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## The Crystal Structure of *m*-Tolidine

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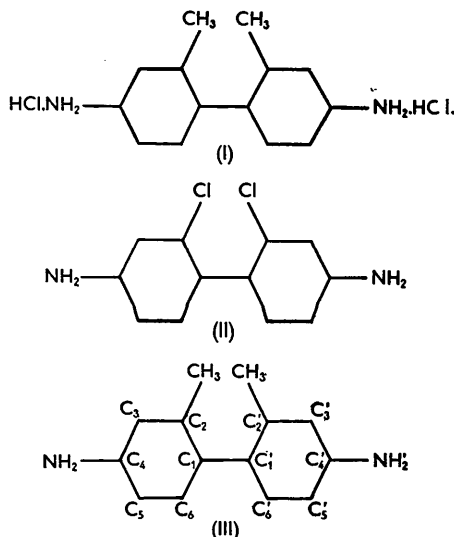
Standard single-crystal methods show that the unit cell of *m*-tolidine is orthorhombic, with  $a = 7.60$ ,  $b = 14.81$ ,  $c = 21.05$  Å; the cell contains eight molecules and has space group *Pcab*. The atomic co-ordinates are obtained by two-dimensional Fourier methods, together with the methods of steepest descents and error syntheses.

The two phenyl rings in each molecule are mutually inclined at an angle of  $86^\circ$ . The diphenyl link is  $1.55$  Å and the C-C bonds vary considerably with values between  $1.31$  and  $1.41$  Å. The structure is racemic with four right-handed and four left-handed molecules in the unit cell.

### Introduction

The work described is a contribution to a survey of a number of substituted diphenyls; a preliminary

chloride (I) was determined by Hargreaves (1940) and refined by Fowweather & Hargreaves (1950). Smare (1948) determined the structure of 2-2'dichlorobenzidine (II).



account of the survey has been given by Hargreaves & Taylor (1941). The structure of *m*-tolidine dihydro-

### Physical and X-ray data

*m*-Tolidine (III) is difficult to crystallize and forms soft, transparent rectangular plates, which cleave easily only parallel to the edge [010] of the plate face (001). The melting point is  $89-90^\circ$  C.

X-ray rotation, oscillation and Weissenberg photographs show that the crystals are orthorhombic with axial lengths

$$a = 7.60 \pm 0.03, b = 14.81 \pm 0.06 \text{ and } c = 21.05 \pm 0.1 \text{ \AA.}$$

The density measured by flotation in a mixture of chloroform and alcohol is  $1.18 \pm 0.01$  g.cm.<sup>-3</sup>. There are eight molecules per unit-cell, giving a calculated density of  $1.182$  g.cm.<sup>-3</sup>.

Absent spectra determine the space group to be *Pcab*- $D_{2h}^{15}$ .

Zero-layer-line Weissenberg photographs were taken with Cu  $K\alpha$  radiation, the crystal being rotated about the  $a$  and  $b$  axes. It was difficult to cut the soft crystals, and in addition the plates were thin, with a thickness

always less than 0.05 mm., which resulted in the crystal fragments chosen for the photographs being of tabular shape. Multiple-film technique (Robertson, 1943) was used for the intensity measurements, and the reflexions were visually compared with calibration spots of known relative exposure. The method developed by Broomhead (1948) was used to correct the intensities for spot shape. An approximate absolute scale was obtained by applying Wilson's method (1942). The effect of primary absorption was neglected since the linear absorption coefficient is small ( $6.45 \text{ cm.}^{-1}$ ).

### Determination of the structure

#### (i) Approximate structure

The space group  $Pcab$  has eight special positions—symmetry centres—in the unit-cell; if the molecules occupy these positions the two phenyl rings will have to be coplanar and there will then be steric hindrance between the methyl groups and the phenyl rings; hence it can be assumed that the molecules are in general positions. A long molecule similar to the *m*-tolidine dihydrochloride molecule can be expected for *m*-tolidine. The orientation of the molecule was obtained from a Patterson synthesis for the [100] projection, which suggested that the long molecules were parallel to the  $z$  axis and separated from the next molecule by a distance of  $\frac{1}{2}b$ . Space-group considerations place the diphenyl link of the molecule at  $y = \frac{1}{8}b$  and operations of the symmetry elements will give molecules parallel to  $z$  separated by  $\frac{1}{2}b$ . The approximate structure was finally obtained by trial-and-error methods, helped by structure factor graphs (Bragg & Lipson, 1936).

