

## Hexamethylenetetramine Sebacate, an Incommensurate Structure with Large Nonsinusoidal Modulations: Comparison of Two Refinement Strategies

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### Abstract

The organic salt hexamethylenetetramine sebacate presents a 1D modulation with strong satellite reflections. Single-crystal X-ray intensities of main reflections and satellites up to sixth order have been measured at room temperature and used to refine this incommensurate structure. Two incommensurate structure models of hexamethylenetetramine (hexamine) sebacate are proposed and compared. The first is based on displacive atomic modulation functions and the second one uses displacive modulation and occupational step functions. Both models require high-order harmonic terms to describe the strongly nonsinusoidal modulation components. The structural characteristics of hexamine sebacate are similar in the two models. The structure is a layer structure consisting of alternating sheets of hexamine and sebacic acid connected by H bonds. Each layer of sebacic acid molecules consists of close-packed aliphatic chains with their axis slightly tilted with respect to the layer normal. The chains form alternating areas, each of which is characterized by a common orientation of the chains. These characteristics have also been observed in hexamethylenetetramine suberate.

### 1. Introduction

The incommensurate (IC) structure of hexamethylenetetramine (hexamine) sebacate is determined based on single-crystal X-ray diffraction data at room temperature. Hexamine sebacate belongs to the family of hexamine and aliphatic diacids and presents the same characteristic type of modulation as hexamine suberate (Bussien Gaillard, Paciorek, Schenk & Chapuis, 1996). In both compounds, the modulations affecting the hexamine atoms have small amplitudes, whereas rotational modulations with large amplitudes affect the acid molecules. The refinement of strong modulations using the IC formalism (de Wolff, Janssen & Janner, 1981) is a challenging task with the refinement programs currently available for IC structure refinements. They do not provide the appropriate tools to describe rotational modulations with large amplitudes.

The main purpose of this paper is to propose two approaches to describe the structure of hexamine sebacate and to compare the structural models obtained. The first approach describes the modulation of the compound by atomic displacive modulation functions including harmonic terms up to eighth order. The second approach uses only harmonic terms up to fourth order and describes the displacement between the two main different positions of the acid chain by means of two superimposed and pre-rotated chains. They are linked together by occupational modulation described by a step function, which makes them mutually exclusive. This refinement uses the concept of the crenel function as described earlier for the refinement of TaSi<sub>0.414</sub>Te<sub>2</sub> by Petříček, van der Lee & Evain (1995).

### 2. Experimental part

The adduct of N<sub>4</sub>(CH<sub>2</sub>)<sub>6</sub> · (CH<sub>2</sub>)<sub>8</sub>(COOH)<sub>2</sub> was obtained by mixing stoichiometric amounts of hexamine and sebacic acid in ethanol for 1 h at 350 K. Single crystals were grown by recrystallization in acetonitrile. For the measurements, the faces were protected from ambient humidity by a film of silicone oil (Paratone).

Room-temperature precession photographs revealed monoclinic symmetry (Fig. 1) with a one-dimensional planar modulation vector. The following reflection conditions were observed:  $0k00$ ,  $k = 2n$ , and  $h0lm$ ,  $m = 2n$ , with the monoclinic axis  $b$ . They indicate the superspace group  $P2_1/m(\alpha 0 \gamma)0s$  (No. 11.2 in *International Tables for Crystallography*, 1993). A DSC (differential scanning calorimetry) analysis of the compound revealed a single phase transition of second order at 356 K.

A single crystal was measured at room temperature on a Syntex  $P2_1$  diffractometer (driven by a modified version of  $P3$  for satellite measurements) with Cu  $K\alpha$  radiation ( $2\theta$ - $\omega$  scans, graphite monochromator). 16 centred main reflections ( $46 \leq 2\theta \leq 71^\circ$ ) were used to evaluate the cell parameters. The components of the modulation vector  $\mathbf{q} = \alpha \mathbf{a}^* + \gamma \mathbf{c}^*$  were obtained by averaging the fractional parts of  $\mathbf{a}^*$  and  $\mathbf{c}^*$  over 12 centred satellite reflections of order 1 to 3 ( $18 \leq 2\theta \leq 52^\circ$ ). The

full width at half-maximum values (FWHM) are similar for main and satellite reflections in the same range of intensities (Table 1).

Main and satellite reflections were chosen as standards. The two categories of reflections presented identical linear decays of approximately 20% during approximately 1000 h of measurement. The reflections of

half a sphere were collected ( $3 \leq 2\theta \leq 116^\circ$ ). No violation of the reflection conditions given above were detected. The data reduction included scaling based on six standard reflections, an absorption correction based on the crystal shape and orientation, a Lorentz-polarization correction and averaging of equivalent reflections in accordance with the superspace-group symmetry. The resulting data set included 3378 unique reflections. Table 1 summarizes the measurement conditions.

### 3. Structure determination and refinement

As in the previous study of hexamine sebacate (Bussien Gaillard, Paciorek, Schenk & Chapuis, 1996), no plausible average structure could be determined for hexamine sebacate from the main reflections only, either from the direct or any other method. To obtain a relevant starting model for the refinement of the IC structure, a commensurate approximation was proposed.

Since  $\alpha \approx 0$  and  $\gamma \approx \frac{1}{4}$ , the following supercell was chosen:

$$\mathbf{a}' = \mathbf{a}^*, \quad \mathbf{b}' = \mathbf{b}^* \quad \text{and} \quad \mathbf{c}' = \frac{1}{4}\mathbf{c}^*. \quad (1)$$

In this cell, the new indices are

$$h' = h, k' = k, l' = 4l \quad \text{for main reflections} \quad (2)$$

$$h' = h, k' = k, l' = 4l + m \quad \text{for satellite reflections.} \quad (3)$$

These transformations lead to the following reflection conditions:  $h'0l'$ ,  $l' = 2n$ , and  $0k'0$ ,  $k' = 2n$ , which correspond to the approximate space-group symmetry  $P2_1/c$ .

With this approximation, the structure could be solved by direct methods using the XS program of SHELXTL5.0.3 (Sheldrick, 1996). Two independent hexamines and two independent acid chains could be located on an E map. The zigzag planes of the two acid chains differ by an angle close to  $65^\circ$  (Fig. 2).

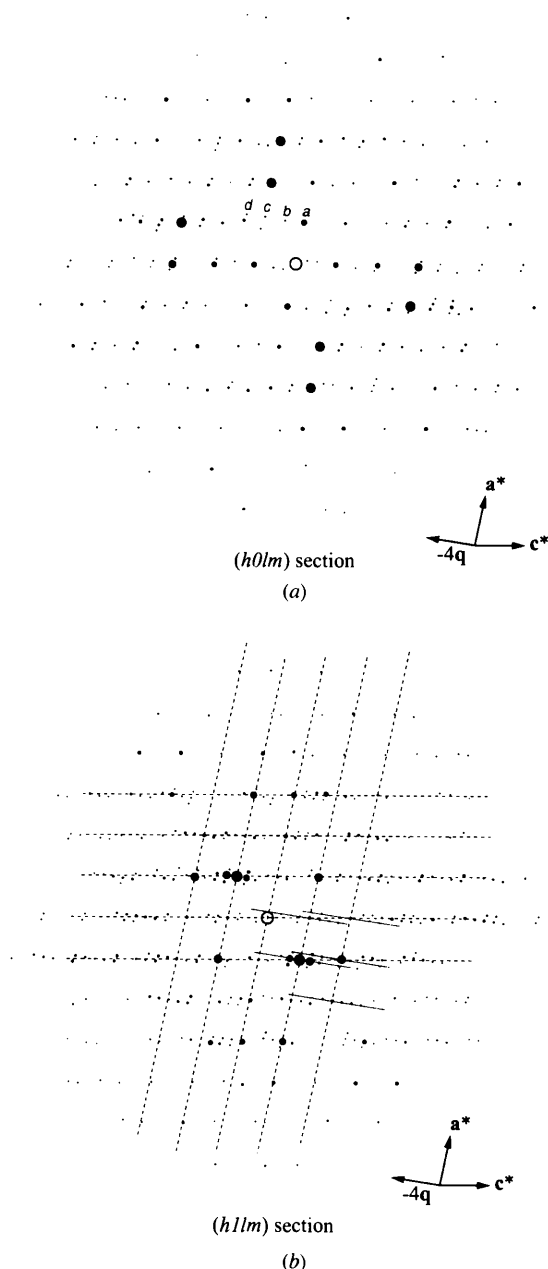


Fig. 1. Schematic representation of two layers of the reciprocal space. The size of the dots is proportional to the intensities of the peaks. Only reflections larger than  $3\sigma$  are represented. Open circles indicate the origin of the reference system. As an example, the 4D indices of the reflections  $a$ ,  $b$ ,  $c$  and  $d$  on (a) are, respectively, 1000, 1002, 1004 and 100 $\bar{6}$ .

