Acta Cryst. (1977). B**33**, 314

The crystal structures of methyl 1,5-dithio-α-D-ribopyranoside quarterhydrate and methyl 1,5-dithio-β-D-ribopyranoside: errata.

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Errors are corrected in Tables 1 and 3 of Girling & Jeffrey [*Acta Cryst.* (1974), B**30**, 327–333].

In Table 1 of Girling & Jeffrey (1974), the atomic parameters given for methyl 1,5-dithio-α-D-ribopyranoside and methyl 1,5-dithio-β-D-ribopyranoside are those for the L enantiomers. The correct values are obtained by reversing the signs of the y coordinates. For methyl 1,5-dithio-α-D-ribopyranoside, molecule A, the following parameters for C(4) were omitted: x 4139, y −288, z 7182, β_{11} 9·9 (5), β_{22} 256 (19), β_{33} 56 (3), β_{12} 4 (3), β_{13} 7 (1), β_{23} 28 (7). For methyl 1,5-dithio-α-D-ribopyranoside, molecule B, the coordinates given for O(3) refer to O(4). The coordinates for O(3) were omitted; they are as follows: x 4990, y −6301, z 3321, β_{11} 8·7 (4), β_{22} 303 (14), β_{33} 63 (3), β_{12} −12 (2), β_{13} 0·4 (8), β_{23} 33 (5). These coordinates are for the D enantiomer.

In Table 3, the signs of the torsion angles for (I*A*) and (I*B*) refer to the L enantiomer. They have to be reversed for the D enantiomer.

Reference

GIRLING, R. L. & JEFFREY, G. A. (1974). *Acta Cryst.* B**30**, 327–333.

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Comment on *The crystal and molecular structure of phenothiazine*, by J. J. H. McDowell.

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There are strong indications that the data reported by McDowell [*Acta Cryst.* (1976), B**32**, 5–10] on the structure of phenothiazine are affected by disorder and that the precision of the molecular dimensions is overestimated.

A crystal structure investigation of phenothiazine was undertaken in this laboratory some years ago. The cell parameters measured by us were only slightly different from those recently reported by McDowell (1976) (see Table 1).

Moreover, the positional and thermal parameters we arrived at differ by no more than 1·5 s.d. from those reported by McDowell. The following observations led us to the conclusion that our results suffered from disorder and that no high accuracy could be claimed:

(1) Weissenberg photographs about the orthorhombic a axis reveal marked diffuse streaking parallel to **c***. In addition, it was found that even after long exposures no reflexions could be recorded in large regions corresponding to $k \gtrsim 10$, indicating comparatively high values for anisotropic thermal parameters β_{22}.

(2) Refinement of the structure, with isotropic thermal parameters only, resulted in a residual R of $\simeq 0{\cdot}25$. An electron density difference map at this stage clearly showed two phenothiazine molecules shifted by about 0·3 Å in opposite directions along a perpendicular to the plane $y = \frac{1}{4}$. There was a sharp drop in the residual to $R \simeq 0{\cdot}08$ when anisotropic thermal parameters were included in the refinement.

Table 1. *Comparison of cell parameters*

	van de Waal & Feil	McDowell (1976)
a	7·918 (2) Å	7·916 (10) Å
b	20·945 (3)	20·974 (10)
c	5·882 (2)	5·894 (10)
Space group	*Pnma*	*Pnma*

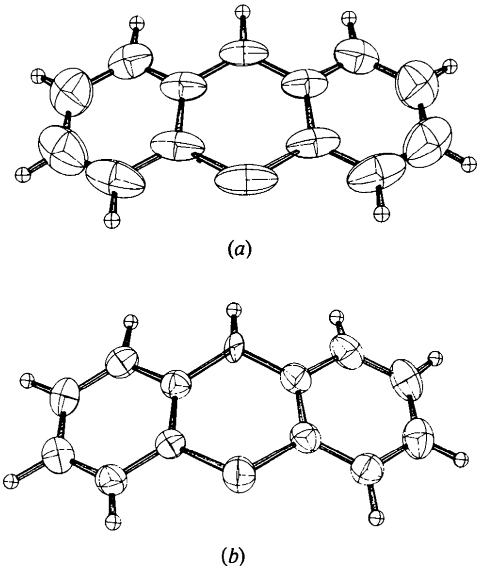
(3) Low-temperature Weissenberg photographs (recorded at 120 K) revealed a number of features, not observed at room temperature: (*a*) *hk*0 reflexions with h odd, forbidden by *Pnma* space-group symmetry, were clearly present. The behaviour of the intensities of these reflexions with increasing temperature is strongly indicative of an order–disorder transition. At the transition point (224·6 K) these reflexions have completely disappeared. (*b*) No unusual 'black' regions. (*c*) Diffuse streaking [see (1) above] has disappeared. (*d*) All reflexions split into two components in a way which is consistent with the superposition of two reciprocal monoclinic lattices, related by a 180° rotation about the (monoclinic) c^* axis.