#### (ii) Fourier syntheses

The electron density was evaluated at intervals of  $a/60$ ,  $c/120$  and  $b/60$ ,  $c/120$  in the [010] and [100]

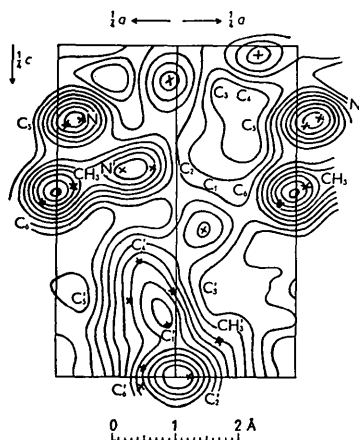


Fig. 1. Electron density in *m*-tolidine projected on (010). Contour lines are drawn at intervals of  $1 \text{ e.}\text{Å}^{-2}$ ; the lowest contour line represents  $2 \text{ e.}\text{Å}^{-2}$ .

projections respectively. Four syntheses were made of each projection. There was overlap of atoms in both projections and it was difficult to determine their maxima when this occurred. An empirical method was used to find the maxima in the case of overlap; this consisted of building up the contours by superimposing atoms of known shape. This method gives only approximate co-ordinates, since ideal spherical atoms are assumed and diffraction effects are neglected.

The contour diagrams for the [010] and [100] projections are reproduced in Figs. 1 and 2 respectively.

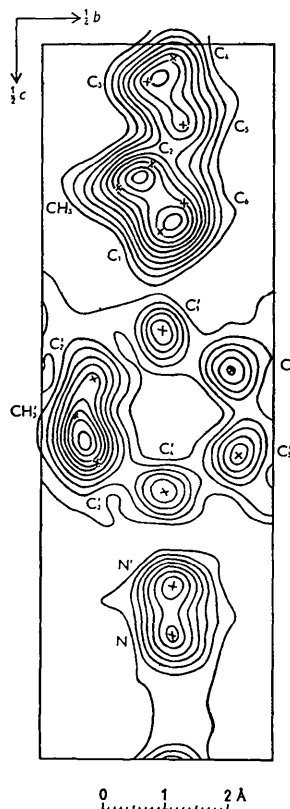


Fig. 2. Electron density in *m*-tolidine projected on (100). Contour lines are drawn at intervals of  $1 \text{ e.}\text{Å}^{-2}$ ; the lowest contour line represents  $2 \text{ e.}\text{Å}^{-2}$ .

The structure was further refined by using the methods of steepest descents and error syntheses. The calculated  $F$  values obtained by these methods are given with the observed values in Table 1 for the [010] projection and in Table 2 for the [100] projection. The quantity  $\sum ||F_o| - |F_c|| \div \sum |F_o|$  has the value 0.28 for the [010] projection and 0.25 for the [100] projection. These high values are probably due to the incomplete refinement of the structure because of poor resolution and to the small average value of observed structure amplitude.

