

Structure of the Fourth Form of 1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane* (γ -HMX), $2C_4H_8N_8O_8 \cdot 0.5H_2O$

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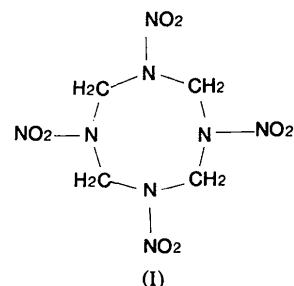
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Abstract. $M_r = 601.3$, monoclinic, Pn , $a = 13.27$ (1), $b = 7.90$ (1), $c = 10.95$ (1) Å, $\beta = 106.8$ (1)°, $V = 1099$ (3) Å³, $Z = 2$, $D_x = 1.82$, $D_m = 1.78$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 1.19$ cm⁻¹, $F(000) = 618$, $T = 293 \pm 3$ K, $R = 0.046$ for 1267 observed diffractometer-measured reflexions. The fourth form of the title compound is a hydrate. The two independent molecules in the unit of structure are similar to those in the α and δ polymorphs of HMX. Bond distances and angles and intermolecular contacts are similar to those in the α , β and δ polymorphs. Closest contacts to O of H₂O (site-occupation factor 0.5) are O...O (3.06, 3.00, 2.91, 3.10 Å), C...O (3.13 Å). Mean e.s.d. of bond lengths 0.011 Å.

Introduction. The structures of three of the four polymorphs of 1,3,5,7-tetranitro-1,3,5,7-tetracyclooctane (HMX) (I) have already been reported. The structure of the β form, stable at room temperature, was determined independently by Small (1947) and Eiland & Pepinsky (1955); it was subsequently refined using neutron data by Choi & Boutin (1970). The structure of the α form, stable between 377 and 429 K, was determined at room temperature by Cady, Larson & Cromer (1963). The form stable above 429 K, designated δ , was determined at room temperature by Cobbleddick & Small (1974). Molecules in the β form possess a crystallographic centre of symmetry and are quite different from those in the α polymorph which have twofold axial symmetry as a space-group requirement. Molecules with near, but not precise, twofold axial symmetry similar to those in the α form are found in δ -HMX. In the complex of HMX and dimethylformamide (Cobbleddick & Small, 1975) molecules are of the α type with crystallographic twofold axial symmetry [a second form of this complex, reported by

Haller, Rheingold & Brill (1983), has since been shown by Marsh (1984) to be identical to the one reported earlier].



The form of the HMX molecule with twofold symmetry or near twofold symmetry will be referred to henceforth as the α form and the 'axis' of this molecule will imply the twofold axial direction.

The remaining polymorph of HMX, γ , which has frequently been described as metastable for all temperatures at atmospheric pressure, is usually formed under conditions of rapid crystallization. Crystals of this form may be kept for long periods when solvent-free, although rapid transformation to the β form occurs on contact with solvent at room temperature.

Experimental. The crystals used in this investigation were prepared by the method described by Cady & Smith (1961) in which water is slowly dripped into a hot, almost saturated, acetone solution of HMX. The crystals were thin plates tabular on {100} showing also the forms {011}, {001} and {101}; the morphology strongly indicated no higher symmetry than class m .

Using Cu $K\alpha$ ($\lambda = 1.542$ Å) cell dimensions were obtained from oscillation and Weissenberg photographs; from systematic absences space group Pn assigned with two independent molecules as the unit of structure. Intensity data collected at 293 ± 3 K on a STADI-2 automatic two-circle diffractometer using graphite-monochromatized Mo $K\alpha$ from the layers $h0l$ to $h8l$

* Other names: cyclotetramethylenetetranitramine, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetraazocine.

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(1788 unique reflexions). A standard for each layer was measured every ten reflexions with an observed variation no greater than 1%. $2\theta_{\max} = 52^\circ$; beyond this value no measurable reflexions could be observed. No correction for absorption or secondary extinction. Data reduction and refinement of the structure performed with *SHELX76* (Sheldrick, 1976). Intensity statistics indicated an acentric distribution confirming the choice of non-centrosymmetric space group.

