

Table 3. Torsion angles ( $^{\circ}$ ) in (8*t*) and (8*c*)

Since the atomic coordinates listed for molecule *B* (8*c*) correspond to the opposite chirality from *A*, the signs of all the calculated torsion angles for molecule *B* have been changed. This enables a direct comparison with molecule *A*, and (8*t*).

	(8 <i>t</i> )	(8 <i>c</i> ), <i>A</i>	(8 <i>c</i> ), <i>B</i>
C(15)–C(1)–C(2)–C(3)	–64.4 (6)	–72.3 (9)	–71.1 (9)
C(1)–C(2)–C(3)–C(8)	103.6 (5)	105.0 (8)	104.9 (8)
C(2)–C(3)–C(8)–C(9)	–69.6 (6)	–49.9 (9)	–49.8 (8)
C(3)–C(8)–C(9)–C(10)	–32.3 (7)	–50.1 (10)	–50.3 (10)
C(8)–C(9)–C(10)–C(11)	53.6 (7)	54.4 (10)	53.7 (10)
C(9)–C(10)–C(11)–C(15)	47.6 (7)	59.2 (9)	63.4 (9)
C(10)–C(11)–C(15)–C(1)	–114.6 (5)	–112.4 (7)	–115.5 (8)
C(11)–C(15)–C(1)–C(2)	71.5 (5)	66.7 (8)	65.4 (8)
C(2)–C(3)–C(4)–C(5)	–147.0 (5)	–103.2 (9)	–107.1 (9)
C(3)–C(4)–C(5)–C(6)	–0.1 (8)	–3.5 (14)	2.3 (13)
C(4)–C(5)–C(6)–C(7)	–12.6 (8)	10.0 (13)	7.2 (13)
C(5)–C(6)–C(7)–C(8)	44.6 (6)	–38.2 (10)	–38.2 (10)
C(6)–C(7)–C(8)–C(3)	–63.8 (5)	59.9 (9)	59.6 (9)
C(7)–C(8)–C(3)–C(4)	47.7 (5)	–49.9 (8)	–48.4 (8)
C(8)–C(3)–C(4)–C(5)	–18.5 (7)	24.1 (10)	18.8 (10)
C(1)–C(15)–C(11)–C(12)	60.2 (6)	59.4 (8)	61.7 (9)
C(15)–C(11)–C(12)–C(13)	–0.9 (7)	1.4 (10)	–1.2 (10)
C(11)–C(12)–C(13)–C(14)	–58.2 (6)	–58.2 (9)	–55.7 (9)
C(12)–C(13)–C(14)–C(1)	56.2 (6)	50.9 (8)	49.7 (9)
C(13)–C(14)–C(1)–C(15)	0.6 (6)	6.3 (8)	6.6 (9)
C(14)–C(1)–C(15)–C(11)	–56.6 (5)	–60.7 (7)	–60.5 (8)
C(14)–C(1)–C(15)–C(20)	57.9 (6)	55.3 (8)	55.7 (8)
C(1)–C(15)–C(20)–C(21)	–59.6 (6)	–63.0 (8)	–64.4 (9)
C(15)–C(20)–C(21)–C(13)	–0.5 (7)	3.8 (8)	4.3 (10)
C(20)–C(21)–C(13)–C(14)	60.7 (7)	59.2 (8)	59.0 (9)
C(20)–C(21)–C(13)–C(12)	–55.5 (7)	–57.8 (8)	–57.6 (9)
C(17)–C(8)–C(9)–O	30.4 (7)	–106.5 (8)	–107.2 (8)
C(7)–C(8)–C(9)–O	–84.7 (6)	10.5 (9)	10.2 (9)

O...C(19), 3.38 Å in (8*t*) and 3.40, 3.34 Å in (8*c*). Short intramolecular distances which are equivalent because of the different configuration at C(8) are O...C(17), 2.73 Å in (8*t*) and O...C(7), 2.66, 2.64 Å in (8*c*). Thus in both the C(8) epimers there is steric crowding of three *B* ring substituents, namely the O atom, the C(19) methyl group and either the C(17) methyl group in (8*t*) or the C(7) methylene group in

(8*c*). There are no unusually short intermolecular distances.

