The Crystal Structure of the Complex Formed Between 1,3,5,7-Tetranitro-1,3,5,7-Tetraazacyclooctane (HMX) and *N,N*-Dimethylformamide (DMF)

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The crystal structure of $C_4H_8N_8O_8.C_3H_7NO$ has been determined by direct methods with counter-measured X-ray data. The crystals are rhombohedral, space group $R\bar{3}c$ or $R3c$ with hexagonal cell dimensions $a = 15.989$ (8), $c = 30.920$ (12) Å and 18 molecules of HMX and DMF in the hexagonal unit cell. The final R was 0.063 for 1521 observed reflexions assuming space group $R\bar{3}c$. The HMX molecule has crystallographic twofold symmetry and is similar in shape to the α and δ polymorphs. The DMF molecules are disordered and the closest contacts between HMX and DMF molecules are between CH_2 groups and the carbonyl O atom.

Introduction

1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane (HMX) has four polymorphic forms (α, β, γ and δ) and the crystal structures of the α (Cady, Larson & Cromer, 1963), β (Small, 1947; Eiland & Pepinsky, 1955; Choi & Boutin, 1970) and δ polymorphs (Cobbledick & Small, 1974) have been reported. The ability of HMX to form solvates with a variety of organic solvents has been described (George, Cady, Rogers & Rohwer, 1965; Selig, 1967, 1969). These HMX solvates gradually lose solvent in air and become opaque pseudomorphs. The solvent complex formed between HMX and *N,N*-dimethylformamide (DMF), which is relatively stable, was chosen for a full structure determination. It is of interest to compare the shape of the HMX molecule in the solvate with that in the pure polymorphs and to investigate whether there are specific interactions, such as hydrogen bonding, between the HMX and DMF molecules.

Experimental

Crystals of HMX–DMF were grown by allowing a warm saturated solution of β-HMX in DMF to cool to room temperature. The crystals lose solvent slowly on removal from solution and were consequently sealed in Lindemann glass tubes. Preliminary photographs showed the crystals to be rhombohedral and the reflecting conditions $-h+k+l=3n$ for hkl and $l=2n$ for $h\bar{h}l$ indicated space group $R3c$ or $R\bar{3}c$. Cell dimensions based on a hexagonal unit cell were obtained from a least-squares refinement of θ values measured on a three-circle diffractometer (Small & Travers, 1961) with Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). Measurement of the density by flotation indicated a 1:1 molecular ratio of HMX to DMF which was confirmed by thermogravimetric analysis. Crystal

data are shown in Table 1. The cell dimensions are similar to those of the room temperature stable polymorph of the solvate formed between HMX and *N*-methyl-2-pyrrolidinone ($a = 16.60$, $c = 31.55$ Å) and the space group the same (George *et al.*, 1965).

Table 1. *Crystal data*

Chemical formula $C_4H_8N_8O_8.C_3H_7NO$
Rhombohedral, space group $R\bar{3}c$ or $R3c$

Hexagonal	$a = 15.989$ (8) Å
unit-cell	$c = 30.920$ (12)
dimensions	$V = 6845.2$ Å^3
	$Z = 18$
	$D_o = 1.614$ g cm^{-3}
	$D_c = 1.612$

Intensities were measured on the diffractometer with a crystal about $1.0 \times 1.0 \times 1.0$ mm. With Cu radiation out to $\sin\theta/\lambda = 0.64$ Å^{-1} 1709 unique integrated intensities were measured, of which 188 were classed as unobserved [$I < \sigma(I)$]. The intensities were corrected for Lorentz and polarization effects but not for absorption. The $N(z)$ test (Howells, Phillips & Rogers, 1950) showed a centric distribution.

Determination and refinement of the structure

The structure was solved by direct methods with *MULTAN* (Germain, Main & Woolfson, 1971). For $R\bar{3}c$ with $Z = 18$ the HMX molecules are required to lie in special positions (either centres of symmetry or twofold axes) and the DMF molecules to be disordered. For $R3c$ no such symmetry requirements are necessary. The 220 reflexions with $E > 1.5$ were used, the space group being treated as $R3c$ and also as $R\bar{3}c$. Both calculations revealed nearly identical structures both in terms of the HMX molecules and in disordering of the DMF molecules. In $R3c$ the HMX molecules have

approximate twofold symmetry with the DMF molecules occupying two sites (related by the pseudo-twofold axis through the HMX molecules) with approximately equal probability and in $R\bar{3}c$ the HMX molecules lie on crystallographic twofold axes and the DMF molecules are disordered in two sites related by the twofold axis as a requirement of the space-group symmetry. The space group thus was assumed to be $R\bar{3}c$ in the least-squares refinement with an asymmetric unit consisting of half a molecule of HMX and half a formula unit of DMF. The coordinates of the DMF atoms for one of the sites were used in the refinement with site occupancy factors of 0·5. R for the starting model was 0·416.

