

Table 2. Bond lengths (Å), calculated bond lengths from Hückel calculations, and bond angles (°) for the nonhydrogen atoms

The errors are derived from the full inverse matrix.

Experimental	Hückel	Experimental	Hückel		
C(1)–C(2)	1.382 (4)	1.38	C(1)–C(12b)	1.379 (3)	1.40
C(2)–C(3)	1.387 (4)	1.39	C(3)–C(4)	1.355 (5)	1.38
C(4)–C(4a)	1.425 (4)	1.41	C(4a)–C(5)	1.420 (3)	1.44
C(4a)–C(12b)	1.424 (3)	1.42	C(5)–C(6)	1.364 (3)	1.38
C(6)–C(6a)	1.458 (3)	1.44	C(6a)–C(7)	1.435 (3)	1.39
C(6a)–C(12a)	1.444 (3)	1.44	C(7)–C(7a)	1.426 (3)	1.40
C(7)–C(14)	1.504 (3)	1.44	C(7a)–C(8)	1.474 (4)	1.42
C(7a)–C(11a)	1.426 (3)	1.44	C(8)–C(9)	1.377 (4)	1.38
C(9)–C(10)	1.395 (4)	1.40	C(10)–C(11)	1.389 (4)	1.38
C(11)–C(11a)	1.442 (3)	1.42	C(11a)–C(12)	1.463 (3)	1.41
C(12)–C(12a)	1.407 (3)	1.39	C(12)–C(13)	1.510 (3)	
C(12a)–C(12b)	1.490 (4)	1.46	C(14)–O	1.358 (3)	
C(15)–O	1.418 (4)				

Mean C–H distance 0.99 (3) Å.

C(2)–C(1)–C(12b)	120.2 (3)	C(1)–C(2)–C(3)	123.8 (3)
C(2)–C(3)–C(4)	117.9 (3)	C(3)–C(4)–C(4a)	119.6 (3)
C(4)–C(4a)–C(5)	120.4 (3)	C(4)–C(4a)–C(12b)	121.9 (3)
C(5)–C(4a)–C(12b)	117.5 (3)	C(4a)–C(5)–C(6)	121.0 (3)
C(5)–C(6)–C(6a)	124.3 (2)	C(6)–C(6a)–C(7)	123.7 (2)
C(6)–C(6a)–C(12a)	115.8 (2)	C(7)–C(6a)–C(12a)	120.4 (2)
C(6a)–C(7)–C(7a)	121.0 (2)	C(6a)–C(7)–C(14)	121.0 (3)
C(7a)–C(7)–C(14)	118.0 (3)	C(7)–C(7a)–C(8)	123.6 (3)
C(7)–C(7a)–C(11a)	117.9 (2)	C(8)–C(7a)–C(11a)	118.5 (3)
C(7a)–C(8)–C(9)	121.9 (3)	C(8)–C(9)–C(10)	119.5 (3)
C(9)–C(10)–C(11)	120.2 (3)	C(10)–C(11)–C(11a)	123.4 (3)
C(7a)–C(11a)–C(11)	116.4 (3)	C(7a)–C(11a)–C(12)	121.0 (2)
C(11)–C(11a)–C(12)	122.6 (3)	C(11a)–C(12)–C(12a)	119.9 (2)
C(11a)–C(12)–C(13)	118.8 (2)	C(12a)–C(12)–C(13)	121.1 (2)
C(6a)–C(12a)–C(12)	118.2 (2)	C(6a)–C(12a)–C(12b)	117.2 (2)
C(12)–C(12a)–C(12b)	124.6 (2)	C(1)–C(12b)–C(4a)	116.3 (2)
C(1)–C(12b)–C(12a)	121.9 (2)	C(4a)–C(12b)–C(12a)	121.6 (2)
C(7)–C(14)–O	108.6 (2)	C(14)–O–C(15)	109.7 (3)

methyl H atoms on C(13) with those on C(1). The shortest contact distance is H(1)…H(132) at 2.05 (4) Å. For a planar molecule this would be *ca* 1.8 Å. The bay-region distortion seems to increase polycyclic hydrocarbon carcinogenic activity (Glusker, 1982).

The *K*-region bond length, C(5)–C(6), is 1.364 (3) Å. Short bonds are also found between C(3)–C(4), 1.355 (5) Å, and C(8)–C(9), 1.377 (4) Å. Presumably these are preferred sites for hydroxyl and epoxide group addition which is a postulated intermediate step in the interaction between DNA and the hydrocarbon.

Simple Hückel MO theory calculations were performed for the unsubstituted benz[a]anthracene skeleton assuming planarity. Bond lengths (*d*) were calculated from bond orders (*b*) via:

$$d = 1.37 + 0.04(0.8-b) + 0.6(0.8-b)^2$$

and these are included in Table 2. The agreement is good with an r.m.s. deviation of 0.02 Å confirming that torsion alone is sufficient to reduce overcrowding in the bay region without significantly reducing π -orbital delocalization. The positions of the shortest bonds also correspond to experimental results. Three deviations exceed 0.03 Å. This is due to the substitution of the skeleton by the methyl and methoxymethyl groups.

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SHORT COMMUNICATIONS

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Concerning a second polymorph of the HMX–DMF complex.*

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Abstract

The monoclinic phase recently reported for the 1:1 complex between octahydro-1,3,5,7-tetrinitro-1,3,5,7-tetrazocine

(HMX) and *N,N*-dimethylformamide is almost certainly identical with the rhombohedral phase reported earlier, and should be described in space group $R\bar{3}c$ rather than $C2/c$.

Recently, Haller, Rheingold & Brill (1983; HRB) described the crystal structure of a second monoclinic polymorph of the 1:1 complex between octahydro-1,3,5,7-tetrinitro-1,3,5,7-tetrazocine (HMX) and *N,N*-dimethylformamide (DMF).

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They reported that, when crystals were isolated from a freshly prepared solution of HMX in DMF, they were rhombohedral as described by Cobbley & 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 $a = 22.627$ (10), $b = 16.000$ (4), $c = 13.849$ (6) Å, $\beta = 114.09$ (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 $a_h = 16.000$ (4), $b_h = 15.996$ (7), $c_h = 30.977$ (14) Å, $a_h = 89.97$ (3), $\beta_h = 90.00$, $\gamma_h = 120.01$ (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 $a_r = b_r = 13.856$ (5), $c_r = 13.849$ (6) Å, $a_r = \beta_r = \gamma_r = 70.53$ (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 Cobbley & Small was also described in space group $R\bar{3}c$; the cell dimensions are

$a_h = 15.989$ (8), $c_h = 30.920$ (12) Å [leading to $a_r = 13.836$ (7) Å, $a_r = 70.59$ (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 Cobbley & 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 Cobbley & 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 [$a = 10.68$ (1), $b = 3.853$ (2), $c = 15.31$ (1) Å, $\beta = 93.3$ (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 $h\bar{k}\bar{l}$ 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 $w = 1/\sigma^2(F_o^2)$.

* Hexachloro-1,8-epidithionaphthalene.

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