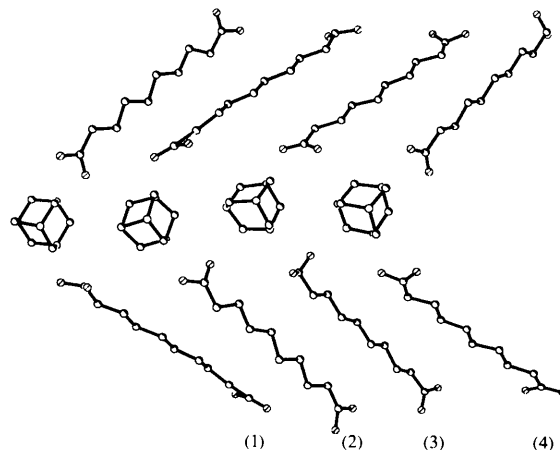


Fig. 2. Projection along  $c$  of the commensurate approximation of hexamine sebacate solved by direct methods in space group  $P2_1$ .

Table 1. Summary of crystal and experimental data

Morphology	{001}, {010}, {111}, {110}, {210}
Crystal habit	Tabular (platelet)
Dimensions (mm)	0.05 × 0.3 × 0.3
Superspace group	$P2_1(\alpha 0 \gamma)000$
Lattice parameters (Å, °)	$a = 5.8769(6)$ , $b = 27.7772(24)$ , $c = 5.9039(8)$ , $\beta = 102.192(9)$
Volume (Å <sup>3</sup> )	942.05 (17)
Modulation vector	$q = -0.02(5) a^* + 0.24(5) c^*$
Z	2
$M_r$ (g mol <sup>-1</sup> )	342.44
$D_x$ (g cm <sup>-3</sup> )	1.19
$\lambda$ (Å)	1.5418
$\mu$ (Cu K $\alpha$ ) (mm <sup>-1</sup> )	0.68
$F(000)$	372
T measurement (K)	295 (2)
2 $\theta$ range (°)	3 ≤ 2 $\theta$ ≤ 116
Scan width (°)	0.90 above K $\alpha_1$ and below K $\alpha_2$
Scan speed (° min <sup>-1</sup> )	1.04–14.65
Standard reflections [ $hklm$ , FWHM (°), relative integrated intensity]	1000, 0.15, 70; 0030, 0.15, 32; 0600, 0.1, 100; 0231, 0.2, 18; 1012, 0.2, 5; 0632, 0.2, 4
Weights	$w = 1/\sigma^2(F)$

	All	$m = 0$	$m = \pm 1$	$m = \pm 2$	$m = \pm 3$	$m = \pm 4$	$m = \pm 5$	$m = \pm 6$
Number of measured reflections	21618	2641	5330	5302	3220	1724	1708	1693
Number of reflections [ $I \geq 3\sigma(I)$ ]	6120	1229	2313	1688	661	71	95	63
Independent reflections [ $I \geq 3\sigma(I)$ ]	3378	661	1229	942	386	52	63	45
Average intensities [ $I \geq 3\sigma(I)$ ]		8892	2630	739	409	262	302	191
$R_{\text{int}}$ without absorption correction (%)	3.1	3.0	2.9	4.0	6.4	11.1	9.5	10.1
$R_{\text{int}}$ with absorption correction (%)	2.5	2.3	2.4	3.8	6.2	11.1	9.2	10.1

The model was refined using the XLS program of the *SHELXTL5.0.3* package. For the refinement, only data with  $|m| = 0$  and 1 have been selected. The anisotropic displacement parameters (ADP) were refined for all non-H atoms. The H-atom positions were deduced from the geometry of the CH<sub>2</sub> groups; bond lengths were restricted to literature values (Housty & Hospital, 1966; Becka & Cruickshank, 1963). Planar restraints were used for the chains of sebacic acid.

In addition to  $P2_1/c$ , the noncentrosymmetric space group  $P2_1$  was also tested. The corresponding results are given below.

	No. of reflections	No. of restraints	No. of parameters	$wR$
$P 2_1/c$	2332	52	433	0.1064
$P2_1$	2334	139	865	0.0784

#### 4. Refinement of the IC structure

The commensurate approximation revealed that the sebacic molecule adopts in different cells two orientations that subtend an angle of  $\sim 65^\circ$  (Fig. 2). In order to describe this large rotational modulation, two models were tested using the refinement programs *MSR* and *JANA*.

The first model consists of an average structure including one hexamine and one sebacic acid molecule. In order to reproduce the rotation of the zigzag plane of the chain, atomic displacive modulation functions

including harmonics up to eighth order are added to the coordinates of the average structure and included in the refinement.

The average structure of the second model consists of one molecule of hexamine and two superimposed molecules of sebacic acid with zigzag planes rotated by an angle of  $\sim 65^\circ$ .

##### 4.1. Refinement using the program *MSR* (Paciorek, 1991)

The IC structure was refined with a modified version of the *MSR* program. The parametrization chosen for the atomic modulation functions was

$$u_i^\mu(\bar{x}_4^\mu) = \sum_{n>0} [c_{i,n}^\mu \cos(2\pi n \bar{x}_4^\mu) + s_{i,n}^\mu \sin(2\pi n \bar{x}_4^\mu)], \quad (4)$$

where  $i = 1, 2, 3$  and  $m$  denotes the atom. The order of the harmonic terms is characterized by  $n$ .

The new version of *MSR* allows different choices for the fourth coordinate (Paciorek, Bussien Gaillard, Schenk & Chapuis, 1996). In this refinement, the fourth coordinate has been chosen according to de Wolff *et al.* (1981):

$$\bar{x}_4^\mu = \mathbf{q} \cdot \mathbf{r}^\mu + t. \quad (5)$$

In order to initiate the refinement of the IC structure, two hexamines and two acid chains [(1) and (2) in Fig. 2] were projected onto the original cell and their coordinates averaged to obtain one unit of hexamine sebacate. The atomic coordinates and atomic modulation functions

Table 2. *R* factors and overall scaling ratio (OSR) for the modulated structure, with *Axe* correction and anisotropic displacement parameters, as refined with MSR

Number of reflections	4621		
Number of parameters	1457		
Satellite order	<i>R</i>	<i>wR</i>	OSR
-6	0.2822	0.2984	0.8375
-5	0.2594	0.2527	0.9035
-4	0.2692	0.2727	0.9117
-3	0.1743	0.1440	0.9571
-2	0.1152	0.0989	0.9716
-1	0.0808	0.0747	0.9916
0	0.0669	0.0740	0.9817
1	0.0758	0.0739	0.9951
2	0.1093	0.0864	0.9788
3	0.1504	0.1319	0.9515
4	0.2749	0.3135	0.8917
5	0.2263	0.2096	0.9190
6	0.3333	0.3430	0.7515
All satellites	0.1080	0.0920	0.9772
All reflections	0.0970	0.0874	0.9784
GOF	2.1844		
Number of restraints	104		
Axe correction factor	0.03275 (9)		

were refined in the superspace group  $P2_1(\alpha 0 \gamma)$  (see §5.1 for justification). The *Axe* correction (Axe, 1980) was applied. No symmetry restrictions were necessary as all atoms are located on general positions. ADP's were refined for the non-H atoms, except for N4, C2 and C11 (Fig. 3).

The positions of the two H atoms of the COOH groups, namely H11 and H31 (Fig. 3), have been calculated from the positions of the COO atoms (Gao, Weber & Craven, 1994). In the refinement, H11 and H31 were also considered as modulated. An isotropic displacement parameter was assigned to H11 and H31.

