

The Crystalline Structure of Anthracene

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XVI. *The Crystalline Structure of Anthracene.* By SIR W. H. BRAGG, F.R.S.

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ABSTRACT.

The author in an address recently published* put forward evidence for regarding the benzene ring as an actual structure of ascertainable size and form, and deduced that the unit cells of naphthalene and anthracene should have two of their axes equal, the third axis being longer for anthracene than for naphthalene by the width of one ring. The experimental data then available supported this hypothesis only roughly; in the present Paper it is shown that more reliable data, subsequently obtained from small but perfect anthracene crystals, agree with it very closely. It is pointed out that the X-ray data furnish a new and accurate method of determining the density of a crystal.

In an Address which as President I gave to this Society on November 11th, 1921, I described certain experiments on the structure of organic crystals. Among these were measurements on the dimensions of the crystal units of naphthalene and anthracene. The comparison of the two sets of results was used to show that the molecule in each case lay with its longest dimension in the direction of the *c* axis. The anthracene data were not entirely satisfactory, since only one X-ray measurement could be made, and that not very accurately: this was the spacing of the cleavage plane 001. The dimensions of the unit were calculated also from the crystallographic data given by Groth and from a determination of the specific gravity quoted in Kaye and Laby's tables. The results were, however, sufficiently accurate to show that the major length of the molecule lay along the *c* axis, because the difference between the lengths of the *c* axes of naphthalene and anthracene was 2.9, while the width of the benzene ring as found in the diamond was 2.5. It was assumed that the molecule of anthracene might be expected to be longer than the molecule of naphthalene by the width of the extra ring, and that the small difference between the two values did not affect the argument.

Recently, through the kindness of Dr. Brady, I have had the opportunity of measuring the anthracene constants, using some minute but perfect crystals which he gave me. The results are set out below in a form which allows comparison with the naphthalene constants. It will be seen that there is now much better agreement between results as calculated and as expected. The *c* axis of anthracene is really 11.18, not 11.6 as calculated from the data previously available. Using, therefore, the X-ray data alone, we find that the difference between the *c* axes of the two crystals is 2.5 exactly, which was the figure anticipated.

The quite considerable difference between the new and the old results is due for the most part to the value previously adopted for the specific gravity. Now that the constants of the crystal unit are more accurately known, it is possible to calculate the specific gravity of a perfect crystal. It is to be expected that this will always be higher than the specific gravity found by ordinary means. It is, in fact, usual for crystallographers to make several measurements of specific gravity and to accept the highest as the most correct (Tutton, "Crystallography," new edition, page 625). The value of the specific gravity is now shown to be 1.255.

There is remarkable similarity between the naphthalene and anthracene observations. Not only are the crystals isomorphous, but the same planes are in each case the

* Proc. Phys. Soc., Vol. 34, Dec. (1921).

best reflectors, and the spacings of the 100 and the 010 are almost exactly the same; it is only in the length of the c axis that there is any marked difference. The cell contains two molecules in each case, while the symmetry number is 4, that is to say, if the molecule were unsymmetrical it would be necessary to employ four of them to make up a cell having the symmetry of the monoclinic prismatic class to which the crystals belong. As two molecules are able to give fourfold symmetry, each must have a twofold symmetry. The nature of that symmetry is indicated by the results. In both cases the 010 plane is exactly halved. Also in the 010 zone, that is in the case of the planes passing through the b axis, 100 and $10\bar{1}$ are halved, 001 and $20\bar{1}$ are not halved. These results show that the crystal molecule possesses a centre of symmetry, and that if one set of molecules all alike to each other be placed at the corners of the cell, the centres of the other molecules lie at the centres of the ab face.

ANTHRACENE.

Monoclinic prismatic. Two molecules in the crystal unit. Assume:—

$$a=8.58; b=6.02; c=11.18; \beta=125^{\circ}0'$$

	<i>Assumed.</i>	<i>Observed.</i>	
100	7.02	3.51	Strong
010	6.02	3.01	Moderate
001	9.16	9.16	Strong. Also 2nd & 4th orders, 3rd order weak.
	<i>Calculated.</i>	<i>Observed.</i>	
$10\bar{1}$	8.34	4.16	
$20\bar{1}$	4.17	4.16	Moderate
110	4.58	4.57	Very strong
$11\bar{1}$	4.88	4.90	Weak
$21\bar{1}$	3.43	3.43	Strong
210	3.04	3.04	Strong

Axial ratios in accordance with the above are

$$a : b : c = 1.423 : 1 : 1.857, \beta = 125^{\circ}0'$$

Groth gives (*Chemische Krystallographie* V., p. 437):

$$a : b : c = 1.4220 : 1 : 1.8781, \beta = 124^{\circ}24'$$

Specific gravity (calculated from the X-ray data) = 1.255

Specific gravity (redetermined by using Dr. Brady's crystal) = 1.250.

NAPHTHALENE.

(See Structure of Organic Crystals, Proc. Phys. Soc., 34, December 15, 1921)
Monoclinic prismatic. Two molecules in the unit cell.

$$a=8.34; b=5.98; c=8.68; \beta=122^{\circ}44'$$

These values are in better agreement with the experimental results described in the Paper referred to than the values calculated from the crystallographic data; the differences are small, however.

DISCUSSION.

Dr. D. OWEN inquired whether the measurements show identical dimensions for all the unit cells of a given substance, whatever the specimen taken ; or whether the results vary with the state of strain of a crystal, which might be expected to affect its density.

Dr. E. A. OWEN said that metallurgists would agree with the remark made by the author in presenting his Paper, that X-ray measurements were more dependable than direct measurements of the density of a crystal. In alloys particularly the densities of the component crystals would be difficult to find.

Mr. J. GUILD said he was interested in the statement that by X-ray measurements it was possible to determine the density of a crystalline substance despite the presence of impurities which would vitiate ordinary density measurements. Would it be possible in a matrix of two or more crystalline substances to determine the density of each ? For example, could the density of the cementite in a pearlitic steel be determined ?

Dr. H. BORNS said that in neutralising H_2SO_4 with lime in organic work chemists often obtain fine crystals of various shapes which after all turn out to be impure $CaSO_4$. Have such and similar crystals been examined as to the identity of their unit cells ?

Dr. F. L. HOPWOOD said that the structure of mixed crystals has been investigated by Vegard,* who showed that the lattice of Thorite ($Th SiO_4$), which belongs to the Zircon group, was completely broken down, only the outer form being preserved.

AUTHOR'S reply : Such evidence as is available supports the idea that the size and form of the crystal unit cell is always the same to a high degree of accuracy, except, of course, that strain or expansion of the crystal is shared by the cell. Each kind of crystal in a matrix gives its own spectrum quite independently. For instance, if cementite crystals occurred in sufficient quantity in a powdered mass the Debye-Hull photograph would show the spectrum of cementite with others due to other crystals. If the cementite lines could be disentangled and interpreted, and if the chemical composition is known, the density is found.

The author is not aware of any systematic measurement of $CaSO_4$ crystals, but does not doubt that they all have the same unit cell no matter what the outside form may be.