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The Crystal Structure of α-HMX and a Refinement of the Structure of β-HMX*

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The crystal structure of the α form of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, commonly known as cyclotetramethylene-tetranitramine or α-*HMX*, has been determined by single-crystal X-ray methods. The unit cell is orthorhombic, space group *Fdd*2 with

$$a = 15{\cdot}14,\ b = 23{\cdot}89,\ c = 5{\cdot}913\ \text{Å}.$$

There are eight molecules in the unit cell. The molecules have a basketlike shape with twofold symmetry. Bond lengths and angles all have normal values, but there are two rather short intermolecular C–O distances of 3·04 and 3·20 Å.

Introduction

The compound octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine is a well known explosive commonly called cyclotetramethylene-tetranitramine or HMX. There are four known polymorphic forms, the optical properties of which have been described by McCrone (1950). The crystallographic data on these forms are summarized in Table 1. The stable form at room temperature is β-HMX. The infrared spectra of α, γ and δ-HMX are similar to each other but are substantially different from that of β-HMX in the longer wavelength regions (Cady & Smith, 1961). In part I of this paper we give the crystal structure of α-HMX. In part II we present the results of a further refinement of the structure of β-HMX, based on the data of Eiland & Pepinsky (1955), hereafter referred to as EP.

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Part I.

Crystal structure of α-HMX

Experimental

The temperature range in which α-HMX is stable is approximately 103 to 162 °C (Cady & Smith, 1961). A mixture of tris(β-chloroethyl) phosphate and β-HMX was heated, with stirring, at 140 °C for about 24 hours. During this time complete conversion to α-HMX occurred and a few single crystals of suitable size and quality for X-ray work were obtained. The length, parallel to the *c* axis, of the selected crystal was about 200 μ. It had a triangular cross section bounded by (010), (110) and (1$\bar{1}$0). The width of the base of this triangle, which was the (010) cleavage face, was about 100 μ and its height was about 80 μ.

Precession and Weissenberg photographs were taken of this crystal and the space group was uniquely established as *Fdd*2 by systematic extinctions. Lattice

Table 1. *Summary of crystallographic data on HMX polymorphs*

Form	Space group	*a*	*b*	*c*	β	*Z*	d_m	d_c	Reference
α	*Fdd*2	15·14	23·89	5·913	—	8	1·84	1·839	This work
	*Fdd*2	15·14	23·75	5·92	—	8	1·83	1·848	Claringbull & Small (1961)
		15·17	24·03	5·92	—	8		1·823	Armour Research Foundation (1958)
β	$P2_1/n$	6·54	11·05	7·37	102·8	2	1·90	1·894	Eiland & Pepinsky (1955)
		6·50	10·93	7·32	103·3	2	1·91	1·943	Llewellyn & Small (1961)
γ	*Pc* or								
	*P*2/*c* or	10·95	7·93	14·61	119·4	4		1·78	Cady & Smith (1961)
	*P*2/*n*	13·28	7·93	10·95	106·5	4		1·78	
	*P*2/*n*	13·15	7·93	10·93	105·5	4	1·76	1·79	Claringbull & Small (1961)
δ	$P6_122$ or								
	$P6_522$	7·66	—	32·49	—	6	1·80	1·786	Claringbull & Small (1961)
		7·69	—	32·67	—	6		1·764	Armour Research Foundation (1958)

constants were measured on a carefully aligned General Electric Co. single-crystal orienter and found to be

$$a=15{\cdot}14,\ b=23{\cdot}89,\ c=5{\cdot}913\ \text{Å}$$
$$(\lambda\ \text{Mo}\ K\alpha_1=0{\cdot}70926\ \text{Å})\ .$$

With $Z=8$, the calculated density is 1·839 g.cm^{-3}. Literature values for the density range between 1·83 (Claringbull & Small, 1961) and 1·87 g.cm^{-3} (McCrone, 1950).

Intensity measurements were made with Mo $K\alpha$ radiation and a single-crystal orienter equipped with a scintillation counter. The crystal was mounted on its a axis. Background corrections were made by the balanced filter technique. Reflections within a sphere limited by $2\theta \leq 40°$ were examined. This sphere included reflections somewhat beyond the detection limit by film techniques. Since one half of the hemisphere was investigated, most of the equivalent reflections were measured twice. The agreement between equivalent values of $|F_{hkl}|^2$, expressed as

$$\Sigma||F_H|^2-|F_{H'}|^2|/\Sigma(|F_H|^2+|F_{H'}|^2)\ ,$$

where $H=hkl$ and $H'=hk\bar{l}$, was 4·8%. Within this sphere, 261 non-equivalent reflections were observed out of a possible 282. The usual Lp corrections were applied to give a set of observed $|F_{hkl}|^2$ values on a relative scale. No absorption corrections were applied.

