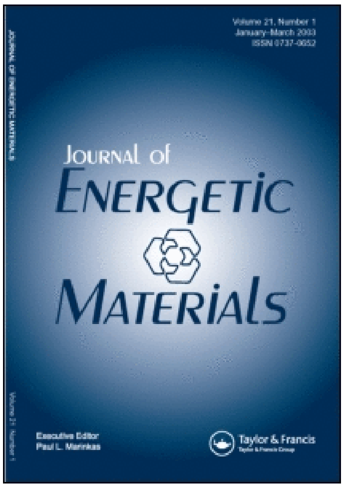

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2,5-dipicryl-1,3,4-oxadiazole: a shock-sensitive explosive with high thermal stability (thermally-stable substitute for petn)

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2,5-DIPICRYL-1,3,4-OXADIAZOLE: A SHOCK-SENSITIVE EXPLOSIVE WITH HIGH THERMAL STABILITY (THERMALLY-STABLE SUBSTITUTE FOR PETN)

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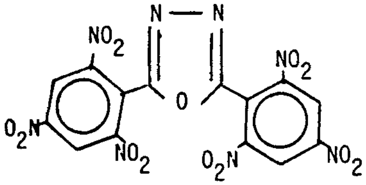
ABSTRACT

The preparation and properties of 2,5-dipicryl-1,3,4-oxadiazole (DPO), a thermally stable substitute for PETN, are discussed. Results of short pulse shock tests on DPO are also given.

INTRODUCTION

From the mid 1960's, a number of research groups, including our own, have been involved in the study of 2,4,6-trinitrophenyl substituted heterocyclic compounds for use as heat-resistant explosives.[1] One of the compounds prepared during the course of our study was 2,5-dipicryl-1,3,4-oxadiazole (DPO) (1). DPO was found to be quite impact sensitive (20 cm) but yet had high



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thermal stability [0.6 cc/g/hr (2 hr period) at 260°C], a combination of thermal stability and impact sensitivity that is unique. When DPO was first prepared, there were few needs for a material with its properties, but recently there has been a renewed interest in thermally stable shock sensitive explosives for use in detonation transfer compositions. This has led to the reinvestigation of DPO reported here, which includes further study of the sensitivity and the synthesis of this unusual explosive.

RESULTS AND DISCUSSION

A. Impact Sensitivity and Thermal Stability of DPO.

The thermal stability and impact sensitivity of DPO are given in TABLE 1 along with data for other heat-resistant explosives whose properties are most similar to those of DPO.

TABLE 1

Impact Sensitivities of Thermally Stable Explosives.

Explosive	Thermal Stability[2] at 260°C, cc/g/hr (2 hr)	Impact[3] Sensitivity cm
2,5-dipicryloxadiazole	0.6	20
NONA[4]	0.5	39
HNS[5]	0.5	45
2,5-dipicryl-3,4-dinitrofuran[6]	0.8 at 230°C	23

Inspection of TABLE 1 shows that there are explosives (HNS and NONA) which are similar in thermal stability to DPO but they are not as impact sensitive. Likewise, 2,5-dipicryl-3,4-dinitrofuran is similar in sensitivity to DPO but is not as thermally stable. Thus it is believed that DPO has a combination of thermal stability and impact sensitivity that is unique and DPO can meet requirements which are not attainable by other explosives.

