anomalous scattering element are present in the unit cell.

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The Crystal Structure of β-Naphthol

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The non-centrosymmetric structure of β-naphthol has been determined with the aid of optical transforms and refined by two-dimensional Fourier methods. Every molecule is attached by hydrogen bonds to two neighbours, and in this way the molecules are linked into chains; adjacent molecules in any chain are crystallographically non-equivalent. Each chain runs throughout the crystal with its length parallel to the *a* axis of the monoclinic unit-cell.

1. Introduction

The crystal structure of β-naphthol has been examined by several research workers. In a paper which includes a review of previous investigations (Hargreaves & Watson, 1957) the authors show that the space group is almost certainly *Ia* and that the unit cell contains two sets of non-equivalent molecules. It was previously assumed that the length of the *c* axis is only half that now established, and that the unit cell contains only one set of equivalent molecules arranged in the space group $P2_1/a$; with these assumptions Kitaijgorodskij (1945, 1947) derived details of the structure of β-naphthol based partly on X-ray evidence and partly on geometrical considerations. The structure determination described in this paper is based wholly on X-ray evidence and confirms that the correct space group is *Ia*.

Wherever possible use has been made of optical-transform methods, and the considerable help afforded by these methods in determining the orientations of the non-equivalent molecules is emphasized in the following sections of the paper.

2. Experimental data

The determination of the space group and unit-cell dimensions are described in the earlier paper (Hargreaves & Watson, 1957) and only the results will be quoted here:

$$a=8.185\pm0.015, \quad b=5.950\pm0.003, \quad c=36.29\pm0.01 \text{ Å};$$
$$\beta = 119° 52'\pm7' .$$

X-ray data show that the space group is either *Ia* or *I2/a*. Pyroelectric tests and statistical tests on the X-ray intensities indicate that the crystals are almost certainly non-centrosymmetric; this suggests that the centrosymmetric space group *I2/a* should be rejected and that the correct space group is *Ia*. There are 4 equivalent general positions in *Ia* and therefore the 8 molecules in the cell will occupy 2 non-equivalent sets of general positions.

Reflexions *h0l* and *0kl*, recorded in zero-layer-line Weissenberg photographs using unfiltered Cu *Kα* radiation, provided the data from which the final atomic positions were deduced. The intensities of the

reflexions were measured by visual comparison with calibration spots of known relative exposure. The cross-sections of the crystal specimens used for taking both sets of Weissenberg photographs are rectangular in the plane perpendicular to the axis of oscillation; the cross-sectional dimensions are 0·24 mm. × 0·10 mm. (b-axis specimen) and 0·16 mm. × 0·10 mm. (a-axis specimen). No absorption corrections have been made; it is estimated that errors in structure amplitudes caused by neglecting the absorption will not exceed 5% for the $h0l$ reflexions and 2% for the $0kl$ reflexions.

3. Determination of the structure

(i) *The* [010] *projection*

The determination of the shape and orientation of the projections of benzene rings from weighted reciprocal-lattice sections is discussed in detail by Hanson, Lipson & Taylor (1953). The $h0l$ weighted reciprocal-lattice section of β-naphthol is shown in Fig. 1; the weights are related to the unitary structure
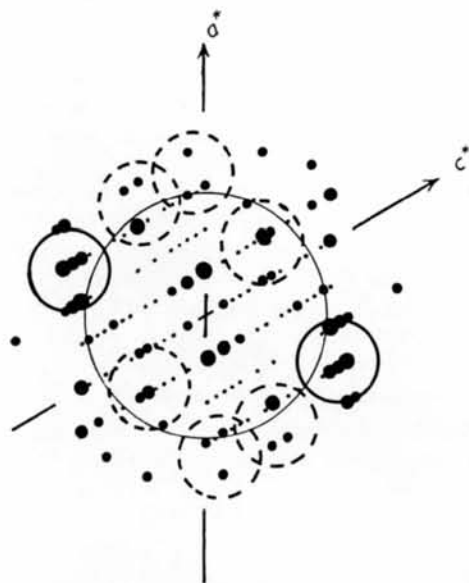

Fig. 1. The $h0l$ section of the weighted reciprocal lattice. Peaks associated with the transform of the benzene molecule surrounded by full lines (principal peaks) or broken lines (subsidiary peaks).

factors. Only two peaks can be seen on or outside the benzene circle; because of the large tilt of the molecule the other four principal benzene peaks are outside the range of reflexions observed with Cu $K\alpha$ radiation. However, the transform of a benzene ring has six subsidiary peaks which lie at smaller distances from the origin than the principal peaks, and these can be distinguished in the weighted reciprocal lattice. The approximate molecular orientation was deduced from the positions of both the two principal peaks and the six subsidiary peaks. The optical transform of the

single 'naphthalene molecule' (i.e. β-naphthol with the oxygen atom omitted) was then compared with the weighted reciprocal lattice. Reasonable agreement was obtained in the peak regions, but it was obvious that not all the large reflexions contained in the two benzene peaks could be produced by further slight adjustments in the orientation of the single naphthalene molecule; since equivalent molecules are parallel in this projection it follows that the two sets of non-equivalent molecules must have slightly different orientations.

