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The unit cell of chrysotile.

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In a recent paper Padurow (1950*a*) has presented some new measurements of the fibre-diffraction pattern of chrysotile from Quebec, Canada, and by the use of affine lattice constants (Padurow, 1950*b*) has concluded that this mineral is triclinic. This result is contrary to the conclusions of previous workers (Warren & Bragg, 1930; Warren & Hering, 1942; Aruja, 1943); and, although the departure from monoclinic symmetry proposed by Padurow is not large, it is important in that if it were accepted it would seriously affect the interpretation of the disorder effects in chrysotile which has been proposed by Warren & Hering and by Aruja (1943). A critical examination of Padurow's conclusions has therefore been made, and the application of his results to more extensive diffraction data has been considered. The ambiguities inherent in the interpretation of fibre photographs preclude the achievement of certainty, but it is concluded that the triclinic cell proposed by Padurow cannot be confirmed and that the previously accepted monoclinic cell is much more probable.

In Table 1 are presented the unit-cell parameters which have been found by various authors for clino-chrysotile, as distinct from ortho-chrysotile (Whittaker, 1951). The question of the doubled a parameter need not detain us; it is required only in the indexing of certain very weak reflexions not observed by all the workers. Therefore, apart from the doubled b parameter of Warren & Bragg, which is also without significance for the present discussion, the differences to be noted are the high value of the a parameter reported by Padurow and, of course, his values for α and γ.

Table 1. *Unit-cell parameters*

	Warren & Bragg	Warren & Hering	Aruja	Padurow	Whittaker
a (Å)	14·66	7·33	14·62	7·36	14·65
b (Å)	18·5	9·24	9·2	9·26	9·2
c (Å)	5·33	5·33	5·32	5·33	5·33
α	90°	90°	90°	92° 50′	90°
β	93° 16′	93° 16′	93° 12′	93° 11′	93° 7′
γ	90°	90°	90°	89° 50′	90°

The value of Δ_γ was found not to differ significantly from zero, but it could not be determined with any degree of accuracy. If it is taken to be exactly zero and the values of Δ_α and Δ_β given by Padurow are accepted, then one obtains the reported value of $\gamma = 89° 50'$. The accuracy of the determination of Δ_γ is, however, insufficient to make this value of γ significantly different from 90°, so that the reported value has no bearing on the discussion of the correct crystal system.

Two lines of evidence are offered for the departure of α from 90°. The major evidence comes from the positions of the spots indexed as 011, 031, 051 and 221 on the first layer line, and those indexed as 022, 052 and $0\bar{5}2$ on the second layer line. Supporting evidence is adduced from the positions of the $h02$ spots. These two arguments will be considered in order.

The derivation of a triclinic angle α from the discrepancies between the positions of the spots 011, 031, 051 and 022 and the positions which they would be expected to occupy on the assumption of monoclinic symmetry and a b value of 9·25Å is unexceptionable, although alternative indices for 022 are possible with the doubled a axis. These four reflexions cannot be indexed as they stand on the basis of a monoclinic cell having the b dimension which is obtained from the 060 reflexion, and assumption of triclinic symmetry is a sufficient but not a necessary explanation of this fact. An alternative explanation based on a disordered monoclinic structure has been put forward by Aruja (1943). It is therefore necessary to examine the supporting evidence for triclinic symmetry given by Padurow, and also to consider the effect of extending his treatment to the higher layer lines and weaker reflexions which he did not observe.

The remaining reflexions used by Padurow in the derivation of Δ_α are indexed as 221, 052 and $0\bar{5}2$, but the positions of these spots cannot be considered to advance the argument materially since they are not indexed uniquely. The two latter sets of indices are indeed only possible if triclinic symmetry is accepted on other grounds.

The remaining evidence adduced in support of the triclinic cell arises from the discrepancy in the values of t_β $(= -\cot\beta)$ obtained from the $h02$ reflexions with positive and negative values of h on the assumption of a monoclinic cell. This evidence is critical, since the observed discrepancies would not be explained by Aruja's theory. Examination of the calculations shows, however, that the discrepancy arises entirely from the unusually large value of a obtained by Padurow from the $h00$ reflexions. If we use an average value of a as obtained by other workers and apply it to the evaluation of Padurow's measurements for the $h02$ reflexions, no significant discrepancy remains.