Determination and refinement of the structure

There are eight molecules in the unit cell. Space group $Fdd2$ has a sixteenfold general position so that one half of the molecule is the asymmetric unit. The molecule is therefore required to have twofold symmetry, and the axis of the molecule must lie on a twofold symmetry axis. Because $Fdd2$ is a polar space group, the position of the molecule along the z axis is chosen arbitrarily. Fisher–Hirschfelder molecular models were assembled. These models could be formed into a large variety of shapes without breaking the bonds. These shapes ranged from the centric molecule found in β-HMX to a basketlike molecule with symmetry $4m$. Two different molecular models with twofold symmetry could be packed into the unit cell. One model, which subsequently proved to be correct, was basket shaped with all nitro groups on the same side of the ring. The other model had adjacent nitro groups on opposite sides of the ring.

A three-dimensional sharpened Patterson synthesis was computed. Only the first of the above models was compatible with the Patterson synthesis. Also, the orientation of the molecule with respect to rotation about the z axis could be established. This orientation was within the range estimated by packing.

Approximate x and y coordinates of the atoms, other than the hydrogen atoms, were determined from the $z=0$ section of the sharpened Patterson. Estimates of the z coordinates were determined from

Table 2. *Final α-HMX least-squares parameters*

Atom	x	y	z	B_{11} ×10^5	B_{22} ×10^5	B_{33} ×10^5	B_{12} ×10^5	B_{13} ×10^5	B_{23} ×10^5	B
C_1	0·0995±7	−0·0416±4	0·0	263±62	151±27	1753±423	118±67	−242±258	−151±165	
C_2	0·0660±7	0·0618±5	−0·0140±24	341±63	107±22	1724±446	−84±55	88±275	65±147	
N_1	0·0181±5	0·0599±3	0·1035±18	300±56	83±14	1257±373	1±45	−227±213	27±112	
N_2	0·1230±5	0·0153±3	0·0590±18	237±37	94±16	2052±297	−98±46	68±192	−91±132	
N_3	0·0210±6	−0·0726±3	0·3264±17	408±65	118±16	1901±479	−35±50	246±288	122±145	
N_4	0·2060±5	0·0266±3	0·1374±21	281±50	171±20	1734±339	−25±53	−180±184	−243±141	
O_1	−0·0493±5	−0·0877±3	0·4138±20	385±41	225±16	1820±254	−169±44	−35±177	310±117	
O_2	0·0903±5	−0·0670±3	0·4272±19	442±45	295±21	1988±262	−123±45	−904±239	19±122	
O_3	0·2563±4	−0·0133±3	0·1712±21	232±32	175±17	2279±226	58±38	−445±153	93±113	
O_4	0·2245±4	0·0757±3	0·1717±21	272±30	169±14	3638±280	−191±37	−137±177	404±122	
H_1	0·088 ±5	−0·043 ±3	−0·178 ±17							0 ±1·8 Å^2
	(0·087)	(−0·042)	(−0·175)							
H_2	0·142 ±6	−0·062 ±4	0·038 ±16							0 ±2·3
	(0·157)	(−0·063)	(0·035)							
H_3	0·060 ±8	0·059 ±5	−0·154 ±25							3·6±3·8
	(0·070)	(0·055)	(−0·180)							
H_4	0·102 ±5	0·099 ±3	0·027 ±14							0 ±1·8
	(0·108)	(0·095)	(0·037)							

Table 3. *Observed and calculated magnitudes of the structure factors for α-HMX*

The column headings are K, $10|F_o|$ and $10|F_c|$. If $|F_o|$ is negative the minus sign means 'less than'

