508. *The Crystal Structures of Some Analogues of Perylene.*

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By comparing some of the crystallographic properties of terrylene (II) and quaterrylene (III) with those of perylene (I), the assignment of formulæ to the first two hydrocarbons is confirmed. Corresponding *X*-ray diffraction photographs of all three compounds are strikingly similar, proving that the arrangement of the respective molecules in their crystals is almost identical.

THE crystal structure of perylene (I) was determined by Donaldson, Robertson, and White.[1] The second member in the series of *peri*-condensed naphthalene analogues (II), terrylene, has been synthesised by Clar, Kelly, and Laird,[2] who described it as a deep red hydrocarbon, m. p. 510°. The third member (III), quaterrylene, was described [2] as a very dark green compound, m. p. >570°. It had been obtained from a sodium chloride–aluminium chloride melt of perylene. However, the products also included a red-brown hydrocarbon, m. p. 467—469°, which must have originated in some other mode of combination of two perylene molecules, *e.g.* (IV). There might therefore be some error in the identification of the green hydrocarbon with quaterrylene. For instance, Zinke, Nussmüller, and

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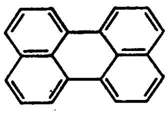
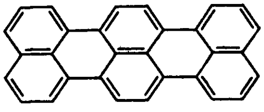
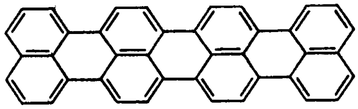
[1] Donaldson, Robertson, and White, *Proc. Roy. Soc.*, 1953, *A*, **220**, 311.

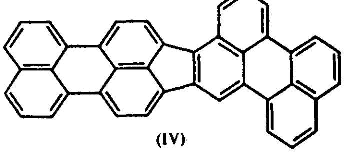
[2] Clar, Kelly, and Laird, *Monatsh.*, 1956, **87**, 391.

Ott[3] believed they had synthesised quaterrylene from perylene and 1-bromonaphthalene, whereas their product has been shown to be terrylene.[2] Since series of similarly analogous aromatic hydrocarbons often have closely related crystal structures,[4] a comparison of the crystallographic properties of these two hydrocarbons with those of perylene might provide conclusive evidence that the compounds are indeed related as formulæ (I)—(III) require.


(I)


(II)


(III)


(IV)

Experimental

Crystals of the red hydrocarbon, obtained from trichlorobenzene, consisted of small rectangular leaflets, with the (001) face as the only form to show appreciable development. Viewed normally to this face in polarised light, the crystals gave oblique extinction and marked pleochroism. Though they were too thin for easy handling, several *X*-ray rotation and oscillation photographs were obtained at various settings of a single crystal. From them it was possible to derive approximate values for the unit-cell parameters (see Table).

Unit-cell parameters.

		a	b	c	β	d_m	d_c	Z	Space group
Perylene	$C_{20}H_{12}$	11·35	10·87	10·31	101°	1·32	1·342	4	$P2_1/a$
Terrylene	$C_{30}H_{16}$	$11{\cdot}_4$	10·7	$14{\cdot}_7$	(102°)	—	1·42	4	$P2_1/a$
Quaterrylene ...	$C_{40}H_{20}$	11·4	$10{\cdot}6_2$	19·7	103°	1·42	1·429	4	$P2_1/a$

More satisfactory crystals of the green hydrocarbon were grown by sublimation. Again rectangular and with the (001) face most prominently developed, they possessed a number of other faces. Lying on the (001) face, the platelets normally appeared black, though—when thin enough—they were dark green, with oblique extinction. Viewed in an edge-on aspect, they showed a less intense colour, despite the fact that the transmitted light then had to traverse a greater thickness of material. The unit-cell parameters listed in the Table were derived from an adequate set of rotation, oscillation, and moving-film photographs. Copper K_α-radiation was used. The data shown for perylene are those cited by Robertson.[4] Axial translations are in Å, d_m is the measured density found by flotation and d_c that calculated, and Z is the number of molecules per unit cell. Different crystals of quaterrylene appeared to differ appreciably in density; the value given has been biased in favour of the higher densities observed. The space group of terrylene was not completely determined, but no reflexions inconsistent with $P2_1/a$ were recorded, and this group appears to be fully justified by the considerations set out below.

