*Acta Cryst.* (1960). **13**, 162

# The structure of methyl 1:2-benzanthraquinones. I. Crystal data.

By R. P. Ferrier and J. Iball,
*Chemistry Department, Queen's College, Dundee, Scotland*

(*Received* 29 *October* 1959)

The carcinogenic action of the methyl substituted 1:2-benzanthracenes depends on the position at which a methyl group is attached. No satisfactory correlation of biological activity with any other property of these compounds has been found. In the course of an investigation of the properties of these compounds and of possible metabolites a series of quinones was prepared by J. W. Cook, A. M. Robinson and F. Goulden (Cook, 1930, 1932, 1933; Cook, Robinson & Goulden, 1937) and measurements were made of the oxidation-reduction potentials (Iball, 1940). Most of the quinones gave very satisfactory single crystals and a study of their unit cells and space groups was undertaken with the object of choosing, for detailed analysis, a suitable quinone related to a carcinogenic hydrocarbon and one which is related to an inactive hydrocarbon. The two selected were 5-methyl-1:2-benzanthraquinone (5-methyl-1:2-benzanthracene is an active carcinogen) and 2′-methyl-1:2-benzanthraquinone (the hydrocarbon is inactive).

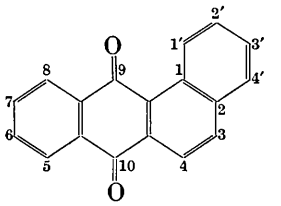


Fig. 1. Numbering of carbon atoms in 1:2-benzanthraquinone.

In Part I we give the unit cells and space group of all the quinones studied and Parts II and III will deal with the detailed structure of the 5-methyl and 2′-methyl quinones. The structures of the latter compounds are being refined by 3-dimensional least-squares techniques. Fig. 1 gives the numbering of the carbon atoms.

### 1:2-Benzanthraquinone

Thin dark-yellow plates were obtained on crystallization from ethyl acetate. They are monoclinic and the main face is (010).

$a = 10{\cdot}96$, $b = 11{\cdot}70$, $c = 19{\cdot}23$ Å; $\beta = 96{\cdot}8°$.

8 mol. ($C_{18}O_2H_{10}$) per unit cell;
$d_o$ (26·3 °C.) = 1·398 g.cm.$^{-3}$; $d_c$ = 1·400 g.cm.$^{-3}$.

Systematic absences, $hkl$ when $(h+k)$ is odd and $h0l$ when $l$ is odd.
The space group is $Cc$ or $C2/c$.

### 3-Methyl-1:2-benzanthraquinone

The data on this compound has already been published (Iball, 1938) but it is included for completeness.

Yellow needles are obtained by crystallization from ethyl acetate. They are monoclinic with $a$ parallel to the needle axis and they show the forms {011} and {100}.

$a = 7{\cdot}54$, $b = 16{\cdot}84$, $c = 11{\cdot}65$ Å; $\beta = 118{\cdot}9°$.

4 mol. ($C_{19}D_2H_{12}$) per unit cell;
$d_o$ (20 °C.) = 1·396 g.cm.$^{-3}$, $d_c$ = 1·403 g.cm.$^{-3}$.

Systematic absences, $h0l$ when $h$ is odd and $0k0$ when $k$ is odd.
The space group is therefore $P2_1/a$.

### 4-Methyl-1:2-benzanthraquinone

Needle crystals, light-brown in colour were obtained by crystallization from ethyl acetate. They are monoclinic with $c$ parallel to the needle axis.

$a = 11{\cdot}80$, $b = 15{\cdot}50$, $c = 3{\cdot}99$ Å; $\beta = 117{\cdot}8°$.

2 mol. ($C_{19}O_2H_{12}$) per unit cell;
$d_o$ (22·0 °C.) = 1·400 g.cm.$^{-3}$; $d_c$ = 1·397 g.cm.$^{-3}$.

