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BY George R. Jordan, USCC

JANUARY

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NATIONAL DEFENSE RESEARCH COMMITTEE
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OSRD No. 452

Serial No. 274

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DIVISION B

**NATIONAL DEFENSE RESEARCH COMMITTEE
OF THE
OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT**

Section B-2

Report on "The Preparation of HMX" (Problem No. OD-12)

Endorsement (1) From F. C. Whitmore Chairman, Section B-2 to Roger Adams, Chairman, Division B. Forwarding report and noting:

"Complete directions for the preparation of HMX are presented along with a discussion of the properties and preliminary crystallographic measurements. The results should be useful in explaining and understanding some of the properties of Bachmann RDX which are due to the small amount of HMX present in it. It should be noted that HMX and products containing it may appear in highly sensitive forms. This problem is being actively studied at Michigan, Cornell and Pennsylvania State College.

(2) Twenty-three copies forwarded to Dr. Irvin Stewart, Secretary of the National Defense Research Committee, as Progress Report under Contract -(B-130, OEWar 243) with Pennsylvania State College.

**Roger Adams, Chairman
by Harris M. Chadwell
Technical Aide**

THE PREPARATION OF HMX

ABSTRACT

Interest in the properties of HMX made it necessary to prepare samples for testing. The details of the method used to prepare samples for du Pont, Bruceton and Dr. J. R. Johnson are given in this report. Analytical and crystallographic data on HMX and its intermediate DPT are included. The HMX was prepared according to the directions given by Wright (Progress Report, Project C.E.-12, November 1 - 30, 1941). Essentially, this involved the conversion of hexamethylenetetramine to the dinitrate, treatment of the dinitrate with acetic anhydride to get DPT (dinitropentamethylenetetramine), followed by nitration of the DPT in acetic anhydride with ammonium nitrate-nitric acid mixture.

Hexamethylenetetramine dinitrate was obtained in 88-97% yields from hexamethylenetetramine. The dinitrate was converted to DPT in yields of 11-32% and yields of 50-55% of HMX were obtained by nitrating DPT.

This report includes complete experimental data on each step of the process.

Crystallographic measurements and photomicrographs of two forms of HMX are included.

EXPERIMENTAL

I. The Preparation of Hexamethylenetetramine Dinitrate.

Hexamethylenetetramine dihydrate was prepared according to Bachmann's directions (Report Serial No. 88, page 12). To 700 ml. of water there was added 400 g (2.88 moles) of hexamethylenetetramine. The solution was cooled to 10°C. and 435 ml. (6.9 moles) of 70% nitric was added with stirring and cooling. The temperature was kept between 5° and 15°C. during the addition. After all of the nitric acid had been added, the suspension was cooled to 5°C and the dinitrate removed by filtration, washed with about a liter of acetone, and dried in air. The size of some of the runs was increased to one and one-half times the above amount.

increase in temperature above an undetermined point, or possibly, to the accumulation of a catalysing gas. Preliminary evidence indicated the importance of efficient stirring.

Based on the above observations the following procedure was used for the preparation of DPT.

To 305 g. (1.32 moles) of hexamethylenetetramine dinitrate, in a five liter round bottomed flask fitted with a thermometer and a stirrer, there was added 500 ml. (540 g., 5.29 moles) of acetic anhydride. The mixture was stirred vigorously. After the temperature rose 3° to 6°C . above that of the laboratory (25° to 27°C .), the reaction mixture was cooled to 15° to 20°C . by placing tap water in a bath surrounding the reaction flask. The suspension was stirred for a total of forty-eight hours. At the end of this time the mixture was filtered. The product was washed well with cold water, then allowed to dry in air for one or two days.

The filtrate from the DPT was diluted with 10 volumes of water. A gummy precipitate separated immediately. After standing from four to six hours the acetic acid-water solution was decanted from the precipitate. The precipitate was stirred with the same amount of water as used for the first dilution of the filtrate. After standing overnight in contact with the fresh water the precipitate was in the form of clumps which could be powdered easily. It was filtered and dried in air. The dry material had a strong odor of formaldehyde. It melted at 152° to 153°C . The melt was colored yellow-brown. At 142°C . some of the material sublimed leaving a white residue.

The precipitates recovered in this manner from the filtrates of all of the DPT runs were combined and saved for further investigation.

Data on a series of DPT runs are summarized in Table 1. Any variations from the procedure given above are shown in the Table.