That DPO has high thermal stability is not surprising since diaryl-1,3,4-oxadiazoles, in general, have excellent thermal stability[7] and DPO has no groups on the center ring that could give lowered stability due to interaction with the attached trinitrophenyl groups (similar to steric interaction around the center ring of NONA which lowers its stability relative to octanitroterphenyl[8]). That DPO is more impact sensitive than similar polynitroaromatic explosives is, however, somewhat unexpected. Generally, with all other factors being equal, the impact sensitivity of a polynitroaromatic explosive will increase as the oxidant balance (OB_{100}) increases[3] and one would expect NONA ($OB_{100} = -0.79$) and 2,5-dipicryl-3,4-dinitrofuran ($OB_{100} = -0.34$) to be more impact sensitive than DPO ($OB_{100} = -1.22$). That this is not the case suggests that there is an additional factor controlling the sensitivity of DPO. The structures of DPO, NONA and dipicryldinitrofuran are similar in that they consist of trinitrophenyl groups attached to a center ring and it would appear that the oxadiazole ring (presumably the N-N bond) in DPO is providing a "trigger linkage"[3] to increase the impact sensitivity of DPO relative to NONA and dipicryldinitrofuran.

B. Shock Sensitivity of DPO.

Short pulse shock tests (exploding foil) on DPO showed that it has a shock sensitivity similar to that of pentaerythritol tetranitrate (PETN)[9a] (see TABLE 2). Moreover, the tests also showed that DPO has a sharp threshold of initiation (standard deviation of the Threshold Flyer Velocity is small), a desirable property for an initiating explosive.

TABLE 2

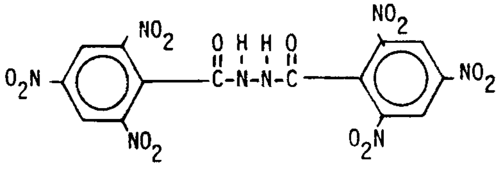
Short Pulse Shock Test Results[9a, 9b]

Explosive	Threshold Flyer Velocity (km/sec)	Density (g/cc)	Consolidation Pressure (MPa)
PETN, Class 2	2.21	1.50	103.4
DPO	2.33	1.61[a]	103.4

(a) The crystal density (flotation method) of DPO is 1.77 g/cc.

C. Previous Procedures for DPO.

All published procedures for DPO involve cyclization of N,N'-bis(2,4,6-trinitrobenzoyl)hydrazine (2). While we were developing our procedures for DPO (cyclization of 2 with phosphorus pentoxide or phosphorus pentachloride)[1a], Russian workers reported the



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synthesis of DPO from 2 and phosphorus oxychloride[10]. The report stated that 1 was prepared by subjecting 2 to cyclization in the presence of phosphorus oxychloride at the b.p. of the reaction mixture but attempts, at that time, to repeat the Russian procedure gave only trace amounts of DPO along with mainly recovered starting material (reaction product analyzed by TLC). In a later publication[11], the Russian workers provided more details of their procedure and state that refluxing 2 mmol (1.2 g) of 2 in 100 ml of phosphorus oxychloride for 20 hours gave a 54% yield of DPO, mp 310-311°C.[12] Again, attempts to repeat this more detailed procedure gave mainly recovered starting material (2) along with only small amounts (approximately 5%) of DPO (as detected by NMR).

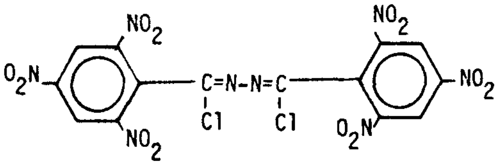
D. Improved Procedure for DPO.

To prepare adequate quantities of DPO for future experimental investigations, improvements were necessary in the existing procedures[1a] which use phosphorus pentoxide or phosphorus pentachloride in nitrobenzene to cyclize 2 to 1 in 30-35% yield. In these procedures, the DPO was isolated from the nitrobenzene reaction solvent by pouring the reaction mixture into a second solvent (methanol) or by steam distillation of the nitrobenzene. (Nitrobenzene was initially chosen as the reaction solvent because the starting material (2) has better solubility in this solvent than other common organic solvents which are compatible with phosphorus pentoxide or phosphorus pentachloride). Thus, in order to make scale-up of DPO practical, it was desirable not only to increase the yield of DPO but also to achieve easier solvent recovery and isolation of DPO. It was recently discovered that these goals can be met by using 1,2-dichloroethane (b.p. 83°C) as the reaction solvent. Even though 2 is nearly insoluble in this solvent and therefore longer reaction times (2.5 hr vs 10 min for nitrobenzene) are required, the product DPO, which is also essentially insoluble in dichlorethane, can simply be removed by filtration and easily purified. A significant amount of a by-product is also formed, but it remains in the dichlorethane filtrate (see section E below) and does not interfere with the isolation of DPO. However, this by-product, when treated with water, gives a recovered polymorph of 2 (mp 285°C, dec) hereafter referred to as 2-P (see experimental section). The recovered polymorph (2-P) is recycled to provide a 60% yield of DPO.

