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NOLTR 62-82

HEAT RESISTANT EXPLOSIVES.
XIII. PREPARATION AND PROPERTIES
OF 3,3'-DIAMINO-2,2',4,4',6,6'-
HEXANITROBIPHENYL (DIPAM) (C)

RELEASED TO ASTIA
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16 May 1962

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HEAT RESISTANT EXPLOSIVES. XIII. PREPARATION AND PROPERTIES OF
3,3'-DIAMINO-2,2',4,4',6,6'-HEXANITROBIPHENYL (DIPAM) (C)

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ABSTRACT: A new oxidative procedure wherein the methyl group in substituted trinitrotoluene derivatives is replaced by hydroxyl has been applied to the preparation of the title compound, a new thermally stable high explosive. The six-step synthesis involved the sequence: m-bromotoluene to bromotrinitrotoluene to dimethylhexanitrobiphenyl to dipicric acid to dipyridinium dipicrate to dichlorohexanitrobiphenyl to DIPAM. The overall yield was 39.5%. DIPAM appears to have attractive potentialities for high temperature mild detonating fuse and similar applications. (C)

CHEMISTRY RESEARCH DEPARTMENT
U. S. Naval Ordnance Laboratory
White Oak, Silver Spring, Maryland

NOLTR 62-82

16 May 1962

↓
This report describes the preparation of 600 grams of a new thermally stable high explosive which may be useful in mild detonating fuse for stage separation in advanced POLARIS missiles. ↑ The work was started under Task FR-44, but as the potential applications became apparent it was transferred to RUME 3E017. The newly-discovered reaction described in NOLTR 62-32 furnished the basis for this synthesis.

W. D. COLEMAN
Captain, USN
Commander

Albert Lightbody
ALBERT LIGHTBODY
By direction

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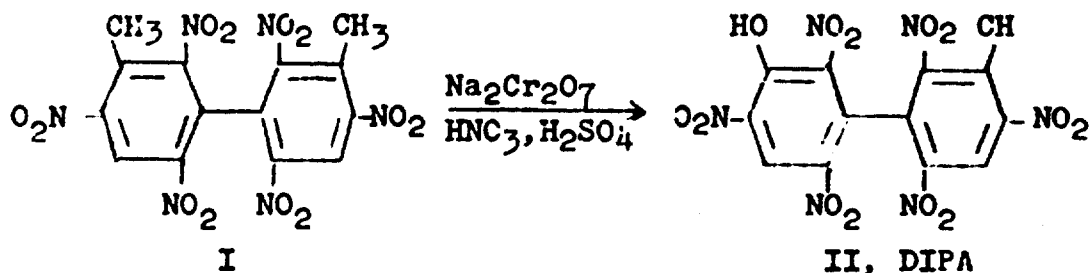
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NOLTR 62-82

TABLE OF CONTENTS

	Page
INTRODUCTION	1
DISCUSSION	2
a) m-Bromotoluene to 3-Bromo-2,4,6-trinitrotoluene ...	2
b) 3-Bromo-2,4,6-trinitrotoluene to 3,3'-Dimethyl- 2,2',4,4',6,6'-hexanitrobiphenyl	3
c) 3,3'-Dimethyl-2,2',4,4',6,6'-hexanitrobiphenyl to Dipicric Acid	4
d) Dipicric Acid to Dipyridinium Dipicrate	4
e) Dipyridinium Dipicrate to Dipicryl Chloride	5
f) Dipicryl Chloride to Dipicramide	6
PROPERTIES OF DIPAM	7
EXPERIMENTAL	8
3-Bromo-2,4,6-trinitrotoluene	8
3,3'-Dimethyl-2,2',4,4',6,6'-hexanitrobiphenyl	8
Dipicric Acid (DIPA)	9
Dipyridinium Dipicrate	10
3,3'-Dichloro-2,2',4,4',6,6'-hexanitrobiphenyl (DIPICL)	10
3,3'-Diamino-2,2',4,4',6,6'-hexanitrobiphenyl (DIPAM)	11
REFERENCES	12