The H atoms of the CH<sub>2</sub> groups were included as riding atoms (Paciorek, Bussien Gaillard, Schenk & Chapuis, 1996) with an overall isotropic temperature factor for the H atoms of the hexamine molecule and an additional one for the H atoms of the sebacic acid molecules. The overall isotropic temperature factors have been refined. Harmonic terms up to the eighth order were included in the model. The agreement factor of each class

of reflections is presented in Table 2. The atomic coordinates and ADP's of the structure at  $t = 0.0$  are presented in Table 3.† The errors were calculated according to Rollet (1965).

The geometry of the compound was strongly restrained in order to avoid unreasonable geometries of the molecules. A selection of geometrical parameters is presented in Table 4.

#### 4.2. Refinement using the program JANA (Petříček, 1996)

The IC structure was refined with a preliminary version of JANA96. For the displacive modulation functions, expression (4) has been used. For the occupational modulation functions, crenel functions were applied.

The atomic coordinates and modulation functions were refined in  $P2_1(\alpha 0 \gamma)$ . A nonstandard setting has been chosen for this superspace group. The representative elements are:

$$\begin{aligned} 1 & \{x, y, z, t\} \\ 2_1 & \{-x, y + 1/2, -z, 1/2 - t\} \end{aligned}$$

To initiate the refinement of the IC structure, the projection described in §4.1 was also used. The coordinates of the hexamine molecules were averaged in order to obtain a starting model consisting of one hexamine and two sebacic acid molecules. The starting positions of two superimposed chains were estimated from the shape of the modulation functions obtained from a preliminary refinement.

The hexamine molecule and the chains were treated as rigid bodies in order to limit the number of refined parameters. The rigidity of the chains, however, was only approximate. To give them more flexibility, each rigid chain was divided into two subchains and the COO ends of the chains were completely released from the corresponding rigid group but their occupation was identical. The coordinates of the rigid groups were

† A list of modulation amplitudes, structure factors and geometrical parameters have been deposited with the IUCr (Reference JS0053). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

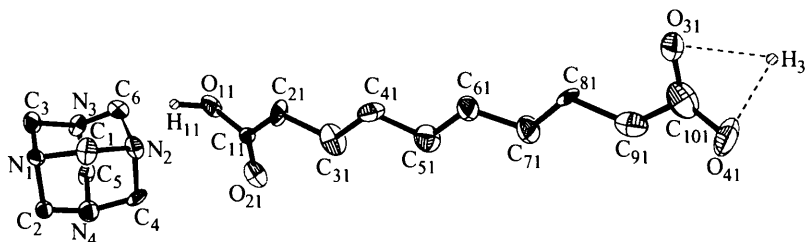


Fig. 3. Representation of hexamine sebacate at  $t = 0.0$  as refined by MSR. The ADP's are represented at the 30% probability level (SHELXTLS.0.3; Sheldrick, 1996).

Table 3. Atomic coordinates and anisotropic displacement parameters (isotropic for H11 and H31) of the MSR structure refinement at  $t = 0.0$ 

	x	y	z							
N1	0.4728 (6)	0.2344 (4)	-0.3654 (5)							
N2	0.5726 (10)	0.2156 (3)	0.0622 (10)							
N3	0.2261 (6)	0.2651 (4)	-0.1044 (6)							
N4	0.6122 (10)	0.2990 (3)	-0.0773 (10)							
C1	0.586 (14)	0.2020 (4)	-0.1780 (11)							
C2	0.6086 (12)	0.2800 (4)	-0.3124 (10)							
C3	0.2365 (6)	0.2475 (4)	-0.3378 (7)							
C4	0.7050 (6)	0.2617 (4)	0.1011 (6)							
C5	0.3718 (11)	0.3080 (4)	-0.0450 (12)							
C6	0.3232 (11)	0.2252 (3)	0.0478 (14)							
O11	0.6979 (11)	0.1434 (2)	0.3456 (11)							
O21	0.9856 (12)	0.1750 (3)	0.5299 (11)							
O31	1.9328 (14)	-0.1726 (3)	1.6388 (13)							
O41	2.2963 (16)	-0.1439 (3)	1.7851 (14)							
C11	0.9074 (11)	0.1364 (3)	0.4668 (11)							
C21	0.9944 (15)	0.0862 (4)	0.5383 (15)							
C31	1.2002 (16)	0.0817 (4)	0.7346 (16)							
C41	1.2667 (16)	0.0326 (4)	0.8298 (17)							
C51	1.4769 (17)	0.0271 (4)	1.0160 (17)							
C61	1.5254 (18)	-0.0215 (4)	1.1212 (16)							
C71	1.7266 (16)	-0.0342 (4)	1.3154 (16)							
C81	1.7757 (12)	-0.0865 (3)	1.3784 (12)							
C91	1.9813 (16)	-0.0945 (4)	1.5808 (17)							
C101	2.0837 (18)	-0.1402 (4)	1.6847 (19)							
H11	0.6029 (86)	0.1503 (11)	0.1949 (78)							
H31	2.2139 (70)	-0.1991 (13)	1.9254 (69)							
	$U^{11}$ ( $U_{iso}$ )	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$				
N1	0.047 (3)	0.031 (5)	0.035 (3)	-0.010 (6)	0.015 (2)	-0.002 (5)				
N2	0.039 (4)	0.082 (5)	0.026 (4)	0.009 (3)	0.015 (3)	0.006 (4)				
N3	0.035 (3)	0.040 (5)	0.029 (3)	0.010 (5)	0.007 (3)	-0.019 (5)				
C1	0.060 (6)	0.052 (7)	0.044 (6)	0.023 (5)	0.019 (4)	-0.005 (5)				
C3	0.044 (4)	0.060 (5)	0.040 (4)	0.022 (7)	0.001 (3)	0.023 (7)				
C4	0.036 (3)	0.056 (4)	0.039 (4)	-0.010 (6)	0.002 (3)	-0.027 (6)				
C5	0.020 (6)	0.080 (9)	0.016 (5)	-0.002 (6)	-0.000 (4)	-0.009 (5)				
C6	0.059 (6)	0.011 (6)	0.065 (7)	-0.004 (5)	0.026 (5)	-0.013 (5)				
O11	0.046 (5)	0.054 (5)	0.067 (5)	0.015 (4)	0.013 (4)	0.037 (4)				
O21	0.055 (6)	0.054 (5)	0.058 (5)	0.018 (4)	0.033 (4)	0.007 (4)				
O31	0.081 (7)	0.070 (6)	0.050 (6)	-0.002 (5)	-0.004 (4)	0.007 (5)				
O41	0.106 (9)	0.084 (7)	0.089 (7)	0.005 (6)	-0.056 (6)	-0.004 (5)				
C21	0.043 (8)	0.048 (7)	0.055 (8)	0.012 (6)	-0.014 (6)	0.019 (6)				
C31	0.098 (10)	0.040 (7)	0.111 (9)	0.031 (7)	0.008 (7)	0.052 (6)				
C41	0.041 (9)	0.050 (7)	0.085 (10)	-0.012 (6)	0.006 (7)	0.000 (7)				
C51	0.061 (8)	0.054 (7)	0.087 (9)	0.008 (6)	0.009 (7)	0.011 (7)				
C61	0.089 (9)	0.053 (7)	0.048 (8)	-0.012 (6)	-0.003 (6)	0.014 (6)				
C71	0.096 (9)	0.049 (8)	0.057 (8)	-0.003 (7)	-0.004 (7)	0.011 (6)				
C81	0.036 (5)	0.052 (7)	0.023 (6)	-0.017 (5)	-0.002 (4)	-0.029 (5)				
C91	0.089 (9)	0.057 (9)	0.070 (9)	-0.018 (7)	0.029 (7)	-0.025 (7)				
C101	0.131 (12)	0.048 (8)	0.154 (13)	0.021 (7)	-0.005 (9)	0.035 (8)				
N4	0.032 (2)									
C2	0.040 (3)									
C11	0.025 (2)									
H11	0.080 (0)									
H31	0.080 (0)									

refined independently whereas their displacive modulations were treated as rigid and the temperature parameters were refined as TLS tensors. The refined width of the occupation function defines the interval  $x_4$  where one of the chains exists. The second occupies the other part of the interval. The refinement was not possible without the use of crenel functions.

