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Ab initio structure determination of monoclinic 2,2-dihydroxymethylbutanoic acid from synchrotron radiation powder diffraction data: combined use of direct methods and the Monte Carlo method

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The crystal structure of 2,2-dihydroxymethylbutanoic acid ($C_6H_{12}O_4$) in monoclinic form has been determined ab initio from synchrotron radiation powder diffraction data. Two O and five C atoms were first derived by direct methods. Two missing O atoms and one C atom were found by the Monte Carlo method without applying constraint to their relative positions. Positional and isotropic displacement parameters of these non-H atoms were refined by the Rietveld method. Molecules are linked by hydrogen bonds and they make sheet-like networks running parallel to the (010) plane. The Monte Carlo method is demonstrated to be a powerful tool for finding missing atoms in partially solved structure.

1. Introduction

In the coating industry the development of environment-friendly materials is strongly required and one of the solutions is to replace volatile organic materials with water-soluble materials. 2,2-Dihydroxymethylbutanoic acid, $C_6H_{12}O_4$ (hereinafter DMBA), having a tertiary carboxyl group and two reactive primary hydroxyl groups, has been developed as a new waterborne coating material. DMBA also has excellent solubility in an organic solvent, such as acetone, with a magnitude of more than one order compared with that of 2,2-dihydroxymethylpropanoic acid, $C_5H_{10}O_4$ (DMPA). DMBA can be polymerized without protecting the tertiary carboxyl group, giving easy handing in the polymerization process. Therefore, DMBA is expected to be a promising material as a monomer for water-soluble polyurethane and water-soluble polyester.

DMBA is known to be crystallized in two forms with triclinic and monoclinic symmetries, depending on crystallization conditions. The crystal structure of triclinic DMBA (t-DMBA) has been determined by one of the authors (YK) using a single-crystal method. It has a space group and contains two independent molecules of $C_6H_{12}O_4$ in an asymmetric unit (Kojima, 2001). It was, however, difficult to obtain a single-crystal of monoclinic DMBA (m-DMBA) for structure analysis. Therefore, in the present study synchrotron radiation powder diffraction data are used for the structure determination of m-DMBA.

With developments of whole-powder-pattern decomposition methods (Pawley, 1981; Le Bail et al., 1988) and computer softwares for phasing (Cascarano et al., 1992; Altomare et al., 1994, 1995), a number of crystal structures have been solved ab initio from powder diffraction data. Direct methods, modified for treating powder diffraction data, have been used as major tools for solving crystal structures (see, for example, a

review by Giacovazzo, 1996), while many other techniques have also been developed over the past decade (see, for example, a review by Harris & Tremayne, 1996). Direct methods require extraction of integrated intensities of individual reflections from the powder diffraction pattern and whether a structure can be solved or not depends on the percentage of independently resolved reflections (Estermann & Gramlich, 1993). On the other hand, the Monte Carlo method (Harris *et al.*, 1994) and the simulated annealing method (Tremayne *et al.*, 1996) directly fit the calculated pattern to the observed pattern and they do not require the integrated intensities.[1] Therefore, these methods are applicable not only to well resolved patterns, but also low-resolution data as often exhibited by organic materials. In these methods the rigid-body model is usually introduced for grouping atoms, to reduce the number of unknown parameters and to avoid falling into false minima. In the present study, the Monte Carlo method has been applied to finding missing atoms in the structure, partially solved by direct methods, without using the rigid-body model.

2. Experimental

2.1. Sample preparation

The present sample of *m*-DMBA was synthesized by following the procedure established as an industrial process. 2,2-Dihydroxymethylbutanal was first synthesized by the condensation reaction of 2-hydroxymethylbutanal with formaldehyde (HCHO) at temperatures of 323–333 K, using triethylamine as a catalyst. Then DMBA was synthesized by oxidizing 2,2-dihydroxymethylbutanal with hydrogen peroxide (H_2O_2). The product was a white-coloured powder. *m*-DMBA was obtained by crystallization at < 278 K in 4-methyl-2-pentanone solution. On the other hand, *t*-DMBA was obtained by crystallization in ethyl acetate solution (Kojima, 2001).