The approximate intermolecular separation of the two sets of non-equivalent molecules was determined by examination of the fringing through the peaks which appear in the weighted reciprocal-lattice section. With this information an optical transform of the two non-equivalent molecules in different orientations (Fig. 2) was obtained which showed very good agree-

(a)

(b)
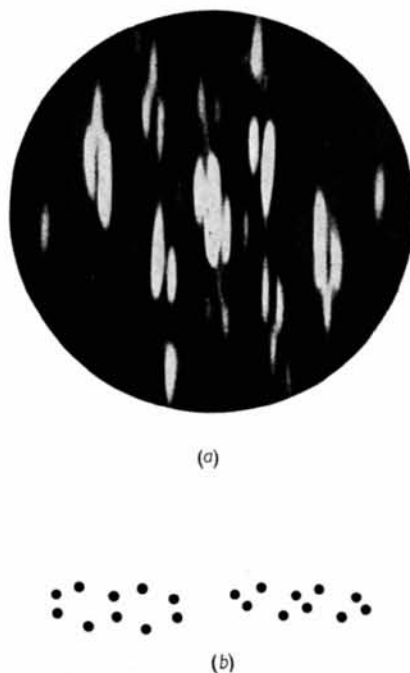
Fig. 2. (a) Optical transform of the [010] projection of the two non-equivalent molecules. (b) Projected molecules giving optical transform in (a).

ment with the weighted reciprocal lattice section (Fig. 1).

(ii) *Refinement of the* [010] *projection*

Using the atomic positions derived optically for the carbon atoms and the scattering-factor curves given in the *International Tables* (1935), real and imaginary parts of the structure factors were calculated by the Manchester University digital computer. The agreement residual $R = \Sigma ||F_o| - |F_c|| \div \Sigma |F_o|$ at this stage was 44%. The calculated phases were used to compute a two-dimensional Fourier synthesis which showed

(a)

(b)

Fig. 3. (a) Projection of electron density along [010]. Contours are at intervals of 1 e.Å^{-2}; the 1 e.Å^{-2} contour is broken.
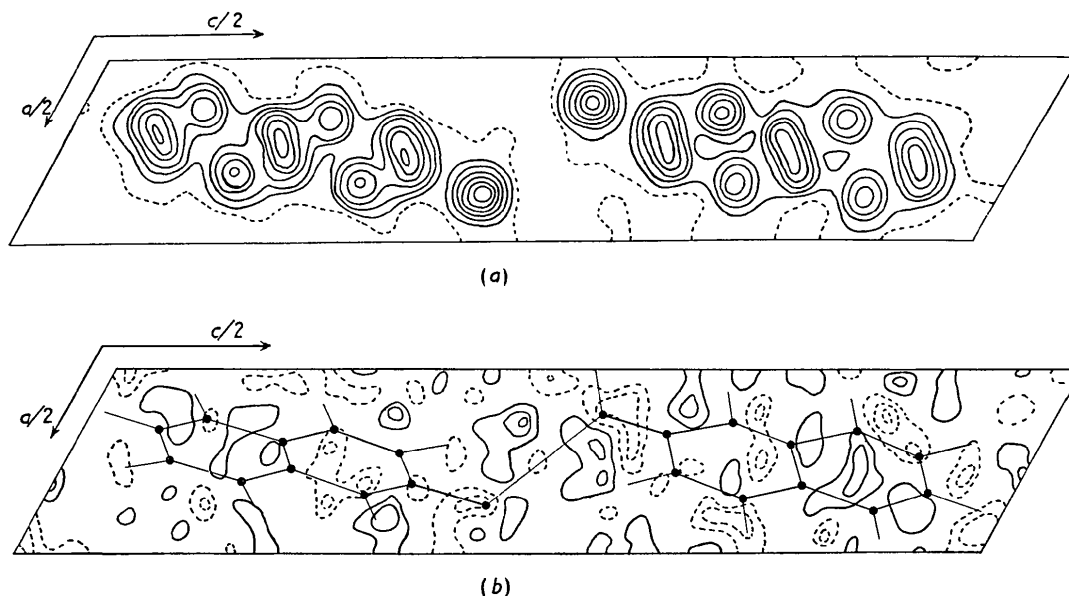(b) Projection of $(\varrho_o - \varrho_c)$ along [010]. Contours are at intervals of 0·2 e.Å^{-2}; negative contours are broken and the zero contour is omitted.

peak heights of approximately 4 e.Å^{-2} in positions which, from stereochemical considerations, are possible oxygen positions. With the oxygen atoms now included the residual R reduced to 40%.