Solvents other than dichlorethane were tried but they gave less desirable results. For example, no significant reaction of 2 with phosphorus pentachloride in carbon tetrachloride occurred apparently because of near total insolubility of 2 in this solvent. Reaction of 2 with phosphorus pentachloride in phosphorus oxychloride did give 1 but lower yields and the hazardous, corrosive nature of phosphorus oxychloride made this solvent less attractive than dichloroethane.

E. By-Product in the Dichloroethane Filtrate. (see sect. D above)

Phosphorus pentachloride is reported to react with diaroylhydrazines to give 1,4-diaryl-1,4-dichloroazines[13], thereby suggesting the possibility that the by-product in the dichloroethane filtrate is 1,4-dipicryl-1,4-dichloroazine (3), which would be expected to react with water to give 2. However, all attempts to prove this by either directly isolating the



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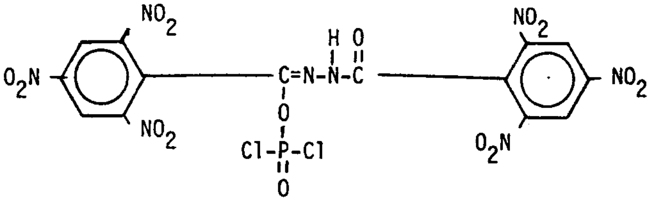
by-product or reacting it to give a product other than 2-P were unsuccessful. Eventually it was discovered that if the dichloroethane filtrate was not directly treated with water, but just allowed to stand exposed to atmospheric moisture, a crystalline precipitate slowly formed. It seemed that this precipitate would be 2-P, but it was found to be yet another product (4) (m.p. 160°C, vigorous decomposition) which also gives 2-P upon treatment with water. Even though 4 is also reactive toward moisture, it was sufficiently stable to obtain evidence



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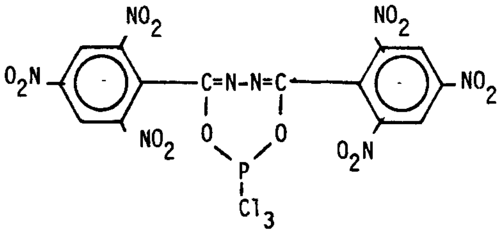
to propose a structure. If the proposed structure for 4 is correct, the calculated elemental composition would be 26.8% carbon, 17.9% nitrogen, 11.3% chlorine and 4.9% phosphorus.

Elemental analysis (Galbraith Laboratories, Inc., Knoxville, Tenn.) of 4 showed 4.82% phosphorus as well as 27.98% carbon, 16.75% nitrogen and 9.79% chlorine, values which are probably only approximate since 4 reacts readily with atmospheric moisture during handling (a sample of 4 allowed to stand exposed to the atmosphere overnight was completely changed to 2-P). The elemental analysis, showing the presence of phosphorus, does rule out 3 as a possible structure for the by-product. The infrared spectrum (KBr) of 4, taken immediately after sample preparation, is noticeably quite different than that of 2-P especially in the C=O region (peak at 1695 for 4; peak at 1710 and at 1630 for 2-P). After a short time, however, the spectrum changed to that of 2-P, presumably because of hydrolysis of 4 in the KBr pellet. The above data suggest that a likely structure for the by-product in the dichloroethane filtrate is the cyclic phosphate (5). Compound 5, once formed, would probably not proceed to DPO but could hydrolyze stepwise to give 4 and eventually 2-P.