After several attempts to solve the structure with *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) a successful solution was obtained by the use of a version of *MULTAN* employing random starting phases. Refinement (on *F*) of positions and anisotropic temperature factors of C, N and O atoms for the two molecules proceeded using 1267 reflexions for which $I > 3\sigma(I)$. In the later cycles of the least-squares refinement methylene H's were included at calculated positions with C—H = 1.08 Å and individual isotropic temperature factors. When *R* was 0.057 the refinement appeared to have converged, but an ($F_o - F_c$) map showed one highly significant peak four times greater than any other feature. As this single maximum was approximately 3 Å from any other atom it was included as an O atom; the best refinement was obtained with a site-occupation factor of 0.5 and no improvement was obtained by making the temperature factor anisotropic. When the refinement had converged with shifts of any parameter less than 0.01 e.s.d. and no feature greater than 0.3 e Å⁻³ on the ($F_o - F_c$) map, the value of *R* was 0.046 (unit weights). Atomic scattering factors from *International Tables for X-ray Crystallography* (1962). The final coordinates are given in Table 1.*

As the most likely explanation of the isolated O atom was an interstitial water molecule, examination of the material was carried out (a) by a Karl Fischer titration and (b) by IR spectroscopy.

(a) A sample (0.8 g) of freshly prepared γ -HMX was dried in air for 24 h and then for 3 h over silica gel in a desiccator. It was left in contact with dry pyridine (12 g) in which it is only slightly soluble; after four days the γ -HMX was transformed to the β form and any water present transferred to the pyridine. The supernatant pyridine was removed and analysed for water content using a BTL Karl Fischer titration apparatus; a blank titration was also performed on the original dried pyridine. Water was found to be present in the γ -HMX [1.18 (15)% by weight], the amount expected from the structure determination (site occupation 0.5) being 1.47% by weight.

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42260 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and U_{eq} ($\times 10^4$)

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

	x	y	z	$U_{eq}(\text{Å}^2)$
C(1A)	6270*	6258 (11)	6525*	355
C(2A)	6780 (11)	3453 (10)	5730 (13)	352
C(3A)	4851 (10)	2784 (11)	4811 (12)	355
C(4A)	4352 (10)	5609 (11)	5578 (12)	359
N(1A)	6718 (9)	5238 (9)	5723 (11)	359
N(2A)	5927 (10)	2705 (9)	4722 (11)	362
N(3A)	4433 (9)	4458 (9)	4561 (11)	340
N(4A)	5210 (9)	6824 (8)	5883 (12)	394
N(5A)	7153 (10)	6087 (12)	4878 (12)	515
N(6A)	6184 (11)	1575 (11)	3903 (12)	501
N(7A)	3952 (9)	4891 (13)	3326 (12)	492
N(8A)	4983 (10)	8506 (10)	5702 (12)	410
O(1A)	7071 (10)	7631 (10)	4845 (12)	770
O(2A)	7557 (10)	5229 (11)	4255 (12)	850
O(3A)	7105 (10)	1422 (10)	3934 (11)	622
O(4A)	5471 (10)	746 (9)	3197 (10)	555
O(5A)	3933 (9)	3839 (12)	2510 (11)	609
O(6A)	3579 (11)	6299 (12)	3138 (12)	773
O(7A)	4081 (9)	8917 (8)	5155 (11)	547
O(8A)	5710 (9)	9511 (8)	6125 (12)	553
C(1B)	1975 (10)	1966 (12)	6679 (12)	410
C(2B)	1595 (10)	-875 (11)	5549 (12)	396
C(3B)	-345 (10)	-270 (11)	4968 (13)	421
C(4B)	6 (11)	2602 (13)	6079 (13)	493
N(1B)	1976 (9)	830 (9)	5630 (11)	377
N(2B)	533 (9)	-1027 (9)	4638 (10)	359
N(3B)	-334 (10)	1553 (10)	4963 (11)	427
N(4B)	1091 (9)	3155 (9)	6365 (11)	443
N(5B)	2238 (9)	1478 (12)	4584 (12)	442
N(6B)	348 (12)	-2106 (10)	3633 (12)	544
N(7B)	-534 (10)	2348 (14)	3787 (13)	531
N(8B)	1334 (11)	4853 (11)	6348 (12)	557
O(1B)	2498 (10)	2968 (10)	4663 (12)	644
O(2B)	2156 (9)	549 (10)	3691 (11)	543
O(3B)	1143 (10)	-2893 (10)	3513 (11)	629
O(4B)	-513 (10)	-2269 (11)	2926 (11)	624
O(5B)	-877 (10)	1448 (12)	2858 (11)	658
O(6B)	-352 (10)	3845 (11)	3785 (12)	748
O(7B)	579 (11)	5800 (10)	6202 (14)	854
O(8B)	2234 (11)	5294 (9)	6502 (13)	686
O(9)†	3224 (20)	-347 (27)	1803 (26)	1183‡

* Fixed value.

