They reported that, when crystals were isolated from a freshly prepared solution of HMX in DMF, they were rhombohedral as described by Cobbledick & Small (1975), but if the crystals were allowed to stand in the mother liquor for three months or more they transformed to the monoclinic modification. They further report that 'the two polymorphs of HMX–DMF are subtly, but genuinely, different'. The difference is probably not genuine.

The monoclinic cell dimensions reported by HRB are $a = 22{\cdot}627\ (10)$, $b = 16{\cdot}000\ (4)$, $c = 13{\cdot}849\ (6)$ Å, $\beta = 114{\cdot}09\ (3)°$, with space group $C2/c$, $Z = 12$. The vectors [010], $[-\frac{1}{2},-\frac{1}{2},-1]$, $[-1,0,1]$ describe an effectively hexagonal cell with $a_h = 16{\cdot}000\ (4)$, $b_h = 15{\cdot}996\ (7)$, $c_h = 30{\cdot}977\ (14)$ Å, $\alpha_h = 89{\cdot}97\ (3)$, $\beta_h = 90{\cdot}00$, $\gamma_h = 120{\cdot}01\ (3)°$, $Z = 24$; a primitive rhombohedral cell based on $[-\frac{1}{2},\frac{1}{2},0]$, $[-\frac{1}{2},-\frac{1}{2},0]$, $[0,0,1]$ has dimensions $a_r = b_r = 13{\cdot}856\ (5)$, $c_r = 13{\cdot}849\ (6)$ Å, $\alpha_r = \beta_r = \gamma_r = 70{\cdot}53\ (3)°$, $Z = 8$. (The e.s.d.'s are only guesses, covariances being lacking.) The corresponding transformation $x_h = -\frac{1}{3}x + y - \frac{1}{3}z$, $y_h = -\frac{2}{3}x - \frac{2}{3}z$, $z_h = -\frac{2}{3}x + \frac{1}{3}z$ (or $x_r = -x + y$, $y_r = -x-y$, $z_r = z$), when applied to the parameters in Table 1 of HRB, leads to atomic coordinates that are compatible with space group $R\bar{3}c$ within about 0·006 Å for the HMX molecule and about 0·016 Å for the disordered DMF molecule – about 20% larger than the reported e.s.d.'s. Thus the structure reported by HRB conforms to space group $R\bar{3}c$ nearly as closely as the reported precisions would demand.

The modification reported by Cobbledick & Small was also described in space group $R\bar{3}c$; the cell dimensions are $a_h = 15{\cdot}989\ (8)$, $c_h = 30{\cdot}920\ (12)$ Å [leading to $a_r = 13{\cdot}836\ (7)$ Å, $\alpha_r = 70{\cdot}59\ (2)°$]. The coordinates they report in their Table 2 agree, within the combined e.s.d.'s, with the $R\bar{3}c$-averaged coordinates of HRB for the HMX molecule and for the carbon atoms of the DMF molecule; no comparison is possible for the N and O atoms of the DMF, since HRB treated them as single atoms while Cobbledick & Small treated them as disordered across twofold axes, with final positions 0·2–0·3 Å from these axes. This difference in treatment could be compensated for – in large part, at least – by differences in the anisotropic B's.

In summary: the structure described as monoclinic by HRB has the symmetry of $R\bar{3}c$, essentially within the e.s.d.'s; and both the cell dimensions and the atomic coordinates agree with the $R\bar{3}c$ structure reported by Cobbledick & Small. Thus there seems no valid reason to presume that the crystals underwent a phase transition during the three-month period of standing in their mother liquor. It seems more likely that, in the case of the aged crystal, the metric symmetry of the lattice happened not to have been recognized by the computer software (*SHELXTL*).

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Hexachloronaphthalene-1,8-disulfide:* further refinement in space group $P2_1/n$.†

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Abstract

The crystal structure of $C_{10}Cl_6S_2$, originally described in space group Pn, has been more satisfactorily refined in space group $P2_1/n$. In the revised structure, the molecule is disordered across a center of symmetry. The bond lengths and non-bonded contacts are now normal; the molecule is slightly non-planar, forming a very shallow boat or skullcap. The final R is 0·083 for 485 reflections, compared to 0·098 for the earlier refinement in Pn.

The crystal structure of $C_{10}Cl_6S_2$ has recently been reported as monoclinic [$a = 10{\cdot}68\ (1)$, $b = 3{\cdot}853\ (2)$, $c = 15{\cdot}31\ (1)$ Å, $\beta = 93{\cdot}3\ (1)°$], space group Pn, with $Z = 2$ (Noordik & Kleijburg, 1982; NK). Surprising features of this structure included a very long S—S bond at 2·49 Å and, at the opposite side of the molecule, an uncomfortably short Cl···Cl contact of 2·74 Å. We also noted that the center of the molecule lay at approximately $y = \frac{1}{4}$ (relatively to the n-glide plane at $y = 0$), so that if the molecule were centrosymmetric the structure would conform to space group $P2_1/n$. The center of symmetry could be achieved if the troublesome S and Cl atoms were disordered.

Because of the shortness of the b axis, only two $0k0$ reflections with k odd – 010 and 030 – were recorded and their F_o values at 2·75 (6) and 2·3 (12) were inconclusive. Accordingly, we undertook additional least-squares refinement, based on the original data. This refinement indicates that the structure should indeed be described as disordered in space group $P2_1/n$.

As described earlier (NK), symmetry-equivalent reflections hkl and $\bar{h}k\bar{l}$ were averaged, yielding 763 independent intensities; one reflection (101) was then deleted, since the two measurements were severely disparate. Full-matrix refinement was based on the remaining 762 reflections, the quantity minimized being $\sum w(F_o^2 - F_c^2)^2$ with $w = 1/\sigma^2(F_o^2)$.