A sample for the refinement of unit-cell parameters was prepared by mixing *m*-DMBA with Si powder used as an internal standard reference material (National Institute of Standards and Technology, Standard Reference Material 640*b*) in a *m*-DMBA/Si weight ratio of 4:1.

2.2. Synchrotron radiation experiment

Synchrotron radiation powder diffraction data were collected at the beamline BL-4B$_2$ with a bending magnet light source at the Photon Factory in Tsukuba. Synchrotron radiation with a wavelength λ of 0.7086 (1) Å was obtained with a water-cooled double-crystal Si(111) monochromator and it was focused horizontally by a cylindrical mirror installed after the monochromator. Diffracted intensities were measured using a powder diffractometer with a multiple-detector system (MDS; Toraya *et al.*, 1996). A 2θ-step scan

[1] The Monte Carlo method and the simulated annealing method can also be applied to an integrated intensity data set rather than profile intensities.

technique was used in a capillary-specimen transmission geometry.

After having derived a structure model of *m*-DMBA, we had another chance of collecting intensity data with synchrotron radiation at λ = 1.2085 (2) Å using MDS. Diffraction data had much higher intensity than those collected at λ = 0.7086 Å and they were used for Rietveld refinement. In the following intensity data sets collected at λ = 0.7086 and 1.2085 Å are designated SR07 and SR12, respectively, according to their wavelength values. Absorption correction was not necessary even for SR12, since $\mu r < 0.1$ (a packing density 33%). The details of the synchrotron radiation experiments are described in Table 1.

2.3. Data collection with laboratory X-rays

Powder diffraction data of *m*-DMBA + Si specimen were measured using Cu $K\alpha_1$ radiation monochromated with a Johansson-type Ge(111) crystal, which was mounted on the incident-beam side of a powder diffractometer (Rigaku Co., RINT1500). A θ–2θ step-scan technique was used in a flat-specimen reflection geometry. Experimental details are given in Table 1.

3. Structure solution and refinement

3.1. Crystallographic data

Peak positions of the first 40 reflections from the low-angle side of SR07 were determined by the computer program *PROFIT* (Version 3.00) for individual profile fitting (Toraya, 1986). They were used by the computer program *ITO* for auto-indexing based on the zone-finding method (Visser, 1969): a monoclinic cell with the dimensions $a = 6.400$, $b = 11.085$, $c = 11.200$ Å and $\beta = 106.12°$ was derived at a figure-of-merit of 86.1.

Overlapping reflections of SR07 in the 2θ range of 5–30° were resolved by the computer program *WPPF* (Version 3.00) for whole powder-pattern decomposition based on the Pawley algorithm (Toraya, 1986). The split-type pseudo-Voigt function was used for modeling the profile shape. An output list of refined integrated intensity parameters for 320 reflections indicated systematic absences of reflections with indices of $l = 2n + 1$ (*n*: integer) for $h0l$, $k = 2n + 1$ for $0k0$, and $l = 2n + 1$ for $00l$, deriving uniquely a space group of $P2_1/c$.

Unit-cell parameters of *m*-DMBA were refined by *WPPF* using laboratory X-ray data in the 2θ range 5–145°. The systematic peak shift $\Delta(2\theta)$ was corrected with the function $\Delta(2\theta) = t_0 + t_1 \cos 2\theta + t_2 \sin 2\theta + t_3 \tan \theta$. Following the procedure proposed by Toraya (1993), the unit-cell parameters of *m*-DMBA and the parameters t_0–t_3 in $\Delta(2\theta)$ were refined simultaneously, while the unit-cell parameter of the Si powder was fixed at a literature value of $a = 5.430940$ (35) Å (Rasberry, 1987) during the whole powder-pattern fitting.

From a comparison of calculated density of *m*-DMBA with that of *t*-DMBA ($D_x = 1.31$ g cm^{-3}), the number of chemical formula units, Z, was estimated to be four. Crystal data are given, together with those of *t*-DMBA, in Table 2.

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Table 1
Experimental details.