† Site occupation 0.5.

‡ U_{iso} .

(b) The presence of water in the crystals was confirmed by the presence of O—H stretching frequency bands in the IR spectrum. The bands were at 3672 and 3595 cm⁻¹ (compared with 3756 and 3657 cm⁻¹ for water vapour and 3445 and 3219 cm⁻¹ for liquid water). The sample was of material prepared as for the Karl Fischer analysis and was incorporated in a pressed KBr disc. A similarly prepared sample of β -HMX was entirely free of bands due to water.

Discussion. The two molecules of HMX and their relation to the crystal axes are shown in Fig. 1(a). A comparison with part of the structure of α -HMX, Fig. 1(b), shows that both molecules of the structural unit are of the α type. Pairs of molecules have their axes approximately parallel, Fig. 2, and are related by a pseudo glide plane parallel to (100) which probably accounts for the initial difficulty in solving the structure. Further comparison of Fig. 1(a) and (b) indicates some resemblance between the structures of γ - and α -HMX. An important difference, however, is that in α -HMX (space group *Fdd2*) the molecules all have their axes parallel to *c*, but in γ -HMX the axes of molecules

related by the n glide are staggered. A fuller discussion of the relations between the polymorphs together with new data on other forms will be presented in a later paper.

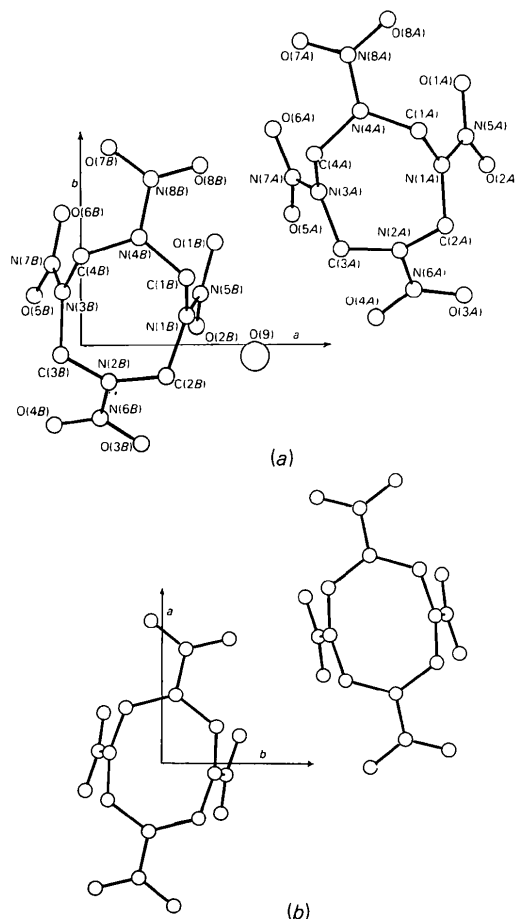


Fig. 1. (a) γ -HMX, projection along c . (b) α -HMX, projection along c .

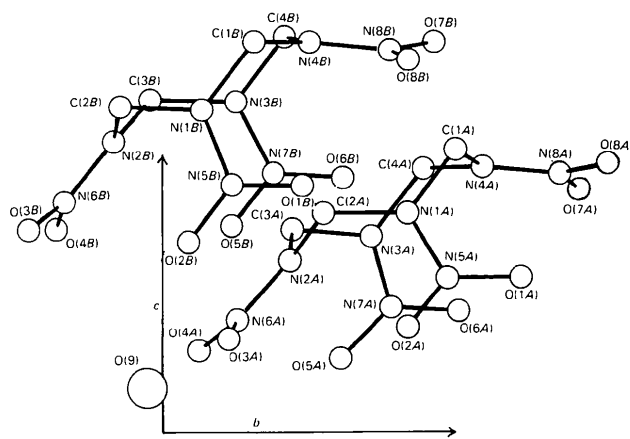


Fig. 2. γ -HMX, projection along a .

