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Structures of Two Binary *n*-Alkane Solid Solutions

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Abstract

From X-ray diffractometer single-crystal data, the structures of two binary *n*-alkane phases have been determined. (I) β-$C_{24}H_{50}$, $C_{26}H_{54}$, β-tetracosane–hexacosane, mole fraction of $C_{24}H_{50}$ 0.77, hence effective molecular weight 345.39, space group $Bb2_1m$ (No. 36), $a = 4.992$ (1), $b = 7.503$ (3), $c = 67.448$ (8) Å, $Z = 4$, $D_x = 0.91$ g cm^{-3}, 201 significant reflections out of 588, $R = 0.11$ and $wR = 0.09$. The structural motif gives an *n*-alkane backbone 27 carbons long with C-atom sites well resolved on the *F* map. The outer three C-atom sites at each end of the motif have occupancies less than unity. (II) β_0-$C_{20}H_{42}$, $C_{22}H_{46}$, β_0-icosane–docosane, mole fraction of $C_{20}H_{42}$ 0.72, hence effective molecular weight 290.41, space group *Fmmm*, $a = 5.020$ (1), $b = 7.711$ (4), $c = 58.6$ (2) Å, $Z = 4$, $D_x = 0.85$ g cm^{-3}, 36 significant reflections out of 302, $R = 0.16$ and $wR = 0.12$. The *F* map showed no resolved C-atom peaks, probably due to high thermal disorder.

Introduction

In Fig. 1 we reproduce the phase diagram, determined by differential scanning calorimetry, of the C_{20},C_{22}† system (Lüth, Nyburg, Robinson & Scott, 1974). The regions of particualr interest to the present investigation are those labelled β and β_0. The β solid solution is present only at temperatures below 288 K and the β_0 solid solution is present only above this temperature. It is to be expected that other pairs of even *n*-alkanes separated by a length of two C atoms would have similar phase diagrams (Mnyukh, 1960). We surmised correctly that the increase in average molecular weight in going from C_{20},C_{22} to C_{24},C_{26} would mean that β would be the stable phase at room temperature. β-C_{24},C_{26} proves to be isostructural with the structure of β-C_{20},C_{22} proposed by Lüth *et al.* (1974).

Although several phase diagrams of binary *n*-alkane systems were known prior to the work of Lüth *et al.* (1974, and references therein) and more have been studied since (Dorset, 1990*a*), knowledge of the crystal structures of any of the solid-solution phases has remained rudimentary and speculative. Smith (1957) published a preliminary report on single-crystal studies of the C_{24},C_{26} solid solution. He reported finding very long *c* parameters for these solid solutions (137.2, 202.0 Å). This differs from the results presented here and no further work seems to have been published by Smith on this topic. X-ray powder-diffraction data have been recorded for several binary phases and although these have yielded information concerning variations in long spacing (Retief, Engel & Boonstra, 1985), it is usually difficult to be confident about the indices of the shorter spacings, hence about the cell dimensions and, *a fortiori*, the space group of these phases. The only unequivocal method of establishing the crystal structure of a binary-solid solution is to obtain three-dimensional diffraction data from a single crystal.

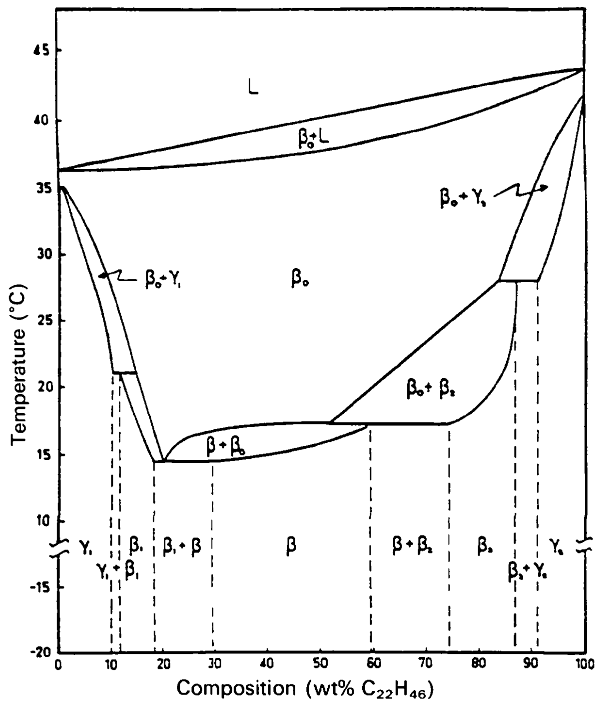

Fig. 1. C_{20},C_{22} phase diagram [Lüth *et al.*, (1974), reproduced by permission]. γ_1 refers to the triclinic $Z = 1$ structure found for pure and near-pure C_{20}. γ_2 is the isostructural phase found for pure and near-pure C_{22}.