The positions of the H atoms of the CH<sub>2</sub> groups and also their displacive modulation amplitudes have been calculated from the corresponding C atoms.

Table 5 summarizes the refinement conditions of this model. The agreement factor of each class of reflections is presented in Table 6. As the two chains are related by crenel functions, the two chains are mutually exclusive.

Table 4. Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for the model with anisotropic displacement parameters, as calculated with MSR

The superscript (i) refers to the symmetry operation  $(-x + 3, y - 0.5, -z + 2, -t)$ . The minimum, maximum and average (with standard deviation) distances and angles are given.  $\Delta d$  is the interval between minimum and maximum values.

Atoms			Min.	Max.	Ave	$\Delta d$	
N2	O11		2.58	2.85	2.73 (5)	0.27	
N2	O21		3.26	3.54	3.40 (5)	0.28	
N4 <sup>i</sup>	O31		2.38	3.75	3.05 (5)	1.37	
N4 <sup>i</sup>	O41		2.44	3.63	2.97 (5)	1.19	
H11	O11		0.92	0.99	0.95 (15)	0.07	
H11	N2		1.91	1.98	1.95 (13)	0.07	
H31	N4 <sup>i</sup>		1.02	2.00	1.28 (15)	0.98	
H31	O31		1.84	2.83	2.16 (15)	0.99	
H31	O41		1.84	2.42	2.15 (15)	0.58	
O11	C11		1.26	1.34	1.30 (5)	0.08	
O21	C11		1.15	1.25	1.20 (5)	0.10	
O31	C101		1.21	1.30	1.25 (6)	0.09	
O41	C101		1.20	1.31	1.26 (6)	0.11	
N2	H11	O11	120.65	155.74	137.99 (21)	35.09	
N4 <sup>i</sup>	H31	O31	94.94	173.44	126.80 (18)	78.50	
N4 <sup>i</sup>	H31	O41	76.09	175.59	129.34 (18)	99.50	
O11	C11	O21	106.91	130.48	121.13 (6)	23.57	
O31	C101	O41	105.30	138.41	118.89 (8)	33.11	
O11	C11	C21	101.55	122.69	111.37 (6)	21.14	
O21	C11	C21	111.79	137.73	127.22 (6)	25.94	
O31	C101	C91	103.49	136.63	117.27 (8)	33.14	
O41	C101	C91	100.20	137.64	123.38 (8)	37.44	
N2	H11	O11	O21	0.32	359.93	130.28 (40)	359.61
N4 <sup>i</sup>	H31	O31	O41	149.86	354.02	234.51 (34)	204.16
O21	O11	C11	C21	168.11	195.55	180.92 (10)	27.44
O41	O31	C101	C91	169.72	200.73	181.01 (14)	31.01

Table 5. Refinement conditions used for the atomic coordinates, the displacive and occupational modulation functions and the displacement parameters for the model refined with JANA

x, y, z	N involved in		Chain 1	Chain 2	O atoms chain 1	O atoms chain 2
	Hexamine atoms	N...H...O bond				
Positional modulation	Individual	Individual	Individual	Individual	Individual	Individual
Occupational modulation	Rigid group	Individual	Rigid group	Rigid group	Individual	Individual
Temp. parameters	–	–	Rigid group	Rigid group	Rigid group	Rigid group
No. of harmonics	Rigid-group TLS	Individual	Rigid-group TLS	Rigid-group TLS	Individual	Individual
	5	3	5	5	3	3

The domain of existence of the first chain (1) is  $0.000 \leq t < 0.150$  and  $0.630 < t \leq 1.000$  and the domain of existence of the second chain (2) is  $0.150 \leq t \leq 0.630$ . Table 7 lists the atomic coordinates and ADP's of the structure at  $t = 0.000$  and  $t = 0.500$ . Fig. 4 illustrates the refined structure at  $t = 0.000$  and  $t = 0.500$ .

A selection of geometrical parameters is presented in Table 8. These parameters could not be restrained in the program JANA.

## 5. Results and discussion

### 5.1. General remarks

The reflection conditions derived from precession photographs indicate the superspace group  $P2_1/m(\alpha 0 \gamma)0s$ . However, models refined in this superspace group did not yield satisfactory results either with

MSR or with JANA. In  $P2_1/m(\alpha 0 \gamma)0s$ , the difference Fourier maps calculated with JANA for different values of  $t$  reveal strong difference maxima around the COOH groups of the sebacic acid chains. This was a convincing indication of the noncentrosymmetric character of the structure. Therefore, the noncentrosymmetric superspace subgroup  $P2_1(\alpha 0 \gamma)$ , which is also compatible with the systematic absences observed on precession photographs, was chosen for the refinement of both models (Fig. 5).

### 5.2. Structure of hexamine sebacate

The two models refined by MSR or by JANA reveal the same general features of hexamine sebacate. The structure is characterized by a sequence of alternating sheets of hexamine and sebacic acid linked via H bonds between the H atom of the COOH groups and the N atom

Table 6. *R* factors for the modulated structure, with anisotropic displacements parameters, as refined with *JANA*

Number of reflections	4621	
Number of parameters	608	
Satellite order	<i>R</i> (obs.)	<i>wR</i> (obs.)
0	0.0576	0.0810
1	0.0621	0.0795
2	0.0791	0.0905
3	0.0983	0.1091
4 and higher	0.1698	0.1884
All reflections	0.0691	0.0876

of the hexamine. The zigzag planes of the acid chains are roughly parallel to one of the mirror planes of the hexamine. The chains adopt a herringbone arrangement of the chains separated by sheets of hexamines as previously observed for example in  $(C_{10}H_{21}NH_3)_2CdCl_4$  (Schenk & Chapuis, 1988) and in hexamine suberate (Bussien Gaillard, Paciorek, Schenk & Chapuis, 1996).

In the hexamine sheets, each molecule is surrounded by four neighbours at a distance  $\frac{1}{2}|\mathbf{a} + \mathbf{c}|$  and two additional ones at a distance *a*. This neighbourhood can be interpreted as a deformation of the close-packed layer observed for hexamine (Becka & Cruickshank, 1963) in the (110) plane. Both models reveal this arrangement.

Each sheet of suberic acid chains is subdivided into two types of areas. In each area, the zigzag planes and the chain axes are roughly parallel and the chains adopt a  $T_{||}$  packing according to the notation of Segerman (1965)

and Abrahamsson, Dahlén, Löfgren & Pascher (1978). In adjacent areas, the zigzag planes are rotated by an angle of approximately  $65^\circ$ . In addition, the chain axes deviate from the parallel direction by an angle of approximately  $15^\circ$  (Fig. 6).

The periodicity of the pattern in the *c* direction is approximately four chain units, two in the first orientation followed by two others in the second orientation. This period is a consequence of the magnitude of the component  $\gamma$  ( $=0.24$ ) of the modulation vector. The main difference between a sheet of suberic acid chains described by *MSR* or *JANA* models is the period of the pattern in the *a* direction. For the model obtained with *MSR*, the period is approximately 7 chains in the first orientation followed by 7 chains in the second orientation, whereas, for the model obtained with *JANA*, this period is approximately 12 chains. The difference is due to the small component  $\alpha$  ( $=-0.02$ ) of the modulation vector, which induces large uncertainties on the amplitudes of the modulation functions along *a*.

5.2.1. *The COOH groups.* As previously observed for the structure of hexamine suberate (Bussien Gaillard, Paciorek, Schenk & Chapuis, 1996), the model refined with *MSR* reveals that the two COOH groups of the sebacic acid are independent and have different chemical characteristics. The H31—O31—C101—O41 group must be considered as a carboxylate group, whereas the H11—O11—C11—O21 group has the typical carboxylic geometry (Fig. 7).