Table 1. *Observed and calculated values of  $F_{h0l}$* 

$\sin \theta$	<i>hkl</i>	$F_o$	$F_c$
0	000	—	784
0.073	002	49	-49
0.146	004	0	-10
0.203	200	88	88
0.206	201	45	60
0.211	202	103	-142
0.220	006	60	-74
0.230	203	41	47
0.250	204	59	57
0.273	205	29	15
0.293	008	11	3
0.299	206	23	24
0.311	207	15	4
0.356	208	7	8
0.367	0,0,10	26	17
0.387	209	49	-52
0.406	400	55	43
0.408	401	24	19
0.413	402	28	15
0.419	2,0,10	18	4
0.421	403	10	-4
0.432	404	6	1
0.440	0,0,12	11	9
0.445	405	11	-18
0.451	2,0,11	12	-15
0.462	406	15	-17
0.483	407	11	2
0.484	2,0,12	21	18
0.501	408	0	-8
0.513	0,0,14	16	-17
0.518	2,0,13	9	21
0.523	409	21	-12
0.547	4,0,10	10	-13
0.552	2,0,14	0	-11
0.572	4,0,11	19	16
0.586	0,0,16	8	2
0.586	2,0,15	0	-10
0.598	4,0,12	23	-20
0.609	600	15	-19
0.610	601	0	-1
0.613	602	0	-12
0.619	603	0	7
0.620	2,0,16	15	-20
0.626	4,0,13	27	27
0.626	604	29	21
0.636	605	17	17
0.648	606	11	19
0.653	4,0,14	11	-9
0.655	2,0,17	23	-7
0.658	607	17	13
0.660	0,0,18	11	-3
0.676	608	0	1
0.683	4,0,15	10	5
0.690	2,0,18	37	-34
0.692	609	0	-10
0.711	6,0,10	0	7
0.713	4,0,16	7	11
0.725	2,0,19	15	-14
0.730	6,0,11	0	-2
0.733	0,0,20	28	15
0.744	4,0,17	6	3
0.751	6,0,12	0	-5
0.760	2,0,20	7	2
0.773	6,0,13	0	-5
0.774	4,0,18	0	0
0.791	6,0,14	0	0
0.796	2,0,21	0	5
0.806	0,0,22	0	-3
0.806	4,0,19	0	-3
0.812	800	6	3
0.813	801	0	-6

Table 1 (cont.)

$\sin \theta$	<i>hkl</i>	$F_o$	$F_c$
0.814	802	6	3
0.816	803	0	-5
0.820	6,0,15	0	1
0.821	804	0	2
0.828	805	0	-5
0.831	2,0,22	0	3
0.838	4,0,20	0	1
0.839	806	0	0
0.845	6,0,16	0	2
0.848	807	0	-1
0.861	808	0	-8
0.866	2,0,23	0	-1
0.869	6,0,17	0	-6
0.870	4,0,21	0	0
0.872	809	8	-3
0.880	0,0,24	0	1
0.888	8,0,10	5	7
0.896	6,0,18	0	-5
0.900	2,0,24	0	5
0.903	4,0,22	13	-6
0.907	8,0,11	0	7
0.921	6,0,19	0	4
0.921	8,0,12	5	-3
0.936	2,0,25	0	0
0.936	4,0,23	7	-4
0.938	8,0,13	0	-4
0.951	6,0,20	0	-2
0.953	0,0,26	10	-5

Table 2. *Observed and calculated values of  $F_{h0}$* 

$\sin \theta$	<i>hkl</i>	$F_o$	$F_c$
0	000	—	784
0.073	002	50	-51
0.090	012	33	-33
0.104	020	16	-18
0.127	022	51	-45
0.146	004	0	13
0.155	014	56	-58
0.172	032	59	-51
0.180	024	9	9
0.208	040	194	-218
0.212	034	40	-33
0.220	006	61	-71
0.220	042	132	-119
0.226	016	37	28
0.243	026	0	-8
0.253	044	81	73
0.268	052	56	30
0.270	036	34	26
0.292	008	10	6
0.296	018	0	8
0.298	054	59	-51
0.302	046	11	8
0.310	028	0	11
0.313	060	42	44
0.319	062	53	41
0.331	038	0	5
0.340	056	43	35
0.344	064	16	-5
0.358	048	20	1
0.366	0,0,10	24	16
0.369	072	43	30
0.370	0,1,10	101	-65
0.380	066	0	-7
0.381	0,2,10	29	6
0.390	058	0	-4
0.390	074	17	-14
0.398	0,3,10	40	-28
0.417	080	41	43

Table 2 (cont.)