INTRODUCTION

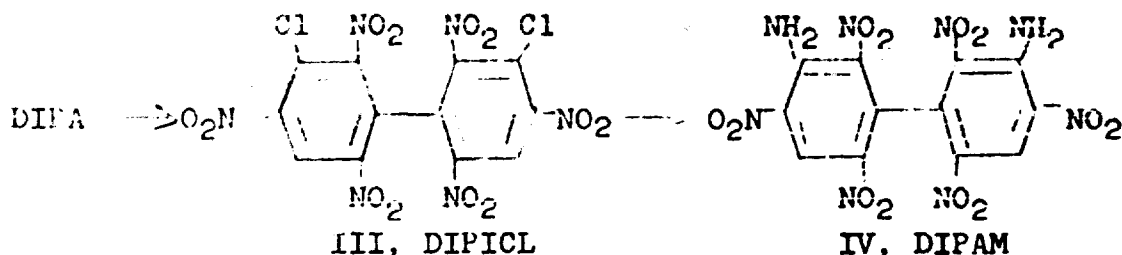
We have reported (1) that oxidations of TNT and 3-substituted 2,4,6-trinitrotoluene derivatives with mixtures of dichromate, nitric acid and sulfuric acid generally effected their conversion to the correspondingly substituted trinitrophenols. In the case of 3,3'-dimethyl-2,2',4,4',6,6'-hexanitrobiphenyl (I), the main product was 3,3'-dihydroxy-2,2',4,4',6,6'-hexanitrobiphenyl (dipicric acid, DIPA, II) rather than the 3,3'-dicarboxylic acid as earlier workers had suggested (2).



Although DIPA has long been known, a number of investigators having reported its preparation by the mixed-acid nitration of 3,3'-dihydroxybiphenyl (3), the novel dichromate oxidation provided for the first time a convenient method for its synthesis. With its availability in moderate quantities, DIPA merited consideration per se as a candidate for high-temperature booster explosive applications (1) but of greater immediate interest was its potential as an intermediate for further synthesis.

Treatment of the dipyridinium salt with phosphorus oxychloride, a procedure which has been reported to effect the high-yield transformation of picric acid to picryl chloride (4) and styphnic acid to styphnyl chloride (5), afforded a convenient method for the conversion of II to 3,3'-dichloro-2,2',4,4',6,6'-hexanitrobiphenyl (dipicryl chloride, DIPICL, III). DIPICL, with ethanolic ammonia, was readily converted to 3,3'-diamino-2,2',4,4',6,6'-hexanitrobiphenyl (dipicramide, DIPAM, IV), the subject of the present report.

CONFIDENTIAL
NOLTR 62-82

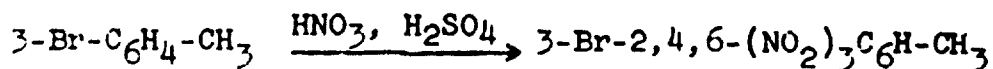


Shortly after the first preparation of DIPAM, there came to our attention an urgent requirement for a thermally stable high explosive which was relatively non-volatile at advanced temperatures and reduced pressures and which would propagate detonation in relatively small diameters, this material to be used in mild detonating fuse (MDF) for stage separation in advanced POLARIS missiles. Preliminary experiments in our laboratories, vide infra, indicated that our new product might satisfy the former requirement; from its chemical similarity to picramide*, we felt it might prove adequate in the latter regard. For this reason we undertook the preparation of over six hundred grams of DIPAM for evaluation both at NOL and in the laboratories of Lockheed Aircraft Corporation.

DISCUSSION

From commercially available m-bromotoluene, the synthesis of DIPAM involves the six-step sequence: m-bromotoluene-(a) $\rightarrow$ 3-bromo-2,4,6-trinitrotoluene -(b) $\rightarrow$ I -(c) $\rightarrow$ DIPA -(d) $\rightarrow$ dipyridinium salt of DIPA -(e) $\rightarrow$ DIPICL -(f) $\rightarrow$ DIPAM.

a) m-Bromotoluene to 3-Bromo-2,4,6-trinitrotoluene.-



* For a chemically related series of aminonitrobenzenes the following failure diameters have been reported: TATB, 1.3 cm; DATB, 0.53 cm; picramide, 0.3 cm (6). This is the only investigation of which we are aware in which variation of any detonation parameter with regularly changing chemical structure was ever studied. We cannot overemphasize the value of the results of such an approach to the synthetic chemist.