H= 0 L= 0	H= 6 L= 0	H= 14 L= 0	H= 5 L= 1	H= 0 L= 2	H= 6 L= 2	H= 1 L= 3	H= 9 L= 3	H= 6 L= 4
	10-105 56	6 267 238	21 392 394	218271849	14 311 284	17-120 117	9 428 432	8-113 146
418041850	12-106 114	H= 1 L= 1	H= 7 L= 1	619541995	16 143 145	19 216 196	11 590 594	10 367 425
828932900	14 221 204	118531878	1 481 495	10 617 603	18 224 239	H= 3 L= 3	13 376 367	12 441 465
1213131339	16 165 99	312991319	3 501 507	14 206 197	H= 8 L= 2	1 291 298	H= 11 L= 3	H= 8 L= 4
16 602 595	18-118 65	519741962	5 196 187	18 262 255	2 852 834	3 295 266	1 147 136	0 465 459
20 556 587	20 465 471	71003 999	7 223 200	H= 2 L= 2	413871347	5 899 887	3 354 361	2 388 390
H= 2 L= 0	H= 8 L= 0	9 726 717	9 501 491	034453467	6 520 503	7 578 560	5 380 389	4 145 87
2 228 238	0 708 711	11 622 615	11 811 767	2 432 432	8 157 116	9 204 191	7 454 456	6 454 452
4 -90 17	2 414 395	13 589 607	13 226 220	4 490 489	10 281 247	11 385 378	H= 0 L= 4	8 368 375
631323096	4 948 962	15 571 565	15 460 432	6 831 827	12 182 147	13 615 627	010381073	10 317 324
8 -99 72	6 392 424	17 466 453	17 177 157	8 451 418	14 454 483	15 199 218	4 122 117	H= 10 L= 4
1011961170	8 524 537	19 387 392	19 348 351	10 314 307	16 260 279	17-116 89	8 162 165	2 203 217
1211711125	10 224 195	21 276 314	H= 9 L= 1	12 965 960	H= 10 L= 2	H= 5 L= 3	12 481 483	4 393 389
14 425 444	12 225 216	H= 3 L= 1	1 888 860	14 492 456	0 286 298	1 740 713	16-115 108	H= 1 L= 5
16 687 696	14 215 211	1 564 550	3 656 607	16 340 358	2 208 248	3 359 352	H= 2 L= 4	1 143 129
18 473 493	18 572 576	312801276	5 434 412	18 452 454	4 371 403	5-106 104	2 713 685	3 160 169
20 225 210	H= 10 L= 0	5 728 711	7 528 501	20 501 495	6 203 176	7 328 337	4 143 77	5 281 285
22-125 29	2 268 237	7 882 856	9 429 429	H= 4 L= 2	8-119 143	9 449 444	6 517 475	7 195 193
H= 4 L= 0	4 109 71	910831082	11 201 248	219871970	10 202 206	11 437 438	8 348 333	9 320 376
016561694	6-105 102	11 418 406	13 171 167	4 964 966	12 209 219	13 250 211	10-114 48	H= 3 L= 5
2 632 694	8 245 201	13 663 652	15 219 225	6 184 168	14 501 525	15 324 318	12 392 378	1 177 185
4 305 286	10 606 622	15 436 444	17 424 444	8 436 436	H= 12 L= 2	17 201 185	14 364 355	3 178 157
614431474	12 717 674	17 778 786	H= 11 L= 1	10 412 393	2 239 217	H= 7 L= 3	16-128 109	5-116 75
8 683 659	14 292 312	19 463 493	1 161 133	12 388 392	4 178 183	1 445 435	H= 4 L= 4	7 225 223
10 246 187	16 417 399	21 449 476	3 199 164	14 378 386	6 346 343	3 138 147	010391018	9 265 267
12 842 838	H= 12 L= 0	H= 5 L= 1	5-106 136	16 387 383	8 213 191	5 265 232	2 284 240	H= 5 L= 5
14 127 77	0 167 149	1 858 878	7 292 303	18 162 160	10 298 336	7 186 162	4 592 586	1 752 769
16 329 326	2 9931004	3 401 393	9 387 363	20 170 161	H= 1 L= 3	9 296 308	6 440 414	3 237 264
18 291 273	4 170 76	5 873 883	11 591 625	H= 6 L= 2	112251186	11 409 438	8 710 716	5 227 230
20 291 303	6 689 707	7 558 543	13 685 687	0 659 659	3 829 818	13 349 362	10 173 164	7 326 372
22 267 207	8 249 254	9 842 824	H= 13 L= 1	2 335 336	5 660 651	15 185 192	12 179 223	
H= 6 L= 0	10 684 711	11 674 635	1 282 291	4 434 427	7 597 571	H= 9 L= 3	14-113 78	
217711761	12-135 211	13 716 717	3 351 350	6 147 186	9 472 453	1 192 177	H= 6 L= 4	
413161324	H= 14 L= 0	15 362 340	5 706 729	81012 992	11 432 435	3 374 366	2 785 786	
6-105 95	2-142 108	17 169 155	7 578 612	10 441 426	13 502 488	5 332 344	4 831 850	
8 318 360	4 730 732	19 206 223	9 203 172	12 388 354	15 373 359	7 244 266	6 474 446	

the Fisher–Hirschfelder model. The coordinates were used as starting parameters in a least-squares refinement which minimized $\Sigma(\Delta F)^2$. Form factors were used in functional form with parameters given by Forsyth & Wells (1959). The full matrix was used and all observations were given unit weight. Isotropic temperature factors were initially applied. The z of C_1 was arbitrarily fixed at 0. The problem quickly converged and showed that the trial structure was correct. After four cycles the value of R was 8·9% including unobserved reflections. All atoms were then allowed to become anisotropic and R was reduced to 5·5% with unobserved reflections omitted. A difference-Fourier synthesis was then calculated in an attempt to locate the hydrogen atoms. Peaks of about 0·25 e.Å^{-3} in height were observed in reasonable locations. There were a few peaks of about 0·20 e.Å^{-3} but these were not in acceptable positions. The standard deviation of the electron density is estimated to be 0·1 e.Å^{-3} by Cruickshank's (1949) formula. The hydrogen atoms were not included in the phase calculations for the difference-Fourier synthesis; therefore the observed peak heights are about half their true value.

