It is felt that alternative (*a*) is the more feasible in the amphibole structure, but no decision as to which is correct can be made in the present circumstances.

It may be that some of the structural features common to this actinolite and to crocidolite are characteristic of the more nearly fibrous members of the amphibole series. It is hoped that similar and in some cases more extensive studies of other amphiboles including a pure tremolite, to be made in due course, may throw light on this and other problems encountered in the course of the present and previous investigations.

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A Comparison of Optical Methods and Difference Synthesis in the Location of Hydrogen

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A comparison has been made between optical methods of testing possible positions of hydrogen atoms in a crystal and the more objective method of a difference synthesis. The (010) projection of diphenylene naphthacene was used in the investigation. The results show that the optical methods give a quick guide, but that the difference synthesis is more definite. Optical methods can, however, be used for non-centrosymmetrical projections, whereas the difference synthesis cannot. The inclusion of hydrogen in the structure-factor calculations for diphenylene naphthacene reduced the agreement residuals from 0·18 to 0·11 for the ($h0l$) zone and from 0·21 to 0·14 for the ($0kl$) zone. This has important implications concerning the lengths of C–C bonds.

Optical methods

Bennett & Hanson (1953) have published a structure for diphenylene naphthacene which included some apparently anomalous C–C bond distances. No great accuracy was claimed, however, the comparatively large values of $\Sigma(|F_o|-|F_c|)\div\Sigma|F_o|$ (0·18 for $h0l$, 0·21 for $0kl$) being attributed to lack of accuracy in the visually observed X-ray intensities. The present work was undertaken to see if by optical methods the hydrogen atoms could be detected. The techniques used were essentially those described by Pinnock & Lipson (1954), in which the optical transform of a mask representing assumed positions of hydrogen atoms only is superimposed on the reciprocal-lattice net. The first trial indicated clearly that the signs and magnitudes of the transform peaks were such as to effect a considerable reduction in (F_o-F_c) for the majority of reflexions.

Since it is possible to deduce from the transform pattern the changes in atomic parameters most likely to produce an improvement in the agreement, an arrangement of the hydrogen atoms was arrived at which improved the agreement residual for the $h0l$ zone from 0·18 to 0·13, structure-factor calculations being carried out only for those reflexions for which the transform indicated a significant contribution.

Further refinement was effected by punching two separate masks, each corresponding to half of the hydrogen atoms. Since their transforms are additive, this technique shows the contribution of each group of atoms to any particular reflexion. This, combined with some 'atom by atom' refinement by means of an instrument devised by Hughes & Taylor (to be published), reduced the $h0l$ residual to 0·12.

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Difference synthesis

The increased confidence in the X-ray data derived from the reduced residual indicated that a difference synthesis might reveal the hydrogen peaks. This was carried out for the (010) projection, using all observed reflexions. The resulting Fourier map (Fig. 1) shows that seven of the eight independent hydrogen atoms are fairly well defined, the highest peaks being slightly less than 0·5 e.Å^{-2}. The remaining atom (No. 6 in Fig. 1) was placed in the position shown with the aid of the optically derived position. It is noticeable that the well defined peaks lie close to the 'optical' positions (shown by crosses in Fig. 1).

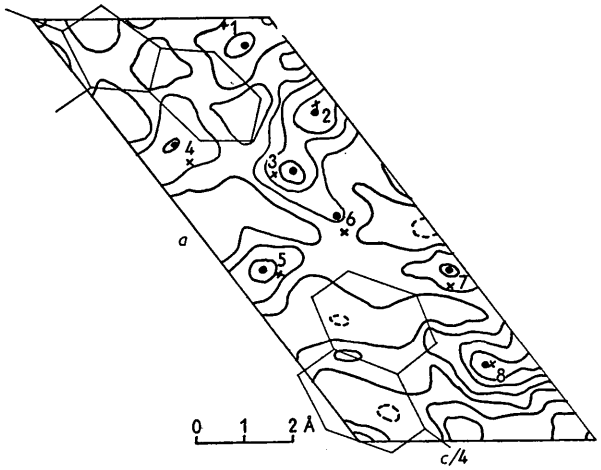

Fig. 1. Difference synthesis map, (010) projection. Contours at intervals of 0·1 e.Å^{-2}, zero contours omitted, negative contours broken. Hydrogen atom positions determined from difference synthesis denoted by dots; those using optical methods by crosses.

