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Correlations between the crystalline long *c*-parameter and the number of carbon atoms of pure *n*-alkanes

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Abstract

Linear relationships of variations of crystalline *c*-parameters of orthorhombic, triclinic and monoclinic *n*-alkane structures as a function of *n*, the carbon atom number, are established by linear least square fitting the data taken from the literature and compared with the relationships previously determined. In particular, the results correspond well with the predictions of Nyburg and Potworowski for Pbcm orthorhombic structures: they allow the precise determination of the mean carbon–carbon distance projected onto the chain axis that is equal to 1.2724 Å and the gap value of 3.1476 Å between the end-methyl-group carbon atom planes of the two consecutive molecule layers. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The first structural study on normal alkanes (hereafter denoted by C_n) was carried out by Müller and Saville [1]. Since then, the crystalline structures of C_n's have been the subject of several publications in the literature; in particular, Turner [2], Heyding et al. [3], Gerson et al. [4] and Craig et al. [5] have presented exhaustive monographs and results. The aim of this review is to summarize current findings on the relationships between n_c, (carbon atom number), chain length and long crystalline parameter, *c*, of C_n structures.

2. Literature results

Müller and Saville [1] observed in experiments that the first X-ray long-spacing increases linearly as a function of n_c, the carbon atom number; the numerical value of this increase is close to 1.3 Å per carbon atom. From the results of Müller [6], Hengstenberg [7], Kohlhaus [8] and Bunn [9] and his own experiments, Teare [10] gave the value of 1.270 ± 0.01 Å for this increase which corresponds to the carbon–carbon distance projected onto the chain axis.

Then, Broadhurst [11] analysed the solid phase behaviour of C_n*'s* and established a relationship between the crystalline *c*-parameter of the orthorhombic structures of the C_n*'s* and their n_c carbon atom number (Table 1).

Later, Nyburg and Potworowski [12] predicted laws of linear variation of the *c*-parameter (Table 1) from *Z*-coordinates of carbon atoms in "key structures":

1. "C_{23} Pbcm" orthorhombic structure of the odd-numbered C_{2p+1};
2. "C_{18}-$P\ \bar{1}$" triclinic structure of the even-numbered $C_{2p}(6 \leq n \leq 36)$;
3. "C_{36}-$P2_1/a$" monoclinic structure of the even-numbered $C_{2p}(26 \leq n \leq 38)$;
4. "C_{36}-$Pca2_1$" orthorhombic structure of the even-numbered $C_{2p}(n \geq 36)$.

Finally, Craig et al. [13] used an equation determined by Stokhuyzen [14] for the orthorhombic structures (Table 1).

3. Discussion

3.1. Pbcm orthorhombic structures of odd-numbered n-alkanes

Craig et al. [5] determined unit-cell crystallographic

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Table 1
Linear relationships of crystalline c-parameter variations vs. n_c carbon atom number in C_n structures

C_n structures	c (Å) orthorhombic	$c/2$ (Å) orthorhombic or c (Å) triclinic and monoclinic	Chain length + gap (Å)
Broadhurst [11]	$2.54n_c + 3.96$	$1.27n_c + 1.98$ [11]	$1.27(n_c - 1) + 3.25$
Key structure Pbcm-C_{23} Nyburg and Potworowski [12]	$2.546n_c + 3.75$ [12]	$1.273n_c + 1.875$	$1.273(n_c - 1) + 3.148$
Stokhuyzen [14]	$2.54n_c + 6.46$	$1.27n_c + 3.23$	$1.27(n_c - 1) + 4.5$ [14]
Pbcm $13 \leq 2p + 1 \leq 41$ this work	$2.5448n_c + 3.7504$	$1.2724n_c + 1.8752^a$, $R^2 = 1$	$1.2724(n_c - 1) + 3.1476$
Key structure Pca2_1-C_{36} Nyburg and Potworowski [12]	$2.54n_c + 3.693$ [12]	$1.27n_c + 1.8465$	$1.27(n_c - 1) + 3.1165$
Triclinic P$\bar{1}$-C_{2p}			
$6 \leq 2p \leq 36$ [12]		$1.265n_c + 2.156^b$, $R^2 = 1$	
$14 \leq 2p \leq 26$ [5]		$1.1169n_c + 4.876^a$, $R^2 = 0.9977$	
Monoclinic P2_1/a-C_{2p}			
$26 \leq 2p \leq 38$ [12]		$1.2746n_c + 2.49^b$, $R^2 = 1$	
$28 \leq 2p \leq 36$ [5]		$0.9615n_c + 11.367^a$, $R^2 = 1$	