Table 1

The Preparation of DPT

The Ac ₂ O was measured in ml., the wt. was calculated from the density									
HADN and Ac ₂ C used per run	Run No.	Reaction Time hrs.	Max. obs. Temp °C	DPT as isolated			M.p. with decomp. °C	Vol. of filtrate ml.	Wt. of ppt from filtrate Grams
				Grams	Moles	Yield %			
HADN									
133g.(0.5 moles)	T-1	48		14.9	0.068	13.67	192-198		
Ac ₂ O 222 ml									
240g. 2.35 moles									
HADN 440.2 g.									
1.66 moles	T-2	45	30	44.3	0.203	12.28	179-189		
Ac ₂ O 626 ml.									
675.6g. 6.62 moles									
HADN									
	A	52		85.9	0.394	29.85			
	B	52		86.6	0.397	30.01			
350 g.	C	52		83.6	0.384	29.05			
1.32 moles	D	72	30	75.3	0.345	26.17	195-205		
Ac ₂ O	E	48	36	81.6	0.374	28.36	195-202		
500 ml.	F	72	32	85.3	0.391	29.64	187-197		
540g.	G	47	28	93.1	0.427	32.35	192-199		
5.29 moles	H	48	30	86.5	0.397	30.06	197-204		
	I	48	27	68.2	0.313	23.70	193-204		
	J	24	25	77.6	0.356	26.97	198-205		
HADN									
	L	48	28	155.5	0.713	27.02	195-200	1210	9.7
700 g.	M	48	29	163.4	0.750	28.39	196-205	1110	8.4
2.64 moles	N	48	28.5	181.0	0.830	31.45	191-201	1100	14.8
Ac ₂ O	O	48	30	159.2	0.730	27.66	194-199	1130	14.0
1000 ml.	P*	48	31	66.8	0.306	11.61	196-203	1320	12.3
1080 g.	Q	72	30	143.9	0.660	25.00	183-187	1070	23.8
10.58 moles	R	50	31	164.8	0.756	28.64	185-189	1090	21.6
Total				1917.5	8.796	26.08			
HADN									
8973 g.									
19.8 lbs.									
33.73 moles									
Ac ₂ O									
10,748 ml									
13,876 g.									
30.6 lbs.									
136.04 moles									

*During this run the stirrer stopped during the night of the first 24 hours.

Table 2
Overall Yields on DPT Runs
Stirred for Different
Lengths of Time

Data from Runs T-1, T-2 and P are omitted									
No. of Runs	HADN		Acetic Anhydride			Reaction Time hrs.	DPT as isolated		
	Grams	Moles	ml.	Grams	Moles		Grams	Moles	Yield
1	350	1.32	500	540	5.29	24	77.6	0.356	26.97
8	4200	15.79	6000	6480	63.53	47-48	988.5	4.534	28.73
4	1750	6.58	2500	2700	26.47	50-52	420.9	1.931	29.34
2	1050	3.95	1500	1620	15.88	72	229.2	1.051	26.63

An examination of the tabulated data (Tables 1 and 2) shows that yields varying from 11 to 32% were obtained from reaction mixtures stirred for twenty-four to seventy-two hours. The variation between the yields from duplicate runs was of the same order of magnitude as the variation between reactions run for different lengths of time. However, from Table 2, which summarized the overall yields obtained from reactions run at different temperatures, it appears that a forty-eight to fifty hour period of stirring is the most satisfactory.

The Properties of DPT.

The properties of DPT determined in this laboratory and those described by Wright are listed below.

A. Properties Determined in this Laboratory.

1. The "melting point" of DPT, isolated as described above, was 193-205°C. The variation between the products from individual runs is shown in Table 1. All samples melted with decomposition and became colored (brown) about 15 degrees below "melting point". As the DPT "melted" some material sublimed. The portion of

sublimate appearing just above the melting DPT was crystalline (clear well formed crystals) while that higher in the tube appeared to have no definite crystalline form.

During combustion, in a micro determination of carbon and hydrogen, the sample of DPT twice gave flashes resembling an electrical discharge in an evacuated tube. At the same time as the flash, sublimed material appeared on the wall of the combustion tube. Later a sample of DPT was sublimed by heating to ca. 125° (ca. 1mm.) for a period of about ten hours. Both sublimate and residue were white and both gave a melting point of 202° - 205°C . (uncorr.) coloring at 193°C . Both of these melting points were typical for DPT, i.e., the melting was merely a tar formation rather than a well defined liquification.