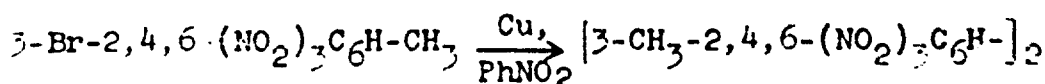
m-Bromotoluene may be made by reactions described in "Organic Syntheses" (7): p-toluidine $\rightarrow$ p-acetotoluidide $\rightarrow$ 4-acetylamino-3-bromotoluene $\rightarrow$ 4-amino-3-bromotoluene $\rightarrow$ m-bromotoluene. Its laboratory price, \$11.00 per hundred grams (8), is undoubtedly more a reflection of demand than of cost in manufacture.

The best literature method for the preparation of 3-bromo-2,4,6-trinitrotoluene (9, 10) involved a two-step nitration with separation of the intermediate 3-bromo-4,6-dinitrotoluene. We have found that the trinitration may conveniently be carried out in a single operation and in excellent yield by using an essentially anhydrous nitric acid - sulfuric acid mixture and by holding the reaction mixture at about 55° for several hours before heating to reflux for several hours. The product precipitates directly on cooling the reaction mixture; the work-up involves simply drowning in excess ice.

Prior to the DIPAM program, preliminary trials on 0.04, 0.1, 0.2 and 0.6 mole scales had resulted in yields of crude product ranging from 92 to 96%. Acetone was a satisfactory recrystallization solvent; yields of recrystallized bromotrinitrotoluene were 84-88%.

In the present program three preparations were carried out on a 1.2 mole scale and a final preparation using 3.5 moles. In the latter instance the total reactant volume was 3.7-3.8 liters. From 1,238 g of m-bromotoluene, 1900 g (86%) of pure bromotrinitrotoluene was carried over to the next step. An additional 50-100 g might have been recovered by further work-up of mother liquors.

b) 3-Bromo-2,4,6-trinitrotoluene to 3,3'-Dimethyl-2,2',4,4',6,6'-hexanitrobiphenyl.



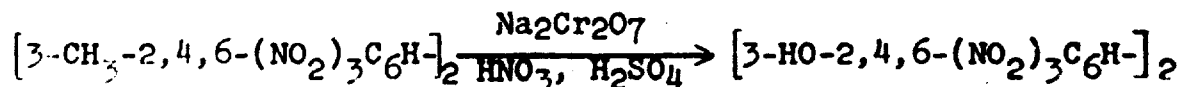
For initial experiments in the Ullmann reaction the procedure of Fock, Moyer and Adams (2) was followed exactly. This involved reacting the bromotrinitrotoluene with activated copper in purified nitrobenzene at 175-185°. To obtain a decently crystalline product it was necessary to remove the major proportion of the solvent by steam distillation, this being the most tedious and time-consuming part of the operation.

CONFIDENTIAL
NOLTR 62-82

In subsequent trials it was found that the relative quantities of nitrobenzene and copper could be reduced substantially with consequent shortening of the steam distillation and no apparent ill effects on yields. The product separated as a black semi-crystalline solid in the pot-residue from the steam distillation. For preliminary purification this material was taken up in hot acetone, decolorized with charcoal and the acetone removed. A further recrystallization from acetone-acetic acid gave a product sufficiently pure for the next step.

One reaction was carried out on a 0.35 mole, four reactions on 0.7-0.8 mole and two reactions on 1.44 mole scales*. Yields of purified dimethylhexanitrobiphenyl ranged from 70 to 81%. From 1,900 g of bromotrinitrotoluene, 1,077 g (77%) of dimethylhexanitrobiphenyl was carried over to the next step.

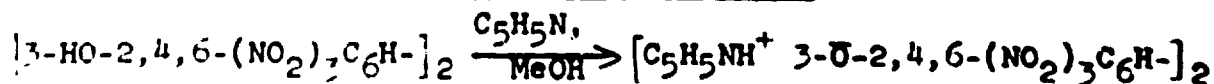
c) 3,3'-Dimethyl-2,2',4,4',6,6'-hexanitrobiphenyl to Dipicric Acid.-



This reaction has been discussed in detail in reference 1. In the course of the present program five preparations were carried out using essentially identical conditions. Improvements in yield from 55 to 80% were achieved by varying dichromate concentrations. Syntheses were carried out on 0.12, 0.27 and 0.55-0.61 mole scales. Reactant volumes in the larger-scale experiments were 4.0-4.2 liters and 12-15 liters of reactor capacity were required for the drowning.

