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Phenylene lattices

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A modified choice of unit-cell vectors resolves an apparent discrepancy in the indexation of the most intense *para*-sexiphenyl reflections compared with other known *para*-phenylenes.

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The *para*-*n*-phenylenes with n = 2, 4, 5, 6, 7 form a textbook example of a series of simple molecular structures. All molecules are linear and consist of n coplanar phenyl rings attached to each other by single bonds. Moreover, all molecules crystallize in the monoclinic space group $P2_1/a$ (Rietveld *et al.*, 1970; Delugeard *et al.*, 1976; Baker *et al.*, 1993). However, in diffraction studies, *para*-sexiphenyl (n = 6) seems to behave somewhat differently than the other phenylenes: some of most intense reflections have indices other than the intense reflections of the remaining members of the family. This is particularly evident in thin film studies (Yanagi & Okamoto, 1997; Yoshida *et al.*, 1999; Kintzel *et al.*, 2001; Smilgies *et al.*, 2002; Plank *et al.*, 2002; Kintzel, 2002), where only a few of the strongest reflections are observed.

The indexing problem can be resolved by looking into the determination of the unit cells. Based on the space group, lattice vectors **a** and **b** are fixed except for inversion. However, **c** is merely chosen by convention that it should have a minimum length and that β should be larger than 90°. Hence, other choices of **c** of the form **c** + m**a**, with m an integer, are still compatible with the space group. For the particular transformation $\mathbf{c}' = \mathbf{c} + \mathbf{a}$, keeping β larger than 90° and a right-handed basis implies $\mathbf{a}' = -\mathbf{a}$, $\mathbf{b}' = -\mathbf{b}$. The full basis transformation has the matrix S

$$\begin{pmatrix}\mathbf{a}'\\ \mathbf{b}'\\ \mathbf{c}'\end{pmatrix} = S\begin{pmatrix}\mathbf{a}\\ \mathbf{b}\\ \mathbf{c}\end{pmatrix} = \begin{pmatrix}-1 & 0 & 0\\ 0 & -1 & 0\\ 1 & 0 & 1\end{pmatrix}\begin{pmatrix}\mathbf{a}\\ \mathbf{b}\\ \mathbf{c}\end{pmatrix}.$$

Table 1 lists all the known *para*-phenylene lattices for two choices of **c**. Choices from the literature and the results of the above calculation are marked as such. Table 2 lists the Miller indices of the strongest reflections, as they are affected by the basis change

$$\begin{pmatrix}h' & k' & l'\end{pmatrix} = \begin{pmatrix}h & k & l\end{pmatrix}\mathbf{S}^T,$$

and indeed the new indexation for *para*-sexiphenyl now matches the other phenylenes. From Table 1 it can be clearly seen that *para*-sexiphenyl agrees well with the other phenylenes, when using the new unit cell (Choice I in Table 1). c and c' as well as β and β' have almost degenerate values for *para*-sexiphenyl. Interestingly, the unit cell of *para*-septiphenyl in the literature (Baker *et al.*, 1993) is consistent with the cases n = 3, 4, 5, although **c** does not have the shortest possible length. Nonetheless, this choice should be maintained for consistency with the other phenylene lattices.

As the transformed basis for *para*-sexiphenyl proposed here provides the lower Miller indices for the most intense reflections (see Table 2), it is suggested that the *para*-sexiphenyl unit cell (Choice II) reported by Baker *et al.* (1993) should be changed to Choice I so that it fits better with the remainder of the *p*-phenylene lattices. To this effect the atomic coordinates (x,y,z) from the literature (Baker *et al.*, 1993) need to be transformed as $(x' \quad y' \quad z') = (x \quad y \quad z)S^{-1}$.

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Table 1
Lattice constants for the two choices of basis vectors.

	Common	Common	Choice	I		Choice	II	
n	*a* (Å)	*b* (Å)	*c* (Å)	*β* (°)	Ref.	*c*′ (Å)	*β*′ (°)	Ref.
3	8.106	5.613	13.613	92.02	(*a*)	15.597	119.28	(*b*)
4	8.110	5.610	17.910	95.80	(*c*)	18.899	109.47	(*b*)
5	8.070	5.581	22.056	97.91	(*d*)	22.419	102.98	(*b*)
6	8.091	5.568	26.338	99.53	(*b*)	26.241	98.17	(*d*)
7	8.034	5.547	30.577	100.52	(*d*)	30.163	94.66	(*b*)

References: (*a*) Rietveld *et al.* (1970); (*b*) this work; (*c*) Delugeard *et al.* (1976); (*d*) Baker *et al.* (1993).

Table 2
Indices of equivalent reflections for the two choices of basis vectors.

Choice I	Choice II
00*l*	00*l*
110	$11\bar{1}$
111	$11\bar{2}$
210	$20\bar{3}$
211	$21\bar{3}$

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