2. Recrystallization of DPT from either acetone or nitromethane did not raise the melting point. The sample decomposed and sublimed as described above. It should be noted that in no case during melting point determinations did we get a melting point but rather a charring and extreme decomposition.
3. A 10 g. sample of DPT was boiled under reflux for eighteen minutes with 60 ml. of water. A vigorous evolution of formaldehyde occurred and a white solid separated on the walls of the condenser. No precipitate formed on cooling the clear solution remaining in the flask. This solution was basic to litmus paper.
4. HMX was prepared by adding DPT slowly to 98% Navy nitric acid, cooled with dry ice. A 21.1% yield of this material, m.p. 274° - 275°C ., was obtained.
5. Crystallographic data.

The DPT isolated from the reaction mixture was crystalline

but the crystals were pitted and slightly cloudy. On crystallization from nitromethane the crystals were transparent and the crystalline form was more regular. Optical measurement of these crystals is now in progress.

B. Properties given in Wright's Reports.

1. Melting point 205° - 206°C . (corr). Mp. after recrystallization from nitromethane, 203° - 208°C .
2. Anal. Calc. for $\text{C}_5\text{H}_{10}\text{N}_6\text{O}_4$: C, 27.51%, Found (wet method): C, 27.4%.
3. DPT is decomposed by dilute nitric acid.
4. DPT was converted to HMX by direct nitration with 100% nitric acid in a yield of 21%.
5. DPT decomposes to hexamine and paraformaldehyde at its melting point.
6. DPT decomposes when heated with water.

III. The Preparation of HMX.

The procedure described by Wright (Progress Report, Project C.E. - 12, November 1-30, 1941) was used for the preparation of HMX. Variations were introduced in several runs to observe their effect on the yield.

After making several trial runs of the preparation of HMX, the following procedure was used. A 54.5 g. (0.25 mole) sample of DPT was placed in a one liter, three necked flask fitted with a thermometer, a stirrer and a burette. To this, 251 ml. (271.3 g., 2.66 moles) of acetic anhydride was added. The temperature of the suspension was raised to 65°C . A solution of 59.6 g. (0.745 moles) of ammonium nitrate in 73.3 ml. (107.7 g., 1.71 moles) of Navy 98% nitric acid (vol. of solution was 107 ml.) was added to the suspension over a period of 30-40 minutes. The reaction temperature was maintained between 65° and 70°C . during the addition of the ammonium nitrate-nitric acid solution, by means of a water bath. After completing the addition of the nitrating reagent the reaction

mixture was aged for about 20 minutes at 55°-63°C., then cooled to 25°C. and held at that temperature for 10 minutes. The above time periods varied from run to run due to the difficulty in maintaining the desired temperature during the aging period.

The following observations were made during the course of the reaction. They illustrate the difficulties mentioned above.

During the addition of the first 50 ml. of nitrating solution there was a rise in the temperature of the reaction mixture immediately after the addition. At first this rise was rapid on adding 2 to 4 ml. of nitrating agent. After 15 to 20 ml. had been added the suspension almost cleared to form a solution. During the addition of the next 2 to 5 ml. a precipitate started to form, the amount of which gradually increased during the continued addition of the nitrating solution. After the addition of 40 to ml. the rise in temperature after addition became sluggish and a larger volume was required to give an equivalent rise in temperature, i.e., 10 to 15 ml. instead to 2 to 4 ml. While adding the rest of the nitrating solution, brown fumes were observed, which increased in amount until all of the reagent had been added and continued during the aging period at 55-63°C. At this point the suspension was very heavy and hard to stir. Aging at 55°-63°C. usually proceeded smoothly for the first 5 to 10 minutes, after which there was a tendency for the temperature to rise rapidly. This rise was accompanied by an evolution of brown fumes and was difficult to control even by cooling externally with ice. It was found that if a solution of 10 ml. of acetic anhydride and 90 ml. of acetic acid was added at this point the temperature could easily be lowered and controlled for the remaining aging period. No trouble was encountered in aging the reaction at 35°C., i.e. no tendency for the temperature to rise was exhibited at this temperature.