Although pure DIPA melts at 311-312° (dec), material melting above 300° was deemed satisfactory for subsequent operations, *vide infra*. From 1,075 g of dimethylhexanitrobiphenyl, 817 g (75%) of dipicric acid was carried over to the next step.

d) Dipicric Acid to Dipyridinium Dipicrate.-



*In the large-scale preparations total reactant volume was ~1.2 liters. A five liter flask was required for the steam distillation.

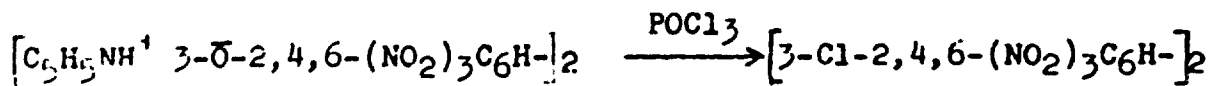
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NOLTR 62-82

The salt precipitated immediately on addition of pyridine to a methanolic solution of DIPA. The reaction mixture was chilled and filtered and the product was washed with ether and dried. When pure DIPA was used and the mother liquors worked up, the yield was close to quantitative. With DIPA prepared as in (c), however, a first crop of high-grade dipyrindinium dipicrate was obtained in about 90% yield, but additional material recovered from mother liquors was of very much lower purity. It was considered that losses in attempting to further purify the dipicric acid would more than offset this 10% decrease in yield*.

Reactions were carried out on a 0.33 mole scale and the reactant volume was ca 1.7 liters. From 772.5 g of DIPA, 914 g (89%) of dipyrindinium dipicrate was carried over to the next step.

e) Dipyrindinium Dipicrate to Dipicryl Chloride.-



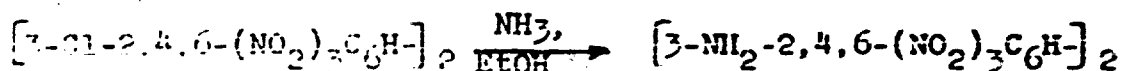
The dipyrindinium salt was converted to DIPICL in virtually quantitative yield by adding to an excess of phosphorus oxychloride, heating on the steam bath, allowing to cool and drowning. The method of drowning is critical and requires extreme caution. If the reaction mixture is added to ice or an ice-water mixture the reaction is initially quite slow, but as the ice melts it becomes more rapid and undergoes autoacceleration. This has, on one occasion, led to boiling and splattering in the mixture.

The preferred method was to add the reaction mixture slowly to water with vigorous agitation, adding ice as necessary to keep the temperature at 30°. For a typical reaction on a 0.25 mole scale this required 3-4 liters of ice and water.

For purification the crude DIPICL was washed with water, then stirred with hot methanol in which it is only very slightly soluble and filtered. From 914 g dipyrindinium salt there was obtained 729 g (99%) of DIPICL.

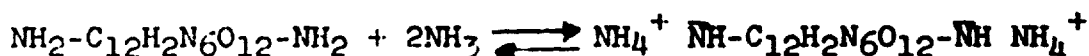
* The main impurity in the DIPA appears to be monohydroxy-hexanitrobiphenyl (m-picrylpicric acid, PIPA).

2) Dipicryl Chloride to Dipicramide.-



Neither DIPICL nor DIPAM is soluble in cold ethanol. When DIPICL was added portionwise to saturated ammoniacal ethanol at 10°, however, it dissolved completely to give a deep-red solution. If this solution was slowly heated to the reflux and the ammonia allowed to boil out, it lightened in color and DIPAM began to precipitate. Distilling off a portion of the ethanol, chilling, filtering and washing with ethanol resulted in a 95-96% yield of DIPAM, m. p. 296-80°.

We interpret this behavior as being due to immediate conversion of DIPICL to DIPAM whose amine hydrogens are sufficiently acidic that the material will form a soluble salt with excess ammonia. As the ammonia boils out the equilibrium is drawn to the left and DIPAM precipitates.



The reaction on a 0.45 mole scale involved 2.7-2.8 liters of reactant volume. From 729 g DIPICL there was obtained 643 g (95.7%) of DIPAM which may be sufficiently pure for the intended application.

For evaluation purposes, however, it was deemed desirable to supply the purest material obtainable. A variety of solvents were tried for recrystallization; an acetone-ethanol pair was found least inconvenient. To dissolve 200 g of crude DIPAM, 7,500 ml of acetone was required and 4,000 ml of absolute alcohol was added during the process of concentration. A total of 599 g (90%) of pure DIPAM, m. p. 298-299°(dec) was obtained together with a further 19.5 g (3%), m. p. 295-296°(dec).