The refinement of a non-centrosymmetric structure is necessarily slow; after five F_o syntheses R fell to 25%.

Using McWeeny's scattering-factor curves (McWeeny, 1951) five successive $(F_o - F_c)$ syntheses were next computed, incorporating all but the very-low-angle reflexions which suffer from possible absorption and extinction errors. The atomic movements indicated by the $(\varrho_o - \varrho_c)$ maps were calculated from the electron-density gradients (Cochran, 1951). After the third difference synthesis the presence of electron density in probable hydrogen positions was indicated and so the hydrogen atoms were included in the succeeding syntheses. The agreement residual R for the observed reflexions, using the final co-ordinates, is 13%. The last difference synthesis and an F_o synthesis using the final calculated phase angles give the electron-density distributions shown in Fig. 3.

(iii) *The* [100] *projection*

The molecular orientation of β-naphthol in the [100] projection has been determined by optical methods without assuming any knowledge of the molecular orientation derived from the [010] projection.

The $0kl$ weighted reciprocal-lattice section of β-naphthol is shown in Fig. 4; the weights are proportional to the unitary structure factors. Twelve peak regions can be seen near the benzene circle.

Equivalent molecules related by the glide plane a will, in general, have different orientations in the [100]

projection. It is possible, therefore, for a single set of equivalent molecules to produce 12 peak regions near the benzene circle. If the non-equivalent molecules are also in different orientations a total of 24 benzene peaks is possible. Examination of optical transforms, using only carbon atoms, quickly indicated that each of the 12 observed peaks represents two superimposed benzene peaks from *equivalent* molecules; thus peaks produced by non-equivalent molecules are resolved from one another.

(iv) *Refinement of the* [100] *projection*

Using co-ordinates for the carbon atoms obtained partly by the optical method and partly by adopting
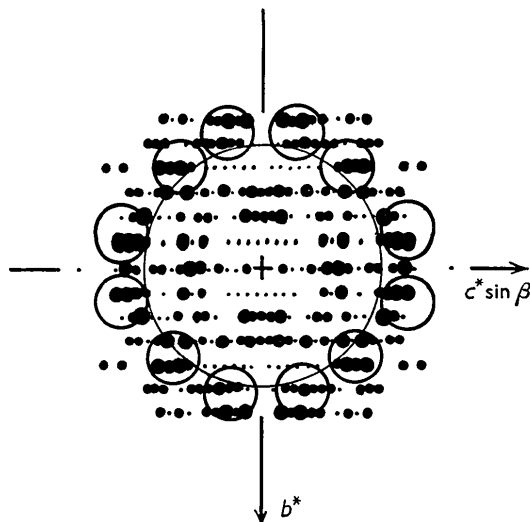

Fig. 4. The $0kl$ section of the weighted reciprocal lattice.

Table 1. *Observed and calculated structure amplitudes and calculated phase angles for h0l and 0kl reflexions*