Crystallographic calculations were carried out using minicomputer programs written or modified by Dr R. Shiono (Shiono, 1980). We are grateful to Dr R. F. Stewart for fostering this collaborative effort.

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## The Structure of the Complex Between Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and *N,N*-Dimethylformamide (DMF), C<sub>4</sub>H<sub>8</sub>N<sub>8</sub>O<sub>8</sub>·C<sub>3</sub>H<sub>7</sub>NO.A Second Polymorph

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**Abstract.** The structure of a previously unknown polymorph,  $\alpha$ -HMX–DMF, is reported.  $M_r = 369.3$ , monoclinic,  $C2/c$ ,  $a = 22.627$  (10),  $b = 16.000$  (4),  $c = 13.849$  (6) Å,  $\beta = 114.09$  (3) $^{\circ}$ ,  $V = 4577.0$  (30) Å<sup>3</sup>,  $Z = 12$ ,  $D_x = 1.607$  g cm<sup>–3</sup>,  $MoK\alpha$ ,  $\lambda = 0.71073$  Å,  $\mu = 1.38$  cm<sup>–1</sup>,  $F(000) = 2304$ ,  $T = 297$  K,  $R = 0.0618$  for

1858 observed reflections. The DMF molecule exhibits twofold disorder. Overall, this polymorph and a previously reported polymorph of HMX–DMF are very similar. The most important non-hydrogen-atom intermolecular interactions between HMX molecules are O...CNC and O...CNNO contacts. These are the same types of heavy-atom associations that dominate the pure HMX polymorphs, which suggests that

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HMX–HMX interactions remain important to the cohesion of the crystal lattice even when HMX co-crystallizes with strongly polar solvents.

**Introduction.** The energetic material octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) co-crystallizes with nearly one hundred organic molecules to produce stoichiometric solids (George, Cady, Rogers & Rohwer, 1965; Selig, 1982). Interest in this area is fueled by the need for information on the intermolecular interactions in the solid which might be important in its stability and decomposition. The only reported crystal structure of an HMX solvate is the 1:1 complex between HMX and *N,N*-dimethylformamide (DMF) (Cobbledick & Small, 1975). An *R*3̄c or *R*3c space group was assigned. The structures of additional HMX solvates would be valuable to have to underpin conclusions about the most important interactions in the solid phase (Brill & Reese, 1980), as well as to learn more about the structural requirements of dopant molecules.

While we confirm by X-ray diffraction that rhombohedral crystals form in freshly crystallized HMX–DMF, we found that HMX–DMF also crystallizes in a second polymorph having a space group of *C*2/c. Pure HMX is rich in polymorphs with four known at present (McCrone, 1950). Crystal-structure determinations are available for  $\alpha$ -HMX (Cady, Larson & Cromer, 1963),  $\beta$ -HMX (Choi & Boutin, 1970; Eiland & Pepinsky, 1955) and  $\delta$ -HMX (Cobbledick & Small, 1974). Differences in the molecular ring conformation exist in addition to the lattice modifications. Thus, it is of interest to investigate the polymorphism of HMX solvates in light of the potential for conformational polymorphism. The identity of the dominant intermolecular interactions in the HMX system is important for understanding how lattice dopants can be accommodated by the HMX structure.

**Experimental.** Prepared from 0.68 mmol of HMX dissolved in 3 ml of DMF (Bedard, Huber, Myers & Wright, 1962), freshly isolated crystals rhombohedral as described by Cobbledick & Small (1975). If crystals allowed to stand in mother liquid for three months or more, transformation to monoclinic morphology occurs. That the HMX–DMF complex which first crystallizes from solution converts with time in the presence of DMF to a second phase suggests that the initially crystallized product is slightly less stable than the final product; we have, therefore, labeled the solvate studied here as  $\alpha$ -HMX–DMF and that studied by Cobbledick & Small as  $\beta$ -HMX–DMF.