[a] Relationships determined by optimization from the data of Craig et al. [5].
[b] Relationships determined by optimization from the data of Nyburg and Potworowski [12].

parameters of the homologous series C_{13}–C_{60}, which were derived from high-resolution synchrotron X-ray powder diffraction. From their accurate and self-consistent data, it is possible to establish linear equations (Table 1) of the variation of orthorhombic c-parameters as a function of the n_c carbon atom number by linear least square fitting, particularly for the orthorhombic C_{2p+1}s, in the range C_{13}–C_{41}, crystallizing with the C_{23}-Pbcm key structure [5]:

$$\frac{c}{2}(\text{Å}) = 1.2724n_c + 1.8752$$

i.e.,

$$c(\text{Å}) = 2.5448n_c + 3.7504$$

with an excellent factor of correlation $R^2 = 1$ (Fig. 1).

This expression for the c-parameter fully verifies the predictions of Nyburg and Potworowski [12] for the C_{2p+1} Pbcm structures (Table 1).

The $c/2$ value of the orthorhombic unit-cell, which corresponds to the $d(002)$ experimental first X-ray long-spacing, represents the sum of the chain length of carbon atoms and of the gap between the planes of end-methyl-group ($-CH_3$) carbon atoms of two consecutive molecule layers. The slope

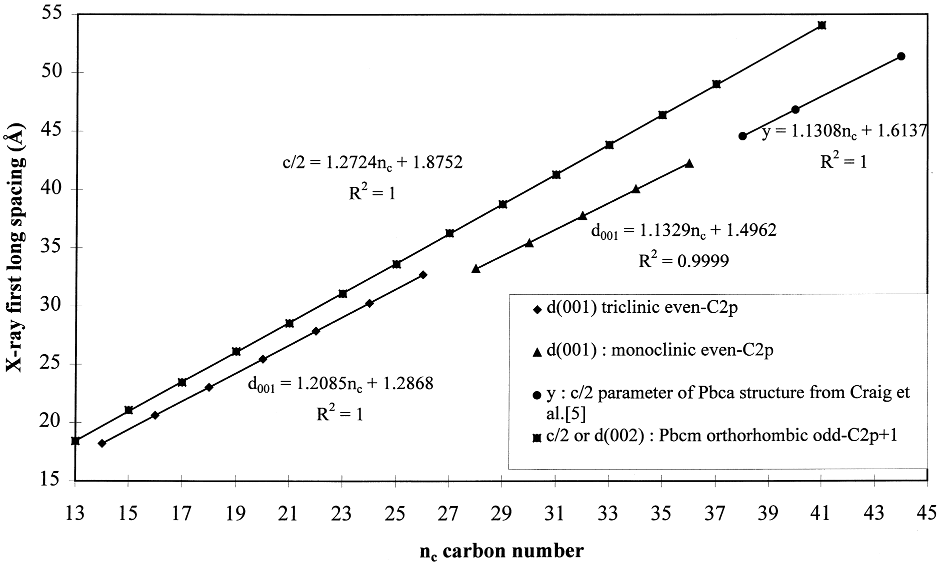

Fig. 1. Plot of the variations in the experimental first X-ray long-spacing as function of n_c, the carbon atom number: (i) $d(002)$ of the Pbcm orthorhombic structures of odd-C_{2p+1} which are equal to the half value of the crystalline c-parameters of the orthorhombic unit-cells; (ii) $d(001)$ of the triclinic and monoclinic structures; (iii) the $c/2$ Pbca orthorhombic values. All the values have been determined from the data of Craig et al. [5].