$\sin \theta$	$hkl$	$F_o$	$F_c$
0.420	082	49	47
0.421	0,4,10	10	-11
0.424	076	26	15
0.429	068	10	-9
0.439	084	36	-24
0.440	0,0,12	10	13
0.443	0,1,12	9	5
0.448	0,5,10	41	37
0.452	0,2,12	0	-2
0.465	0,3,12	23	-28
0.466	078	20	-16
0.469	086	21	13
0.470	092	0	10
0.480	0,6,10	28	-13
0.486	0,4,12	8	-1
0.489	094	12	17
0.508	088	13	-5
0.511	0,5,12	26	9
0.513	0,0,14	15	-17
0.515	0,1,14	0	-6
0.516	0,7,10	14	17
0.516	096	0	-3
0.521	0,10,0	46	-57
0.522	0,2,14	0	-3
0.523	0,10,2	0	-9
0.536	0,3,14	0	3
0.538	0,6,12	9	-7
0.538	0,10,4	0	2
0.550	098	10	-14
0.552	0,4,14	0	-9
0.554	0,8,10	10	7
0.563	0,10,6	0	4
0.569	0,7,12	23	11
0.572	0,5,14	10	-13
0.575	0,11,2	0	-5
0.586	0,0,16	9	9
0.588	0,11,4	0	-3
0.589	0,1,16	0	-8
0.593	0,9,10	21	-12
0.596	0,2,16	13	-12
0.596	0,10,8	0	4
0.598	0,6,14	15	20
0.604	0,8,12	0	-6
0.607	0,3,16	0	16
0.610	0,11,6	0	-5
0.621	0,4,16	23	15
0.625	0,12,0	44	-38
0.626	0,7,14	0	11
0.626	0,12,2	35	22
0.636	0,10,10	0	4
0.640	0,9,12	0	-10
0.640	0,11,8	0	-3
0.640	0,12,4	17	-17
0.641	0,5,16	33	19
0.657	0,8,14	9	18
0.659	0,12,6	0	4
0.660	0,0,18	11	-1
0.661	0,1,18	13	-7
0.663	0,6,16	9	4
0.668	0,2,18	0	-3
0.677	0,3,18	12	6
0.677	0,13,2	12	-13
0.678	0,11,10	0	2
0.680	0,10,12	0	-1
0.687	0,12,8	0	-2
0.688	0,7,16	16	9
0.689	0,13,4	0	-2
0.692	0,4,18	0	-3
0.692	0,9,14	9	13
0.708	0,5,18	9	14
0.708	0,13,6	0	-3

Table 2 (cont.)

$\sin \theta$	$hkl$	$F_o$	$F_c$
0.718	0,8,16	25	-22
0.720	0,11,12	0	-2
0.722	0,12,10	0	2
0.728	0,6,18	17	21
0.729	0,10,14	15	-7
0.730	0,14,0	10	26
0.731	0,14,2	0	-1
0.733	0,0,20	27	16
0.733	0,13,8	0	-2
0.734	0,1,20	0	-6
0.739	0,2,20	0	-5
0.740	0,14,4	0	-4
0.748	0,3,20	0	-1
0.750	0,9,16	17	-19
0.752	0,7,18	0	-6
0.757	0,14,6	0	2
0.760	0,4,20	0	-7
0.761	0,12,12	0	-5
0.766	0,11,14	9	-9
0.767	0,13,10	16	18
0.776	0,5,20	0	0
0.780	0,8,18	17	10
0.781	0,15,2	0	4
0.782	0,14,8	0	-1
0.783	0,10,16	0	-6
0.792	0,15,4	0	2
0.794	0,6,20	0	0
0.804	0,13,12	12	9
0.805	0,12,14	0	-2
0.806	0,0,22	0	-1
0.807	0,9,18	10	-7
0.807	0,15,6	0	5
0.808	0,1,22	0	0
0.813	0,2,22	0	2
0.814	0,14,10	0	2
0.816	0,7,20	0	-4
0.818	0,11,16	0	-4
0.821	0,3,22	0	-1
0.830	0,15,8	0	2
0.832	0,4,22	0	2
0.833	0,16,0	0	2
0.834	0,16,2	0	-3
0.839	0,10,18	10	-11
0.840	0,8,20	0	1
0.842	0,16,4	0	1
0.846	0,13,14	0	5
0.847	0,5,22	0	-2
0.847	0,14,12	0	4
0.854	0,12,16	0	5
0.857	0,16,6	0	5
0.860	0,15,10	0	-4
0.864	0,6,22	0	-1
0.867	0,9,20	0	2
0.872	0,11,18	15	6
0.878	0,16,8	0	0
0.880	0,0,24	0	-3
0.881	0,1,24	0	2
0.884	0,7,22	0	-2
0.884	0,17,2	0	-2
0.886	0,2,24	0	0
0.887	0,14,14	0	-3
0.892	0,13,16	0	6
0.892	0,15,12	0	0
0.893	0,3,24	0	0
0.893	0,17,4	12	5
0.896	0,10,20	7	-3
0.904	0,4,24	0	-1
0.906	0,12,18	0	5
0.906	0,16,10	0	-1
0.907	0,8,22	0	1
0.908	0,17,6	13	-5