When hydrogen atoms in these positions were included in the calculated structure factors, R was reduced to 3·9%. An attempt was made to least-square isotropic hydrogen atoms with all other atoms anisotropic, and R was further reduced to 3·5%. The positions of the hydrogen atoms converged, but the temperature factors of three of these atoms tended to become negative. This anomalous behavior on the part of the hydrogen atoms probably arose from the fact that we now had 106 parameters and only 261 observations, even though the observations were reasonably accurate.

The final least-squares parameters are given in Table 2. The hydrogen positions from the difference-Fourier synthesis are given in parentheses in Table 2. The final observed and calculated structure factors, for which $R=3{\cdot}5\%$ with unobserved reflections excluded, are given in Table 3. The calculated values in Table 3 were made with the least-squares parameters of Table 2. As fractions of the standard deviations, the maximum shift was 0·023 and the mean shift 0·0067 in the last cycle. These values do not include the hydrogen atoms.

Discussion of the structure of α-HMX

A drawing of the molecule and a portion of the unit cell as viewed along the twofold z axis is shown in Fig. 1. A view along the y axis is shown in Fig. 2 and one along the x axis in Fig. 3. Hydrogen atoms are not shown in these figures. The interatomic distances and angles are given in Table 4. Distances and angles involving hydrogen atoms located by the difference-Fourier synthesis are given in parentheses. Many of these distances and angles are also shown in Figs. 1 and 2. The basketlike shape of the molecule can be seen clearly in these figures.

The bond distances all agree well with normal values and are essentially the same as found in β-HMX. The only unusual features in the structure of β-HMX are the two rather short intermolecular O–C distances of 3·04 and 3·14 Å. In α-HMX there

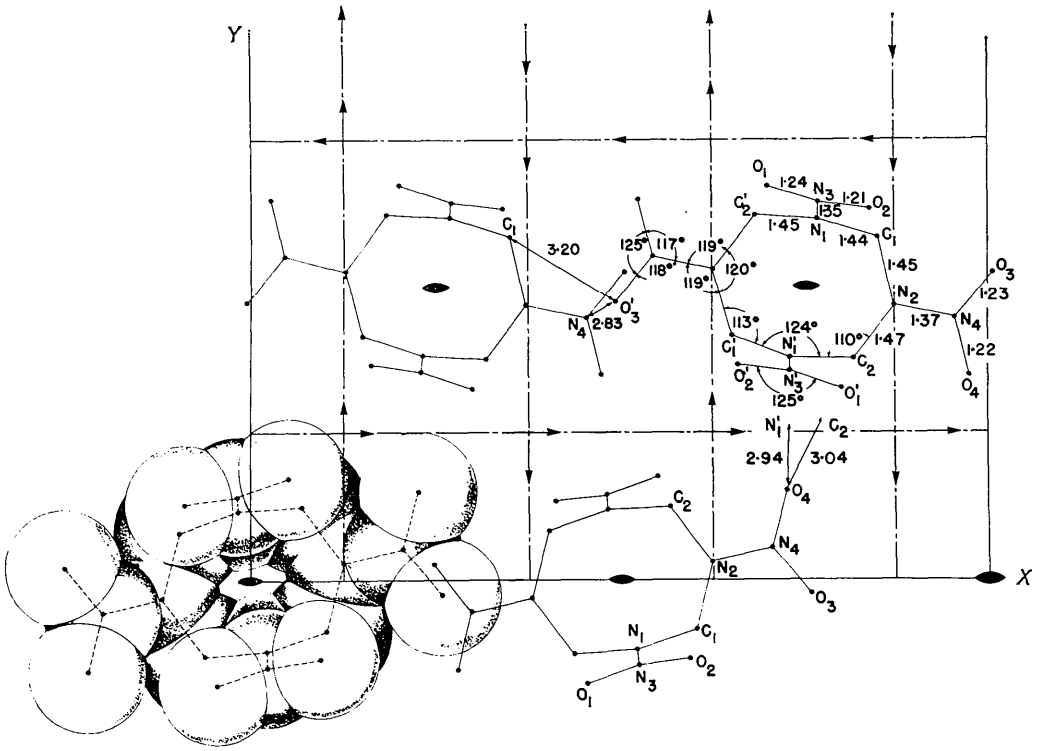


Fig. 1. α-HMX molecule and a portion of the unit cell as viewed along the z axis.