Data collection			
Temperature	297		
Crystal form	Powder		
Crystal color	White		
Wavelength (Å)	0.7086 (1)	1.2085 (2)	1.540562
Radiation type	Synchrotron		Laboratory X-ray (Cu $K\alpha_1$)
Diffractometer	MDS†		Rigaku RINT1500
Monochromator	Si(111) double crystal		Johansson-type Ge(111) crystal
Analyzer	Ge(111) flat crystal		–
Data collection method	2θ step scans		θ–2θ step scans
Measurement mode	Capillary specimen transmission		Flat specimen reflection
Specimen mounting	Glass capillary 1.0 mm φ		Flat specimen holder
Specimen rotation (r s^{-1})	1	1	1
2θ range (°)	2.0–154.9	2.0–154.8	5.0–145.0
Step size, 2θ (Å)	0.004	0.004	0.02
Step counting time (s)	3.5	3.5	20
Absorption correction	None	None	–
Refinement			
Refinement on profile intensities			
Profile shape function	Pseudo-Voigt function		
Structure refinement program	*PFLS* (Toraya, 2000)		
No. of reflections	876		
No. of parameters refined	64		
Weighting scheme	$w_i = 1/y_{oi}^e$ ($e = 2.2$)		
Preferred orientation correction	Symmetrized harmonic expansion		
Source of atomic scattering factors	*International Tables for X-ray Crystallography* (1974, Vol. IV)		
R_p	0.0707		
R_{wp}	0.0709		
R_{Bragg}	0.0927		
R_F	0.0927		

$R_p = \sum_i |y_{oi} - y_{ci}|/\sum_i y_{oi}$; $R_{wp} = [\sum_i w_i(y_{oi} - y_{ci})^2/\sum_i w_i y_{oi}^2]^{1/2}$; $R_{Bragg} = \sum_j |I_{oj} - I_{cj}|/\sum_j I_{oj}$; $R_f = \sum_j |I_{oj}^{1/2} - I_{cj}^{1/2}|/\sum_j I_{cj}^{1/2}$.
† MDS: synchrotron radiation powder diffractometer with multiple-detector system.

3.2. Application of direct methods

Integrated intensity parameters of 320 reflections of SR07 (2θ range 5–30°) were converted into structure amplitudes $|F(hkl)|$ with appropriate corrections for Lorentz–polarization and the multiplicity of reflections. Among them, 123 reflections were equi-partitioned (38% of total reflections). Values of 0.01 were assigned to $|F(hkl)|$ of 39 reflections with zero or negative intensities (12%). A set of $|F(hkl)|$ thus obtained was
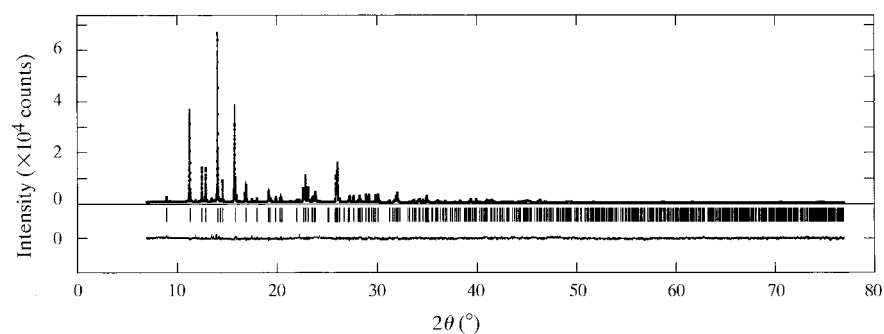

Figure 1
Final fitting result of Rietveld refinement. Filled squares and solid lines represent the observed and calculated profile intensities, respectively. The diagram at the bottom gives weighted difference plots by $5 \times (w_i)^{1/2}(Y_{oi} - Y_{ci})$. Short vertical bars represent Bragg reflection positions.

used as input data for the computer program *SIRPOW*97 for direct methods (Altomare *et al.*, 1994). From an estimated Z value of 4, six C and four O atoms were assumed to be present as asymmetric units in a unit cell, whereas H atoms were ignored in solving structure.

Positional parameters of ten C atoms and three O atoms were derived from *SIRPOW*97, giving the R_{wp} value of 30.4%. Comparisons of a molecular structure thus derived with those of *t*-DMBA and 1,1,1-tris(hydroxymethyl) propane (TRMP) (Sake Gowda *et al.*, 1982) clearly indicated that the positions of five C and two O atoms were correctly found, whereas those of the remaining six atoms, some of which have much longer bond lengths than the literature values, were considered to be ghosts.