Systematic absences, $0k0$ when $k$ is odd.

The space group can theoretically be either $P2_1$ or $P2_1/m$. The latter space group would, however, require the molecules to have a centre of symmetry and since this is impossible with this compound the space group must be $P2_1$.

### 5-Methyl-1:2-benzanthraquinone

Crystallization from ethyl acetate gave long pale-yellow needles. The crystals were orthorhombic with $c$ parallel to the needle axis and a well-developed face (010) was present on most of them.

$a = 14{\cdot}13$, $b = 23{\cdot}27$, $c = 3{\cdot}94$ Å.

4 mol. ($C_{19}O_2H_{12}$) per unit cell;
$d_o$ (24·5 °C.) = 1·389 g.cm.$^{-3}$; $d_c$ = 1·395 g.cm.$^{-3}$.

Systematic absences, $h0l$ when $(h+l)$ is odd and $hk0$ when $k$ is odd.

Two space groups, $P2_1nb$ and $Pmnb$ are consistent with the above absences but the latter requires 8 asymmetric units and since this compound cannot have any molecular symmetry the space group must be $P2_1nb$.

### 6-Methyl-1:2-benzanthraquinone

Pale yellow needles were obtained by crystallization from amyl acetate. They were triclinic with $c$ along the needle axis.

$a = 13{\cdot}12$, $b = 13{\cdot}69$, $c = 7{\cdot}68$ Å;
$\alpha = 103{\cdot}0°$, $\beta = 94{\cdot}8°$, $\gamma = 83{\cdot}1°$.

4 mol. ($C_{19}O_2H_{12}$) per unit cell;
$d_o$ (23.0 °C.) = 1·359 g.cm.$^{-3}$; $d_c$ = 1·358 g.cm.$^{-3}$.

Space group $P1$ or $P\bar{1}$. With 4 molecules per unit cell it is probable that $P\bar{1}$ is the correct space group with 2 molecules forming an asymmetric unit.

### 7-Methyl-1:2-benzanthraquinone

Many attempts were made to obtain reasonable single crystals from a variety of solvents but all were unsuccessful. The compound always crystallized in the form of an extremely fine yellow powder.

### 8-Methyl-1:2-benzanthraquinone

Pale-yellow needles were obtained by crystallization from ethyl acetate. They appeared to be good single crystals when examined under the microscope but in nearly every needle examined by X-rays multiple diffraction spots appeared. The unit cell is monoclinic with $c$ parallel to the needle axis.

$a = 10{\cdot}37,\ b = 16{\cdot}91,\ c = 7{\cdot}57$ Å; $\beta = 100{\cdot}5°$.

4 mol. ($C_{19}O_2H_{12}$) per unit cell;
$d_o$ (22.0 °C.) = 1·388 g.cm.$^{-3}$; $d_c$ = 1·393 g.cm.$^{-3}$.

Systematic absences, $h0l$ when $l$ is odd and $0k0$ when $k$ is odd.
The space group is therefore $P2_1/c$.

### 1'-Methyl-1:2-benzanthraquinone

Yellow needles were obtained by crystallization from ethyl acetate. They were monoclinic with $b$ parallel to the needle axis and most of them had well developed (100) faces.

$a = 31{\cdot}78,\ b = 3{\cdot}94,\ c = 23{\cdot}84$ Å; $\beta = 120{\cdot}4°$.

8 mol. ($C_{19}O_2H_{12}$) per unit cell;
$d_o$ (24·0 °C.) = 1·396 g.cm.$^{-3}$; $d_c$ = 1·405 g.cm.$^{-3}$.

Systematic absences, $hkl$ when $(k+l)$ is odd and $h0l$ when $h$ is odd.

The space group could be either $Cc$ or $C2/c$ but with 8 molecules in the unit cell the latter group is probably the correct one.