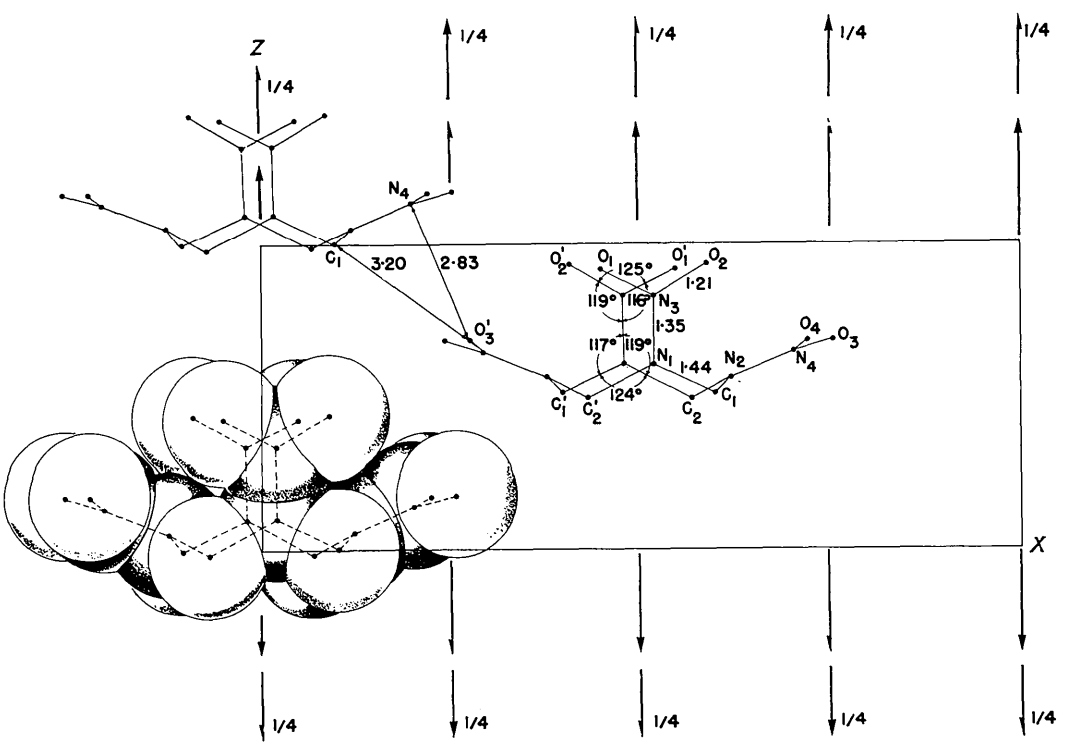


Fig. 2. α-HMX molecule and a portion of the unit cell as viewed along the y axis.

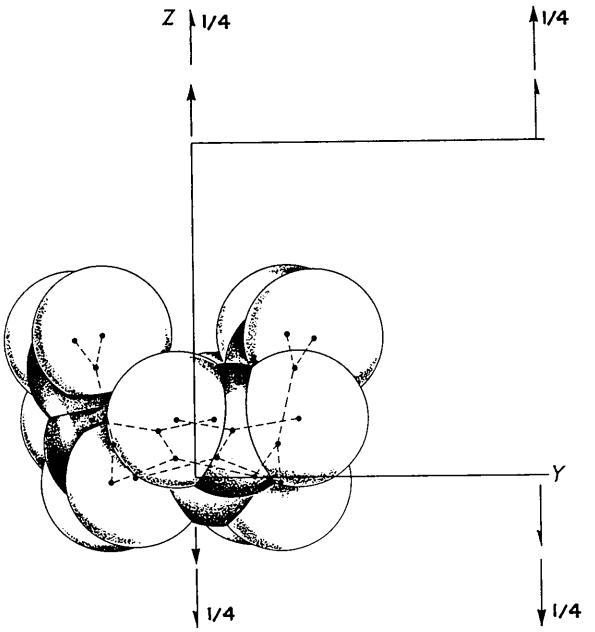


Fig. 3. α-HMX molecule as viewed along the x axis.