The reaction mixture was usually a heavy slurry after aging. It was poured on a mixture of 500 g. of ice and 200 cc. of water. A curdy, pale yellow

precipitate formed immediately. After standing from 2 to 4 hours the precipitate was filtered and washed with water. The water washings and filtrate were discarded. The precipitate had an odor of nitrogen oxides. It was "fumed off" with enough 70% nitric acid to give a clear solution when hot. On cooling this solution a crystalline precipitate of HMX formed. This was filtered and allowed to dry in air.

The data on the various runs are summarized in Tables.

It was observed that during the aging at 55°-63°C., if the water bath was removed, the temperature of the reaction mixture rose slowly at first but more rapidly after it reached 65-68°C. At this point the temperature was lowered to 60-63°C. with an ice bath, then the bath was removed and the temperature allowed to rise again. This process was in some instances repeated until the temperature of the reaction mixture began to fall on continued stirring. This accounts for the aging time in excess of 20 minutes as shown in the table.

An examination of the tabulated data shows.

- a) The best yields were obtained when the reaction was run at about 65°C., aged at 55°-62°C. for 20 to 40 minutes and at 25°C for 10 minutes (Yield 50-55%).
- b) Increasing the reaction temperature to about 75°C. caused the yield to be lowered (Yield 34%).
- c) Lowering the reaction temperature to about 60°C. had little effect on the yield (Yield 47%).
- d) Adding the dry DPT portionwise as in the Bachmann RDX preparation lowered the yield (Yield 36.2%).
- e) Adding all of the ammonium nitrate to the suspension of DPT - acetic anhydride at the beginning of the reaction caused a great decrease in the yield (Yield 6.9%).
- f) Treating the DPT with acetone to get it in a crystalline condition did not improve the yield when used to prepare HMX.

Preparation of P_8

Run	DPT used	Acetic Anhydride	% HNO_3	$10H_2NO_3$	Temp	Boiling Time	Aging Time	Yield	M_p										
No	Gms	Mols	ml	Gms	Mols	Temp	Temp	Mols	°C										
T-1	10	0.046	46.2	50.0	0.49	13	19.1	0.304	11.1	0.39	62.72	55.60	24	5	None	7.8	0.026	524	270
T-2	10	0.046	46.2	50.0	0.49	13.2	19.7	0.313	11.1	0.39	64.6	50	10	None	7.9	0.026	580	270	
T-3	10	0.046	46.2	50.0	0.49	13.4	19.7	0.319	11.1	0.39	65.70	15	20	None	7.2	0.026	523	270	
PSC-1	80	0.367	370	400	3.93	108	157	2.52	83.8	1.10	65.68	57	None	None	42.9	0.105	39.5	273	273
PSC-2	40	0.184	306	325	3.18	54	79.4	1.26	44.4	0.55	63.70	50.60	25.1	15	12	27.7	0.094	571	276
PSC-3	40	0.184	185	200	1.96	54	79.4	1.26	44.4	0.55	65.71	52.60	22	20	10	26.7	0.090	48.8	273
PSC-4	54.5	0.25	231	271.3	2.66	73.3	107.7	1.71	57.6	0.785	62.65	50.60	24	20	10	35.0	0.118	47.3	273
PSC-5	"	"	"	"	"	"	"	"	"	"	64.48	50.60	37	30	10	40.8	0.158	55.1	271
PSC-6	"	"	"	"	"	"	"	"	"	"	64.68	50.60	34	39	10	40.8	0.138	55.1	273
PSC-7	"	"	"	"	"	"	"	"	"	"	73.75	57.67	46	26	10	37.4	0.127	51	263
PSC-8	"	"	"	"	"	"	"	"	"	"	73.79	65.70	86	21	20	25.6	0.086	34.6	264
PSC-9	"	"	"	"	"	"	"	"	"	"	64.68	50.60	115	4	-	26.8	0.091	36.2	275
PSC-10	"	"	"	"	"	"	"	"	"	"	65.67	40.53	38	32	-	5.1	0.017	6.84	270
PSC-11	"	"	"	"	"	"	"	"	"	"	65.67	50.60	38	46	-	33.0	0.112	44.6	270
PSC-12	"	"	"	"	"	"	"	"	"	"	64.66	50.60	34	42	10	41.0	0.134	55.4	275

* DPT boiled with acetone.

○ Added HNO_3 only.

† Added a mixture of 10cc Ac_2O + 90cc $AcOH$ at end of reaction time.

‡ DPT added dry in portions.