Results

Table 1(a) shows the structure factors for all observed $h0l$ reflexions, using x and z parameters (listed in Table 2) corresponding to the positions shown by dots in Fig. 1. Hartree f_0 values for hydrogen were used with a temperature factor $B = 4{\cdot}0$ Å^2. A replot of log ($|F_o| \div |F_c|$) against $\sin^2\theta$, using the amended F_c's, did not indicate any worthwhile change in the scale factor or temperature factor used by Bennett & Hanson. In fact, the overall agreement was found to be virtually unaffected by changes in any parameter,

Table 1(a)

$h\,k\;\;l$	F_o	F_c with hydrogen	F_c without hydrogen
0 0 2	50·3	53·9	62·8
0 0 4	58·0	−55·2	−60·0
0 0 6	7·8	6·5	4·8
0 0 8	15·8	−17·1	−15·4
0 0 12	13·5	12·9	13·9
1 0 0	72·0	59·1	67·0
1 0 2	28·2	29·8	29·8
1 0 4	7·6	5·0	4·4
1 0 10	12·8	11·2	9·3
1 0 12	9·0	8·8	9·3
1 0 $\bar{2}$	30·4	33·6	40·5
1 0 $\bar{4}$	5·7	7·0	5·1
1 0 $\bar{6}$	5·1	7·5	8·2
1 0 $\overline{10}$	8·6	7·7	4·4
1 0 $\overline{12}$	11·2	9·3	9·0
1 0 $\overline{16}$	9·2	−8·5	−8·7
2 0 0	52·6	−47·6	−47·0
2 0 2	31·0	28·6	31·0
2 0 4	7·1	−4·6	−3·8
2 0 6	8·3	6·5	4·0
2 0 8	26·2	22·3	23·0
2 0 10	6·3	4·7	4·4
2 0 $\bar{2}$	35·2	−38·5	−41·7
2 0 $\bar{4}$	28·4	30·6	35·5
2 0 $\bar{6}$	14·1	−16·5	−14·6
2 0 $\bar{8}$	5·9	7·0	3·4
2 0 $\overline{10}$	18·5	17·9	20·0
2 0 $\overline{12}$	7·7	−7·0	−7·6
2 0 $\overline{18}$	10·8	−10·3	−10·3
3 0 0	11·9	11·5	10·8
3 0 4	14·9	−14·5	−12·8
3 0 8	16·1	8·2	7·9
3 0 $\bar{2}$	6·3	5·7	2·8
3 0 $\bar{4}$	5·0	−3·1	−8·4
3 0 $\bar{6}$	22·4	−23·6	−27·4
3 0 $\bar{8}$	24·5	−24·8	−23·8
3 0 $\overline{12}$	8·0	−8·8	−7·7
3 0 $\overline{16}$	9·7	10·5	11·2
3 0 $\overline{20}$	13·4	−11·4	−11·3
4 0 0	7·3	−3·8	−2·2
4 0 2	27·0	22·8	21·6
4 0 4	6·5	6·1	6·4
4 0 6	13·6	−15·3	−16·9
4 0 $\bar{2}$	27·4	−22·2	−19·2
4 0 $\bar{6}$	25·7	28·1	34·1
4 0 $\bar{8}$	14·3	−11·8	−11·9
4 0 $\overline{10}$	33·6	−37·6	−38·0
5 0 0	20·5	14·2	12·7
5 0 2	15·6	15·0	16·0
5 0 $\bar{2}$	6·7	−6·8	−3·8
5 0 $\bar{4}$	16·3	17·0	12·2
5 0 $\bar{6}$	12·1	13·3	17·3
5 0 $\bar{8}$	6·5	5·3	1·4
5 0 $\overline{10}$	6·4	−7·2	−7·0
5 0 $\overline{12}$	13·2	−12·9	−12·0
6 0 0	15·0	12·9	13·3
6 0 $\bar{2}$	32·0	29·2	28·5
6 0 $\bar{4}$	21·7	22·4	22·6
6 0 $\bar{6}$	10·5	−11·0	−13·1
6 0 $\bar{8}$	14·6	−17·9	−18·6
6 0 $\overline{16}$	11·4	12·1	12·7
7 0 2	7·9	9·3	8·8
7 0 $\bar{6}$	12·5	−11·0	−12·1
7 0 $\overline{14}$	11·9	12·9	14·1
7 0 $\overline{18}$	14·1	−15·8	−15·9
8 0 0	8·6	−8·8	−8·7
8 0 $\bar{6}$	13·2	−15·7	−16·4
8 0 $\bar{8}$	8·8	−6·4	−7·3
8 0 $\overline{16}$	9·1	−9·6	−9·2
8 0 $\overline{18}$	9·7	−12·3	−12·3
9 0 2	7·1	−7·9	−8·1
9 0 $\bar{2}$	8·0	7·1	7·2
9 0 $\bar{8}$	17·7	−17·2	−17·2
9 0 $\overline{10}$	22·4	−22·5	−22·2
10 0 $\bar{2}$	11·9	7·5	7·3
10 0 $\overline{10}$	16·8	−17·2	−16·8
10 0 $\overline{12}$	12·3	−10·4	−10·1