The overall yield for the six steps from m-bromotoluene to pure DIPAM was 39.5%.

For comparison, picramide has a pK_a of 12.25 (11).

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NOLTR 62-32

Properties of DIPAM

Molecular Formula: $C_{12}H_6N_3O_{12}$, Mol. Wt. 454.1

Melting Point: 298-299° (dec).

Oxidant Balance (12): $OB_{100} = -1.52$ (balanced slightly below CO level).

Heat of Formation: The heat of formation of picramide has been determined experimentally (13), $\Delta H_f = -20.1$ Kcal/mole. By adding and subtracting appropriate bond and standardization energies, DIPAM is computed to have $\Delta H_f = -27.6$ Kcal/mole. In the computation it is assumed that, as seems reasonable, there is no interaction between the rings and that DIPAM has twice the heat of sublimation of picramide.

Heat of Detonation: Using the H_2O , CO , CO_2 arbitrary in calculation, DIPAM is computed to have a heat of detonation of 384.4 Kcal/mole or 845 cal/g. If the $[2 CO = CO_2 + C]$ equilibrium is taken into account, the values are somewhat higher.

Crystal Density: 1.79 g/cc.

Impact Sensitivity: 132 cm, $\sigma = 0.23$. Determined on an EHL machine as modified at NOL using type 12 tools. On this machine TNT has a 50% impact height of 160 cm; Comp. A, 70 cm; Tetryl, 32 cm; RDX, 24 cm; PETN, 12 cm.

Vacuum Thermal Stability

At 230°C. gas evolved = 0.3 cc per g per hr (6 hr period).
At 245°C. gas evolved = 0.3 cc per g per hr (2 hr period).
At 260°C. gas evolved = 7.5 cc per g per hr (2 hr period).

Volatility Studies: A weighed sample of the explosive was held in an evacuated Abderhalden drying apparatus over boiling nitrobenzene (ca. 210°) and the loss in weight due to sublimation or other causes was determined after a thirty minute interval. Results for DIPAM and other thermally stable explosives are as follows (compound, pressure, % weight loss): DIPAM, 1.0 mm, nil; TNTACOT, 1.0 mm, 0.1%; TATB, 1.0 mm, 1.1%; DIPICL, 1.0 mm, 2.3%; DATB, 2.5 mm, 53.8%; hexanitrostilbene, 0.9 mm, nil; KEND, 0.6 mm, nil; nonanitroterphenyl, 0.8 mm, 0.5%; hexanitrobiphenyl, 0.5 mm, 0.4%. It should be appreciated that these were crude measurements and that pressure values read from a McLeod gauge near the pump do not accurately describe pressures above the sample.

7
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NOLTR 62-82

EXPERIMENTAL

3-Bromo-2,4,6-trinitrotoluene.-

To a well-stirred mixture of 1500 ml 30% oleum and 1800 ml 90% nitric acid at 55° was added dropwise over a fifty minute period 588 g (3.45 moles) m-bromotoluene (8). The resulting clear orange solution was stirred an additional seventy-five minutes at 55°, then heated to the reflux. A mildly exothermic reaction which was self-sustaining for about fifteen minutes ensued. The solution was held at the reflux for a total of two hours, then allowed to cool slowly with vigorous agitation*.

The cooled reaction mixture was drowned with stirring in 5000 ml ice-water, filtered and the filter cake washed with 8000 ml water and air-dried overnight to yield 985 g (93%) crude bromotrinitrotoluene, m. p. 134-137°. A single recrystallization from 4000 ml acetone furnished three crops, totalling 808 g, m. p. 142-144° and a further crop, 30 g, m. p. 141-143°. The yield of recrystallized material was 88%.

3,3'-Dimethyl-2,2',4,4',6,6'-hexanitrobiphenyl.-

Materials: 440 g (1.44 mole) bromotrinitrotoluene
280 g copper dust**
500 ml dry redistilled nitrobenzene

The bromotrinitrotoluene was dissolved in the nitrobenzene in a three-neck two-liter flask fitted with a mechanical stirrer, thermometer and powder funnel. The solution was heated to 165° on an oil bath and 10 g of copper was added with vigorous stirring. The temperature was slowly raised to 185° and at some

The product begins to precipitate at about 85°. There appears to be considerable heat of crystallization and if the solution is allowed to become too supersaturated the exotherm during the precipitation may cause local splattering. The addition of seed crystals effectively eliminates this possibility.