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† The notation C_n refers to the normal alkane C_nH_{2n+2}.

Apart from Smith's (1957) work, as far as we are aware, there have been no such studies other than those made by Lüth *et al.* (1974) on the β and β_0 phases of C_{20},C_{22} (Fig. 1). Apparently the only Fourier summation of diffraction intensities from such a binary system to have been made in the intervening years has been that from a two-dimensional electron-diffraction pattern (Dorset, 1990*b*) of the presumed β phase of C_{32},C_{36}. The two-dimensional charge-potential map shows the crystal structure in the *x* projection.

Lüth *et al.* (1974) obtained X-ray prcccssion photographs of single crystals of the β and β_0 phases of C_{20},C_{22}. From the qualitative intensities of the indexed reflections, crystal structures, discussed in detail below, were proposed for both phases. In this paper we report an analogous study of the β phase of C_{24},C_{26} and β_0 phase of C_{20},C_{22} this time obtaining quantitative diffraction intensities from a diffractometer.

Experimental

All chemicals were *ex* Aldrich Chemical Co. The method of crystal growth was the same for both systems, C_{20},C_{22} and C_{24},C_{26}. A 1:1 mole ratio of components was dissolved in *n*-dodecane (C_{12}) and the solution cooled at approximately 0.05 K per day until the onset of crystallization. Crystals were filtered off and pieces cut (C_{24},C_{26} 1.0 × 0.3 × 0.04 mm; C_{20},C_{22} 0.9 × 0.5 × 0.05 mm) which showed as much uniform extinction as possible on rotation in cross-polarized light.

Preliminary X-ray photographs were used to check crystal quality. The Laue symmetry and systematic absences for the C_{20},C_{22} mixture were the same as those for the β_0 phase observed by Lüth *et al.* (1974), as was the C_{24},C_{26} systems from the $Bb2_1m$ β phase.

The chosen crystal fragments were mounted in turn on a Picker four-circle diffractometer. Using Ni-filtered Cu $K\alpha$ radiation, unit-cell dimensions were derived from 14 reflections ($55 < 2\theta < 90°$) for the C_{24},C_{26} mixture and from 18 reflections ($15 < 2\theta < 48°$) for the C_{20},C_{22} mixture. On the completion of data collection, the crystals used were subject to gas chromatography mass spectroscopic analysis.

C_{24},C_{26} (β phase)

The unit-cell parameters derived from the diffractometer data at 298 K are: $a = 4.992$ (1), $b = 7.503$ (3), $c = 67.448$ (8) Å, $\alpha = 90.02$ (2), $\beta = 90.00$ (1), $\gamma = 89.95$ (3)°; *a* and *b* are close to those observed by Lüth *et al.* (1974) for β-C_{20},C_{22} with mole fraction of C_{20}, 0.58; $a = 4.971$, $b = 7.392$ Å.

The *c* cell parameters for such solid solutions depend, of course, on the nature of the constituents and on the composition, which are discussed in detail below. Gas chromatography showed the crystal sample to have a mole fraction of C_{24} of 0.77.

Reflections were scanned over 3° in 2θ in the θ–2θ mode covering the range 5–90°. Friedel-related reflections were not measured and no corrections were made for absorption. A standard reflection was measured every 50 reflections and showed no significant decay. The index ranges were $h = 0$ to -4, $k = 0$ to 6 and $l = 0$ to 60. 588 unique reflections were measured, of which 201 were significant [$I > 2.5\sigma(I)$].

Over the mole-fraction range in which the β phase is present, the structural motif, *i.e.* that revealed by Fourier summation, is C_{27}. This is a consequence of the $Bb2_1m$ space group* which requires *m* symmetry at molecular centres normal to the molecular backbone. This cannot be achieved by an *n*-even alkane unless there is disorder. A pure *n*-even alkane can achieve the necessary space-group symmetry by half occupying each of two possible positions. This is shown in Fig. 2 in which, for illustrative purposes, a solid solution of C_4 and C_6 is shown yielding a motif C_7.