(4) The existence of an order–disorder transition at 224·6 K was confirmed by heat-capacity measurements with a powder specimen.

(5) Analysis of anisotropic β values showed them to be unacceptable as parameters describing thermal motion (a detailed discussion is given below).

Table 2. *R.m.s. displacements* (Å) *and direction cosines of principal axes of vibration, calculated from the data of McDowell* (1976) *for phenothiazine*

	$\langle u_1^2\rangle^{1/2}$	$\langle u_2^2\rangle^{1/2}$	$\langle u_3^2\rangle^{1/2}$	C_{11}	C_{12}	C_{13}	C_{21}	C_{22}	C_{23}	C_{31}	C_{32}	C_{33}
S	0·22	0·40	0·17	0·82	0·00	0·58	0·00	1·00	0·00	–0·58	0·00	0·82
N	0·25	0·33	0·16	0·97	0·00	0·26	0·00	1·00	0·00	–0·26	0·00	0·97
C(1)	0·17	0·36	0·19	0·94	0·17	0·30	–0·22	0·97	0·12	–0·27	–0·18	0·95
C(2)	0·19	0·42	0·24	0·83	0·39	–0·41	–0·29	0·92	0·28	0·48	–0·11	0·87
C(3)	0·22	0·40	0·30	0·77	0·60	–0·23	–0·40	0·73	0·55	0·50	–0·33	0·80
C(4)	0·22	0·34	0·33	0·82	0·55	0·13	–0·50	0·60	0·62	0·26	–0·58	0·77
C(5)	0·21	0·33	0·23	0·91	0·40	0·08	–0·37	0·90	–0·23	–0·16	0·18	0·97
C(6)	0·18	0·32	0·19	0·91	0·25	0·33	–0·28	0·96	0·06	–0·31	–0·14	0·94


(*a*)

(*b*)

Fig. 1. Comparison of thermal-vibration ellipsoids at the 50% probability level (Johnson, 1965) for (*a*) orthorhombic phenothiazine (McDowell, 1976) and (*b*) monoclinic ($P2_1$) phenothiazine (Freeman, 1971).

Table 3. *Comparison of unit-cell parameters at* 120 *and* 300 K

	120 K	300 K
a	5·808 (1) Å	5·882 (2) Å
b	7·783 (3)	7·918 (2)
c	22·009 (3)	21·755 (4)
β	69·87 (2)°	74·33 (2)°

We concluded that, at room temperature, pseudosymmetry *Pnma* is generated by polysynthetic twinning about $\mathbf{c}_m^*$ of a monoclinic (*m*) cell, which is related to the orthorhombic (*o*) cell by: $\mathbf{a}_m \simeq \mathbf{c}_o$, $\mathbf{b}_m \simeq \mathbf{a}_o$, $\mathbf{c}_m \simeq \mathbf{b}_o + \mathbf{c}_o$. The true space group is $P2_1/c$.

Since the molecular position is not now restricted by symmetry, the molecule may be shifted somewhat with respect to the position dictated by *Pnma* space-group symmetry. In the other twin individual the shift will be in the opposite direction. Because of the polysynthetic character of the twinning, only *mean* atomic positions can be deduced from X-ray results at room temperature, with necessarily large anisotropic temperature factors, which in fact allow for the displacements.

Since our observations refer to several crystals, grown in different ways, we consider it probable that McDowell's data are based on the same disordered modification.

Using the anisotropic thermal parameters in McDowell's Table 2, we have calculated atomic r.m.s. displacements $\langle u_i^2\rangle^{1/2}$ ranging from 0·16 to 0·42 Å (Table 2). The corresponding values of $B = 8\pi^2\langle u^2\rangle$ are about 2 to 14 Å^2 respectively. In Table 2 we have included the direction cosines C_{ij} of the principal axes of vibration *i* with respect to the crystal axes *j* (*i.e.* *a*, *b* and *c*). Clearly, the largest displacements are nearly all parallel to **b**, indicating positional disorder rather than librational motion. A similar conclusion is reached if the thermal-vibration ellipsoids calculated from McDowell's anisotropic *β*'s are compared with the thermal-vibration ellipsoids found from a structure analysis of an ordered monoclinic ($P2_1$) modification of phenothiazine (Freeman, 1971) (Fig. 1).

Though the estimated separation between the two possible molecular positions amounts to 0·6 Å, molecular dimensions derived from the mean atomic positions may not be grossly in error, particularly when the two molecular positions in the disordered structure are related by pure translation. The precision of the molecular dimensions is likely to be overestimated when only the mean positional atomic parameters are considered and the reported intermolecular distances may be in error by as much as the separation (*i.e.* 0·6 Å) between the two sets of possible molecular positions.

Finally we note that we have collected low-temperature intensity data from twinned crystals of phenothiazine exhibiting sufficient separation between diffraction maxima in reciprocal space to enable observation of diffraction by one twin individual only. The unit-cell parameters (at 120 K) are compared with corresponding values, derived from the orthorhombic unit cell (300 K), in Table 3.

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