Unfortunately, to facilitate the preparation of the amount of HMX required, it was necessary to use DPT from different runs in obtaining the above results. Since the DPT melted with decomposition the melting point is not a good criterion of purity and thus some of the effects observed may be due to the relative purity of the DPT used. Since the primary purpose of the work was to get large amounts of HMX for testing, the above may be considered only preliminary conclusions.

Two additional runs were made in which the reaction mixture was poured on ice at the point at which the suspension cleared, in one instance, and at the point where the addition of nitrating agent effect only a small rise in temperature. Investigation of the products from these runs is being held up until the sensitivity of the products has been determined.

The melting point of HMX isolated as above was in most cases 272° - 274° C. and was accompanied by the evolution of gas.

Since the observed "melting point" is really a point of decomposition, it might be wise to refer to decomposition point (D.p.) in the future rather than melting point.

Anal.

Calc. for $C_4H_8N_8O_8$	C = 16.22%
	H = 2.73%
	N = 37.83%

Found.	C = 16.25%
	H = 2.71%
	N = 37.61%

The examination, microscopically, of the product from a standard preparation of HMX by the Wright process after "fuming off" in 70% nitric acid, showed two crystalline habits; thick prisms and plates and also acicular crystals (Figs. 1 and 2).

Dr. Johnson, in a private communication of April 9, 1942, on the crystal forms of HMX, stated that HMX existed in two forms.

α - form - "elongated orthorhombic pinacoids" - probably orthorhombic

- from - monoclinic bipyramids and pinacoids, and a monoclinic acicular form.

Included are photomicrographs of HMX recrystallized from 70% nitric acid (Fig. 3) and that recrystallized from 35% nitric acid (Fig. 4). The HMX used for the above recrystallizations was the product of numerous preparations by the Wright process and had, previous to recrystallization, been "fumed-off", in 70% nitric acid. The material as pictured in Fig. 3 has a sensitivity of about 60 cm. as determined on the crude sensitivity equipment of this laboratory. The impact sensitivity machine used in this laboratory has usually given fall heights (5 Kg. wt.) 10-20 cm. lower than the Bruceton figures. At present, however, no direct comparison with our results and Bruceton's results can be made.

The HMX prepared in this laboratory, for Bruceton, had a sensitivity of 6 cm. This sample of HMX was the combined product of several preparations according to Wright's method all of which were "fumed-off" in 70% nitric acid. The great difference in sensitivities between the product sent to Bruceton and that obtained by recrystallization from 70% nitric acid (Fig. 3) is not yet accounted for. It should be pointed out, however, that the product sent to Bruceton consisted of about 10% acicular type crystals and about 90% of the bipyramidal and pinacoidal type whereas a sample of the material as pictured in Fig. 3 appeared to be free of the acicular type crystals.

Preliminary work in this laboratory on recrystallization of this sensitive material from other solvents seems to indicate that the sensitivity can be greatly decreased merely by recrystallization.

A sample of the sensitive material sent to Bruceton was recrystallized from nitromethane and showed a sensitivity of about 70 cm. as determined in this Laboratory.