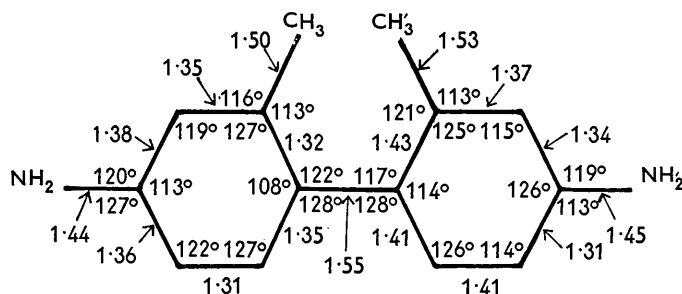
Fig. 3. Bond lengths and bond angles in *m*-tolidine.

Table 2 (cont.)

$\sin \theta$	$hkl$	$F_o$	$F_c$
0.916	0,5,24	0	3
0.927	0,11,20	7	7
0.928	0,17,8	6	4
0.930	0,15,14	0	2
0.932	0,6,24	0	1
0.932	0,9,22	0	1
0.932	0,14,16	8	7
0.936	0,18,0	0	-2
0.937	0,16,12	0	2
0.937	0,18,2	0	-1
0.949	0,13,18	0	0
0.949	0,18,4	0	0
0.951	0,7,24	0	3
0.953	0,0,26	10	-6

The atomic co-ordinates (Table 3) were not obtained directly from the electron-density maps, but were derived on the basis of the best agreement between  $F_o$  and  $F_c$ , using the methods already discussed together with trial-and-error methods.

Table 3. Atomic co-ordinates  
(All values in Ångström units.)

	$x$	$y$	$z_1$	$z_2$
$C_1$	0.42	1.88	2.94	2.94
$C_2$	-0.38	1.75	1.93	1.89
$C_3$	-0.04	1.75	0.63	0.57
$C_4$	1.25	2.10	0.21	0.19
$C_5$	2.05	2.36	1.28	1.26
$C_6$	1.66	2.26	2.52	2.48
$CH_3$	-1.75	1.23	2.23	2.23
$N$	1.63	2.10	-1.20	-1.18
$C'_1$	-0.11	1.92	4.39	4.41
$C'_2$	0.23	0.82	5.25	5.25
$C'_3$	-0.07	0.89	6.58	6.60
$C'_4$	-0.61	2.01	7.10	7.10
$C'_5$	-0.76	3.15	6.46	6.50
$C'_6$	-0.57	3.06	5.10	5.10
$CH'_3$	0.68	-0.52	4.66	4.66
$N'$	-0.84	2.10	8.53	8.53

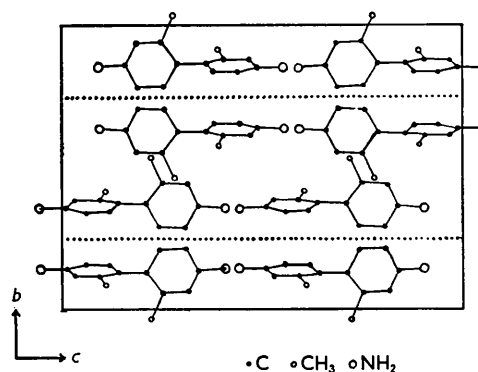
$z_1$  co-ordinate from the [010] projection,  $z_2$  co-ordinate from [100] projection.

### Description of the structure

The values of bond lengths and bond angles for *m*-tolidine can be calculated for each phenyl ring and are represented in Fig. 3. Similar values should be expected for the same bond in the two rings, but values differing by as much as 0.10 Å are found, which

may indicate that the accuracy is of the order of  $\pm 0.05$  Å. The planes of the two phenyl rings have been calculated by a least-squares method, the mean displacement of the atoms from these planes being 0.03 Å. The angle between the mean planes of the two phenyl rings is 86°, which makes the methyl-methyl separation 3.86 Å, in reasonable agreement with Pauling's (1944) value of about 4.0 Å. In *m*-tolidine dihydrochloride the two rings are inclined at an angle of 70.6° which brings the methyl groups into contact; this is probably due to the strong ionic forces between the  $NH_3^+$  groups and the  $Cl^-$  ions. There are no abnormally short distances in the *m*-tolidine unit-cell, the shortest molecular distance being 3.60 Å between atoms  $CH_3$  and  $C'_6$  and the closest distance between adjacent molecules being 3.94 Å.