h	k	ℓ	$|F_o|$	$|F_c|$	$\alpha(°)$
0	0	2	21	23	180
0	0	4	95	104	186
0	0	6	40	39	195
0	0	8	34	34	190
0	0	10	39	42	194
0	0	12	28	32	186
0	0	14	64	69	202
0	0	16	60	62	11
0	0	18	33	31	36
0	0	20	10	9	201
0	0	22	23	21	25
0	0	24	17	17	201
0	0	26	-	5	233
0	0	28	11	8	203
0	0	30	23	22	40
2	0	0	175	193	1
2	0	2	21	19	33
2	0	4	23	22	18
2	0	6	-	4	166
2	0	8	25	21	8
2	0	10	15	11	15
2	0	12	32	33	194
2	0	14	68	76	204
2	0	16	37	40	18
2	0	18	-	2	90
2	0	20	9	10	24
2	0	22	-	1	90
2	0	24	-	3	0
2	0	26	19	23	218
2	0	28	-	3	90
2	0	$\bar{30}$	14	12	35
2	0	$\bar{2}$	23	28	264
2	0	$\bar{4}$	165	202	179
2	0	$\bar{6}$	22	33	27
2	0	$\bar{8}$	87	106	174
2	0	$\bar{10}$	13	13	9
2	0	$\bar{12}$	20	27	174
2	0	$\bar{14}$	25	30	338
2	0	$\bar{16}$	13	14	106
2	0	$\bar{18}$	44	37	333
2	0	$\bar{20}$	22	24	178
2	0	$\bar{22}$	40	36	337
2	0	$\bar{24}$	23	22	183
2	0	$\bar{26}$	26	21	342
2	0	$\bar{28}$	22	17	115
2	0	$\bar{30}$	18	14	168
4	0	0	35	35	191
4	0	2	-	12	24
4	0	4	-	10	197
4	0	6	-	8	14
4	0	8	-	3	342
4	0	10	25	22	23
4	0	12	15	15	192
4	0	14	-	8	225
4	0	16	-	3	315
4	0	18	-	2	333
4	0	20	-	1	315
4	0	22	-	6	198
4	0	24	-	2	0
4	0	26	12	11	214
4	0	$\bar{2}$	21	31	329
4	0	$\bar{4}$	33	32	178
4	0	$\bar{6}$	21	21	31
4	0	$\bar{8}$	39	45	174
4	0	$\bar{10}$	14	10	32

h	k	ℓ	$|F_o|$	$|F_c|$	$\alpha(°)$
4	0	$\bar{12}$	15	19	174
4	0	$\bar{14}$	-	5	127
4	0	$\bar{16}$	35	40	342
4	0	$\bar{18}$	11	12	35
4	0	$\bar{20}$	11	13	337
4	0	$\bar{22}$	8	5	310
4	0	$\bar{24}$	8	10	299
4	0	$\bar{26}$	-	3	45
4	0	$\bar{28}$	18	14	111
4	0	$\bar{30}$	71	68	155
4	0	$\bar{32}$	32	29	131
4	0	$\bar{34}$	18	15	146
4	0	$\bar{36}$	-	4	297
4	0	$\bar{38}$	-	3	315
4	0	$\bar{40}$	-	7	321
4	0	$\bar{42}$	-	3	315
4	0	$\bar{44}$	-	6	279
4	0	$\bar{46}$	11	16	142
6	0	0	22	16	191
6	0	2	-	3	135
6	0	4	-	6	198
6	0	6	-	3	252
6	0	8	-	6	239
6	0	10	-	5	169
6	0	12	-	6	81
6	0	14	15	17	21
6	0	$\bar{2}$	19	11	338
6	0	$\bar{4}$	32	27	8
6	0	$\bar{6}$	13	14	0
6	0	$\bar{8}$	9	4	207
6	0	$\bar{10}$	9	11	138
6	0	$\bar{12}$	-	4	297
6	0	$\bar{14}$	14	17	194
6	0	$\bar{16}$	61	60	346
6	0	$\bar{18}$	-	7	45
6	0	$\bar{20}$	14	10	143
6	0	$\bar{22}$	9	10	169
6	0	$\bar{24}$	-	2	243
6	0	$\bar{26}$	8	12	169
6	0	$\bar{28}$	13	11	170
6	0	$\bar{30}$	39	31	151
6	0	$\bar{32}$	29	26	342
6	0	$\bar{34}$	34	33	322
8	0	0	-	2	63
8	0	$\bar{2}$	-	1	0
8	0	$\bar{4}$	16	17	0
8	0	$\bar{6}$	12	12	209
8	0	$\bar{8}$	-	2	207
8	0	$\bar{10}$	-	4	124
8	0	$\bar{12}$	-	1	0
8	0	$\bar{14}$	-	2	90
8	0	$\bar{16}$	18	15	352
8	0	$\bar{18}$	-	7	304
8	0	$\bar{20}$	21	22	166
8	0	$\bar{22}$	-	3	135
8	0	$\bar{24}$	-	4	0
8	0	$\bar{26}$	-	4	236
8	0	$\bar{28}$	-	6	198
8	0	$\bar{30}$	-	7	16
8	0	$\bar{32}$	-	8	35
8	0	$\bar{34}$	21	21	354
8	0	$\bar{36}$	12	12	190