Crystal 0.42 × 0.31 × 0.18 mm, epoxied to a glass fiber and coated with varnish to prevent solvent evaporation, Nicolet R3 diffractometer, systematic absences consistent with *C*2/c and *C*c, *C*2/c confirmed by successful solution and refinement of structure;

unit-cell parameters from least-squares analysis of 24 accurately centered reflections,  $24 \leq 2\theta \leq 28^\circ$ ; intensity data collected with  $2\theta$  scans for  $3 < 2\theta < 45^\circ$ , variable scan speed ( $4\text{--}20^\circ \text{ min}^{-1}$ ), three check reflections measured every 97 reflections, no decay; 2633 reflections measured, 2434 unique, 1858 observed,  $I \geq 2\sigma(I)$ ; atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Direct methods, *SOLV*, contained in the Nicolet program package *SHELXTL* (Sheldrick, 1978); initial *E* map revealed non-hydrogen atoms of an entire HMX molecule, subsequent difference maps showed that the asymmetric unit consisted of one and one-half formula units of the HMX–DMF complex. The HMX half-molecule is positioned on a twofold axis and the disordered DMF half-molecule has its nitrogen and oxygen atoms lying on the twofold crystallographic axis. The nitrogen and oxygen atoms of the DMF half-molecule were refined at half-occupancy and the remaining carbon atoms of the DMF half-molecule were set at half-occupancy to keep their thermal parameters consistent with those of the carbon atoms of the DMF whole molecule. The disorder of the DMF molecule was modeled after that used by Cobbledick & Small (1975). Structure refined with block-cascade procedure (on *F*) with *SHELXTL*, hydrogen atoms located in idealized positions on the carbon atoms of the HMX molecules, non-hydrogen atoms refined anisotropically;  $R = 0.0618$ ,  $R_w = 0.0617$  ( $R_w = \sum w^{1/2} |\Delta| / \sum w^{1/2} |F_o|$ ),  $w^{-1} = \sigma^2(F_o) + G |F_o|^2$ ,  $G = 0.0015$ ,  $S = 1.249$ ; inspection of  $F_c$  vs  $F_o$  values for 20 low-angle reflections of high intensity indicated a correction for secondary extinction required;\* maximum  $\Delta\rho$  excursion =  $0.32 \text{ e } \text{Å}^{-3}$ ,  $\Delta_{\text{mean}}/\sigma_{\text{max}} = 0.186$  for the final cycle.†

**Discussion.** Table 1 gives the atomic positional coordinates.

The conformation of the tetrazocine ring is chair–chair in both HMX–DMF polymorphs. This conformation is the same as that in the  $\alpha$  and  $\delta$  modifications of pure HMX and also is believed to occur in  $\gamma$ -HMX (Landers, Apple, Dybowski & Brill, 1983). The chair conformation is found in  $\beta$ -HMX. Because the bond distances and angles for the two types of HMX and DMF molecules in  $\alpha$ -HMX–DMF given in Tables 2 and 3 do not differ in any important features from one another and are the same in essential detail as those found in  $\alpha$ - and  $\delta$ -HMX and in  $\beta$ -HMX–DMF, they

\*  $F_{\text{corr}} = F_c / [1.0 + 0.002 (X) (F_c)^2 / \sin(2\theta)]^{0.25}$ , where *X* refined to 0.0006 in final run.

† Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and full lists of bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38705 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

will not be discussed further here. The packing of the molecules is shown in Fig. 1. For convenience, the two NO<sub>2</sub> groups lying more or less in the tetrazocine ring plane will be referred to as 'equatorial', while those oriented more or less perpendicular to the ring plane are 'axial' NO<sub>2</sub> groups.