Sections of generalized 4D difference-electron-density maps were evaluated with *JANA* from the model without

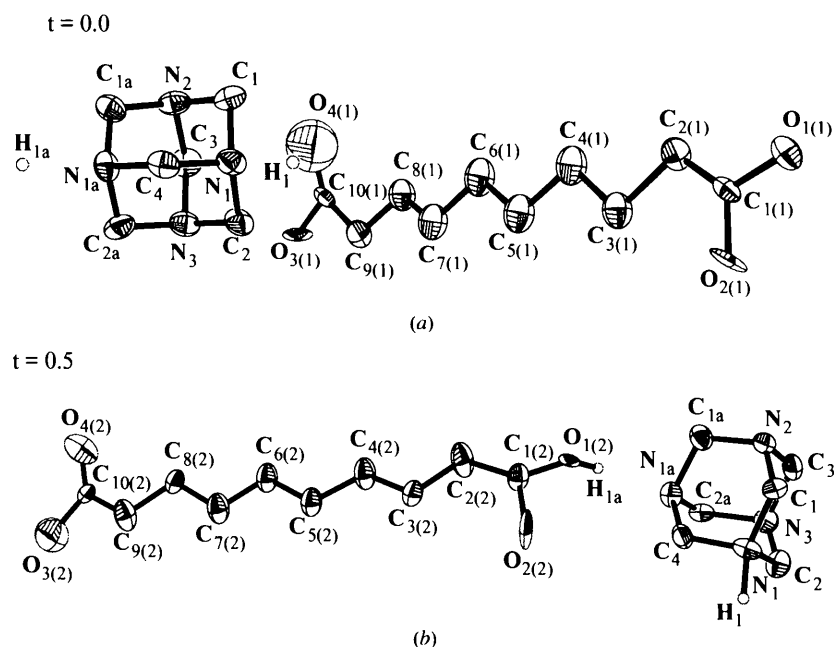


Fig. 4. Representation of hexamine sebacate as refined by *JANA* at (a)  $t = 0.0$  and (b)  $t = 0.5$ . The ADP's are represented at the 30% probability level.

Table 7. Atomic coordinates and displacement parameters of the structure as refined with JANA at  $t = 0.0$  for the hexamine and the first chain (1) and at  $t = 0.5$  for the hexamine and the second chain (2)

	x	y	z			
N1	0.571 (1)	0.3054	0.555 (1)			
N1a	0.576 (2)	0.2196 (2)	0.450 (2)			
N2	0.218 (2)	0.2619 (5)	0.412 (2)			
N3	0.484 (2)	0.2832 (4)	0.152 (2)			
C1	0.334 (2)	0.2994 (4)	0.590 (2)			
C1a	0.336 (2)	0.2166 (4)	0.459 (2)			
C2	0.589 (2)	0.3200 (4)	0.316 (2)			
C2a	0.604 (2)	0.2357 (4)	0.221 (2)			
C3	0.239 (2)	0.2789 (5)	0.176 (2)			
C4	0.693 (2)	0.2574 (4)	0.623 (2)			
O1(1)	1.106 (2)	0.6380 (4)	1.501 (2)			
O2(1)	1.264 (3)	0.6174 (8)	1.214 (3)			
C1(1)	1.066 (3)	0.6143 (7)	1.287 (3)			
C2(1)	0.848 (3)	0.5905 (7)	1.177 (3)			
C3(1)	0.877 (3)	0.5645 (7)	0.940 (3)			
C4(1)	0.631 (3)	0.5391 (7)	0.847 (3)			
C5(1)	0.641 (3)	0.5141 (7)	0.615 (4)			
C6(1)	0.402 (3)	0.4913 (7)	0.502 (4)			
C7(1)	0.414 (3)	0.4672 (7)	0.277 (3)			
C8(1)	0.188 (3)	0.4487 (8)	0.142 (3)			
C9(1)	0.188 (3)	0.4243 (7)	-0.080 (3)			
C10(1)	-0.048 (3)	0.3982 (8)	-0.177 (4)			
O3(1)	-0.035 (3)	0.3840 (6)	-0.374 (3)			
O4(1)	-0.176 (4)	0.3818 (9)	-0.068 (4)			
H1	0.720 (12)	0.3439 (25)	0.751 (11)			
H1a	0.657 (11)	0.1621 (23)	0.483 (11)			
N1	0.600 (1)	0.2858	0.435 (1)			
N1a	0.601 (2)	0.2018 (2)	0.540 (2)			
N2	0.226 (2)	0.2422 (5)	0.396 (2)			
N3	0.482 (2)	0.2271 (4)	0.126 (2)			
C1	0.346 (2)	0.2900 (4)	0.466 (2)			
C1a	0.345 (2)	0.2051 (4)	0.542 (2)			
C2	0.591 (2)	0.2730 (4)	0.185 (2)			
C2a	0.603 (2)	0.1903 (4)	0.296 (2)			
C3	0.240 (2)	0.2319 (5)	0.152 (2)			
C4	0.704 (2)	0.2482 (4)	0.596 (2)			
H1	0.758 (12)	0.3177 (25)	0.491 (11)			
H1a	0.689 (11)	0.1351 (23)	0.675 (10)			
O1(2)	1.278 (2)	0.6388 (4)	1.158 (2)			
O2(2)	0.957 (4)	0.6620 (7)	1.016 (4)			
C1(2)	1.106 (4)	0.6239 (7)	1.012 (4)			
C2(2)	1.027 (4)	0.5799 (7)	0.874 (4)			
C3(2)	0.798 (4)	0.5742 (7)	0.733 (4)			
C4(2)	0.739 (4)	0.5279 (7)	0.624 (4)			
C5(2)	0.513 (4)	0.5188 (7)	0.461 (4)			
C6(2)	0.472 (4)	0.4705 (7)	0.350 (4)			
C7(2)	0.245 (4)	0.4617 (7)	0.210 (4)			
C8(2)	0.210 (4)	0.4110 (7)	0.095 (4)			
C9(2)	-0.034 (4)	0.4047 (7)	-0.053 (4)			
C10(2)	-0.082 (4)	0.3565 (7)	-0.156 (4)			
O3(2)	-0.312 (3)	0.3651 (6)	-0.259 (3)			
O4(2)	0.060 (3)	0.3303 (6)	-0.197 (4)			
	$U^{11}$ ( $U_{\text{iso}}$ )	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
N1	0.0354 (27)	0.0661 (1)	0.0592 (30)	-0.0148 (5)	0.0136 (22)	-0.009891 (5)
N1a	0.0580 (30)	0.0443 (1)	0.0354 (26)	-0.0102 (5)	0.0018 (21)	0.000341 (4)
N2	0.0369 (7)	0.0740 (1)	0.0517 (14)	0.0147 (4)	0.0103 (6)	0.000016 (6)
N3	0.0560 (13)	0.0697 (1)	0.0378 (7)	-0.0024 (6)	0.0123 (6)	-0.001486 (4)
C1	0.0479 (30)	0.0677 (1)	0.0583 (28)	0.0171 (5)	0.0180 (19)	-0.004369 (4)
C1a	0.0487 (27)	0.0666 (1)	0.0501 (26)	0.0005 (4)	0.0103 (17)	0.011962 (4)
C2	0.0718 (29)	0.0636 (1)	0.0323 (27)	-0.0043 (4)	0.0150 (18)	0.003459 (4)
C2a	0.0426 (27)	0.0624 (1)	0.0708 (26)	0.0095 (4)	0.0169 (17)	-0.012441 (4)
C3	0.0484 (9)	0.0738 (1)	0.0461 (10)	0.0150 (5)	0.0002 (7)	0.008381 (5)
C4	0.0390 (9)	0.0690 (1)	0.0430 (10)	0.0093 (6)	0.0066 (7)	0.011515 (5)



Table 7 (cont.)