h	k	ℓ	$|F_o|$	$|F_c|$	$\alpha(°)$
0	0	2	21	19	186
0	0	4	95	108	184
0	0	6	40	44	196
0	0	8	34	34	176
0	0	10	39	46	187
0	0	12	28	28	176
0	0	14	64	53	199
0	0	16	60	52	1
0	0	18	33	29	22
0	0	20	10	6	202
0	0	22	23	19	32
0	0	24	17	14	207
0	0	26	-	8	157
0	0	28	11	12	222
0	0	30	23	25	45
0	0	32	-	5	248
0	0	34	-	5	233
0	0	36	-	6	278
0	0	38	-	3	225
0	0	40	6	6	231
0	1	1	21	21	85
0	1	3	17	21	319
0	1	5	42	43	103
0	1	7	28	26	296
0	1	9	8	7	0
0	1	11	9	12	284
0	1	13	33	32	139
0	1	15	11	7	82
0	1	17	37	37	285
0	1	19	-	8	330
0	1	21	7	8	90
0	1	23	-	2	63
0	1	25	15	11	131
0	1	27	19	18	117
0	1	29	21	24	306
0	1	31	8	11	90
0	2	0	46	40	0
0	2	2	27	29	352
0	2	4	74	80	184
0	2	6	11	12	294
0	2	8	28	27	158
0	2	10	12	14	216
0	2	12	34	37	59
0	2	14	24	25	346
0	2	16	5	4	0
0	2	18	17	17	346
0	2	20	12	11	158
0	2	22	7	7	315
0	2	24	9	9	162
0	2	26	31	36	214
0	2	28	8	7	27
0	2	30	7	6	45
0	3	1	36	40	271
0	3	3	47	47	96
0	3	5	28	27	96
0	3	7	13	12	0
0	3	9	36	35	293
0	3	11	16	12	114
0	3	13	25	24	99
0	3	15	9	9	6
0	3	17	33	33	289
0	3	19	10	10	299
0	3	21	26	23	108
0	3	23	11	9	198
0	3	25	8	6	239
0	3	27	8	6	309
0	3	29	8	10	139

h	k	ℓ	$|F_o|$	$|F_c|$	$\alpha(°)$
0	4	0	-	2	0
0	4	2	9	10	73
0	4	4	14	12	309
0	4	6	13	13	86
0	4	8	11	12	215
0	4	10	9	10	96
0	4	12	5	8	240
0	4	14	-	5	127
0	4	16	17	17	263
0	4	18	27	26	182
0	4	20	18	19	354
0	4	22	19	19	42
0	4	24	-	1	90
0	4	26	-	5	189
0	4	28	-	1	153
0	4	30	-	2	90
0	4	32	-	1	0
0	4	34	6	6	187
0	5	1	-	4	33
0	5	3	8	6	351
0	5	5	16	11	105
0	5	7	15	14	240
0	5	9	22	21	287
0	5	11	11	15	176
0	5	13	11	12	66
0	5	15	9	7	219
0	5	17	6	6	59
0	5	19	-	2	297
0	5	21	7	9	90
0	5	23	7	7	164
0	5	25	13	9	311
0	6	0	-	5	0
0	6	2	-	0	~
0	6	4	17	12	190
0	6	6	10	10	217
0	6	8	24	25	7
0	6	10	11	11	355
0	6	12	9	7	196
0	6	14	-	0	~
0	6	16	4	6	189
0	6	18	8	7	0
0	6	20	5	4	104
0	6	22	7	6	18

the intermolecular separation parallel to the *c* axis found in the [010] projection, real and imaginary parts of the structure factors were calculated. As for the [010] projection a Fourier synthesis was computed and the oxygen atoms appeared in the electron-density map with peak heights approxmiately equal to 4 e.Å^{-2}. Three Fourier refinements including the oxygen atoms reduced the residual R from 30% to 19%.

Five successive $(F_o - F_c)$ syntheses were computed, using McWeeny's scattering factor curves. All but the very-low-angle reflexions were used in these refinements. Hydrogen atoms were included in the third $(F_o - F_c)$ synthesis. Structure factors calculated after the fourth difference synthesis gave an agreement residual $R = 12\%$ for the observed reflexions and the succeeding $(\varrho_o - \varrho_c)$ map showed no appreciable slopes at the atomic centres.