3.3. Finding missing atoms by the Monte Carlo method

The Monte Carlo method, used in the present study, follows the procedure described by Harris *et al.* (1994), using the Metropolis importance sampling algorithm. The objective function was the weighted reliability index given by

$$R_{wp} = 100 \times \{[\Sigma w_i(Y_{oi} - Y_{ci})^2]/\Sigma w_i Y_{oi}^2\}^{1/2},$$

where Y_{oi} and Y_{ci} are the observed and calculated profile intensities at the ith step, respectively, and w_i is the weight assigned to the ith observation in the form $w_i = Y_{oi}^{-1}$. The computer program *MCS* (Version 1.00) for the Monte Carlo calculation, which has been developed by the authors' group (Nakamura *et al.*, 2001), was used to find the missing one C and two O atoms in *m*-DMBA by using *SR*07 (2θ range 5–30°). In calculating initial and trial configurations, relative positions of seven independent atoms, derived by direct methods, were kept fixed as a group in a unit cell. In each Monte Carlo move, nine positional parameters (three sets of x, y, z for three missing atoms) were varied, under the constraint of symmetry operations of the space group $P2_1/c$, by random amounts in random directions within the maximum

Table 2
Crystal data of *m*-DMBA and *t*-DMBA.

	m-DMBA	*t*-DMBA
Chemical formula	$C_6H_{12}O_4$	$C_6H_{12}O_4$
Chemical formula weight	148.158	148.158
Cell setting	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	6.3980 (1)	10.282 (2)
b (Å)	11.0866 (2)	10.712 (2)
c (Å)	11.2095 (4)	6.835 (1)
α (°)	90	91.49 (1)
β (°)	106.108 (2)	92.94 (2)
γ (°)	90	90.47 (2)
V (Å^3)	763.90 (4)	753.6 (2)
Z	4	4
D_x (Mg m^{-3})	1.29	1.31

Table 3
Fractional atomic coordinates and isotropic displacement parameters (Å^2).

	x	y	z	U_{iso}
C1	0.1145 (9)	0.3836 (5)	0.2402 (4)	0.012 (1)
C2	0.074 (1)	0.4302 (6)	0.3555 (5)	0.041 (2)
C3	0.2466 (8)	0.4863 (4)	0.1909 (4)	0.024 (2)
C4	−0.111 (1)	0.3434 (5)	0.1487 (5)	0.036 (1)
C5	0.2582 (9)	0.2590 (5)	0.2744 (5)	0.045 (3)
C6	0.470 (1)	0.2776 (4)	0.3769 (5)	0.040 (1)
O1	0.1170 (6)	0.5383 (5)	0.3907 (3)	0.041 (2)
O2	−0.0208 (5)	0.3626 (3)	0.4214 (3)	0.031 (1)
O3	0.3057 (5)	0.4345 (3)	0.0831 (3)	0.035 (1)
O4	−0.2531 (5)	0.4432 (3)	0.1259 (3)	0.031 (1)

displacement of 1.2 Å. An acceptance level was set so as to keep the acceptance rate of ∼40%.

Structural parameters for a configuration, which gave the minimum of 29.7% during 10000 Monte Carlo moves, were further refined by the Rietveld method, reducing the value to 12.1%.

3.4. Rietveld refinement

Positional and isotropic displacement parameters of six C and four O atoms were refined by the Rietveld method using *SR*12 (2θ range of 5–77°) and the computer program *PFLS* (Version 5.00; Toraya, 2000), adopting the same profile model as that of *WPPF*. The contribution of 12 H atoms was not included in the refinement. An intensity correction for preferred orientation was applied by employing the function for symmetrized harmonic expansion (Järvinen, 1993).

In the least-squares fitting the weight function w_i, proposed by Toraya (1998) for taking systematic error into account, was assigned to Y_{oi}. The function has the form $w_i = Y_{oi}^{-e}$, and the parameter e can be optimized in order to obtain uniform distributions of the mean weighted residuals $\langle w_i(Y_{oi} - Y_{ci})^2 \rangle$ and weighted difference plots by $w_i^{1/2}(Y_{oi} - Y_{ci})$. The optimization of the weight function was obtained at $e = 2.2$.