Bond distances and angles in the molecules (Table 2) are, within the limits of error, similar to those found in the other forms of HMX. The closest intermolecular contacts between HMX molecules, $C \cdots O$ (3.01 Å), $O \cdots N$ (2.89 Å) and $O \cdots O$ (2.90 Å), are again similar to those in other polymorphs. It should be noted that in none of the polymorphs involving α -type molecules has any high degree of precision been attained; mean e.s.d.'s are, in α 0.012 Å, in δ 0.020 Å and in the present work 0.011 Å. The most reliable determination of the α -type molecule is that in the HMX-DMF complex (Cobbledick & Small, 1975), mean e.s.d. 0.004 Å.

The additional atom O(9) is situated in a void in the structure, the closest approaches to it being: O(4A), 3.06, O(6A), 3.00, O(2B), 2.91 and O(1A), 3.10 Å. The values of these distances, taken together with the analytical evidence point to the presence of a molecule of water weakly hydrogen-bonded to O of HMX molecules and possibly accepting H from C(2A) and C(3B).

Table 2. Bond distances (Å) and angles ($^\circ$)

C(1A)—N(1A)	1.441 (12)	C(1B)—N(1B)	1.458 (13)
C(1A)—N(4A)	1.450 (11)	C(1B)—N(4B)	1.465 (12)
C(2A)—N(1A)	1.413 (11)	C(2B)—N(1B)	1.432 (12)
C(2A)—N(2A)	1.458 (11)	C(2B)—N(2B)	1.478 (12)
C(3A)—N(2A)	1.460 (11)	C(3B)—N(2B)	1.445 (12)
C(3A)—N(3A)	1.430 (11)	C(3B)—N(3B)	1.441 (12)
C(4A)—N(3A)	1.465 (12)	C(4B)—N(3B)	1.437 (13)
C(4A)—N(4A)	1.453 (11)	C(4B)—N(4B)	1.449 (13)
N(1A)—N(5A)	1.395 (12)	N(1B)—N(5B)	1.387 (11)
N(2A)—N(6A)	1.376 (11)	N(2B)—N(6B)	1.358 (11)
N(3A)—N(7A)	1.361 (11)	N(3B)—N(7B)	1.387 (11)
N(4A)—N(8A)	1.364 (10)	N(4B)—N(8B)	1.381 (11)
N(5A)—O(1A)	1.224 (11)	N(5B)—O(1B)	1.223 (11)
N(5A)—O(2A)	1.193 (11)	N(5B)—O(2B)	1.201 (11)
N(6A)—O(3A)	1.219 (11)	N(6B)—O(3B)	1.263 (12)
N(6A)—O(4A)	1.221 (11)	N(6B)—O(4B)	1.187 (11)
N(7A)—O(5A)	1.215 (12)	N(7B)—O(5B)	1.217 (12)
N(7A)—O(6A)	1.211 (11)	N(7B)—O(6B)	1.207 (12)
N(8A)—O(7A)	1.218 (10)	N(8B)—O(7B)	1.224 (12)
N(8A)—O(8A)	1.233 (10)	N(8B)—O(8B)	1.209 (12)
N(1A)—C(1A)—N(4A)	113.0 (7)	N(1B)—C(1B)—N(4B)	113.1 (7)
N(1A)—C(2A)—N(2A)	111.7 (7)	N(1B)—C(2B)—N(2B)	111.6 (7)
N(2A)—C(3A)—N(3A)	111.1 (7)	N(2B)—C(3B)—N(3B)	113.7 (7)
N(3A)—C(4A)—N(4A)	111.1 (7)	N(3B)—C(4B)—N(4B)	114.0 (8)
C(1A)—N(1A)—C(2A)	126.0 (8)	C(1B)—N(1B)—C(2B)	123.2 (7)
C(1A)—N(1A)—N(5A)	117.2 (7)	C(1B)—N(1B)—N(5B)	118.7 (7)
C(2A)—N(1A)—N(5A)	116.7 (8)	C(2B)—N(1B)—N(5B)	117.6 (8)
C(2A)—N(2A)—C(3A)	119.5 (7)	C(2B)—N(2B)—C(3B)	118.6 (7)
C(2A)—N(2A)—N(6A)	118.2 (8)	C(2B)—N(2B)—N(6B)	120.8 (8)
C(3A)—N(2A)—N(6A)	120.1 (7)	C(3B)—N(2B)—N(6B)	119.5 (8)
C(3A)—N(3A)—C(4A)	122.5 (7)	C(3B)—N(3B)—C(4B)	125.1 (8)
C(3A)—N(3A)—N(7A)	117.8 (8)	C(3B)—N(3B)—N(7B)	117.2 (8)
C(4A)—N(3A)—N(7A)	118.9 (7)	C(4B)—N(3B)—N(7B)	117.2 (8)
C(4A)—N(4A)—C(1A)	119.6 (7)	C(4B)—N(4B)—C(1B)	122.4 (7)
C(4A)—N(4A)—N(8A)	119.0 (7)	C(4B)—N(4B)—N(8B)	120.7 (8)
C(1A)—N(4A)—N(8A)	120.9 (7)	C(1B)—N(4B)—N(8B)	116.9 (8)
N(1A)—N(5A)—O(1A)	116.7 (9)	N(1B)—N(5B)—O(1B)	115.5 (9)
N(1A)—N(5A)—O(2A)	116.5 (9)	N(1B)—N(5B)—O(2B)	117.4 (8)
O(1A)—N(5A)—O(2A)	126.9 (10)	O(1B)—N(5B)—O(2B)	127.1 (9)
N(2A)—N(6A)—O(3A)	118.8 (9)	N(2B)—N(6B)—O(3B)	115.6 (10)
N(2A)—N(6A)—O(4A)	117.6 (9)	N(2B)—N(6B)—O(4B)	120.7 (10)
O(3A)—N(6A)—O(4A)	123.6 (9)	O(3B)—N(6B)—O(4B)	123.7 (9)
N(3A)—N(7A)—O(5A)	117.5 (9)	N(3B)—N(7B)—O(5B)	115.9 (9)
N(3A)—N(7A)—O(6A)	116.8 (9)	N(3B)—N(7B)—O(6B)	117.4 (10)
O(5A)—N(7A)—O(6A)	125.7 (9)	O(5B)—N(7B)—O(6B)	126.7 (11)
N(4A)—N(8A)—O(7A)	118.4 (8)	N(4B)—N(8B)—O(7B)	114.2 (10)
N(4A)—N(8A)—O(8A)	117.2 (8)	N(4B)—N(8B)—O(8B)	120.2 (9)
O(7A)—N(8A)—O(8A)	124.4 (8)	O(7B)—N(8B)—O(8B)	125.5 (9)