At this stage of refinement, which was intended to be the final one, it was noticed that the mutual positions of five adjacent carbon atoms in one of the molecules were such that they represented unusually short and long bond distances between the atoms. Structure factors were therefore calculated using the z co-ordinates deduced from the [010] projection— which had been refined independently—for these five atoms; the residual R fell to 11%. The corresponding $(\varrho_o - \varrho_c)$ map (Fig. 5(b)) indicated that of the five atoms one should be left at its newly assigned position, two should be moved still further away from their previous positions, and two should be moved back towards their previous positions. The refinement could be continued further but it is slow; the peculiar behaviour of these five atoms serves to illustrate the difficulties met in refining non-centrosymmetric struc-
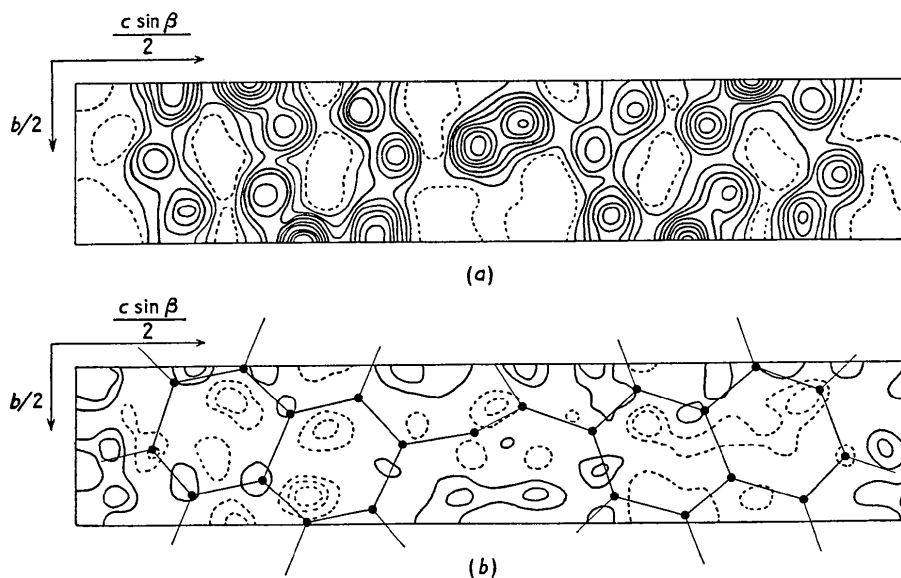
Fig. 5. (a) Projection of electron density along [100]. Contours are at intervals of 1 e.Å^{-2}; the 1 e.Å^{-2} contour is broken. (b) Projection of $(\varrho_o - \varrho_c)$ along [100]. Contours are at intervals of 0·2 e.Å^{-2}; negative contours are broken and the zero contour is omitted.

tures. Fig. 5(b) was used to deduce the final atomic co-ordinates for the [100] projection. An F_o synthesis computed using the final calculated phase angles gives the electron-density map shown in Fig. 5(a).

4. Choice between two possible structures

It is not possible to deduce the structure uniquely from the two projections, parallel to [010] and [100] respectively, shown in Figs. 3(a) and 5(a). There are two possible structures—A and B, say—with different projections parallel to [001] but with homometric projections parallel to the [100] and [010] axes. Structure A may be represented by non-equivalent molecules I and II with positions relative to the origin as indicated in Figs. 3(a) and 5(a). In structure B molecule I occupies exactly the same position as molecule I in structure A; molecule II has the same y and z co-ordinates as molecule II in structure A, but the fractional x co-ordinates are all increased by 0·5. The molecule equivalent to II in structure A and related to it by the glide plane a has x and z co-ordinates identical with those of II in structure B and this accounts for the identity of the [010] projections of II in both A and B.

Both structures have identical bond lengths within the molecule but the intermolecular distances are very different. One of the O–O distances in A is 1·8 Å; the corresponding distance in B has the usual value of 2·7 Å, suggesting that structure B is the correct one. This conclusion has been verified by the examination of a number of general reflexions hkl in a b-axis oscillation photograph. The visually estimated intensities are compared with unitary structure amplitudes cal-

culated for both A and B in Table 2; it is evident that B is the correct structure. Reflexions with h even have the same calculated structure amplitudes for both structures and are therefore omitted from Table 2.

Table 2. *Choice between structures A and B*

Calculated unitary structure amplitudes of reflexions hkl, arranged in order of increasing $\sin \theta$ values, are compared with observed intensities

| hkl	$|U_A|$	$|U_B|$	Intensity
$11\bar{2}$	0·51	0·04	Weak
110	0·04	0·50	Very strong
$12\bar{5}$	0·09	0·02	Absent
123	0·11	0·17	Medium
$31\bar{8}$	0·04	0·11	Weak
$3,1,\overline{10}$	0·08	0·08	Weak
310	0·06	0·03	Absent
312	0·17	0·02	Absent
$3,2,\overline{11}$	0·11	0·06	Absent
$3,2,\overline{13}$	0·05	0·18	Medium
$5,1,\overline{16}$	0·03	0·25	Medium
$5,1,\overline{18}$	0·12	0·04	Absent
$5,1,\overline{20}$	0·11	0·03	Absent