Final reliability indices are given in Table 1. Details of the refinement procedure will be found elsewhere (Toraya, 2000).

4. Results and discussion

A final fitting result of Rietveld refinement is shown in Fig. 1. Final atomic parameters are given in Table 3. Fig. 2 shows the conformation of a molecule of $C_6H_{12}O_4$ in *m*-DMBA. Selected bond lengths and bond angles are given in Table 4.

4.1. Structure of *m*-DMBA

Figs. 3(*a*)–(*d*) show crystal structures of *m*-DMBA and *t*-DMBA, each of which is projected along the [100] and [001] directions. Two independent molecules in *t*-DMBA, designated *A* and *B*, respectively, are approximately in mirror symmetry. The molecule in *m*-DMBA and its mirror image, generated by the *c* glide plane, have virtually the same

conformation as those in *t*-DMBA, whereas their orientations in the unit cell are greatly different from those in *t*-DMBA.

As shown in Fig. 3(*a*), two carboxyl groups in *m*-DMBA face each other, and two molecules, related by the centers of symmetry at (0, 0, 0) and (0, $\frac{1}{2}$, $\frac{1}{2}$), are linked strongly by hydrogen bonds O1···O2 having a distance of 2.596 (5) Å in the (100) plane. The formation of molecular pairs in *m*-DMBA explains why the protection of the carboxyl groups is unnecessary during the polymerization process of *m*-DMBA.

In *m*-DMBA the molecular pairs are linked by two hydrogen bonds of O3···O4 having distances of 2.647 (5) Å in the (100) plane (Fig. 3*a*) and also by two hydrogen bonds of O3···O4 [2.730 (5) Å] along the *a* axis (Fig. 3*b*), while there are no hydrogen bonds along the *b* axis. On the other hand, individual molecules in *t*-DMBA have six hydrogen bonds of O1*A*···O3*B* [2.704 (2) Å], O2*A*···O3*B* [2.604 (2) Å], O4*A*···O4*A* [2.720 (3) Å], O1*B*···O3*A* [2.762 (2) Å], O2*B*···O3*A* [2.602 (2) Å] and O4*B*···O4*B* [2.697 (3) Å], which are all approximately parallel to the (001) plane (Fig. 3*c*), and one hydrogen bond of O4*A*···O4*B* [2.691 (3) Å] along the *c* axis (Fig. 3*d*). Therefore, as shown by dotted lines
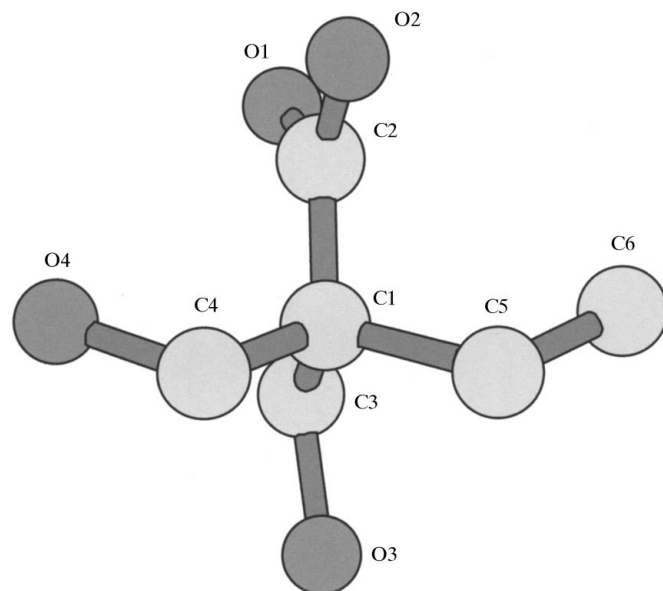

Figure 2
Conformation of the molecule $C_6H_{12}O_4$ in *m*-DMBA.

Table 4
Selected bond lengths (Å) and bond angles (°) of *m*-DMBA.