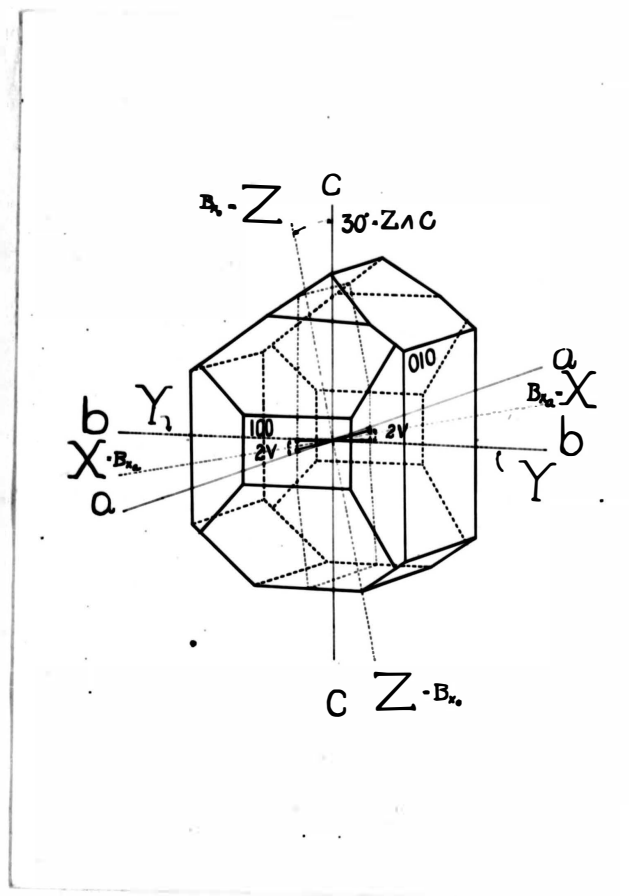


Fig. 1

Refractive Indices at $25^{\circ} \pm 3^{\circ}$ $\alpha = 1.587$ $\beta = 1.595$ $\gamma = 1.597$
 All ± 0.003

Birefringence = 0.010

Optical Axial Angle: $2V$ (Mallard's Constant) = $8^{\circ} \pm 2^{\circ}$

Dispersion: Small

Optical Character: Negative

Crystal System: Monoclinic

Crystal Habit: Thick prisms and tablets

Optical Orientation: Optical axial plane = 010
 $Z \wedge C = 30^{\circ}$ $X = B_{xa}$

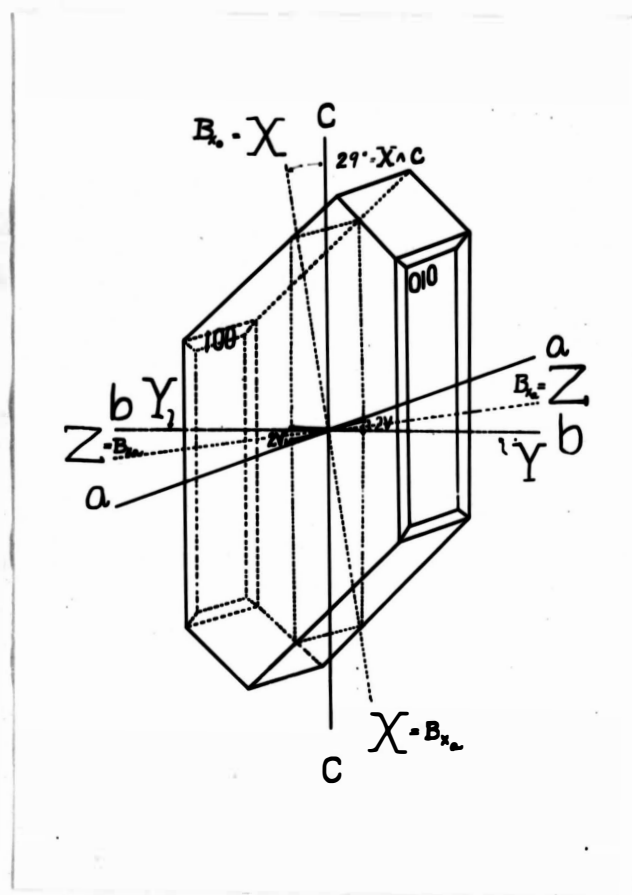


Fig. 2

Refractive Indices at $25^{\circ} \pm 3^{\circ}$ $\alpha = 1.565$ $\beta = 1.575$ $\gamma = 1.640$

Birefringence: 0.075

Optical Axial Angle = $2V = 8^{\circ} \pm 2^{\circ}$

Dispersion: Small

Optical Character: Positive

Crystal System: Monoclinic

Crystal Habit: Acicular

Optical Orientation: Optical axial plane = 010

$B_{x_0} = X$ $X \wedge C = 29^{\circ}$

ATI-30058

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AUTHOR(S): Whitmore, F. C.					
ORIGINATING AGENCY: Pennsylvania State College					
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ABSTRACT: Details of the preparation of HMX are included in this report, along with analytical and crystallographic data on HMX and its intermediate DPT. The preparation of HMX involved the conversion of hexamethylenetetramine to the dinitrate, treatment of the dinitrate with acetic anhydride to get DPT (dinitropentamethylenetetramine) followed by nitration of the DPT in acetic anhydride with ammonium nitrate-nitric acid mixture. Hexamethylenetetramine dinitrate was obtained in 88-97% yields from hexamethylenetetramine. The dinitrate was converted to DPT in yields of 11-32%, and yields of 50-55% of HMX were obtained by nitrating DPT. Complete experimental data on each step of the process are given along with crystallographic measurements and photomicrographs of two forms of HMX.					
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x HMX
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