The β solid-solution phase shows two important structural differences from those that would be expected for a genuine C_{27} structure in the same space group. First, the terminal atoms of the C_{27} motif lie end-to-end with distances much closer than would be allowed by a genuine van der Waals contact between two methyl groups. This 'conflict' is not real, however, since in no unit cell are both terminal sites simultaneously occupied. The second difference shown by C_{24},C_{26} solid solutions, as opposed to a genuine C_{27} structure, concerns the C-atom site occupancies. The occupancies of the three outermost C-atom sites of the C_{27} motif are all less than unity but increase with C_{26} content. If we assume (Fig. 2) that all the possible positions for the molecules to adopt are proportional to their mole fractions, then

* Equivalent positions: $(000,\frac{1}{2}0\frac{1}{2})+$ x,y,z $x,y,\bar{z}$ $\bar{x},\frac{1}{2}+y,\bar{z}$ $\bar{x},\frac{1}{2}+y,z$.

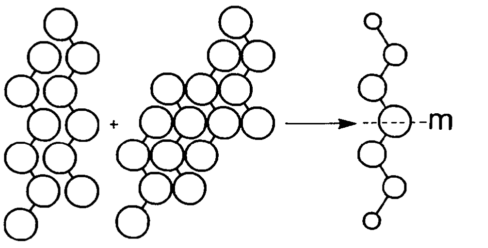

Fig. 2. The possible arrangement of C_4 and C_6 backbones to give a molecular motif C_7. The size of the C atoms gives an indication of occupancy. For a system containing a 0.77 mole fraction of C_4, the theoretical carbon occupancies would be (0.77/4) + (0.23/2) = 0.31. (0.77/2) + 0.23 = 0.62, (0.77 × 3/4) + 0.23 = 0.81, 0.77 + 0.23 = 1, then mirrored: 0.81, 0.62, 0.31.

Table 1. *Atomic fractional coordinates and isotropic temperature factors* ($Å^2$) *for the* β-C_{24},C_{26} *solid solution*

$B_{iso} = (8\pi^2/3)$ trace **U**.

	x	y*	z	B_{iso}	Occupancy
C(1)	0.82 (3)	0.000 (2)	0.245 (2)	5 (3)	0.22 (4)
C(2)	0.72 (2)	0.109 (9)	0.2260 (9)	18 (3)	0.75 (7)
C(3)	0.82 (1)	−0.027 (7)	0.2082 (6)	8 (1)	0.75 (4)
C(4)	0.692 (6)	0.046 (5)	0.1875 (4)	6.6 (3)†	1.00
C(5)	0.816 (6)	−0.043 (5)	0.1705 (4)	6.6 (3)	1.00
C(6)	0.704 (6)	0.030 (5)	0.1517 (4)	6.6 (3)	1.00
C(7)	0.811 (6)	−0.059 (5)	0.1319 (4)	6.6 (3)	1.00
C(8)	0.693 (6)	0.028 (5)	0.1128 (4)	6.6 (3)	1.00
C(9)	0.818 (6)	−0.052 (5)	0.0940 (4)	6.6 (3)	1.00
C(10)	0.695 (6)	0.029 (5)	0.0763 (4)	6.6 (3)	1.00
C(11)	0.813 (6)	−0.060 (5)	0.0572 (4)	6.6 (3)	1.00
C(12)	0.705 (6)	0.032 (5)	0.0372 (4)	6.6 (3)	1.00
C(13)	0.819 (6)	−0.061 (4)	0.0189 (4)	6.6 (3)	1.00
C(14)	0.698 (7)	0.020	0	2.8 (7)	1.00

* In the space group $Bb2_1m$, the position of the origin on the y axis is arbitrary. Here it has been chosen to coincide with the molecular backbone.

† The anisotropic temperature factors for C(4)–C(13) are U_{11} = 6.4 (3), U_{22} = 13.9 (5), U_{33} = 4.9 (3), U_{12} = 1.4 (4), U_{13} = 0.3 (9), U_{23} = 0.8 (7) ($Å^2 \times 100$).