### 2'-Methyl-1:2-benzanthraquinone

This compound was originally purified by crystallization from methyl ethyl ketone and was in the form of thin long yellow needles. When it was recrystallized from the same solvent at room temperature a different crystal modification (Form II) was obtained.

Improved crystals of the original modification (Form I) were obtained, with some difficulty, by recrystallizing from the same solvent at a temperature near 0 °C.

Both modifications were monoclinic needles, Form II had a slightly darker colour than Form I.

*Form I*

Yellow monoclinic needles with $b$ parallel to the needle axis.

$a = 20{\cdot}67,\ b = 4{\cdot}06,\ c = 7{\cdot}77$ Å; $\beta = 90{\cdot}8°$.

2 mol. ($C_{19}O_2H_{12}$) per unit cell;
$d_o$ (23·5 °C.) = 1·380 g.cm.$^{-3}$; $d_c$ = 1·386 g.cm.$^{-3}$.

Systematic absences, $0k0$ when $k$ is odd.

The space group could be $P2_1$ or $P2_1/m$ but in the latter group the mirror plane would require two molecules to be placed along the $b$ axis and this is impossible with an axial length of only 4·06 Å.

The space group is therefore $P2_1$.

*Form II*

Yellow monoclinic needles with $a$ parallel to the needle axis.

$a = 7{\cdot}87,\ b = 16{\cdot}53,\ c = 22{\cdot}35$ Å; $\beta = 113{\cdot}5°$.

8 mol. ($C_{19}O_2H_{12}$) per unit cell;
$d_o$ = (22·0 °C.) = 1·353 g.cm.$^{-3}$; $d_c$ = 1·357 g.cm.$^{-3}$.

Systematic absences, $h0l$ when $l$ is odd and $0k0$ when $k$ is odd.

The space group is $P2_1/c$ and the asymmetric unit must consist of two molecules.

### 3'-Methyl-1:2-benzanthraquinone

Spherical clusters of very small orange-coloured needles were obtained by crystallization from methyl ethyl ketone. The needles, which were of poor quality, were orthorhombic with $c$ parallel to the needle axis.

$a = 21{\cdot}93,\ b = 30{\cdot}75,\ c = 3{\cdot}95$ Å.

8 mol. ($C_{19}O_2H_{12}$) per unit cell;
$d_o$ = (22·3 °C.) = 1·369 g.cm.$^{-3}$; $d_c$ = 1·360 g.cm.$^{-3}$.

Systematic absences, $0kl$ when $(k+l)$ is odd and $hk0$ when $h$ is odd.

Two space groups are consistent with the above absences, viz. $Pn2a$ and $Pnma$. No distinction between them can be made on the evidence available.

### 4'-Methyl-1:2-benzanthraquinone

A yellow crystalline powder was consistently obtained when this compound was re-crystallized from a wide variety of solvents and all attempts to grow crystals large enough for ordinary single-crystal techniques have been unsuccessful.

These compounds have very similar shaped molecules but crystallize in a wide variety of space groups. Although there are similarities in the unit-cell dimensions the arrangement of symmetry elements is very different. For example, the 5-methyl compound has a unit cell with very similar axial lengths and cell shape to Form I of the 2'-methyl compound (the former has one axis doubled) but whereas in the latter the short axis (4·06 Å) is a symmetry axis, the corresponding axis (3·94 Å) of the former is not a symmetry axis.

We are indebted to the British Empire Cancer Campaign and to the Royal Society for grants in support of this investigation.

### References

Cook, J. W. (1930). *J. Chem. Soc.* p. 1087.
Cook, J. W. (1932). *J. Chem. Soc.* p. 456.
Cook, J. W. (1933). *J. Chem. Soc.* p. 1952.
Cook, J. W., Robinson, A. M. & Goulden, F. (1937). *J. Chem. Soc.* p. 393.
Iball, J. (1938). *Z. Kristallogr.* A, **99**, 230.
Iball, J. (1940). *Amer. J. Cancer*, **38**, 372.