An anomalous feature of the physical properties of γ -HMX has been the difficulty in establishing conditions for the interconversion with other polymorphs (apart from the high-temperature conversion to δ -HMX). This structure determination indicates that water must be regarded as a component in the equilibrium. It is intended to pursue further experimental investigations into the thermodynamics of the HMX-H₂O system, in particular to measure vapour pressure and to determine the extent to which the H₂O composition can be varied.

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Structure of 1-(2-Hydroxyethyl)cytosine

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Abstract. C₆H₉N₃O₂, $M_r = 155.16$, orthorhombic, *Pbca*, $a = 12.376$ (1), $b = 7.554$ (1), $c = 15.407$ (1) Å, $V = 1440.3$ (1) Å³, $Z = 8$, $D_m = 1.435$, $D_x = 1.431$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54184$ Å, $\mu = 9.43$ cm⁻¹, $F(000) = 656$, room temperature, $R = 0.049$ for 1109 observed reflexions. The cytosine moieties form a pair through the N(4)–H···N(3) hydrogen bonds around the inversion centre. The hydroxyl group is hydrogen-bonded with the amino group, to form a sheet parallel to the *ac* plane, and with O(2) of an adjacent molecule, which links the sheets. The pyrimidine ring is planar within ± 0.027 Å.

Introduction. To reveal elementary binding patterns in protein–nucleic acid interactions, we have investigated

the structures of model crystals that contain nucleic acid base and an amino-acid side group: carboxyl group (Fujita, Takenaka & Sasada, 1982, 1983, 1984a; Takenaka & Sasada, 1982b), carbamoyl group (Fujita, Takenaka & Sasada, 1984b,c, 1985; Takimoto, Takenaka & Sasada, 1981, 1982), indolyl group (Ohki, Takenaka, Shimanouchi & Sasada, 1977) and imidazolyl group (Takenaka, Takimoto & Sasada, 1984). The hydroxyl group is also a functional group which could play a role in the protein–nucleic acid interactions. We have synthesized several model compounds having both nucleic acid base and a hydroxyl group and examined their crystal structures by X-ray analysis. The present paper deals with the hydrogen-bonding patterns between cytosine and the hydroxyl group.