	$U^{11}$ ( $U_{iso}$ )	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1(1)	0.0922 (45)	0.0749 (2)	0.0574 (58)	-0.0274 (8)	0.0319 (36)	-0.013748 (8)
O2(1)	0.0541 (48)	0.0963 (3)	0.0426 (55)	-0.0236 (9)	0.0324 (37)	0.014398 (10)
C1(1)	0.0476 (41)	0.0442 (2)	0.0379 (34)	-0.0033 (8)	0.0177 (24)	0.014106 (8)
C2(1)	0.0536 (25)	0.0577 (1)	0.0607 (24)	-0.0078 (4)	0.0091 (17)	0.002266 (4)
C3(1)	0.0740 (22)	0.0589 (1)	0.0581 (21)	-0.0035 (4)	0.0010 (14)	0.001681 (4)
C4(1)	0.0758 (16)	0.0664 (1)	0.0719 (18)	-0.0065 (3)	-0.0029 (12)	-0.005035 (3)
C5(1)	0.0825 (16)	0.0672 (1)	0.0716 (18)	-0.0051 (3)	-0.0057 (12)	-0.005563 (3)
C6(1)	0.0824 (16)	0.0673 (1)	0.0718 (18)	-0.0050 (3)	-0.0058 (12)	-0.005603 (3)
C7(1)	0.0760 (16)	0.0668 (1)	0.0722 (18)	-0.0063 (3)	-0.0033 (12)	-0.005295 (3)
C8(1)	0.0724 (20)	0.0593 (1)	0.0605 (20)	-0.0049 (4)	0.0024 (14)	0.000893 (4)
C9(1)	0.0528 (24)	0.0573 (1)	0.0606 (24)	-0.0090 (4)	0.0101 (17)	0.002420 (4)
C10(1)	0.0486 (41)	0.0429 (2)	0.0356 (34)	-0.0035 (8)	0.0186 (24)	0.015040 (8)
O3(1)	0.0379 (53)	0.0886 (3)	0.0771 (64)	-0.0221 (9)	0.0427 (41)	-0.032499 (10)
O4(1)	0.2381 (87)	0.1626 (5)	0.0493 (96)	-0.1513 (16)	0.0469 (64)	0.001705 (17)
H1	0.07 (2)					
H1a	0.07 (2)					
N1	0.0354 (27)	0.0661 (1)	0.0592 (30)	-0.0148 (5)	0.0136 (22)	-0.009891 (5)
N1a	0.0580 (30)	0.0443 (1)	0.0354 (26)	-0.0102 (5)	0.0018 (21)	0.000341 (4)
N2	0.0369 (7)	0.0740 (1)	0.0517 (14)	0.0147 (4)	0.0103 (6)	0.000016 (6)
N3	0.0560 (13)	0.0697 (1)	0.0378 (7)	-0.0024 (6)	0.0123 (6)	-0.001486 (4)
C1	0.0479 (30)	0.0677 (1)	0.0583 (28)	0.0171 (5)	0.0180 (19)	-0.004369 (4)
C1a	0.0487 (27)	0.0666 (1)	0.0501 (26)	0.0005 (4)	0.0103 (17)	0.011962 (4)
C2	0.0718 (29)	0.0636 (1)	0.0323 (27)	-0.0043 (4)	0.0150 (18)	0.003459 (4)
C2a	0.0426 (27)	0.0624 (1)	0.0708 (26)	0.0095 (4)	0.0169 (17)	-0.012441 (4)
C3	0.0484 (9)	0.0738 (1)	0.0461 (10)	0.0150 (5)	0.0002 (7)	0.008381 (5)
C4	0.0390 (9)	0.0690 (1)	0.0430 (10)	0.0093 (6)	0.0066 (7)	0.011515 (5)
O1(2)	0.01810 (67)	0.0289 (2)	0.0552 (73)	-0.0009 (7)	0.0016 (47)	0.0165 (9)
O2(2)	0.1231 (61)	0.0391 (2)	0.0543 (57)	-0.0174 (7)	-0.0419 (41)	-0.0126 (7)
C1(2)	0.0689 (51)	0.0328 (1)	0.0493 (65)	-0.0002 (5)	-0.0037 (44)	0.0020 (8)
C2(2)	0.0873 (33)	0.0405 (1)	0.0859 (37)	0.0012 (4)	-0.0211 (26)	-0.0127 (5)
C3(2)	0.0706 (29)	0.0468 (1)	0.0487 (34)	-0.0098 (3)	0.0052 (23)	-0.0048 (4)
C4(2)	0.0859 (24)	0.0500 (1)	0.0717 (23)	-0.0088 (3)	-0.0087 (17)	-0.0120 (3)
C5(2)	0.0805 (24)	0.0523 (1)	0.0619 (23)	-0.0118 (3)	-0.0009 (16)	-0.0107 (3)
C6(2)	0.0813 (24)	0.0518 (1)	0.0623 (23)	-0.0124 (3)	-0.0012 (16)	-0.0101 (3)
C7(2)	0.0865 (24)	0.0500 (1)	0.0729 (23)	-0.0087 (3)	-0.0095 (17)	-0.0124 (3)
C8(2)	0.0697 (31)	0.0461 (1)	0.0434 (36)	-0.0122 (3)	0.0079 (25)	-0.0019 (4)
C9(2)	0.0872 (34)	0.0402 (1)	0.0806 (38)	-0.0001 (4)	-0.0194 (26)	-0.0103 (5)
C10(2)	0.0537 (56)	0.0344 (1)	0.0303 (74)	-0.0026 (5)	0.0116 (49)	0.0047 (9)
O3(2)	0.1253 (84)	0.0516 (2)	0.1318 (95)	0.0127 (9)	-0.0448 (62)	-0.0845 (11)
O4(2)	0.0651 (75)	0.0746 (2)	0.1298 (88)	0.0394 (8)	0.0236 (58)	-0.0232 (10)
H1	0.07 (2)					
H1a	0.07 (2)					

the H atoms of the COOH groups. The superposition of these sections with the refined positions of the H atoms has been systematically studied for various values of  $t$ . It appears that, for some values, the H atoms move from the centre of the corresponding difference maxima towards a relatively strong difference maximum close to the O atoms. To maintain the H atoms in chemically reasonable positions, it would be necessary to apply geometrical constraints, which, however, are not available in *JANA*. This is the reason why the results differ from those of *MSR* and why the distances are not chemically reasonable in the complete range of  $t$  (Table 8). In *JANA* too, the bridging hydrogen could not be localized for several values of  $t$ .

5.2.2. *The N...H...O bonds.* Each layer of sebacic acid chains is linked to two layers of hexamine via an H bond between the hydrogen of the COOH groups and an N atom of the hexamine. The model refined with *MSR* reveals that the H bonds are different at the two opposite

Table 8. Selected bond distances ( $\text{\AA}$ ) for the model with anisotropic displacement parameters, as calculated with *JANA*

The minimum, maximum and average (with standard deviation) distances are given. The superscript (i) corresponds to the symmetry operation ( $x, y + 1/2, z, 1/2t$ ).

Atoms		Min.	Max	Ave
N1	H1	1.22	2.38	1.77 (7)
N1a	H1a	1.13	2.16	1.57 (6)
H1	O3(1)	0.65	1.55	1.14 (7)
H1	O4(1)	1.30	2.59	2.10 (7)
O1(2)	H1a	0.62	1.85	1.24 (6)
O2(2)	H1a	2.25	2.75	2.52 (6)
N1	O3(1)	2.00	3.23	2.82 (2)
N1	O4(1)	2.89	3.83	3.36 (2)
N1 <sup>i</sup>	O3(2)	2.02	3.61	2.65 (2)
N1 <sup>i</sup>	O4(2)	2.68	4.00	3.44 (2)
N1a	O1(2)	1.94	3.55	2.60 (1)
N1a	O2(2)	3.04	3.81	3.46 (2)
N1a <sup>i</sup>	O1(1)	2.30	3.66	2.88 (1)
N1a <sup>i</sup>	O2(1)	2.75	3.91	3.39 (2)

sebamic acid–hexamine interfaces (Fig. 8). One should mention that the  $N\cdots O$  and  $C—O$  distances were restrained in the refinements and slightly released towards the end of the refinement in order to detect conformational changes of the  $COOH$  form and  $N\cdots O$  bonds as a function of  $t$ . The following results were obtained. For the  $H11—O11—C11—O21$  group,  $H11$  is linked to  $O11$  independently of  $t$  and the  $N2—O11$  distance varies between 2.6 and 2.8 Å, a typical  $N—O$  distance in the presence of an H bond. The second oxygen  $O21$  rotates around the  $N2—O11$  axis and does not participate in the H bond (Fig. 8) as the distance  $N2—O21$  varies between 3.26 and 3.54 Å. For the  $H31—O31—C101—O41$  group, the precise nature of the H bond could not be determined, but the H atom is probably located within the triangle  $O31\cdots N4'\cdots O41$  and both O atoms are involved in the H bond [(i) refers to the symmetry operation  $(-x + 3, y - 0.5, -z + 2, -t)$ ].

