal was separated by hand sorting, and the visible absorption spectra of each type in xylene were identical; there was no evidence of any broadening of the bands from the pale-red crystals. This evidence seems to indicate that any impurity in the pale-red crystals is not a different molecular species, but that the disorder must be due to molecules that are differently oriented in the crystal.

We do not intend to make a more detailed structural investigation on the β-modification, because the limited intensity data make it very unlikely that the structural parameters could be determined as accurately as in the case of the α-modification even although the space group of α is non-centred. The crystallographic data of the two modifications are compared in the Table.

Data for α- and β-dinaphthoperopyrene, $C_{38}H_{18}$.

	α-Form	β-Form
System	Monoclinic	Monoclinic
a	30·73 Å	16·01 Å
b	3·855	7·48
c	19·87	21·51
β	113·0°	118·6°
Cell volume	2167 Å³	2263 Å³
Space group	$C_2{}^3$–$C2$	$C_{2h}{}^5$–$P2_1/c$
Molecules per cell	4	4

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[2] Rossmann, *J.*, 1959, 2601.

[3] Clar, Kelly, Robertson, and Rossmann, *J.*, 1956, 3878.