Table 4. *Interatomic distances and angles in* α-HMX

Bond	Distance (Å)	Angle (°)	
C_1–H_1	1·07 ±0·10 (1·05)	H_1–C_1–H_2	112 ±13 (109)
C_1–H_2	0·83 ±0·09 (1·02)	N_1–C_1–H_1	105 ±6 (105)
C_1–N_1	1·445±0·013	N_1–C_1–H_2	111 ±7 (119)
C_1–N_2	1·447±0·013	N_1–C_1–N_2	113·1±1·5
C_2–H_3	0·84 ±0·15 (1·00)	N_2–C_1–H_1	108 ±6 (107)
C_2–H_4	1·07 ±0·07 (1·06)	N_2–C_1–H_2	107 ±7 (102)
C_2–N_1'	1·450±0·014	H_3–C_2–H_4	110 ±15 (111)
C_2–N_2	1·471±0·014	N_1'–C_2–H_3	113 ±9 (121)
N_3–N_1	1·354±0·010	N_1'–C_2–H_4	112 ±6 (115)
N_3–O_1	1·238±0·013	N_2–C_2–H_3	107 ±9 (98)
N_3–O_2	1·215±0·013	N_2–C_2–H_4	105 ±5 (98)
N_4–N_2	1·367±0·012	N_2–C_2–N_1'	110·5±1·5
N_4–O_3	1·235±0·010	C_1–N_1–C_2'	123·8±1·1
N_4–O_4	1·225±0·010	C_1–N_1–N_3	116·9±1·4
Short intermolecular distances		C_2'–N_1–N_3	119·2±1·1
N_4–O_3'	2·837±0·017	C_1–N_2–C_2	119·7±1·5
C_2–O_4	3·045±0·013	C_1–N_2–N_4	119·4±1·5
C_1–O_3'	3·203±0·015	C_2–N_2–N_4	119·4±1·5
		N_1–N_3–O_1	116·3±1·5
		N_1–N_3–O_2	118·8±1·5
		O_1–N_3–O_2	124·9±1·7
		N_2–N_4–O_3	118·1±1·6
		N_2–N_4–O_4	117·0±1·6
		O_3–N_4–O_4	124·9±1·7

are also two short non-bonded O–C distances, namely C_2–O_4, 3·04 Å, and C_1–O_3', 3·20 Å.

The crystals show good cleavage on (010). The reason for this is made clear from an inspection of Fig. 1. Only intermolecular bonds need be broken when the crystal is cleaved on the glide plane normal to y.

The atoms in the N–NO_2 groups are essentially co-planar. The equations of the two pertinent planes are, for N_1, N_3, O_1 and O_2, $-0{\cdot}2301X+0{\cdot}9488Y+0{\cdot}2163Z+1{\cdot}2965=0$, and for N_2, N_4, O_3 and O_4, $-0{\cdot}3346X-0{\cdot}0770Y+0{\cdot}9393Z+0{\cdot}3255=0$. The distances of the atoms from these planes are given in Table 5. The entire nitramine groups of six atoms are more nearly co-planar in α-HMX than in β-HMX.

Table 5. *Distances of atoms from the* N–NO_2 *planes*

N_1–N_3(O_1,O_2)		N_2–N_4(O_3,O_4)	
N_1	0·003 Å	N_2	0·001 Å
N_3	−0·011	N_4	−0·005
O_1	0·004	O_3	0·002
O_2	0·004	O_4	0·002
C_1	0·003	C_1	−0·103
C_2'	0·102	C_2	−0·200

Table 6. *Magnitudes and direction angles, relative to the crystallographic axes, of the principal axes of the vibration ellipsoids*

Atom	Axis i	B_i (Å²)	α (°)	β (°)	γ (°)
N_1	1	2·9±0·5	20±18	91±18	110±18
	2	1·9±0·3	85±25	14±56	77±53
	3	1·6±0·5	71±18	104±56	24±36
N_2	1	2·6±0·3	56±22	117±21	134±34
	2	1·4±0·3	47±12	44±12	86±10
	3	3·1±0·3	62±24	121±20	44±34
N_3	1	3·9±0·6	19±20	97±20	72±25
	2	3·0±0·4	96±29	40±28	51±27
	3	2·2±0·4	108±16	129±28	44±27
N_4	1	2·8±0·4	30±25	99±16	119±24
	2	4·2±0·4	92±13	21±11	111±11
	3	1·9±0·4	60±25	71±10	37±21
C_1	1	1·9±0·5	31±23	111±32	69±57
	2	4·1±0·5	61±12	36±15	109±15
	3	2·3±0·5	100±54	63±28	29±46
C_2	1	3·5±0·5	30±19	120±20	87±27
	2	2·0±0·5	63±19	41±33	118±46
	3	2·5±0·5	79±31	65±43	28±46
O_1	1	3·1±0·3	32±13	72±10	64±21
	2	6·0±0·3	116± 6	30± 5	77± 5
	3	2·2±0·3	108±19	113± 8	30±19
O_2	1	4·9±0·3	42± 7	68± 8	124± 7
	2	7·1±0·4	110± 7	22± 8	82± 5
	3	1·6±0·3	55± 6	85± 4	36± 7
O_3	1	1·6±0·3	30± 8	102± 6	62± 8
	2	4·1±0·4	82±17	12±12	81±29
	3	3·6±0·3	119± 9	94±32	29±13
O_4	1	1·4±0·2	38± 6	56± 5	77± 5
	2	4·1±0·3	126± 6	54± 9	56±10
	3	5·9±0·3	80± 7	125± 8	37±10