**The copper used was electrolytic dust from Fisher Scientific Company. It was activated by stirring with concentrated hydrochloric acid, filtering, washing with water, methanol and ether and drying in the oven.

point between the two temperatures reaction started. The copper was then added over a period of about thirty minutes in increments of about 10 g. With each addition there was a slight exotherm and a temperature of 184-186° was maintained with very little external heating until about three-fourths of the copper had been added, at which time external heating was increased to maintain this temperature. The mixture was heated for about ten minutes after the addition was complete, then filtered hot to remove the gray inorganic salts*. The precipitate and reaction flask were thoroughly washed with acetone.

Steam distillation to remove the acetone and nitrobenzene from the reaction products required about three hours, after which time the dark semi-crystalline residue was dissolved in hot acetone, treated with charcoal and filtered. The acetone was then allowed to evaporate leaving as a residue 280 g (86%) of crude product.

This was taken up in the minimal amount of boiling acetone, an equal quantity of acetic acid was added and the mixture heated to 25-97° on the steam bath to remove the acetone, then cooled to 5°, filtered and the product washed with ether and dried in the oven at 70-80°. There was obtained 260 g (80.3%) of pure dimethylhexanitrobiphenyl, m. p. 240-241°.

Dipicric Acid, DIPA.-

To 260 g (0.575 mole) dimethylhexanitrobiphenyl in a five-liter three-neck flask fitted with stirrer and thermometer were added with stirring 2600 ml 90-100% nitric acid (no rise in temperature) and sufficient of a total of 905 ml 30% oleum to raise the temperature to 50° and to hold the mixture at this temperature until all or most of the dimethylhexanitrobiphenyl had dissolved. The remaining oleum was then added while cooling the mixture with an ice bath.

With continued cooling to maintain the temperature at about 25° (not above 30°), 750 g of sodium dichromate dihydrate was added portionwise over a several hour period to the well-stirred mixture which turned greenish-black. Cooling was necessary for an additional several hours, after which time the mixture could be left unattended at room temperature. Total stirring time was about 25 hours.

*It is undesirable to allow the reaction mixture to cool to ambient temperatures and stand before filtering. In one case where the mixture stood overnight before filtering, considerable of the product had to be recovered from the inorganic salt by washing with hot acetone.

Crude dipicric acid was obtained as a yellow amorphous product by drowning the reaction mixture on about 10 liters of cracked ice, allowing the precipitate to settle, filtering through a coarse sintered glass funnel and washing the filter cake with 20% hydrochloric acid. For preliminary purification this material was digested with 500 ml ethanol, the solution filtered off through a sintered glass funnel, the residue digested with an additional 750-1000 ml ethanol and the mixture again filtered. Concentrated hydrochloric acid was then added to the combined filtrates until the mixture appeared to be almost colorless.

The mixture was then chilled, filtered and the product air-dried for several hours after which time it still retained considerable water. Taking this material up in acetone and adding an equal volume of benzene caused most of the water to separate as a lower phase which was removed. The organic phase was then dried over Drierite and concentrated to yield two successive crops of DIPA. The first crop, washed with benzene and then with hexane and dried for 24 hrs. at 60° 1 mm, weighed 167 g and melted with decomposition at 311°. The second crop, treated similarly, amounted to 41 g. m. p. 301° (dec). The total yield of DIPA was 19% of theory.

Dipyridinium Dipicrate. -

A solution was made by dissolving 150 g of dipicric acid in 1500 ml of warm absolute methanol then cooled to below 40°. With vigorous stirring 75 ml of pyridine was added in a slow stream and stirring was continued for one-half hour after addition was complete. The reaction mixture was then cooled in an ice-salt bath, filtered and the product washed with ether and dried. The yield was 183 g (90.6%) of bright yellow crystalline solid, m. p. 256-258° (dec).