Table 1. Atom coordinates ( $\times 10^4$ ) for the non-hydrogen atoms

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
C(1)	3299 (3)	-501 (3)	2803 (3)	44 (2)
C(2)	2779 (2)	877 (3)	1933 (3)	41 (2)
C(3)	2001 (2)	797 (3)	2800 (4)	42 (2)
C(4)	2522 (2)	-579 (3)	3662 (3)	41 (2)
N(1)	3316 (2)	392 (2)	2677 (3)	38 (2)
N(2)	3824 (2)	820 (3)	3426 (3)	52 (2)
N(3)	2412 (2)	1299 (2)	2429 (3)	39 (2)
N(4)	2322 (2)	2147 (2)	2323 (3)	49 (2)
N(5)	2376 (2)	297 (2)	3715 (3)	38 (2)
N(6)	2717 (2)	709 (3)	4651 (3)	49 (2)
N(7)	3160 (2)	-730 (2)	3703 (3)	39 (2)
N(8)	3574 (3)	-1251 (3)	4464 (3)	52 (2)
O(1)	4246 (2)	404 (3)	4095 (3)	70 (2)
O(2)	3808 (2)	1584 (2)	3357 (3)	64 (2)
O(3)	2630 (2)	2535 (2)	1922 (3)	69 (2)
O(4)	1946 (2)	2471 (2)	2643 (3)	72 (2)
O(5)	2629 (2)	1464 (2)	4661 (3)	70 (2)
O(6)	3067 (2)	287 (2)	5392 (2)	63 (2)
O(7)	3410 (2)	-1493 (2)	5159 (3)	73 (2)
O(8)	4081 (2)	-1446 (2)	4406 (3)	71 (2)
C(5)	-7 (2)	-2194 (3)	1195 (3)	41 (2)
C(6)	860 (2)	-2205 (3)	3091 (3)	42 (2)
N(9)	614 (2)	-964 (2)	2005 (3)	46 (2)
N(10)	514 (2)	-1804 (2)	2074 (3)	36 (2)
N(11)	639 (2)	-1932 (2)	3886 (3)	39 (2)
N(12)	1075 (2)	-1613 (3)	4821 (3)	53 (2)
O(9)	1019 (2)	-630 (2)	2784 (3)	64 (2)
O(10)	279 (2)	-627 (2)	1164 (3)	69 (2)
O(11)	885 (2)	-1471 (2)	5515 (3)	73 (2)
O(12)	1620 (2)	-1462 (3)	4897 (3)	73 (2)
N(13)	1069 (2)	-1418 (3)	-360 (3)	77 (2)
C(8)	1634 (5)	-1514 (7)	667 (8)	61 (5)
C(8')	1254 (7)	-596 (7)	111 (10)	66 (7)
C(9)	909 (10)	-2369 (9)	-857 (13)	104 (9)
C(9')	453 (7)	-1271 (11)	-1396 (13)	79 (7)
C(7)	1358 (7)	-2126 (8)	-93 (12)	115 (8)
C(7')	704 (6)	-785 (8)	-755 (9)	60 (6)
O(13)	1782 (2)	-732 (3)	1055 (3)	102 (2)
N(14)	5000	-352 (4)	2500	75 (4)
C(11)	4727 (5)	375 (7)	1839 (8)	62 (5)
C(12)	4712 (7)	-1138 (6)	1724 (10)	91 (7)
C(10)	4673 (7)	-470 (8)	1505 (10)	83 (6)
O(14)	5000	1054 (3)	2500	109 (4)