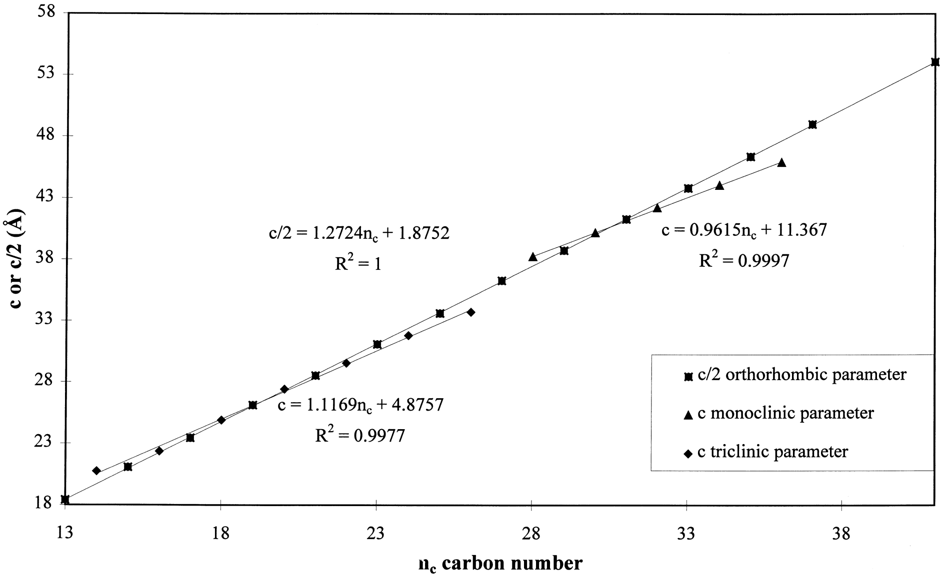

Fig. 2. Comparison between the *c*/2 Pbcm orthorhombic values and the triclinic and monoclinic *c*-parameters (from the data of Craig et al. [5]).

of the linear equation represents the chain length increase per carbon atom and it is equal to the average carbon–carbon distance projected onto the chain axis [10]. For a chain with a carbon atom number, n_c, there are $(n_c - 1)$ carbon–carbon distances and it is possible to write the previous *c*/2 equation as follows:

$$\frac{c}{2}(\text{Å}) = 1.2724(n_c - 1) + 3.1476$$

with:

1. $1.2724(n_c - 1)$: chain length (Å) of n_c carbon atoms;
2. 3.1476 Å: gap value between the planes of end-methyl-group carbon atoms of two consecutive molecule layers.

Moreover, the gap can be calculated from the *Z*-coordinates of the end-group carbon atoms of two consecutive chains which are equal to 1.573 and −1.573 Å, respectively, in the C_{23} Pbcm “key structure”, as determined by Smith [15] and Nyburg and Potworowsky [12]; for this structure, the gap is equal to 3.146 Å. This value is very close to the one obtained from the previous equation.

3.2. Triclinic, monoclinic and orthorhombic structures of even-numbered n-alkanes

For the triclinic ($P\bar{1}: n \le 26$), monoclinic ($P2_1/a: 28 \le n \le 36$) and orthorhombic (Pbca: $n = 38$, 40 and 44) structures of C_{2p}’s [5], the experimental first X-ray long spacing has a lower value than in the Pbcm orthorhombic structure of C_{2p+1}’s as a result of the incline of the molecules. This value varies linearly as a function of the carbon atom number, n_c (Fig. 1), on lines situated below the line representing the variations of the *c*/2 parameter or *d*(002) of the Pbcm orthorhombic unit-cells (Fig. 1). The variation line of the monoclinic first long spacing, *d*(001), is below that of the *d*(001) triclinic spacing, because the molecule axis is more inclined:

- about 27° relative to the normal to the (001) plane in C_{36} monoclinic structure [16];
- nearly 19° in C_{18} triclinic structure [12,17].