3,3'-Dichloro-2,2',4,4',6,6'-hexanitrobiphenyl (DIPICL). -

One hundred eighteen grams of the dipyridinium salt was added to 250 ml of phosphorus oxychloride and warmed on a steam bath. The salt was nearly completely dissolved when the temperature reached 60° at which time the product began to precipitate. After heating for an additional half-hour the

*This material occasionally precipitates in a very fine form and passes quite slowly through the filter. When this occurs the filtration is quite tedious and may be shortened appreciably by allowing the material to settle and first passing the supernatant liquor through the sintered glass funnel.

reaction mixture was cooled to below 40° and drowned slowly, starting with 500 ml water and adding the reaction mixture and ice at a rate sufficient to keep the drowning mixture at about 30° (CAUTION, see discussion). When drowning was complete the volume was 2000-2500 ml. When the exotherm had ceased the product was recovered by filtration and washed with 2 liters of cold water. It was then suspended in 500 ml of methanol and warmed almost to the boiling point with stirring, then filtered and dried. The yield was 94 g (99.5%), m. p. 275-277° (dec).

3,3'-Diamino-2,2',4,4',6,6'-hexanitrobiphenyl (DIPAM).-

To 2200 ml of absolute ethanol saturated with dry ammonia in a five-liter three-neck flask fitted with thermometer, stirrer and condenser was added portionwise over a one-hour period and at a temperature below 12° 226 g of DIPICL. The DIPICL dissolved as added to form a blood-red solution. Anhydrous ammonia was then slowly bubbled in for an additional 15 minutes after which time the solution was slowly heated to the reflux. At about 30-35° an orange solid began to precipitate and the solution lightened in color. The mixture was caused to reflux one-half hour after which time about 500 ml ethanol was boiled off, carrying with it the last of the excess ammonia.

The reaction mixture was cooled to 10°, filtered and the product was washed with 5% aqueous hydrochloric acid, ethanol and ether and dried in the vacuum oven at 80° (30 mm). There was obtained 197.5 g (95%) of an orange-brown powder, m. p. 296° (dec).

For purification this material was taken up in 7500 ml hot acetone, the solution decolorized with charcoal and concentrated, adding 4500 ml of absolute ethanol during the course of the concentration. There was obtained as a first crop 173.5 g of pure DIPAM, m. p. 299° (dec) in the form of a nicely microcrystalline yellow powder. A second crop, 19.4 g, m. p. 294° (dec), was again recrystallized to yield 18.0 g, m. p. 298° (dec). The yield of pure DIPAM from DIPICL was 92%.

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SUBJECT ANALYSIS OF REPORT

Descriptors	Codes	Descriptors	Codes
Explosives	EXPL	Trinitro	TRIT
Heat-resistant	HEAA	Diethyl	DINT
Explosives (Preparation)	EXPLP	DI	DIA
Explosives (Properties)	EXPLF	Picric	PICR
Diamine	DIAM	Acid	ACID
Hexa	HEXA	Pyridinium	PYDN
Nitro	NITRO	Picrate	PCRA
Piperyl	PIPE	Dichloro	DICL
Oxidation	OXIT	Hydroxyl	HYDX
Synthesis	SYNS	Methyl	METY
Bromo	BROM		
Toluene	TOLN		

1. Explosives - Heat resistant 3,3'-diamino- 2,2',4,4',6,6'- hexanitrobiphenyl phenyl Explosives - Preparation Explosives - Properties Title Dacons Joseph C. III. Project	Naval Ordnance Laboratory, White Oak, Md. NOL technical report 62-82 HEAT RESISTANT EXPLOSIVES. XIII. PREPARATION AND PROPERTIES OF 3,3'-DIAMINO-2,2',4,4',6,6'-HEXANITROBIPHENYL (DIPAM) (C₁₂H₆N₆) by Joseph C. Dacons and others. 16 May 1962. 12p. Task PR-44. A new oxidative procedure wherein methyl group in substituted trinitrotoluene derivative is replaced by hydroxyl has been applied to preparation of title compound. A new thermally stable high explosive, six-step synthesis involved sequence: m-bromotoluene to bromotritrinitrotoluene to dimethylhexanitrobiphenyl to dipicric acid to dipyrindinium dipicrate to dichlorohexanitrobiphenyl to DIPAM. Overall yield was 39.5%. DIPAM appears to have attractive potentialities for high temperature mild detonating fuse and similar applications. Abstract card is confidential.	1. Explosives - Heat resistant 3,3'-diamino- 2,2',4,4',6,6'- hexanitrobiphenyl phenyl Explosives - Preparation Explosives - Properties Title Dacons Joseph C. III. Project
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