Table 2. Bond lengths ( $\text{\AA}$ ) in the HMX molecules

C(1)-N(1)	1.443 (6)	C(1)-N(7)	1.451 (7)
C(2)-N(1)	1.455 (5)	C(2)-N(3)	1.444 (7)
C(3)-N(3)	1.471 (7)	C(3)-N(5)	1.445 (5)
C(4)-N(5)	1.450 (5)	C(4)-N(7)	1.443 (7)
N(1)-N(2)	1.376 (5)	N(2)-O(1)	1.222 (5)
N(2)-O(2)	1.225 (5)	N(3)-N(4)	1.371 (5)
N(4)-O(3)	1.222 (7)	N(4)-O(4)	1.224 (7)
N(5)-N(6)	1.376 (5)	N(6)-O(5)	1.224 (5)
N(6)-O(6)	1.215 (4)	N(7)-N(8)	1.371 (5)
N(8)-O(7)	1.228 (7)	N(8)-O(8)	1.222 (7)
C(5)-N(10)	1.445 (5)	C(5)-N(11a)	1.450 (6)
C(6)-N(10)	1.452 (5)	C(6)-N(11)	1.451 (7)
N(9)-N(10)	1.373 (5)	N(9)-O(9)	1.217 (4)
N(9)-O(10)	1.225 (5)	N(11)-N(12)	1.367 (5)
N(11)-C(5a)	1.450 (6)	N(12)-O(11)	1.223 (7)
N(12)-O(12)	1.218 (7)		

Table 3. Bond angles in the HMX molecules ( $^\circ$ )

N(1)-C(1)-N(7)	112.2 (4)	N(1)-C(2)-N(3)	112.8 (4)
N(3)-C(3)-N(5)	112.3 (4)	N(5)-C(4)-N(7)	113.9 (4)
C(1)-N(1)-C(2)	124.0 (3)	C(1)-N(1)-N(2)	117.2 (3)
C(2)-N(1)-N(2)	117.9 (3)	N(1)-N(2)-O(1)	117.0 (4)
N(1)-N(2)-O(2)	116.7 (3)	O(1)-N(2)-O(2)	126.3 (4)
C(2)-N(3)-C(3)	118.6 (4)	C(2)-N(3)-N(4)	120.0 (4)
C(3)-N(3)-N(4)	119.4 (4)	N(3)-N(4)-O(3)	117.7 (5)
N(3)-N(4)-O(4)	118.3 (4)	O(3)-N(4)-O(4)	124.0 (4)
C(3)-N(5)-C(4)	123.7 (3)	C(3)-N(5)-N(6)	117.7 (3)
C(4)-N(5)-N(6)	117.4 (3)	N(5)-N(6)-O(5)	116.9 (3)
N(5)-N(6)-O(6)	116.8 (4)	O(5)-N(6)-O(6)	126.3 (4)
C(1)-N(7)-C(4)	119.3 (3)	C(1)-N(7)-N(8)	119.6 (4)
C(4)-N(7)-N(8)	119.4 (4)	N(7)-N(8)-O(7)	117.7 (5)
N(7)-N(8)-O(8)	118.0 (5)	O(7)-N(8)-O(8)	124.3 (4)
N(10)-C(5)-N(11a)	112.3 (4)	N(10)-C(6)-N(11)	112.7 (4)
N(10)-N(9)-O(9)	117.0 (3)	N(10)-N(9)-O(10)	116.2 (3)
O(9)-N(9)-O(10)	126.8 (4)	C(5)-N(10)-C(6)	123.9 (3)
C(5)-N(10)-N(9)	117.7 (3)	C(6)-N(10)-N(9)	117.5 (3)
C(6)-N(11)-N(12)	119.5 (4)	C(6)-N(11)-C(5a)	119.3 (3)
N(12)-N(11)-C(5a)	119.3 (4)	N(11)-N(12)-O(11)	117.7 (4)
N(11)-N(12)-O(12)	118.0 (5)	O(11)-N(12)-O(12)	124.2 (4)

Table 4. Selected intermolecular distances ( $\text{\AA}$ ) in  $\alpha$ -HMX-DMF