Moreover the ratio of the slope, obtained for the monoclinic or triclinic structures, with the one of the Pbcm orthorhombic structure corresponds to the cosine of the mean incline angle of the molecule chains relative to the normal to their stacking planes. The following values, 27° and 18.23° obtained for the monoclinic and triclinic structures respectively, agree with those previously mentioned.

Nota Bene: It appears that the *c*/2 parameter values of the Pbca orthorhombic structure of C_{38}, C_{40} and C_{44}, determined by Craig et al. [5], are brought into alignment with the *d*(001) values of the monoclinic structure of C_{28}, C_{30}, C_{32}, C_{34} and C_{36} (Fig. 1). This observation confirms the depiction of Boistelle et al. [16] and Craig et al. [5] about the Pbca orthorhombic structure of C_{2p}‘s that this orthorhombic structure is a stacking of alternate monoclinic layers, related one to the other by a twofold axis perpendicular to the (001) plane. The molecule tilt angle in the Pbca orthorhombic structure with a monoclinic subcell is certainly identical to the one of molecules in $P2_1/a$ monoclinic structure.

In the triclinic and monoclinic structures, the crystalline *c*-axis is tilted in relation to the normal to molecule stacking layers, but it is not parallel to the alkane chain axis [12], because the slopes of the corresponding lines (Fig. 2 and Table 1) is not equal to the average increase (1.2724 Å) of the chain length, determined from the Pbcm orthorhombic structure data [5]. Indeed, as the *all-trans* conformation of the alkane molecule is preserved whatever the structure of lower temperature, this increase must be identical in all *n*-alkane structures (for instance, it is found equal to the following mean values: 1.272 Å in C_{18} [17] and 1.279 Å in C_{36} [16]).

According the atom coordinates of literature [12,17,18] and the values of the first long spacing, that corresponds to the thickness of a molecule layer, the average gap between the planes of the end-methyl-group carbon atoms of two consecutive molecule layers is equal to 2.74 Å in triclinic C_{12},C_{14},C_{16},C_{18} and 2.98 Å in monoclinic C_{36} respectively.

The other higher C_{2p}'s present the Pca2_1 orthorhombic structure in which the chains are parallel to the *c*-axis [5].

4. Conclusions

The variation linear equation of the *c*-parameters of the C_{2p+1} Pbcm orthorhombic structure ($13 \leq 2p + 1 \leq 41$), obtained by optimization from the experimental data of Craig et al. [5], and the gap value (3.1476 Å) between the planes of the terminal-methyl-group ($-CH_3$) carbon atoms of two consecutive molecule layers correspond perfectly to the predictions of Nyburg and Potworowski [12], determined from the carbon atom coordinates in the C_{23}-Pbcm key structure (Table 1). However the agreement is not perfect for the linear variation relationships of the *c*-parameters of the triclinic and monoclinic structures (Table 1).

These results can be used to arrive at the following conclusions:

1. The prediction of the crystalline *c*-parameter of the pure C_n unit-cell and of the average *z*-coordinates of carbon atoms is possible when the axes of carbon chains are straight, as described by Nyburg and Potworowski [12].
2. If the first long spacing, measured by diffraction on a pure C_n, is situated clearly below the variation line of the Pbcm orthorhombic structure *c*/2 value, its structure is triclinic, monoclinic or Pbca orthorhombic (Fig. 1) and the molecules are inclined in relation to the normal to the molecule stacking layers.
3. For multicomponent mixtures of C_n's crystallizing in orthorhombic structures, the linear variation relationship, corresponding to the Pbcm structures, allows the determination of the mean number of carbon atoms in the multi *n*-alkane solid solutions as observed by Craig et al. [13], Dirand et al. [19,20], Nouar et al. [21], Chevallier et al. [22,23] and Retief et al. [24]. Moreover the differences measured in relation to this variation line represent the disorder between the molecule stacking layers of the multicomponent solid solutions.
4. It is possible to compare these results obtained from experimental data with the simulations of the interlamellar spacing in model *n*-alkane crystals [25], which lead to values close to 3.02 Å.

However for the very high chain lengths Zeng and Ungar [26] observed that the molecules of C_{194} and C_{246} are not straight and are bent.

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