C1—C2	1.482 (9)	O1—C2	1.265 (8)
C1—C3	1.607 (8)	O2—C2	1.314 (8)
C1—C4	1.583 (7)	O3—C3	1.477 (7)
C1—C5	1.645 (8)	O4—C4	1.412 (7)
C5—C6	1.525 (7)		
C2—C1—C3	106.7 (4)	C1—C5—C6	112.8 (4)
C2—C1—C4	108.4 (5)	C1—C3—O3	106.4 (4)
C2—C1—C5	108.0 (4)	C1—C4—O4	108.6 (4)
C3—C1—C4	116.8 (4)	C1—C2—O1	121.8 (6)
C3—C1—C5	111.0 (4)	C1—C2—O2	120.5 (5)
C4—C1—C5	105.4 (4)	O1—C2—O2	117.4 (6)

in Figs 3(*a*)–(*d*), the molecules in *m*-DMBA constitute a sheet-like network parallel to the (010) plane. On the other hand, the molecules in *t*-DMBA constitute a three-dimensional network. *t*-DMBA has a greater number of hydrogen bonds and a smaller unit-cell volume by 1.6% than *m*-DMBA. These facts suggest that *t*-DMBA is probably energetically more stable than *m*-DMBA. Differences in these structural features of *t*- and *m*-DMBA may be responsible for the fact that *t*-DMBA could be grown up to large crystals with enough sizes for single-crystal structure analysis. On the other hand,

m-DMBA remains as aggregates of fine crystals and of low crystallinity.

4.2. The Monte Carlo method for finding missing atoms

To obtain a complete structure solution becomes difficult with increasing the number of severely overlapping reflections and the degradation of the quality of reflection data is the principal problem in applying direct methods to structure solution using powder diffraction data. In the present sample reflections in 38% of the total reflections were equi-partitioned and three atoms among ten atoms in the asymmetric unit could not be found after the application of direct methods.

Several techniques have been proposed to overcome this difficulty. Some persist in using direct methods to obtain the complete structure solution by improving observed structure amplitudes. Techniques, included in this category, are the fast iterative Patterson squaring (FIPS) method for a sophisticated whole powder-pattern decomposition (Estermann *et al.*, 1992), the computer software *EXTRA*, which feeds back various types of information to the whole powder-pattern decomposition process (Altomare *et al.*, 1995, 1998; Carrozzini *et al.*, 1997) *etc*. A rather classi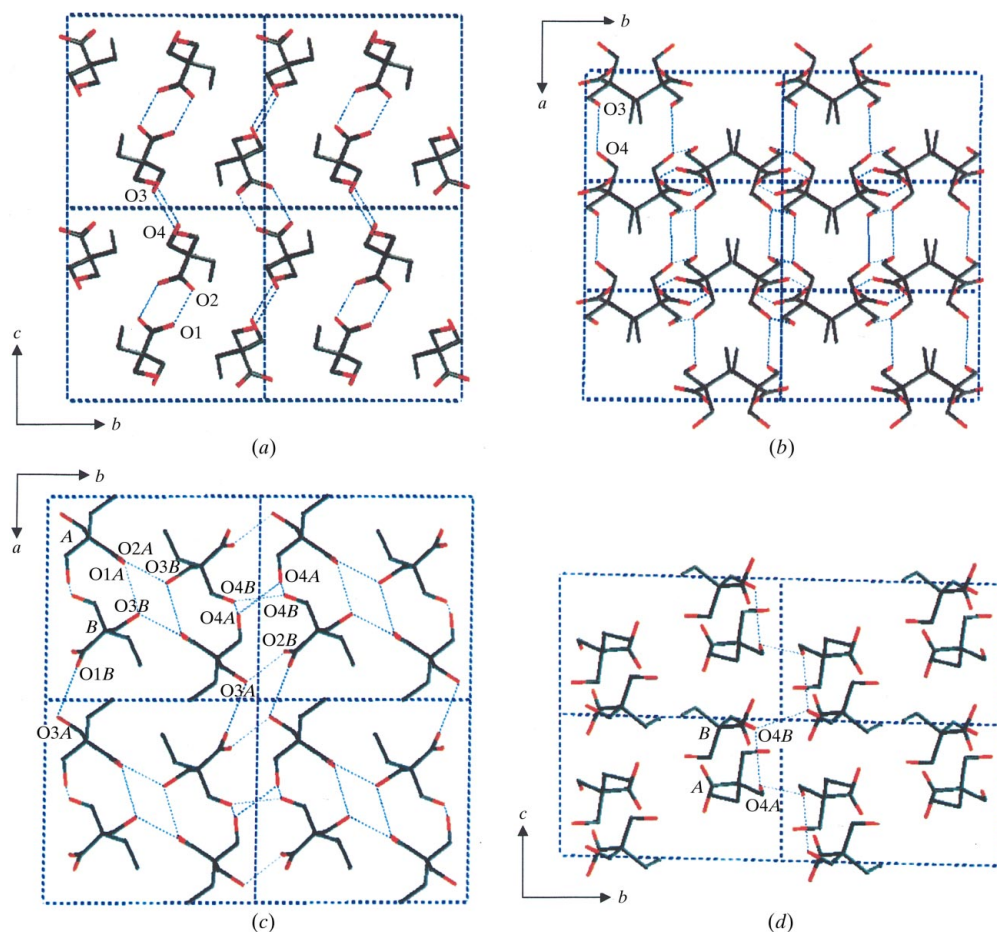cal approach is the use of difference Fourier synthesis to find missing atoms using integrated intensities obtained by the Rietveld decomposition formula (Rietveld, 1969). In many cases in which we need to find missing atoms, however, the quality of intensity data is often not enough to synthesize well resolved difference Fourier maps. The Monte Carlo method, employing the rigid-body model, has been used successfully for structure solutions of organic compounds from powder diffraction data (Harris & Tremayne, 1996). However, the applicability of the method has been limited in cases where we have information to construct the rigid-body model itself. In the present study, the Monte Carlo method is demonstrated to be a powerful tool for finding missing atoms in the structure partially solved by direct methods. The method can be applied not only to organic materials, but also inorganic materials, as has been shown in the structure analysis of