Short axial HMX-HMX interactions			
O(9)···C(4)	3.110 (6)	O(6)···C(2)	3.092 (7)
O(9)···N(5)	3.171 (4)	O(6)···N(1)	3.171 (5)
O(9)···C(3)	3.179 (6)	O(6)···C(1)	3.180 (6)
Short equatorial HMX-HMX interactions			
O(7)···C(6)	3.110 (7)	O(12)···C(2)	3.109 (7)
O(7)···N(11)	3.227 (4)	O(12)···N(3)	3.231 (7)
O(7)···N(12)	3.243 (5)	O(12)···N(4)	3.264 (6)
O(7)···O(12)	3.274 (7)	O(12)···O(3)	3.287 (7)
Long equatorial HMX-HMX interactions			
O(8)···C(5)	3.311 (6)	O(11)···C(3)	3.320 (6)
O(8)···N(12)	3.349 (7)	O(11)···N(4)	3.371 (7)
O(8)···N(11)	3.402 (6)	O(11)···N(3)	3.395 (7)
O(8)···O(11)	3.334 (7)	O(11)···O(4)	3.352 (7)
Selected HMX-DMF interactions			
O(10)···C(8')	3.102 (13)	O(13)···C(2)	3.309 (11)
O(10)···C(7)	3.184 (15)	O(13)···C(3)	3.329 (15)
O(13)···C(1)	3.316 (12)	O(13)···C(4)	3.311 (13)

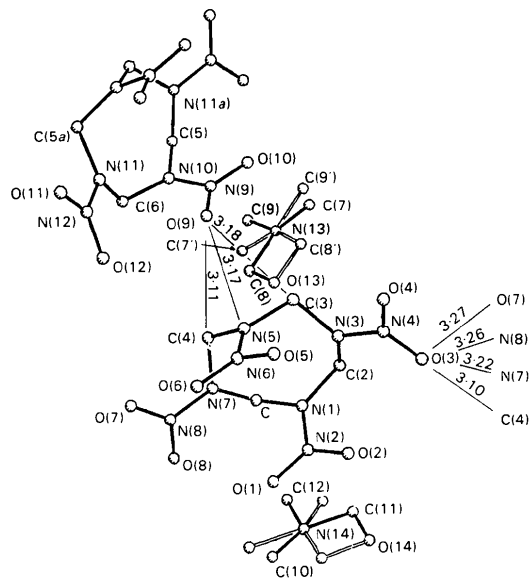


Fig. 1. The O···CNC and O···DMF interactions involving the axial NO<sub>2</sub> group of HMX. Some of the interactions between equatorial NO<sub>2</sub> groups are also represented ( $\text{\AA}$ ).

Disorder of the DMF molecule occurs in both  $\alpha$ - and  $\beta$ -HMX-DMF. However, the N and O atoms of the DMF molecules lie on the twofold axis in  $\alpha$ -HMX-DMF giving rise to two superimposed DMF molecules. In  $\beta$ -HMX-DMF, the DMF molecule also exhibits disorder about a twofold axis, but no atom lies on the axis. The disorder results in bond lengths and angles in the DMF molecule that are not particularly reliable.

The two polymorphs of HMX-DMF are subtly, but genuinely, different. The threefold axis of  $\beta$ -HMX-DMF is absent in  $\alpha$ -HMX-DMF. However, the projection of the unit cell of  $\alpha$ -HMX-DMF along what was the threefold axis of  $\beta$ -HMX-DMF reveals that the positioning of the molecules remains very similar when  $\beta$ -HMX-DMF converts to the  $\alpha$ -polymorph.

The atoms of the HMX molecule have alternating positive and negative charges (Stals, 1969) which contribute to the cohesion of the crystal lattice. Contacts can be analyzed qualitatively by using the van der Waals radii: C...N = 3.07, C...O = 2.97 and O...N = 2.90 Å. Intermolecular atom-atom contacts in  $\alpha$ -HMX-DMF (Table 4) exceed these distances and, therefore, the interactions are probably not strong.