Anisotropic full-matrix least-squares refinement with *CRYLSQ* of the X-RAY System reduced R to 0·099 and a difference synthesis located the methylene H atoms of the HMX molecule and the aldehydic H atom of the disordered DMF as well as the methyl H atoms at a lower level of electron density. The H atoms were included in the model with U_{ij} values of the C atoms to which they are bonded. The C, N and O atomic parameters were refined for two cycles of *CRYLSQ* and finally the positional coordinates of the H atoms were included in the refinement for a further two cycles. The final R was 0·063 for 1521 observed reflexions with a maximum shift-to-error of 0·3 for the heavy atoms on the last cycle. Unit weights were used and scattering factors were from *International Tables for X-ray Crystallography* (1962). The final positional and thermal parameters are given in Tables 2 and 3 respectively.*

Discussion of the crystal structure

The HMX molecule has crystallographic twofold symmetry and is very similar in shape to the α polymorph

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31098 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1 NZ, England.

Table 2. *Fractional atomic coordinates* ($\times 10^5$ *for the heavy and* 10^4 *for the hydrogen atoms*)

	x	y	z
C(1)	8826 (19)	23543 (18)	4536 (9)
C(2)	18049 (19)	42094 (18)	4022 (10)
C(3)	40811 (45)	39200 (44)	8049 (24)
C(4)	41595 (73)	24755 (67)	9318 (39)
C(5)	56371 (56)	40231 (69)	7711 (42)
N(1)	9374 (14)	32697 (14)	3478 (7)
N(2)	17726 (15)	46830 (14)	7967 (7)
N(3)	968 (16)	32579 (17)	2579 (8)
N(4)	19032 (17)	56007 (16)	7749 (9)
N(5)	45950 (105)	34732 (197)	8677 (97)
O(1)	1429 (17)	40378 (17)	2005 (8)
O(2)	−6420 (14)	24714 (16)	2471 (8)
O(3)	19710 (18)	60132 (15)	11162 (8)
O(4)	19374 (18)	59370 (15)	4180 (8)
O(5)	32016 (64)	35163 (122)	8629 (123)
H(1)	588 (24)	1890 (24)	237 (11)
H(2)	1552 (25)	2436 (23)	449 (11)
H(3)	1873 (24)	4602 (24)	118 (11)
H(4)	2369 (24)	4058 (23)	405 (11)
H(5)	4581 (62)	4671 (58)	662 (27)
H(6)	4168 (95)	1950 (79)	757 (35)
H(7)	4462 (102)	2627 (81)	1136 (37)
H(8)	3541 (79)	2263 (78)	845 (42)
H(9)	5822 (68)	4572 (84)	676 (46)
H(10)	5936 (62)	4061 (72)	1094 (35)
H(11)	5880 (59)	3670 (73)	542 (33)

of HMX which also has crystallographic twofold symmetry, and to the δ polymorph which has approximate twofold symmetry. Stereoscopic views of the molecule are shown in Fig. 1. Bond distances and angles are given in Tables 4 and 5 and are comparable with those of α-, β- and δ-HMX. In common with α-, β- and δ-HMX and other nitramines, the nitramine groups are very nearly planar. The C atoms of the puckered eight-membered ring are planar within the limits of experimental error. The equations of least-squares planes and deviations of atoms from them are listed in Table 6; the figures in parentheses are the corresponding values for HMX in the α polymorph.

Table 3. *Thermal vibrational parameters* ($\times 10^4$)

The temperature factor equation has the form $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	418 (14)	362 (12)	663 (16)	223 (11)	18 (12)	−60 (11)
C(2)	403 (13)	362 (13)	657 (17)	177 (11)	26 (12)	−11 (11)
C(3)	525 (33)	480 (31)	947 (47)	265 (27)	−40 (32)	0 (32)
C(4)	734 (62)	568 (45)	1219 (77)	368 (44)	−67 (50)	−13 (51)
C(5)	456 (39)	860 (56)	1579 (89)	354 (41)	91 (47)	120 (57)
N(1)	342 (10)	384 (11)	626 (13)	208 (9)	−19 (9)	−51 (9)
N(2)	470 (12)	295 (10)	630 (13)	195 (9)	−40 (10)	−27 (9)
N(3)	479 (13)	588 (14)	632 (14)	317 (12)	−138 (11)	−134 (11)
N(4)	537 (14)	350 (12)	894 (18)	233 (11)	−51 (13)	−29 (12)
N(5)	457 (46)	599 (126)	808 (107)	331 (73)	−121 (38)	−215 (52)
O(1)	793 (16)	711 (14)	951 (17)	577 (13)	−226 (13)	−116 (12)
O(2)	414 (11)	688 (14)	922 (16)	288 (10)	−189 (10)	−207 (12)
O(3)	910 (17)	440 (12)	922 (16)	352 (12)	−73 (13)	−168 (11)
O(4)	976 (18)	455 (12)	932 (16)	401 (13)	−19 (14)	116 (12)
O(5)	505 (38)	1069 (125)	1176 (82)	502 (63)	71 (65)	69 (116)