Table 1(*b*)

h k	F_o	F_c with hydrogen	F_c without hydrogen
0 0 2	53·4	55·1	64·0
0 0 4	54·8	−55·1	−59·9
0 0 6	10·4	6·7	5·0
0 0 8	18·4	−18·2	−16·5
0 0 12	19·3	14·8	15·8
0 1 1	8·1	9·4	11·9
0 1 2	38·2	52·0	53·1
0 1 3	54·7	56·1	56·0
0 1 4	36·2	33·8	35·1
0 1 6	6·7	− 4·3	− 3·2
0 1 8	15·3	−10·1	− 9·8
0 1 9	19·8	18·1	17·5
0 2 0	5·1	3·7	2·5
0 2 2	13·9	17·2	17·6
0 2 4	18·4	14·7	13·3
0 2 5	16·9	−15·2	−11·0
0 2 7	8·7	−13·8	−14·4
0 2 8	8·5	− 7·3	− 7·0
0 2 9	9·7	7·7	8·0
0 3 1	17·3	11·3	12·4
0 3 9	10·0	−11·2	−11·7
0 4 6	12·7	−10·7	−10·6

Table 2. *Coordinates of hydrogen atoms*

H atom	*x*/*a*	*y*/*b*	*z*/*c*
1	0·067	0·58	−0·200
2	0·227	0·36	−0·220
3	0·366	0·16	−0·150
4	0·307	−0·17	−0·047
5	0·400	−0·46	0·040
6	0·528	−0·64	0·134
7	0·400	−0·86	0·234
8	0·177	−0·55	0·197

including small changes in hydrogen positions, which suggests that the limit of the X-ray data had been reached.

The improvement in the agreement is immediately obvious from Table 1(*a*), the final residual being 0·11. It is interesting that approximately 0·01 of this residual is contributed by a single reflection (100), the inclusion of hydrogen increasing (F_o-F_c) from 3·0 to 12·9. No reasonable hydrogen configuration could change this figure appreciably.

The *y*-coordinates were calculated from the (010) projection using a C–H bond length of 1·07 Å, and the structure factors with and without hydrogen for 0*kl* reflexions are listed in Table 1(*b*). The agreement residual in this case was reduced immediately from 0·21 to 0·14. No attempt at refining was made for this zone on account of the small number of reflexions observed. Again, a single reflexion makes a large contribution to the residual, (012) alone accounting for about 0·03 of the final residual of 0·14.

Discussion

One important consequence of the improvement in the agreement residuals is that greater reliance can be placed on the C–C bond lengths given by Bennett & Hanson, some of which differ considerably from values to be expected from any possible arrangement of double bonds. The greater confidence in the (010) projection is supported by the fact that the difference synthesis does not indicate any significant movement of the carbon atoms. While the rather unsatisfactory (100) projection tends to give comparatively inaccurate *y* coordinates, some of the C–C bonds are almost normal to the *b* axis, and so are non-critical to changes in *y*. Bennett & Hanson's diagrammatic representation of the molecule is reproduced in Fig. 2.

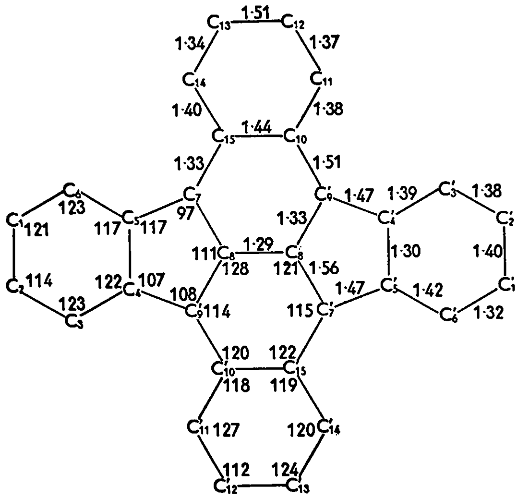

Fig. 2. Diagrammatic representation of the molecule, showing bond lengths (in Ångström units) and angles (in degrees).

Conclusions

This investigation illustrates the value of optical transform methods in the location of hydrogen. They provide a rapid means of testing a possible hydrogen configuration, and of refining such an arrangement. They indicate whether a difference synthesis is likely to be successful, and help in locating poorly defined peaks. Moreover, unlike the difference synthesis, optical methods can be used for non-centrosymmetrical projections.

I wish to express my indebtedness to Prof. H. Lipson and Dr C. A. Taylor for their constant guidance throughout this investigation. I am also grateful to Dr A. W. Hanson for allowing access to the original data of diphenylene naphthacene and for many helpful discussions.

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