The general features of intermolecular interactions in both polymorphs of HMX containing DMF solvate molecules can be summarized similarly. The oxygen atoms of the 'equatorial' NO<sub>2</sub> groups in each HMX molecule interact with a neighboring HMX molecule such that one oxygen atom associates relatively closely (3.10–3.29 Å) with the C<sup>(+)</sup>-N<sup>(-)</sup>-N<sup>(+)</sup>-O<sup>(-)</sup> ribbon of atoms while the other has relatively long interactions (3.26–3.40 Å) with the same set of atoms. The 'axial' NO<sub>2</sub> groups engage in intermolecular interactions with HMX and DMF as shown in Fig. 1. One oxygen atom is positioned at a distance of 3.09–3.19 Å from a neighboring C<sup>(+)</sup>-N<sup>(-)</sup>-C<sup>(+)</sup> band, while the other interacts at a distance of 3.10–3.22 Å with the N<sup>(-)</sup>-C<sup>(+)</sup> unit of the DMF molecule. In both polymorphs the equatorial NO<sub>2</sub> groups engage only in HMX intermolecular interactions, while in the axial NO<sub>2</sub> groups one oxygen atom associates with an HMX molecule and the other associates with a DMF molecule. In all cases the O<sup>(-)</sup>...C<sup>(+)</sup> interactions are the shortest. The DMF molecule in both polymorphs is situated in the face of the tetrazocine ring opposite the NO<sub>2</sub> groups. The oxygen atom is about equidistant (3.31–3.34 Å) from all four carbon atoms in  $\alpha$ -HMX-DMF. In  $\beta$ -HMX-DMF a wider range of O...C distances (3.18–3.45 Å) is found, but the average O...C distance of about 3.32 Å is essentially the same as that in  $\alpha$ -HMX-DMF. Some weak C-H...O hydrogen bonding may be suggested by this result.

In keeping with its lower density, the distances between HMX molecules in the crystal lattice of  $\alpha$ -HMX-DMF are expanded compared to those in pure HMX. Within a radius of 3.20 Å, O<sup>(-)</sup>...C<sup>(+)</sup> intermolecular contacts dominate: eight per molecule occur between HMX molecules and two per molecule

occur between HMX and DMF. The O<sup>(-)</sup>...C<sup>(+)</sup> contact distance between HMX molecules is longer on average by 0.05–0.10 Å than is observed in the unsolvated HMX structure. The shortest O<sup>(-)</sup>...C<sup>(+)</sup> contact is 3.09 Å. There are no O<sup>(-)</sup>...N<sup>(+)</sup> attractions in this range, whereas several occur in the polymorphs of pure HMX. By the same token, there are three O<sup>(-)</sup>...N<sup>(-)</sup> intermolecular repulsions between HMX molecules and two O<sup>(-)</sup>...N<sup>(-)</sup> repulsions between HMX and DMF. Significantly more O<sup>(-)</sup>...N<sup>(-)</sup> repulsions occur in pure HMX (Brill & Reese, 1980). Unlike what is found in pure HMX, no O...O contacts exist within a 3.20 Å radius about any oxygen atom.

Despite the expanded crystal lattice of HMX-DMF, it is informative to notice that a basic structural commonality is retained in all of the HMX structures solved to date. This is the association of the oxygen atoms of one HMX molecule with the CNC and CNNO ribbons of atoms in neighboring HMX molecules. These interactions suggest that the cohesive force within the solid is influenced in an important way by the association of these heavy-atom contacts. Thus, molecules which can be accommodated in the HMX crystal lattice must be able to participate in the same kinds of heavy-atom intermolecular interactions. While C-H...O hydrogen bonding may contribute to some extent, C-H...O interactions are not considered particularly strong (Donohue, 1968). Moreover, the infrared spectrum of the HMX-DMF complex offers little support for significant C-H...O hydrogen bonding (Castelli & Cragle, 1965).

The ring conformation adopted by the HMX molecule is chair-chair in all cases except in the most dense form of HMX,  $\beta$ -HMX. The less dense  $\alpha$ -,  $\gamma$ - and  $\delta$ -polymorphs and the DMF and *N*-methyl-2-pyrrolidinone solvates (Haller, Rheingold & Brill, 1983) all contain the chair ring conformation.