The DMF molecules are disordered about two sites required by the symmetry of the space group with the N and O atoms lying approximately 0·25 Å from two-fold axes. In the refinement one molecule of DMF was used in the model with atomic site occupancy factors of 0·5. The overlap of average positions gives rise to large correlation coefficients, poor atomic coordinates and very high standard deviations. Within the limits

Table 4. Bond distances (Å)

N(2)-C(2)	1·450 (4)	N(5)-C(5)	1·474 (17)
C(2)-N(1)	1·458 (3)	C(1)-H(1)	0·93 (3)
C(1)-N(1)	1·459 (4)	C(1)-H(2)	1·01 (4)
N(1)-N(3)	1·363 (4)	C(2)-H(3)	1·05 (4)
N(2)-C(1')	1·453 (3)	C(2)-H(4)	1·04 (5)
N(2)-N(4)	1·377 (4)	C(3)-H(5)	1·15 (8)
N(3)-O(1)	1·225 (4)	C(4)-H(6)	1·00 (14)
N(3)-O(2)	1·222 (3)	C(4)-H(7)	0·76 (12)
N(4)-O(3)	1·220 (4)	C(4)-H(8)	0·91 (12)
N(4)-O(4)	1·217 (4)	C(5)-H(9)	0·83 (13)
C(3)-O(5)	1·232 (12)	C(5)-H(10)	1·09 (11)
C(3)-N(5)	1·345 (32)	C(5)-H(11)	1·09 (12)
N(5)-C(4)	1·399 (30)		

Table 5. Bond angles (°)

N(2)-C(2)-N(1)	111·8 (2)	N(2')-C(1)-H(1)	111 (2)
C(1)-N(1)-C(2)	123·8 (2)	N(2')-C(1)-H(2)	111 (2)
C(1)-N(1)-N(3)	117·9 (2)	H(3)-C(2)-H(4)	107 (3)
C(2)-N(1)-N(3)	117·5 (2)	N(1)-C(2)-H(3)	106 (2)
C(2)-N(2)-C(1')	119·7 (3)	N(1)-C(2)-H(4)	104 (2)
C(1')-N(2)-N(4)	119·0 (2)	N(2)-C(2)-H(3)	114 (2)
C(2)-N(2)-N(4)	119·3 (2)	N(2)-C(2)-H(4)	112 (2)
N(1)-N(3)-O(1)	117·3 (2)	O(5)-C(3)-H(5)	128 (6)
N(1)-N(3)-O(2)	117·3 (3)	N(5)-C(3)-H(5)	109 (6)
O(1)-N(3)-O(2)	125·4 (3)	N(5)-C(4)-H(6)	132 (6)
N(2)-N(4)-O(3)	117·3 (3)	N(5)-C(4)-H(7)	83 (9)
N(2)-N(4)-O(4)	117·7 (3)	N(5)-C(4)-H(8)	102 (8)
O(3)-N(4)-O(4)	125·0 (3)	H(6)-C(4)-H(7)	116 (15)
N(1)-C(1)-N(2')	111·8 (3)	H(6)-C(4)-H(8)	90 (12)
O(5)-C(3)-N(5)	122·7 (1·4)	H(7)-C(4)-H(8)	140 (14)
C(3)-N(5)-C(5)	117·5 (2·0)	N(5)-C(5)-H(9)	114 (8)
C(3)-N(5)-C(4)	122·5 (1·2)	N(5)-C(5)-H(10)	100 (5)
C(4)-N(5)-C(5)	118·6 (2·2)	N(5)-C(5)-H(11)	114 (4)
H(1)-C(1)-H(2)	100 (3)	H(9)-C(5)-H(10)	110 (10)
N(1)-C(1)-H(1)	113 (3)	H(9)-C(5)-H(11)	107 (11)
N(1)-C(1)-H(2)	110 (2)	H(10)-C(5)-H(11)	111 (9)

Table 6. Deviations of atoms from least-squares planes

The equations of the planes are referred to orthogonal axes a, b', c.