Discussion

These parameters correspond closely: *a* and *b* are nearly the same for all three compounds, whilst there are successive increments of about 4·7 Å in *c*. The length of molecules (I)—(III) would be expected to increase successively by about 4·3 Å, made up of 2·8 Å, the distance between atoms 1 and 4 in a naphthalene residue, and of 1·5 Å, the length of the *peri*-bond. The small discrepancy between 4·7 and 4·3 Å may be attributed to the

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[3] Zinke, Nussmüller, and Ott, *Monotsh.*, 1955, **86**, 853.

[4] Robertson, " Organic Crystals and Molecules," Cornell Univ. Press, 1953, p. 216.

longer molecules' being packed more nearly parallel to the *c*-axis, as is also suggested by the significantly lower value of *b* for quaterrylene. On the evidence of these unit-cell dimensions alone, it is likely that the three compounds are perylene and its analogues, with the greatest lengths of their molecules nearly parallel to *c*.

This conclusion becomes inescapable after a detailed comparison of corresponding *X*-ray photographs has been made. With due allowance for the different lengths of the *c*-axes, the resemblance was very close in every case. It is illustrated in the Plate, where [110] rotation photographs of perylene and quaterrylene are shown separately and then in juxtaposition. In some respects the resemblance is closer without allowance for the changes in *c*. This arises because the Fourier transforms of molecules (I)—(III) are in large part identical, so that—the molecules of the different hydrocarbons being similarly arranged in the crystals—intense reflexions are likely to occur in the same region of corresponding *X*-ray diagrams, irrespective of the particular value of the *l*-index.

There can be no doubt that these crystals are built from closely analogous molecules, arranged in an almost identical manner. It follows that, since the crystal structure of perylene is already known, those of terrylene and quaterrylene can be immediately inferred to a good first approximation. A more detailed study of quaterrylene will be undertaken, though the structure—like that of perylene—is not one that lends itself to accurate analysis by two-dimensional methods.

These three compounds constitute a crystallographic series whose regularity is almost equal to that shown by the normal paraffins and their derivatives. Diphenyl, terphenyl, and quaterphenyl are a comparable family;[5] with each additional phenyl group the *c*-axis increases by about 4·2 Å, as would be expected. (The crystallographic evidence—which is self-consistent, though of an early date [6]—requires each of these molecules to be centrosymmetric, and probably coplanar; but, in the gaseous state, that of diphenyl is not so.[7]) A similar and longer series occurs with naphthalene and its benzologues, which have been studied as far as hexacene;[4] but, though the unit cells correspond, there is a change from monoclinic to triclinic symmetry between anthracene and tetracene. Respective *c*-axes increase by about 2·4 Å, which agrees with the expected increase in molecular length. In the series, coronene–ovalene–circumanthrene,[8] the increment appears in the *a*-axis, and averages at about 3·5 Å, which is greater than the increase in molecular length, 2·4 Å. This increase lies approximately in the direction of the *a*-glide, so that two molecules, rather steeply inclined to *a*, come within the primitive translation.

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[5] Pickett, *Nature*, 1933, **131**, 513.

[6] *Idem, J. Amer. Chem. Soc.*, 1936, **58**, 2299; earlier references are also given here, or in *Strukturbericht.*

[7] Bastiansen, *Acta Chem. Scand.*, 1949, **3**, 408.

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

A comparison of [110] *rotation* X-*ray diagrams for crystals of perylene and quaterrylene.* (a) *Perylene.* (b) *Quaterrylene.* (c) *Both diagrams* (a) *and* (b) *in closer juxtaposition.* (*That for quaterrylene has been displaced upwards by about* 1 *mm.*).