The results obtained for the refinement with *JANA* cannot confirm this result for the reasons explained in §5.2.1.

5.2.3. *Comparison with other structures containing aliphatic chains.* It is interesting to mention here that a

search in the Cambridge Structural Database showed that for 139 ordinary structures containing aliphatic chains with at least 10 C atoms, 55 were published without assessing the validity of the refinement and that most of the others have  $R$  factors larger than 5% (Fig. 9). This phenomenon is mainly due to the quality of the crystals and flexibility of the aliphatic chains, which can easily distort. Moreover, the longer the aliphatic chain is, the more difficult it is to obtain a good crystallization. The results obtained in our refinements must be considered within this perspective. The reliabilities of our models are comparable with the published data of similar structures.

## 6. Characteristics of MSR and JANA

*MSR* and *JANA* exhibit their own properties and characteristics, which are worth mentioning in this context.

### 6.1. Comparison between MSR and JANA refinements

The final  $R$  values obtained for each class of reflection by the two programs cannot be easily compared. The

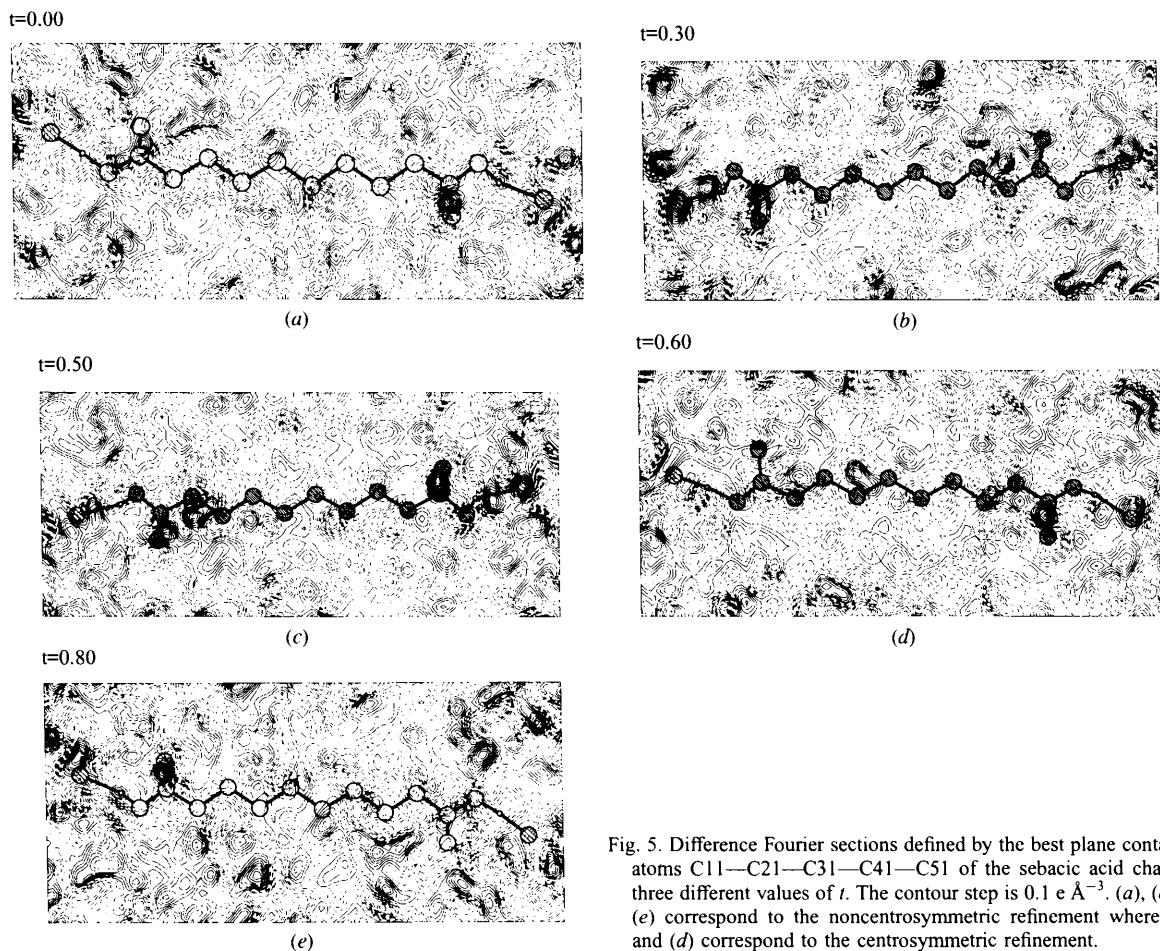


Fig. 5. Difference Fourier sections defined by the best plane containing atoms  $C11—C21—C31—C41—C51$  of the sebamic acid chain for three different values of  $t$ . The contour step is  $0.1 \text{ e } \text{Å}^{-3}$ . (a), (c) and (e) correspond to the noncentrosymmetric refinement whereas (b) and (d) correspond to the centrosymmetric refinement.

results are strongly correlated to the restraints applied to the structure.

*MSR* supplies chemical restraints that ensure reasonable geometry of the model. Moreover, the option called 'riding atom' (Paciorek, Bussien Gaillard, Schenk & Chapuis, 1996) provides directly the coordinates of an atom riding on a refined one for each value of the internal coordinate. This option is especially useful for the H atoms of the CH<sub>2</sub> groups.

*MSR* is limited to atomic modulation functions only. Consequently, the description of rotational modulation

functions has to be simulated by the inclusion of a large number of harmonic terms (Paciorek, Bussien Gaillard, Schenk & Chapuis, 1996).

*JANA* supplies rigid-body displacements and TLS formalism for IC structures. These options were used to describe the atomic displacements and atomic thermal parameters of both the hexamine and sebacic entities. Special shapes of modulation functions were also particularly useful to describe the occupational modulation of the sebacic acid molecule. Their main advantage was to limit the number of parameters to a reasonable