5. Atomic co-ordinates

The atomic co-ordinates are given in Table 3; the values of the z co-ordinates are the unweighted means of the two sets of values deduced respectively from the [010] and [100] projections.
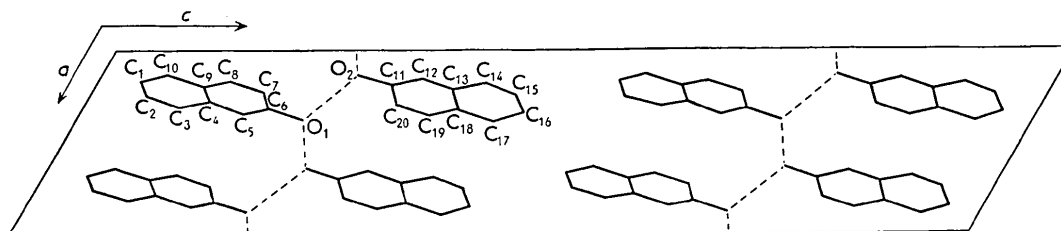
The accuracy of the co-ordinates is not very great, in spite of the large number of Fourier refinements, because the structure is non-centrosymmetric (see § 3(iv)) and because the number of reflexions observed at room temperature (82 $h0l$ reflexions, 91 $0kl$ reflexions) is rather small in relation to the number of

Table 3. *Atomic co-ordinates*

Atom	x (Å)	y (Å)	z (Å)
O_1	3·10	1·26	8·65
O_2	1·07	0·78	9·76
C_1	1·38	1·52	1·66
C_2	2·07	0·32	2·14
C_3	2·52	0·01	3·71
C_4	2·28	0·87	4·66
C_5	2·88	0·58	6·21
C_6	2·58	1·47	7·08
C_7	1·89	2·70	6·49
C_8	1·36	2·94	5·06
C_9	1·64	2·12	4·09
C_{10}	1·07	2·40	2·49
C_{11}	1·53	1·26	11·23
C_{12}	1·23	0·48	12·21
C_{13}	1·78	0·87	13·69
C_{14}	1·47	0·06	14·78
C_{15}	2·03	0·43	16·22
C_{16}	2·80	1·75	16·78
C_{17}	3·22	2·56	15·88
C_{18}	2·61	2·14	14·27
C_{19}	2·92	2·86	13·28
C_{20}	2·38	2·49	11·76

(a)

(b)
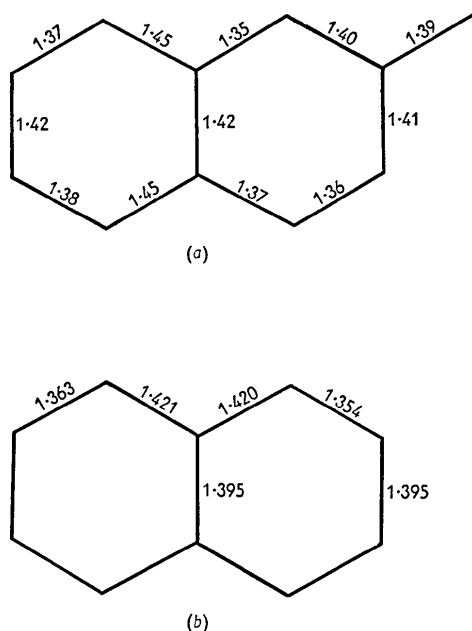
Fig. 6. Bond lengths in (a) β-naphthol, (b) naphthalene.

parameters (44) which has to be determined in each projection.

It is reasonable to assume that the configurations of the two non-equivalent molecules are identical. Comparison of the lengths of corresponding bonds in these molecules thus provides a measure of the accuracy of the structure. It is found that the lengths of the twelve bonds in the molecule differ, on the average, by 0·03 Å from the mean values given in Fig. 6(a); the largest difference is almost 0·07 Å.

6. Description of the structure

The dimensions of the β-naphthol molecule are shown in Fig. 6(a); the bond lengths are the means of the two values obtained for non-equivalent molecules. For comparison the dimensions of the naphthalene molecule (Abrahams, Robertson & White, 1949) are given in Fig. 6(b). It is doubtful, however, whether much significance can be attached to the differences in the lengths of corresponding bonds in the two structures because of the large errors in the bond lengths determined for β-naphthol (§ 5).
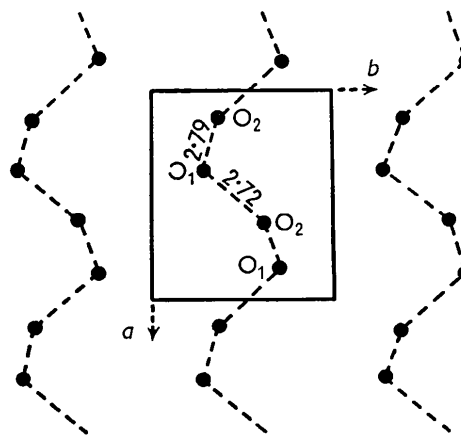

Fig. 8. Hydrogen-bond formation in β-naphthol. The oxygen atoms all lie near the plane $z = \frac{1}{4}$ (or $\frac{3}{4}$) and are viewed along [001].