The normal distances found in *m*-tolidine show that the packing of the molecules is determined by weak van der Waals forces, which account for the softness of the crystals. Fig. 4 shows the arrangements of the

Fig. 4. Structure of *m*-tolidine projected on (100).

molecules in the crystal, and the easy cleavage direction along the  $a$  glide planes is shown by the dotted lines. The molecules lie in sheets parallel to (010), pairs of sheets being at equal distances on either side of the  $a$  glide planes at  $y = \frac{1}{4}$  and  $\frac{3}{4}$ .

The structure is racemic, the unit-cell containing four right-handed and four left-handed molecules.

It is a pleasure to thank Dr H. Lipson and Dr A. Hargreaves for their help and advice throughout the course of this work.

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## The Crystal Structure of *p*-Dichlorobenzene

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The structure of *p*-dichlorobenzene has been determined by means of two electron-density projections. It is found that this compound is isostructural with *p*-dibromobenzene whose structure was previously determined by the authors. All the atoms of each molecule are in the same plane, the benzene ring is a plane regular hexagon of 1.40 Å side, and the chlorine atoms are on the hexagon diagonal.

### 1. Introduction

In previous researches (Bezzi & Croatto, 1942; Croatto & Bezzi, 1949b) we have determined the crystal structure of *p*-dibromobenzene, using X-ray methods with Fourier-Bragg analysis. In the present work we have obtained the structure of *p*-dichlorobenzene. This concludes a program of researches directed not only to establishing the crystalline structure of such substances, but also to throwing light on some controversial problems in isomorphism.

On the one hand Bruni & Gorni (1899, 1900 *a b*), in well known classical researches, consider *p*-dichlorobenzene and *p*-dibromobenzene as typical isomorphous substances, from consideration of their analogous formulae and the close similarity of their crystal constants; on the other hand Hendricks (1933) believed that he had shown that these two substances differed markedly in their crystalline structures. The X-ray work of Hendricks on these substances was carried out by the method of 'trial and error'.

It is worth noting that Hendricks was able to determine only the parameters of the halogens with certainty, and found that they were practically the same for the two substances. In this halogen lattice there are two positions which can be occupied by the benzene ring. Hendricks believed that the benzene rings did not occupy the same positions in both substances, but that one position was occupied in *p*-dichlorobenzene and the other in *p*-dibromobenzene.

It must be observed that Hendricks's choice be-

tween these two positions was made on the basis of X-ray data only in the case of *p*-dichlorobenzene. The choice between the two possible positions for the benzene ring in *p*-dibromobenzene was made on the basis of the optical properties of the crystals.

It seems opportune to take up this study of the above substances again, by means of development in Fourier series.

### 2. Determination of the structure of *p*-dichlorobenzene

The X-ray work on *p*-dichlorobenzene has been carried out with crystals sealed in small tubes of Lindemann glass, to avoid evaporation. We have taken rotation and Weissenberg photographs with rotation about the *b* and *c* axes.

The space group is  $C_{2h}^5-P2_1/a$ ; the unit cell contains two molecules of  $C_6H_4Cl_2$ , and has the following dimensions:

$$a = 14.80, b = 3.99, c = 5.78 \text{ \AA}, \beta = 113^\circ,$$

in good agreement with the previous data of Hendricks.

The four points in general positions of the space group  $C_{2h}^5-P2_1/a$  have the co-ordinates:

$$\begin{aligned} x, y, z; & \frac{1}{2}+x, \frac{1}{2}-y, z; \\ \bar{x}, \bar{y}, \bar{z}; & \frac{1}{2}-x, \frac{1}{2}+y, z. \end{aligned}$$

The reflexions on the Weissenberg photographs were identified by the method of the reciprocal lattice and