Figure 3
(*a*) [100] and (*b*) [001] projections of *m*-DMBA. (*c*) [001] and (*d*) [100] projections of *t*-DMBA.

tobermorite: a zeolitic Ca atom and three water molecules in [Ca$_4$Si$_6$O$_{17}$·2H$_2$O] frameworks were found by the Monte Carlo method (Yamazaki & Toraya, 2001).

4.3. Accuracy of refined positional parameters

Pattison *et al.* (2000) discussed the accuracy of positional parameters, refined by the Rietveld method, of *m*-fluorobenzoic (C$_7$H$_3$FO$_2$) acid (*m*-FBA) at room temperature and 100 K. *m*-FBA consists of ten independent non-H atoms in a monoclinic unit cell and the maximum range of synchrotron radiation powder diffraction data used for Rietveld refinement was 0.51 Å^{-1}. Therefore, Rietveld refinement conditions are mostly the same as those in the present study. Pattison *et al.* (2000) reported that the average deviation in bond lengths from single-crystal values is 0.025 Å for room-temperature data. In the present study, the average deviation of nine bond lengths from single-crystal values of *t*-DMBA was 0.046 Å, being about twice as large as that of *m*-FBA, although we must take into account the fact that the referenced single-crystal values are not of *m*-DMBA, but of *t*-DMBA and that the contribution of H atoms was ignored in the Rietveld refinement.

In a recent study on the accuracy of Rietveld refinement it was pointed out that important factors for obtaining high accuracy are:

(i) sufficiently large $\sin\theta/\lambda$ in the range > 0.8,
(ii) adequate counting statistics,
(iii) correct profile modeling,
(iv) proper weighting and
(v) high-resolution diffraction data (Toraya, 2000).

In the present study the accuracy of positional parameters could be significantly improved by optimizing the weighting on observations in the Rietveld refinement. A still greater average deviation in bond length of *m*-DMBA than that of *m*-FBA is primarily due to the broadening of diffraction lines of *m*-DMBA: a minimum value of the full-width at half maximum (FWHM) was 0.055° for *m*-DMBA (FWHM for the instrumental function of MDS using a 1.0 mm φ-capillary specimen at the BL-4B$_2$ beamline was ~0.018°). On the other hand, the FWHM of *m*-FBA is reported to be 0.012°, indicating that the sample of *m*-FBA is well crystallized, whereas the *m*-DMBA is of low crystallinity.

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