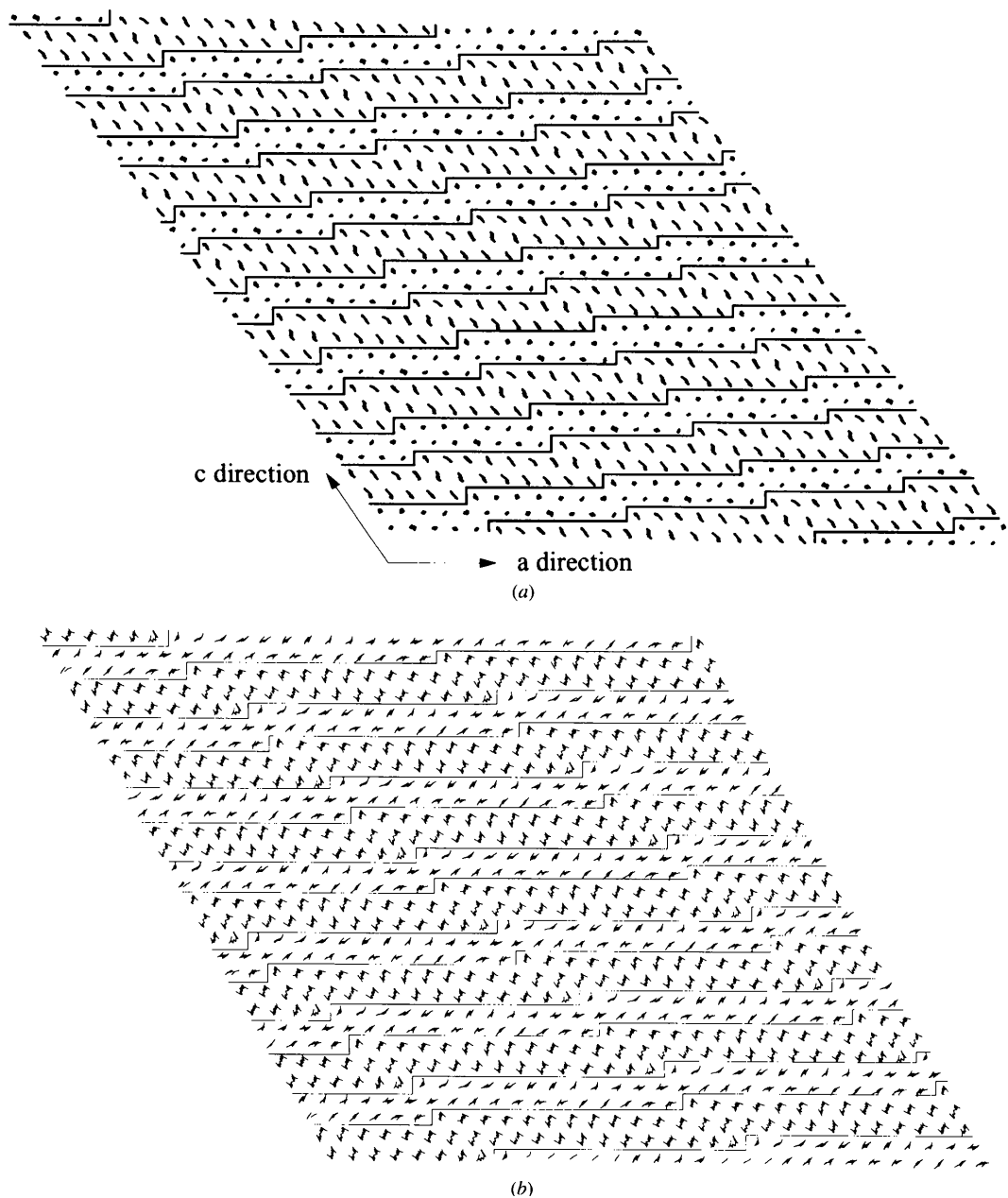


Fig. 6. View of the zigzag planes of the carbon chains along the chain axes in one layer of the IC crystal refined with (a) *MSR* and (b) *JANA*.

level. We should also point out that *JANA* also supplies rotational modulation functions. However, this option uses a rectilinear approximation that is valid only for small rotational angles. Obviously, this approximation could not be used in the study of hexamine sebacate.

For the present structure refinement, the main shortcoming of *JANA* was the lack of control of the geometrical restraints. As a consequence, unreasonable geometrical parameters of the structure appeared for some values of the internal coordinate. Consequently, this increased the difficulty of extracting chemical information from the resulting model.

### 6.2. On the use of geometrical restraints in the refinement of hexamine sebacate

The question can be raised if the use of geometrical restraints in the refinement of hexamine sebacate with *MSR* is justified. In other words and along the lines of Watkin (1994), we are suggesting to the refinement procedure a solution that we would like to see, providing it does not conflict with the X-ray observations. The aim in using geometrical restraints in our model was only to prevent large variations of distances and angles in the molecules in order to ensure a reasonable geometry of the model over the whole  $t$  space. By discarding the restraints, the refinement yields some unreasonable geometries of the model for some values of  $t$ .

### 6.3. On the use of IC description

It should be asked if the results obtained from the commensurate approximation (§3), which gives surprisingly good  $R$  factors, should not be sufficient to describe

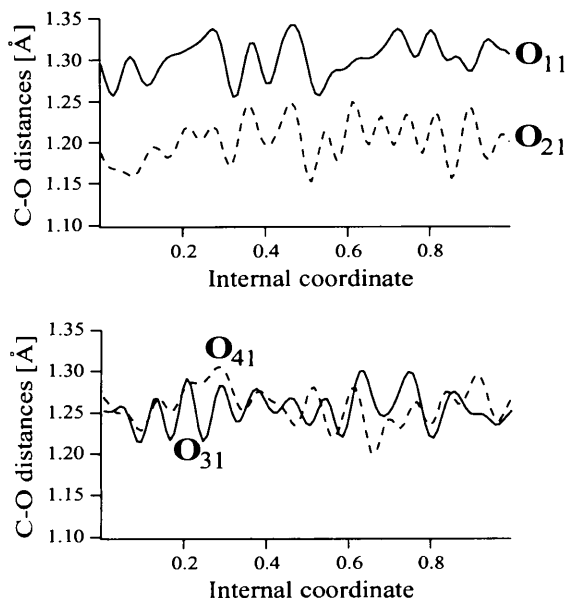


Fig. 7. The C—O distances of the two COOH functional groups are represented for 100 values of  $t$  between 0.0 and 1.0.

the structure of hexamine sebacate. Thus, the use of a heavy IC description could be avoided. The refinement of the commensurate approximation uses only a biased data set with  $[m = 0, 1]$  and omits reflections with weak intensities, an approach that cannot be supported according to the recommendations published by Schwarzenbach *et al.* (1989). Consequently, the IC description of the structure is necessary in order to use all the measured reflections in the refinement process. Moreover, the results of a refinement should not be based only on  $R$  values but also on chemical and physical considerations. The model must be chemically and physically reasonable. This is not the case for the commensurate approximation in which the C—O distances are unreasonably short and the ADP's of some O atoms are not positive definite.

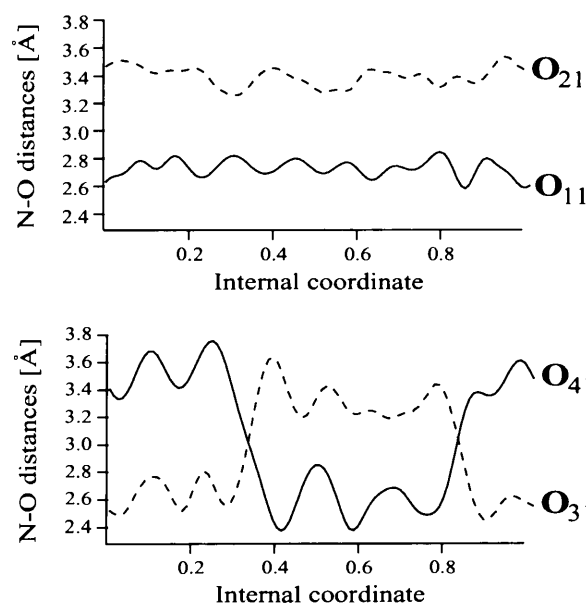


Fig. 8. The N—O distances of the two COOH functional groups are represented for 100 values of  $t$  between 0.0 and 1.0.

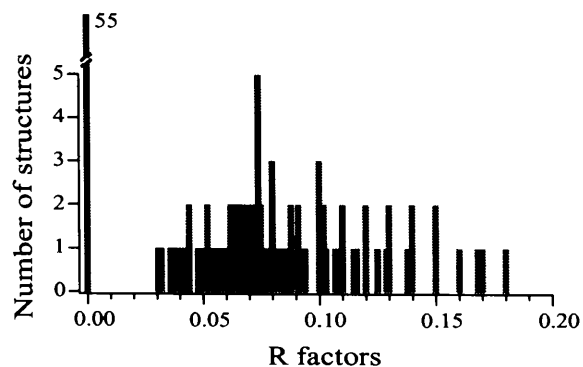


Fig. 9. Histogram presenting the  $R$  factors of structures containing aliphatic chains with at least ten carbon atoms. Of the 139 structures found in the Cambridge Structural Database, 55 have been reported without assessing the reliability of the refinement.

## 7. Conclusions

The main motivation of our present work was to model the IC structure of hexamine sebacate. As mentioned in a previous paper (Bussien Gaillard, Paciorek, Schenk & Chapuis, 1996), the refinement of this type of structure is a challenging task considering the large molecular rotation of the acid molecule. The present refinement programs are not able to handle important rotational modulations. We attempted to reproduce this rotation by two approaches that are not exact but are sufficient to describe the IC structure of hexamine sebacate, even though the resulting models show the limits of the programs *MSR* and *JANA*.

Nevertheless, we hope that this study will shed some light on ongoing projects to solve and refine organic IC structures and suggest ideas to implement new features in the IC structure refinement programs.

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