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* Hexachloro-1,8-epidithionaphthalene.

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Convergence was reached at $R = 0{\cdot}16$ for all 762 reflections and $R = 0{\cdot}12$ for the 485 reflections with $F^2 \geq 3\sigma(F^2)$. This latter value is appreciably larger than the 0·098 obtained for the *Pn* refinement (NK). However, *U*'s for the Cl and S atoms were highly anisotropic and a difference map in the plane of the molecule suggested that these atoms should be split into pairs separated by 0·5 Å or more. The final model was based on disordered, half-occupied sites for each of these peripheral atoms and ordered sites for the C atoms; all atoms were given anisotropic *U*'s for a total 118 parameters.* Full-matrix refinement converged satisfactorily to an *R* of 0·124 for all 762 reflections and 0·083 for the 485 stronger reflections, now convincingly better than the 0·098 obtained in *Pn* with 161 parameters. The $P2_1/n$ parameters are given in Table 1.

The $P2_1/n$ model represents a disorder between two centrosymmetrically related orientations of the peripheral atoms (Fig. 1); although the C atoms are, no doubt, also disordered as they accommodate to the pinching effect of the S—S bond, their disorder can be satisfactorily represented by their anisotropic *U*'s. This model is much more reasonable than the *Pn* model. Thus, the S—S bond length is 1·94 (2) Å rather than the 2·49 (2) Å reported for the *Pn* refinement: a bit shorter than normal, but not far from the range 2·00–2·10 Å commonly found for S—S bonds (*International Tables for X-ray Crystallography,* 1962; Dideberg & Toussaint, 1974). Similarly, the C—C distances are now normal rather than ranging from 1·28 to 1·75 Å. We note that the e.s.d.'s reported here are probably unreliable, owing to large correlations among pairs of disordered atoms. For example, $\langle d(\text{C—Cl})\rangle$ is 1·71 [7] Å, the bracketed sample e.s.d. being about three times as large as the least-squares e.s.d.; the mean agrees well with the expected value of 1·717 (8) Å (Herbstein, 1979). The non-bonded Cl···Cl and Cl···S distances around the periphery of the molecule are remarkably equal at 3·05–3·12 Å, in agreement with earlier values (Herbstein, 1979).

The molecule appears to be somewhat non-planar, having the shape of a shallow skullcap: while the ten C atoms are coplanar within 0·007 Å, the four atoms S(1), Cl(4), Cl(5), S(8) are displaced by an average of 0·05 Å (range, −0·01 to 0·10 Å) and the atoms Cl(2), Cl(3), Cl(6), Cl(7) by an average of 0·12 Å in the same direction (range, 0·05 to 0·15 Å). While the correlation problem casts some doubt on the reliability of these numbers, the deformation appears to be strikingly different from that found in octachloronaphthalene (Herbstein, 1979) and the hexachloronaphthalene-1,8-dithiolate ligand in $[\mathrm{Ni_3(C_{10}Cl_6S_2)_3(PPh_3)_3}]$ (Bosman & Van der Linden, 1977), which form twisted ribbons. This difference in shape presumably arises from the constraint imposed by the covalent S—S bond.

Table 1. *Final coordinates* ($\times 10^4$) *and* U_{eq} *values* ($\text{Å}^2\times 10^3$), *space group* $P2_1/n$

$$U_{\text{eq}} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C(1)	1201 (8)	−363 (25)	−818 (5)	54 (3)
C(2)	2251 (9)	1044 (30)	−359 (7)	71 (3)
C(3)	2124 (10)	2198 (27)	502 (7)	67 (4)
C(4)	1034 (10)	2018 (26)	892 (6)	53 (3)
C(5)	48 (8)	−592 (21)	−443 (5)	41 (3)
†S(1)	1168 (21)	−2090 (72)	−1927 (18)	105 (5)
†Cl(2)	3621 (15)	641 (38)	−992 (10)	96 (4)
†Cl(3)	3608 (12)	3447 (41)	907 (10)	97 (3)
†Cl(4)	1215 (9)	3663 (48)	1924 (10)	75 (3)
†Cl(5)	−1523 (18)	1306 (58)	1819 (15)	71 (4)
†Cl(6)	−3649 (14)	−1928 (36)	683 (9)	82 (3)
†Cl(7)	−3244 (11)	−4148 (30)	−1214 (7)	90 (4)
†S(8)	−583 (11)	−3422 (46)	−1940 (9)	91 (3)

† Half-populated, disordered sites.

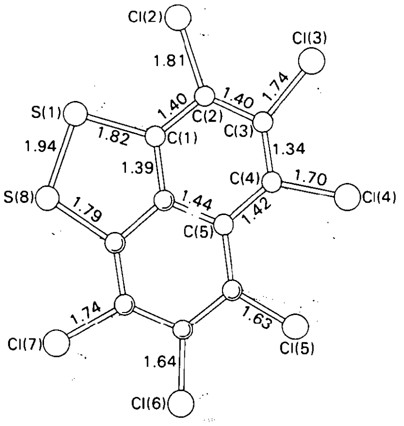

Fig. 1. The disordered structure, space group $P2_1/n$. The dashed atoms are related to the solid ones by the center of symmetry. E.s.d.'s are in the range 0·012–0·015 Å for C—C and 0·017–0·027 Å for C—Cl and C—S; these latter values are subject to relatively large correlations (see text).

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* A list of anisotropic thermal parameters has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39604 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.