The matter has been checked further by consideration of data obtained by the author for the second, third, fourth, fifth and sixth layer lines of clino-chrysotile. The data were obtained using Cu $K\alpha$ and Mo $K\alpha$ radiation, and the specimen consisted of a mixture of ortho-chrysotile and clino-chrysotile from Cuddapah, India (Whittaker, 1951). The clino portion is, however, known to give photographs essentially identical with those of chrysotile from Quebec. No significant difference was found between the t_β values obtained from the $h02$ and $\bar{h}02$ reflexions, or from the $h04$ and $\bar{h}04$ reflexions. Further, if Padurow's triclinic cell is accepted it becomes necessary to re-index all the $0kl$ reflexions with $l > 2$. Such a triclinic cell can certainly provide indices for these reflexions, but they would be of the general type hkl not observed as strong reflexions with $l \leqslant 2$. In particular, a well-exposed Mo $K\alpha$ photograph of chrysotile shows a very marked set of nine reflexions which are distinguished from the rest in two ways: they are all strong relative to their neighbours, and they are distinguished from equally strong reflexions by all having short Debye–Scherrer arcs attached to

them. On the basis of a monoclinic cell these spots receive the following indices:

Zero layer	060	First layer	031 and 091
Second layer	062	Third layer	033 and 093
Fourth layer	064	Fifth layer	095
Sixth layer	066		

The presumption appears strong that the five of these distinctive reflexions with $l > 2$ should have indices of similar form to those with $l \leqslant 2$.

Finally, it should be pointed out that the assumption of triclinic symmetry does not explain the low b value which corresponds to the position of the 020 reflexion. This is observed by Padurow, and has also been systematically observed by other workers. Both this effect, and also the corresponding one on the weak 040 reflexion not observed by Padurow, are accounted for by Aruja's structure. It should also be observed that the reflexion indexed by Padurow as 090 and used in calculating the b parameter is equally well indexed as 700; indeed, photometric studies show that its breadth falls in line with those of $h00$ reflexions but not with those of $0k0$ reflexions.

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The structure of *p*-di-isocyanobenzene.

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Transparent needle-like single crystals of *p*-di-isocyanobenzene (New & Sutton, 1932) have been obtained which show a marked tendency towards chemical decomposition; this is normally complete in about three days and appears to be accelerated in X-radiation. Because of this, complete X-ray data have been obtained only about one axis (c), although there is a small amount of information available about the other two axes.

The X-ray photographs indicate a monoclinic unit cell,

$$a = 9{\cdot}80, \quad b = 7{\cdot}15, \quad c = 4{\cdot}72\,\text{Å}, \quad \beta = 97^\circ\ 11',$$

corresponding to two molecules per unit cell. The absent reflexions correspond to one of the three space groups $C2/m$, $C2$, Cm—probably the first.

Considerations of cell size and Patterson syntheses about all three axes indicate the approximate general positions of the molecules. Trial Fourier syntheses were made for the projection along the c axis, the molecule being assumed to lie in the special twofold positions of the centro-symmetric space group $C2/m$. This led to a satisfactory electron-density map showing a plan of the molecule tilted approximately 45° about the broken line (Fig. 1). Close agreement was found between the thirty observed and calculated structure factors;

$$\Sigma(\Delta F) \div \Sigma F = 18{\cdot}5\,\%$$

(cf. Hanson & Lipson, 1952).

The resulting fractional parameters are:

	x	y	z
C_1	0·100	0	−0·21
C_2	0·050	0·167	−0·11
C_3	−0·050	0·167	0·11
N_1	0·207	0	−0·44
C_4	0·295	0	−0·62

the z parameters being less certain than the x and y parameters, since they were not directly observed. These parameters correspond to the alternative structures II or III (Fig. 1), which, in plan, differ but slightly, and only in the parameter of the terminal carbon atom. Type III seems less probable than II in view of the evidence from other physical measurements (New & Sutton, 1932; Hammick, New, Sidgwick & Sutton, 1930). Any change in the parameters towards a structure of type I is found to spoil agreement between observed and calculated structure factors very considerably.

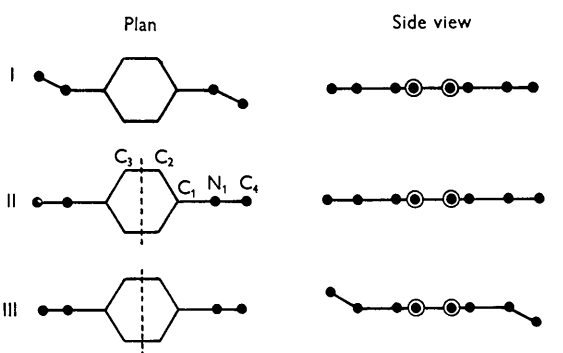

Fig. 1.

When the difficulties connected with the instability of the crystal have been more effectively surmounted, it is hoped to obtain complete data about the other axes. It will then be possible to define the atomic positions more accurately, and to decide finally between structures II and III.

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