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EXPERIMENTAL

^{1}H NMR spectra were determined on a Varian EM-390 spectrometer with TMS as the internal standard and IR spectra were obtained with a Perkin-Elmer Model 283 spectrometer. Melting points were recorded on a Thomas Hoover apparatus and are uncorrected. TLC plates (Silica gel 60) were developed with toluene-acetone (50/50) to detect compound 2 and with toluene-ethanol (98/2) to detect compound 1. The TLC plates were visualized by spraying with 25% potassium hydroxide in methanol.

Impact sensitivities were determined on an ERL machine with type 12 tools and a 2.50 kg weight.[3] Vacuum thermal stabilities were determined by holding 0.2 g of the explosive under vacuum at constant elevated temperature and measuring the volume of gas evolved.[2]

2,4,6-Trinitrobenzoyl Chloride.

A suspension of 67.7 g of crude 2,4,6-trinitrobenzoic acid[14] in 540 ml of benzene was stirred in a water bath at 40-45°C while 57.2 g of phosphorus pentachloride was added in portions after which the solution was heated to the boiling point and 200 ml of benzene were removed by distillation. Hexane (300 ml) was added to the warm solution which was then cooled to 15°C to give 62.9 g, mp 160-162°C. Concentration of the mother liquor gave an additional 5.1 g, mp 159-161°C. (A preparation of trinitrobenzoyl chloride using phosphorus oxychloride is reported in reference 11).

N,N'- Bis(2,4,6-trinitrobenzoyl)hydrazine (2).

This procedure for 2 is simpler and provides a better yield than the previously published procedure[1a]. A slurry of 21.0 g (0.076 mole) of 2,4,6-trinitrobenzoyl chloride in 140 ml of methanol was vigorously stirred in a water bath at 30°C while a solution of 7.1 g (0.12 mole) of 85% hydrazine hydrate in 35 ml of methanol was added over a 50-60 minute period. The mixture was cooled to 20°C and the insoluble material was removed by filtration and washed with methanol until the washings were nearly colorless. The product was then washed with warm water and again with methanol to give 7.46 g (38%) of solid, mp 262°C dec. ^{1}H NMR (DMSO-d_6):9.30 (s with small satellite peaks at 9.45 and 9.15) 12.3 (s); IR (KBr):3360 (sharp peak) (NH), 1730, 1710 (C=O).

2,5-Dipicryl-1,3,4-Oxadiazole (1).

a. Small Scale Preparation of 1.

To 7.4 g (0.0145 mol) of N,N'-bis(2,4,6-trinitrobenzoyl)hydrazine and 65 ml of 1,2-dichlorethane stirred in a 200 ml round bottom flask was added 7.4 g (0.0355 mol) of phosphorus pentachloride. The mixture was heated to reflux temperature in an oil bath and was held at this temperature for 2.5 hrs. The mixture was cooled to room temperature and the insoluble material (3.2 g of crude 2,5-dipicryl-1,3,4-oxadiazole), mp 318°C (dec), was removed by filtration. The crude oxadiazole was dissolved in boiling acetone (300 ml) (charcoal), the solution was filtered and the filtrate was concentrated by distillation until much of the acetone had been removed and an appreciable amount of crystals had formed. Methanol was slowly added with continued distillation until the distillate temperature approached 65°C. The mixture was cooled to room temperature and filtered to give 2.9 g of pure 2,5-dipicryl-1,3,4-oxadiazole, mp 335°C (vigorous decomposition). ^{1}H NMR (DMSO-d_6):9.52 (s).