(a) Plane through N(1), N(3), O(1) and O(2)
$$-0.1997x + 0.0652y + 0.9777z = -1.5678$$

N(1)	0·001 (0·003) Å
N(3)	−0·005 (−0·010)
O(1)	0·002 (0·004)
O(2)	0·002 (0·004)
C(1)	0·110 (0·002)
C(2)	0·124 (0·103)

(b) Plane through N(2), N(4), O(3) and O(4)
$$-0.9238x - 0.3826y + 0.0156z = 1.6025$$

N(2)	0·001 (0·001) Å
N(4)	−0·002 (−0·005)
O(3)	0·001 (0·002)
O(4)	0·001 (0·002)
C(2)	−0·165 (−0·201)
C(1')	−0·188 (−0·102)

(c) Plane through C(1), C(2), C(1') and C(2')
$$1.0000x + 0.0000y + 0.0000z = 0.4751$$

C(1)	0·004 (0·041) Å	N(4)	−0·959 (0·854) Å
C(2)	−0·004 (−0·041)	O(1)	−2·524 (2·488)
N(1)	−0·640 (0·653)	O(2)	−2·527 (2·567)
N(2)	−0·434 (0·390)	O(3)	−1·181 (1·054)
N(3)	−1·975 (1·971)	O(4)	−1·173 (1·057)

(d) Plane through C(3), C(4), C(5), N(5) and O(5)
$$0.0308x + 0.2113y + 0.9769z = -3.7068$$

C(3)	−0·024 Å
C(4)	−0·024
C(5)	−0·022
N(5)	0·071
O(5)	0·000
H(5)	−0·229

(a)

(b)
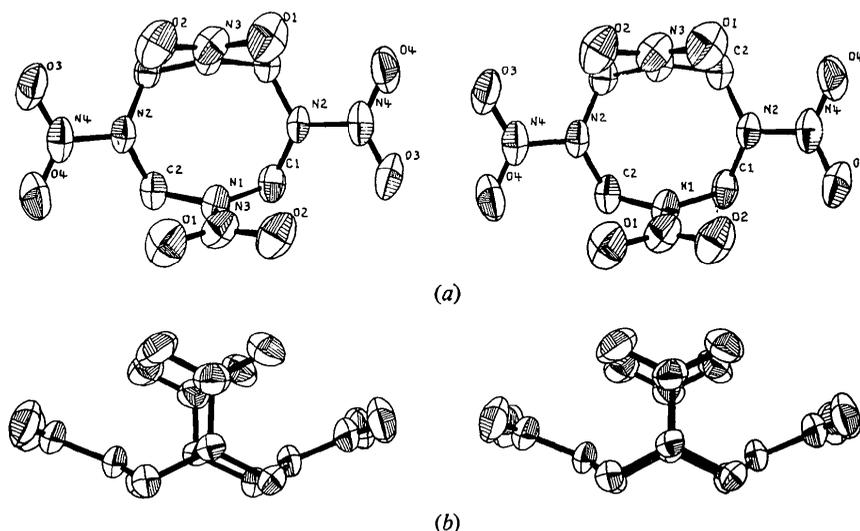
Fig. 1. Stereoscopic views of the HMX molecule drawn with ORTEP (Johnson, 1965), showing thermal ellipsoids with 50 % probability. (a) Molecule viewed from above. (b) Molecule viewed from the side.

of the errors, the bond distances and angles agree reasonably well with those found in the 1:1 complex formed between 1,7-diacetoxy-2,4,6-trinitro-2,4,6-tri-azaheptane (BSX) and DMF (Cobbledick & Small, 1973). The molecule is very nearly planar and details are shown in Table 6.

Table 7. *Intermolecular distances* (Å)

Equivalent positions

x	y	z	Superscript None
$1-y$	$1+x-y$	z	i
$-y$	$x-y$	z	ii
y	$-x+y$	$-z$	iii
$\frac{1}{3}-y$	$\frac{2}{3}-x$	$\frac{1}{3}+z$	iv
$\frac{1}{3}+x$	$\frac{2}{3}+x-y$	$\frac{1}{3}+z$	v
$\frac{1}{3}-x$	$\frac{2}{3}-x+y$	$\frac{1}{3}-z$	vi
$\frac{1}{3}+x-y$	$\frac{2}{3}-y$	$\frac{1}{3}-z$	vii