The anisotropic thermal parameters were transformed to obtain the axes of the ellipsoids of thermal motion and the directions of these axes with respect to the crystallographic axes. The results are given

Table 7. *Least-squares parameters for β-HMX*

Atom	x	y	z	B_{11} $\times 10^4$	B_{22} $\times 10^4$	B_{33} $\times 10^4$	B_{12} $\times 10^4$	B_{13} $\times 10^4$	B_{23} $\times 10^4$
C_1	0·8024±21 (0·810)	0·0656±10 (0·065)	0·7817±15 (0·785)	275±44	80±10	203±24	−49±35	258±53	−22±26
C_2	0·2442±22 (0·245)	0·1144±11 (0·114)	0·0553±15 (0·053)	294±49	93±11	196±25	11±40	241±57	42±27
N_1	0·4055±20 (0·404)	−0·0006±10 (−0·004)	0·7081±14 (0·708)	383±48	85±10	215±24	2±35	288±54	−26±25
N_2	0·6593±18 (0·658)	−0·0260± 9 (−0·027)	0·7070±13 (0·708)	285±41	79± 9	196±21	−2±30	233±47	22±22
N_3	−0·0185±17 (−0·021)	0·1211± 8 (0·122)	−0·0376±12 (−0·039)	332±42	66± 8	192±21	15±28	334±49	−16±20
N_4	−0·1081±20 (−0·100)	0·2021± 9 (0·201)	0·0304±14 (0·032)	362±47	72± 9	219±23	39±32	309±54	13±23
O_1	0·3044±18 (0·311)	0·0719± 9 (0·073)	0·5808±13 (0·581)	434±42	114±10	233±21	47±35	154±47	25±25
O_2	0·2964±17 (0·299)	−0·0606± 9 (−0·060)	0·7597±13 (0·761)	360±40	117±10	280±23	−5±32	411±50	−6±24
O_3	0·0475±19 (0·044)	0·2464± 8 (0·246)	0·1816±13 (0·183)	579±47	89± 9	258±22	−11±35	332±54	−97±24
O_4	0·6692±18 (0·669)	0·2197± 8 (0·220)	−0·0650±13 (−0·063)	397±42	93± 9	285±22	105±30	391±51	28±23