To the dichloroethane filtrate (from which the crude dipicryloxadiazole was removed) was slowly added 10 ml of water. (A precipitate quickly formed after only a small amount of the water had been added). The mixture was heated to reflux for 5 minutes, then was cooled and filtered to give 1.8 g of recovered N,N'-bis(2,4,6-trinitrobenzoyl)hydrazine (2-P). Compound 2-P (mp 277°C dec) is a different crystal form (polymorph) than the N, N'-bis(2,4,6-trinitrobenzoyl)hydrazine (2) [mp 262°C dec, see above] used as the original starting material. (High purity 2-P, obtained by treating 4 with water, has mp 285°C dec.) Compound 2-P gave the correct elemental analysis and its ^{1}H NMR spectrum and thin layer chromatograms were identical to those of the original starting material, but it had a different solid phase (KBr) IR spectrum [3450-3100 (broad peaks) (NH), 1710 (C=O), 1630]. These results are consistent with a polymorph. Treatment of the 1.8 g of 2-P with phosphorus pentachloride in dichlorethane as described above gave an additional 0.7 g of 1 raising the total yield to 3.6 g (51%).

b. Scale Up Procedure for 1

The N,N′-bis(2,4,6-trinitrobenzoyl)hydrazine (2) starting material used for this procedure was obtained from Chemtronics, Inc., Swannanoa, N.C. This material contained 10 percent of a by-product, methyl trinitrobenzoate[15], but a small scale test experiment indicated that this by-product did not interfere with the preparation or purification of 1.

The scale up procedure for 1 was as follows: 125 g of the impure N,N′-bis(2,4,6-trinitrobenzoyl)hydrazine (corresponding to 112.5 g of pure material) was stirred in one liter of dry 1,2-dichloroethane in a 3-neck 2 liter round bottom flask (a mechanical stirrer was used). Phosphorus pentachloride (125 g) was added and the mixture was stirred at reflux temperature for 2.5 hrs. After cooling to room temperature, the mixture was filtered to give 52.2 g (48%) of crude 2,5-dipicryl-1,3,4-oxadiazole. ^{1}H NMR of the crude product shows only 1 with a very small amount of 2.

The dichloroethane filtrate was stirred while 300 ml of cold water was added all at once. A precipitate immediately formed and the temperature of the mixture began to rise slowly. When the temperature reached 65-70°C, small amounts of ice were added to hold the mixture at this temperature. After a short time the temperature began to fall and when the mixture was near room temperature, it was filtered to give 30.3 g of 2-P. Based on recovered starting material, the yield of crude 1 was 66%. The yield of purified product by crystallization from acetone - methanol (as described in the small scale preparation of 1) was approximately 60%.

The crude 2,5-dipicryl-1,3,4-oxadiazole can also be purified by dissolving it in gamma-butyrolactone (1 gram per 5 ml of butyrolactone at 100°C), treating the solution with charcoal, filtering and adding methanol to the filtrate to precipitate the product. Dimethylformamide (DMF) can similarly be used instead of butyrolactone but it is difficult to remove the small amounts of DMF that tend to remain in the product.

Recovery of 4.

A dichloroethane filtrate from the scale up procedure for DPO was allowed to stand overnight unprotected from atmospheric moisture. A crystalline precipitate (4) formed which was removed by filtration, washed with dichloroethane and immediately dried in a vacuum desiccator over drierite to give 6.5 g of 4, m.p. 160°C with vigorous decomposition. The IR (KBr) spectrum of 4, before 4 eventually hydrolyzed in the KBr pellet, was distinctly different from that of 2-P (see RESULTS AND DISCUSSIONS, section E). Attempts to obtain an ^1H NMR spectrum of 4 were not successful possibly because of interaction of 4 with the NMR solvent (DMSO-d_6) or water contained therein. Both direct treatment of 4 with water or allowing 4 to stand overnight unprotected from moisture gave high purity 2-P, m.p. 285°C with decomposition.

ACKNOWLEDGMENTS

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