C(2)···O(5)	3·274 (23)	C(1)···O(2^{iii})	3·088 (4)
H(2)···O(5)	2·65 (4)	H(4)···O(2^{iii})	2·57 (4)
H(4)···O(5)	2·38 (5)	O(3)···H(1^{iv})	2·60 (4)
O(3)···O(3^i)	3·268 (6)	C(4)···O(1^v)	3·209 (13)
N(2)···O(3^i)	3·232 (3)		
N(4)···O(3^i)	3·261 (4)		
H(5)···O(1^i)	2·67 (7)	O(3)···C(1^{vi})	3·101 (3)
O(2)···H(6^{ii})	2·48 (12)	O(1)···C(4^{vi})	3·123 (11)
N(1)···O(2^{iii})	3·174 (4)	O(3)···H(2^{vi})	2·64 (2)
C(3)···O(1^{iii})	3·109 (8)	C(1)···O(5^{vii})	3·180 (16)
C(2)···O(2^{iii})	3·179 (4)	H(2)···O(5^{vii})	2·31 (4)
H(2)···O(2^{iii})	2·52 (3)	H(4)···O(5^{vii})	2·49 (5)

Table 8. *Geometry of the intermolecular* C–H···O *contacts*

C(2)····O(5)	3·27 (2) Å	C(2)–H(4)···O(5)	142°
C(2)–H(4)	1·04 (5)	C(3)–O(5)···C(2)	124
H(4)···O(5)	2·38 (5)	C(3)–O(5)···H(4)	115
C(1)····O(5)	3·45 (2)	C(1)–H(2)···O(5)	136
C(1)–H(2)	1·01 (4)	C(3)–O(5)···C(1)	150
H(2)···O(5)	2·65 (4)	C(3)–O(5)···H(2)	141
C(2')···O(5)	3·39 (2)	C(2')–H(4')···O(5)	143
C(2')–H(4')	1·04 (5)	C(3)–O(5)···C(2')	167
H(4')···O(5)	2·49 (5)	C(3)–O(5)···H(4')	157
C(1')···O(5)	3·18 (2)	C(1')–H(2')···O(5)	144
C(1')–H(2')	1·01 (4)	C(3)–O(5)···C(1')	131
H(2')···O(5)	2·31 (4)	C(3)–O(5)···H(2')	123

Fig. 2 shows the arrangement of molecules in one layer viewed down **c**. Intermolecular distances less than 3·30 Å between heavy atoms and less than 2·70 Å between heavy and H atoms are shown in Table 7. In the BSX–DMF structure an interesting feature is the close approach of the DMF carbonyl O atom to two nitro N atoms of the BSX molecule (2·891 and 2·969 Å). The interaction appears to be of a dipole type similar to the carbonyl–carbonyl interactions which have been observed in a number of structures. The HMX–DMF structure does not have any HMX-to-DMF interactions of this type and the closest contacts are between the DMF carbonyl O atom and CH_2 groups of the HMX molecule. Each DMF carbonyl O atom is in quite close contact with four methylene H atoms and the geometry of the contacts is shown in Table 8. The C–H···O angles are in the range 136–144° and may be attributed to C–H···O hydrogen bonding.
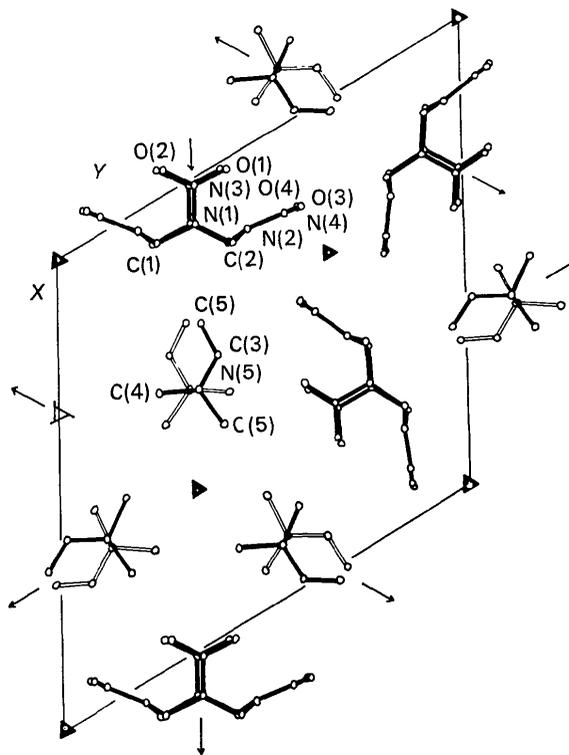
Fig. 2. Projection of the crystal structure showing the arrangement of molecules in one layer.

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