it is straightforward to show that for a 0.77 mole fraction of C_4, the site occupancies of the C_7 motif atoms are 0.31, 0.62, 0.81, 1.0, 0.81, 0.62 and 0.31. Note that the sum of these occupancies is 4.48, corresponding to an overall solid-solution composition of $C_{4.5}$. If this model is appropriate for the C_{24},C_{26} system, we can expect the same occupancies for the three outer C atoms at each end of the C_{27} motif as calculated above. Non-terminal H atoms will have the same occupancies as the C atoms to which they are attached. There will also be terminal H atoms associated with each of the four outer C atoms with occupancies [starting at C(1)] of 0.31, 0.31, 0.19 and 0.19. Although we were confident of the C_{24},C_{26} solid-solution structure, both from our preliminary X-ray photographs and from the work of Lüth *et al.* (1974), we nevertheless generated direct-method E sets using *SOLVER* (Gabe, Le Page, Charland, Lee & White, 1989). The first of these, in order of merit, yielded the expected structure, showing clearly the C_{27} motif. Fractional coordinates were refined for all C atoms. Isotropic temperature factors were refined by least squares for the central C atom [C(14)] and the three end C atoms [C(1), C(2) and C(3)]. The temperature factors of C(1), C(2) and C(3) were refined alternately with the occupancies. The temperature factors of C(4)–C(13) atoms were refined anisotropically as a block. The observed occupancies and resulting refined parameters for the C atoms are given in Table 1. The occupancies are in fair agreement with those given above. C—C bond distances and C—C—C angles are given in Table 2. H positions were located assuming a C—H distance of 1 Å. Three H positions were

Table 2. *Bond lengths* (Å) *and bond angles* (°) *for the* β-C_{24},C_{26} *solid solution*

C(1)—C(2)	1.60 (2)	C(8)—C(9)	1.54 (4)
C(2)—C(3)	1.65 (5)	C(9)—C(10)	1.48 (4)
C(3)—C(4)	1.63 (8)	C(10)—C(11)	1.57 (4)
C(4)—C(5)	1.46 (4)	C(11)—C(12)	1.61 (4)
C(5)—C(6)	1.49 (4)	C(12)—C(13)	1.53 (4)
C(6)—C(7)	1.59 (4)	C(13)—C(14)	1.54 (3)
C(7)—C(8)	1.56 (4)		
C(1)—C(2)—C(3)	100 (7)	C(8)—C(9)—C(10)	110 (3)
C(2)—C(3)—C(4)	107 (4)	C(9)—C(10)—C(11)	110 (3)
C(3)—C(4)—C(5)	111 (3)	C(10)—C(11)—C(12)	112 (2)
C(4)—C(5)—C(6)	110 (3)	C(11)—C(12)—C(13)	111 (2)
C(5)—C(6)—C(7)	116 (3)	C(12)—C(13)—C(14)	110 (2)
C(6)—C(7)—C(8)	113 (3)	C(13)—C(14)—C(13′)	112 (2)
C(7)—C(8)—C(9)	111 (3)		

calculated for C(2), C(3) and C(4), as well as for C(1) as these sites are partially occupied by methyl C atoms. The observed occupancies for the H atoms were also in fair agreement with those calculated above. H positions and calculated occupancies are supplied as supplementary material.* The isotropic hydrogen temperature factors were assumed to be 1.1 times those of the C atoms to which they were attached.

Reflections 004 and 006 were removed from the data set as they both had extremely unequal background intensities. The final R value was 0.11 with $wR = 0.09$, $w = 1/\sigma^2(F_o)$. The goodness-of-fit was 11.4. Refinement of the 54 parameters was based on F values. The z projection is given in Fig. 3(a). The final electron density map is discussed below.

C_{20},C_{22} (β_0 phase)

The derived unit cell data, for mole fraction of C_{20} 0.72, are a = 5.020 (1), b = 7.711 (4), c = 58.6 (2) Å, α = 90.8 (2), β = 89.6, γ = 90.01 (5)°, where a and b are very similar to those of the β_0 phase observed by Lüth *et al.* (1974), *e.g.* a = 5.030, b = 7.646 Å, mole fraction of C_{20} 0.73. The c parameter indicates a bilayer structure containing four molecules per cell.

From the preliminary photographs, the following systematic absences were confirmed, hkl: $h + k = 2n + 1$, $h + l = 2n + 1$, $k + l = 2n + 1$. Of the five possible space groups which give rise to these systematic absences, only $Fmm2$ would not give a bilayer structure. In all other cases a disordered molecule must be present in order to conform to the molecular symmetry. If, as has been found in other orthorhombic n-alkane structures (C_{36}; Teare, 1959), the long axis of the C-atom chain is parallel to the z

* Lists of structure factors and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71496 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI0147]

axis, the other four possible space groups *Fmmm*, *Fm2m*, *F2mm* and *F222* will give rise to identical structures. We used the same space group as suggested by Lüth *et al.* (1974) for the β_0 phase, *Fmmm*.