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## Methyl 3-(4-Chlorobenzoyl)-4-(4-chlorophenyl)-1-cyano-4-hydroxy-2,6-diphenylcyclohexanecarboxylate, $C_{34}H_{27}Cl_2NO_4$

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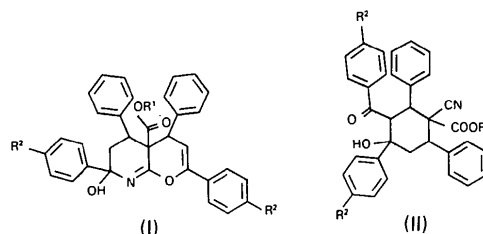
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**Abstract.**  $M_r = 584.5$ , triclinic,  $P\bar{1}$ ,  $a = 11.246$  (3),  $b = 12.265$  (3),  $c = 13.029$  (3) Å,  $\alpha = 86.41$  (2),  $\beta = 72.22$  (2),  $\gamma = 115.71$  (2)°,  $Z = 2$ ,  $V = 1501.7$  (7) Å<sup>3</sup>,  $D_x = 1.292$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.252$  mm<sup>-1</sup>,  $F(000) = 608$ ,  $T = 293$  K. Final  $R = 0.059$  for 2323 observed reflections. The structure proposed from chemical and spectroscopic considerations could be fully corroborated. The cyclohexane ring is in the chair conformation and is slightly strained, probably due to steric reasons. The phenyl rings are essentially planar and approximately perpendicular to the cyclohexane least-squares plane. There is an intramolecular hydrogen bond between the benzoyl O and the hydroxyl group.

**Introduction.** For the 2:1 reaction product from chalcone (1,3-diphenyl-2-propen-1-one) and esters of cyanoacetic acid there are different structures proposed in the literature. One is a non-cyclic structure (Kohler, Graustein & Merrill, 1922), whereas in another case the product from chalcone ( $R^2 = \text{H}$ ) and ethyl cyanoacetate ( $R^1 = \text{Et}$ ) is proposed as (I) (Degny, Zard, Pastor & Cambon, 1981). In the course of syntheses of pteridine analogues (Troschütz & Roth, 1978) the reaction was reinvestigated. From spectroscopic data (<sup>1</sup>H, <sup>13</sup>C, UV) the product from 4-chlorochalcone ( $R^2 = \text{Cl}$ ) and methyl cyanoacetate ( $R^1 = \text{Me}$ ) prepared according to Kohler *et al.* was concluded to possess the monocyclic structure (II). This is also supported by the finding of an

analogous monocyclic product obtained from chalcone and malononitrile (Soto, Seoane & Ciller, 1980). Since, however, (I) could not be discarded unambiguously from the spectroscopic investigations an X-ray analysis had to be undertaken in order to establish the true stereochemistry of the title compound.



**Experimental.** Colourless needles, crystal size  $0.25 \times 0.25 \times 0.3$  mm. Syntex  $P2_1$ , diffractometer, Mo  $K\alpha$  radiation, graphite monochromator. Lattice constants from angular settings of 24 independent reflections ( $15 < 2\theta < 30^\circ$ ). Range of  $hkl$ :  $-10-10$ ,  $-11-11$ ,  $0-13$ .  $2\theta_{\text{max}} = 42^\circ$  ( $2^\circ$  plus  $\alpha_1$ ,  $\alpha_2$  dispersion scan range, variable scan speed  $2-10^\circ \text{ min}^{-1}$ ). One check reflection after every 33 records. 3318 total reflections (omitting standards), adjustment of individual intensities to fluctuations of the standard intensities, 3117 unique reflections, 792 with  $|F| < 3\sigma$ .  $R_{\text{int}} = 0.02$ . No absorption correction. Analysis of normalized structure amplitudes clearly showed structure to be centrosymmetric ( $\langle E^2 - 1 \rangle = 0.97$ ); solved by use of direct-methods program *MULTAN* (Germain, Main &

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