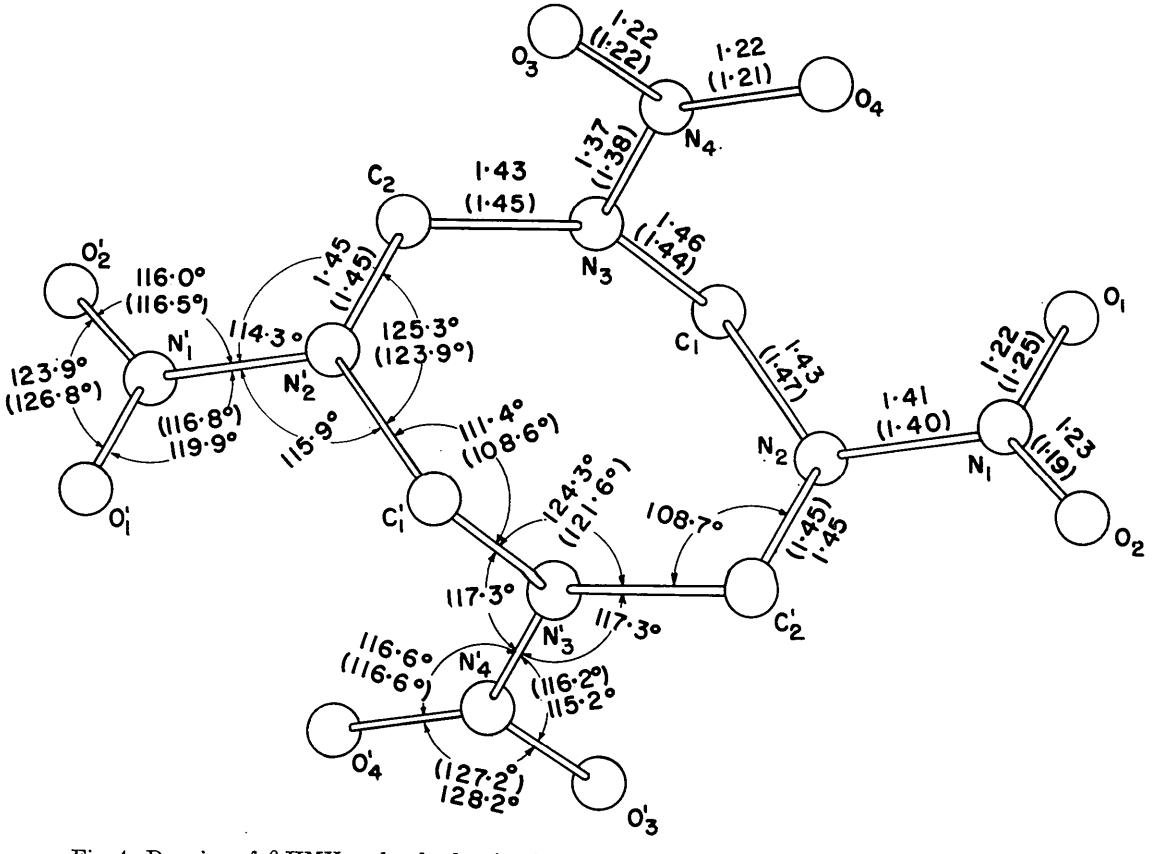


Fig. 4. Drawing of β-HMX molecule showing interatomic distances and angles. The distances given by EP are shown in parentheses.

in Table 6. The directions of the major axes of the vibration ellipsoids bear no consistent relationship to the normals to the planes of the nitramine groups. However, the orientation of most of the ellipsoids is not well defined because of the rather large standard deviation of the thermal parameters.

Part II.
Refinement of the structure of β-HMX

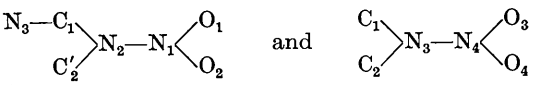
The data of EP for β-HMX (709 non-zero $F(hkl)$) were subjected to a least-squares refinement after transformation of the data from space group $P2_1/n$ to the standard orientation of $P2_1/c$. All details of the least-squares analysis were the same as for α-HMX. For the new orientation,

$$a=6{\cdot}54,\ b=11{\cdot}05,\ c=8{\cdot}70\ \text{Å};\ \beta=124{\cdot}3°.$$

EP report a final R of 18·7%. After least-squares refinement with anisotropic temperature factors, but not including hydrogen, R was reduced to 13·0%. Table 7 gives the final least-squares parameters and, in parentheses, our starting parameters which are the transformed parameters given by EP. Only the parameters x_{C_1}, x_{N_4}, x_{O_1}, and y_{N_1} have changed by more than three standard deviations. As a fraction of the standard deviation, the maximum shift was 0·0012, and the mean shift 0·0002 in the last cycle.

The bond distances and angles for β-HMX are shown in Fig. 4, in which the distances found by EP are shown in parentheses. The least-squares standard deviations of these bonds range between 0·012 and 0·020 Å. The two short intermolecular C–O distances found by EP changed from 3·01 and 3·12 Å to 3·04 and 3·14 Å.

EP state that the groups



are planar. We find that C_2', N_2, N_1, O_1, and O_2 are essentially planar but that N_3 is 0·15 Å and C_1 is 0·44 Å from this plane. Similarly, C_1, N_3, N_4, O_3 and O_4 are planar but C_2 is 0·23 Å from this plane.

Although the final R for α-HMX is very much lower than that for β-HMX, the standard deviations of the bond lengths are essentially the same. This illustrates the importance of having a large quantity of data as well as data of high accuracy. Application of Cruickshank's (1960) formulae to the results for both α and β-HMX shows that the errors in atom positions should be approximately the same for both polymorphs.

An IBM-704 was used for calculating the α-HMX Patterson. All other calculations were made with an IBM-7090 using programs written by the authors.

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Die Struktur des Kaliumpolyphosphats $(KPO_3)_x$

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The structure has been solved by means of a generalized Patterson function. It consists of polyphosphate chains of the same type as the silicate chains in diopside, and contains K^+ ions with 7 and 8 oxygen neighbours respectively.

Allgemeines

Beim Entwässern von KH_2PO_4 bildet sich Kaliumpolyphosphat $(KPO_3)_x$, eine Verbindung, die folgende interessante Eigenschaften besitzt:

Es existieren von ihr mehrere Modifikationen, die sich reversibel ineinander umwandeln (Thilo & Dostál, 1959). Unter Quellung können durch Austausch gegen Kalium organische Kationen, wie z.B. *n*-Hexylammonium-Ionen $C_6H_{13}.NH_3^+$ und Anilinium-Ionen $C_6H_5.NH_3^+$, eingelagert werden, zum Teil vielleicht sogar reversibel (Weiss & Michel, 1958). Es gibt zwei