Fig. 7 shows how the molecules are arranged in the crystal. The molecules pack in sheets which lie parallel to the (001) plane. All molecules in a given sheet are equivalent to one another and to molecules in alternate sheets. Every molecule in a given sheet is linked by a hydrogen bond to a molecule in the same adjacent sheet but is separated from molecules in the other adjacent sheet by the usual van der Waals distances.

Fig. 7. The structure of β-naphthol viewed along [010]. Hydrogen bonds are indicated by broken lines.

The closest approach between carbon atoms in different molecules is 3·5 Å.

The hydrogen-bond formation is indicated more clearly in Fig. 8. There are two types of hydrogen bond, each of which links a pair of non-equivalent molecules; the O–O distances are 2·72 Å and 2·79 Å respectively. Every molecule is linked, by hydrogen bonds between the oxygen atoms, to two neighbours, thus forming chains of molecules; adjacent molecules in any chain are crystallographically non-equivalent. Each chain runs throughout the crystal with its length parallel to the a axis. Although the chains run parallel to the planes of the sheets there are no hydrogen-bond linkages between neighbouring chains; the closest distance of approach between oxygen atoms in neighbouring chains is 4·30 Å (Fig. 8).

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.

Structural relations of UO_2, isometric $PbUO_4$ and orthorhombic $PbUO_4$. By CLIFFORD FRONDEL

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We have synthesized* isometric and orthorhombic polymorphs of $PbUO_4$ that hitherto have not been described crystallographically. The orthorhombic phase may be identical with material synthesized by Zehenter (1904). Both substances contain hexavalent uranium and the formula is more properly written $Pb(UO_2)O_2$.

The isometric polymorph is isostructural with UO_2, with $a_0 = 5·600 \pm 0·002$ Å, in so far as can be determined by X-ray powder diffraction methods. Neutron diffraction study may reveal a multiple and perhaps a non-isometric cell. The phase was obtained by heating U_3O_8 with PbO and excess sheet lead in water at 230°–290° C. It forms orange–brown isotropic cubes with an index of refraction over 2·0. If U_3O_8 is used in molar excess over PbO, mixtures are obtained of $PbUO_4$ with stoichiometric UO_2 ($a_0 = 5·468$ Å). It may be noted that the calculated Eh–pH boundary (at 25 °C.) of the PbO/Pb couple is below that of the U_3O_8/UO_2 couple (Latimer, 1952). The isometric phase apparently is stabilized by the presence of small amounts of U^4 in solid solution. Increase in the amount of UO_2 formed concurrently is accompanied by an increase of U^4 in solid solution, to an apparent

Table 1

Isometric UO_2		Isometric $PbUO_4$		Orthorhombic $PbUO_4$		Orthorhombic $BaUO_4$	
hkl	2θ	*hkl*	2θ	*hkl*	2θ	*hkl*	2θ
111	28·27°	111	27·59°	{ 102	27·14°	102	26·80°
				120	27·62	120	26·95
200	32·76	200	31·96	{ 022	31·40	022	31·05
				200	32·40	200	31·22
220	47·00	220	45·82	{ 004	44·30	004	33·10
				040	45·63	040	44·62
311	55·76	311	54·34	{ 124	52·96	124	52·42
				142	53·81	142	52·85
222	58·47	222	56·96	{ 302	54·65	302	55·03
				204	55·88	204	55·43

$d_{100} = 5·468$ Å $d_{100} = 5·600$ Å $d_{100} = 5·528$ Å
$2d_{110} = 7·733$ $2d_{110} = 7·920$ $d_{010} = 7·952$
$2d_{1\bar{1}0} = 7·733$ $2d_{1\bar{1}0} = 7·920$ $d_{001} = 8·180$

maximum of $x \sim 0·2$ in the formula $Pb(U^6_{1-x}U^4_x)O_{4-x}$. On heating in air, the U^4 is oxidized and the substance then converts to an orthorhombic polymorph. The conversion is rapid over about 450°. We also have synthesized