Reflections were measured over 2.5° in 2θ. A standard reflection was measured every 25 reflections. This showed a significant decay of approximately 10% and was corrected for. The index ranges measured were $h = 0$ to -4, $k = 0$ to -6 and $l = -53$ to 53. 302 unique reflections were collected, of which only 36 were significant $[I > 2.5\sigma(I)]$.

Due to a lack of reflections of significant intensity, direct methods could not be used to solve the structure and probably no definitive structure can be established on the basis of so few significant Bragg reflections. In the space group *Fmmm*, with four motifs per cell, the motif has necessarily *mmm* symmetry. Two models were examined and in both the initial positions of the atoms were such as to give a planar backbone with the C—C distance set at 1.52 Å and the C—C—C angle at 113.4°. (H atoms were not included.) To satisfy *mmm* symmetry, the molecules have to occupy equally four (in general) rotational positions about the *z*-crystallographic axis. The starting position for refinement had the plane of the backbone parallel to the *A* face; rotation about *z* was in 10° steps. For any such rotational position the resulting $\pm x$ and $\pm y$ coordinates are the same for all atoms and were not subsequently allowed to vary. For each such rotational position,

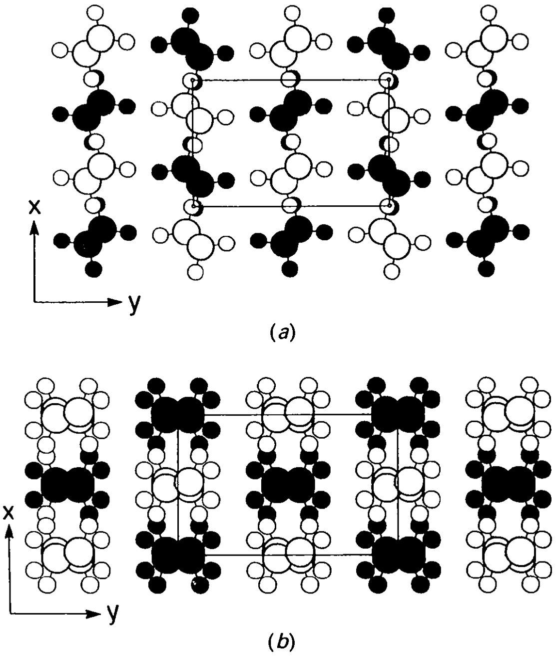

Fig. 3. (*a*) Projection of the β-C_{24},C_{26} system. Solid spheres represent alkane chains $z = 0.5$ lower than the empty spheres. (*b*) Projection of the β_0-C_{20},C_{22} system.

Table 3. *z fractional coordinates, temperature factors and occupancies for the* β_0-C_{20},C_{22} *solid solution*

	z	B_{iso}	Occupancy
C(1)	0.231 (7)	90 (60)	0.13
C(2)	0.211 (4)	40 (10)	0.19
C(3)	0.187 (3)	40 (10)	0.25
C(4)	0.165 (2)	20 (1)	0.25
C(5)	0.141 (2)	20 (1)	0.25
C(6)	0.120 (2)	20 (1)	0.25
C(7)	0.097 (2)	20 (1)	0.25
C(8)	0.074 (2)	20 (1)	0.25
C(9)	0.053 (2)	20 (1)	0.25
C(10)	0.032 (2)	20 (1)	0.25
C(11)	0.009 (3)	20 (1)	0.25

two kinds of longitudinal disorder were assumed. In Model 1, the disorder assumed was of the same kind as in β-C_{24},C_{26} (Fig. 2). The motif is now C_{23} instead of C_{27} and the occupancies of the outer atoms (nor varied) are calculated in the same way. This is the model assumed for β-C_{20},C_{22} by Lüth *et al.* (1974) with a structural motif of C_{23}.

In Model 2, half the C_{22} molecule together with two longitudinally displaced and overlapping C_{20} molecules were allowed to move parallel to the *z*-crystallographic axis until the lowest residual was obtained. In both cases all occupancies were initially set to 1.0. Model 2 gave consistently and significantly lower *R* factors than Model 1 with a minimum of 0.14 (occurring at a rotation of 15°), compared with a lowest *R* value of 0.19 for Model 1. The goodness-of-fit of 17.5 was high and the inclusion of 22 variables (*i.e.* temperature factors and *z*-fractional coordinates of 11 atoms) with only 36 reflections is clearly hard to justify.

Model 2 was further refined by setting occupancies calculated assuming a random distribution of the shorter chain along the length of the longer *n*-alkane chain with weighting appropriate to the mole fraction. These occupancies were not allowed to vary. The isotropic temperature factors of the central 16 atoms were made equal and refined as a block. The final *R* value was 0.16 with $wR = 0.12$ and goodness-of-fit 14.6. The final *z* fractional coordinates, temperature factors and calculated occupancies are given in Table 3. The final *x* and *y* fractional coordinates of the C backbone were $x = 0.21$ and $y = 0.05$. The C(11) atom, that closest to the centre of the motif, lies 0.53 Å from the $z = 0$ plane and hence 1.06 Å from the neighbouring C(12) atom. This compares with the known backbone translation of 1.27 Å between adjacent C atoms in an alkane chain. The *z* projection of the unit cell is given in Fig. 3(*b*).

Discussion

A section, at $y = 0$, of the electron-density map of the refined β-C_{24},C_{26} structure is shown in Fig. 4(*a*). The decreasing carbon occupancies towards the end of the chain can clearly be seen. Fig. 4(*b*) shows the $y = 0$ map of the β_0-C_{20},C_{22} solid solution. In this, no single atom can be distinguished.

The area of the basal plane increases on going from β to β_0. In the C_{20},C_{22} systems, the area of the *C* unit-cell face (*i.e.* normal to the alkane backbone) is larger for β_0 than for β. Since the β to β_0 transition is brought about by a temperature increase, we consider it likely that this expansion and the much greater disorder observed in the β_0 phase is dynamic rather than static.

The *c* cell parameter for a solid solution, given ideal packing, *i.e.* no void formation, can be easily calculated by interpolating between the *c* parameters expected for the pure components (Nyburg & Potworowski, 1973). For an effective number of C's of $(0.77 \times 24) + (0.23 \times 26) = 24.46$ per chain, the predicted *c* cell parameter for the C_{24},C_{26} system would be 66.63 Å. The observed *c* parameter is approximately 1% longer than this. Void formation therefore accounts for only 1% of the volume of the unit cell. The average chain length in the C_{20},C_{22} solid solution is $(0.72 + 20) + (0.28 \times 22) = 20.56$ C's, which theoretically would give rise to a unit cell 55.90 Å long. The observed unit cell is approximately 5% longer than this. It is likely that the end-to-end packing of near-freely rotating molecules would not be as efficient as for static molecules.

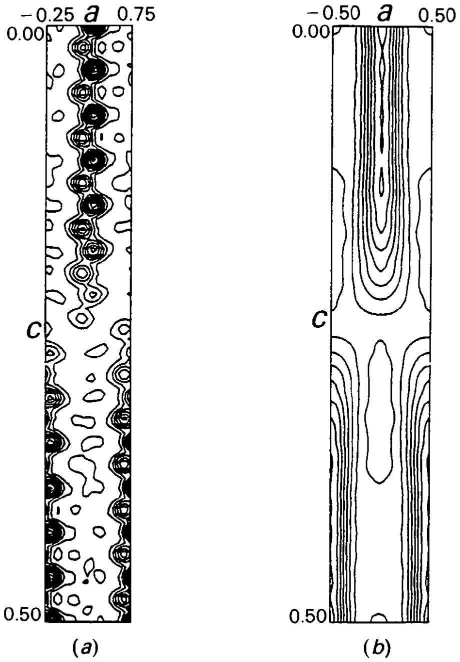

Fig. 4. (*a*) $y = 0$ electron-density map of the β-C_{24},C_{26} system, showing decreasing C-atom site occupancies towards the end of the C-atom chains. (*b*) $y = 0$ electron-density map of the β_0-C_{20},C_{22} system.

The refined occupancies for the C_{24},C_{26} sample are reasonably close to those calculated, namely for C(1), C(2) and C(3): 0.22, 0.75 and 0.75 compared with 0.30, 0.62 and 0.81, respectively. Thus, the observed occupancies correspond to a total composition of $21 + 2\,(0.22 + 0.75 + 0.75) = 24.44$, compared with a theoretical value of 24.45. Discrepancies between the individual calculated and observed occupancies are probably caused by strong correlation with the temperature factors.

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