NSWC/WOL TR 78-31

F – PICRYLDINITROMETHANE. SYNTHESIS AND PROPERTIES

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A completely fluorinated analog of picryldinitromethane has been made as part of a research effort aimed at the synthesis of high-density, zero hydrogen explosives. 1,3,5-Trifluorotrinitrobenzene, used as starting material in the synthesis and of interest in itself as a dense energetic material, was prepared by a new and improved method. In the course of the synthesis, a technique was developed for control of the ambident behavior of

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polynitroalkyl anions which may have general application in reactions of these nucleophiles.

This report describes the synthesis of F-picryldinitromethane (FPDNM) from 1,3,5-trifluorotrinitrobenzene (TFTNB). TFTNB and FPDNM are high-density, zero-hydrogen explosives. This work was carried out under Task Number ZR0130901, IR-144, and Task Number SF33-354-316, the Zero Hydrogen Explosives Program, sponsored by the Naval Sea Systems Command.

Julius W. Enig

JULIUS W. ENIG
By direction

CONTENTS

Page

I. INTRODUCTION..... 3

II. DISCUSSION..... 3

III. SUMMARY..... 8

IV. EXPERIMENTAL..... 8

GLOSSARY.....14

TABLES

Table Page

1 Physical Properties..... 7

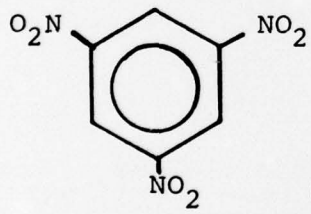
2 Infrared Spectra..... 12

I. INTRODUCTION

F-Picryldinitromethane has been synthesized as part of a program to develop new zero-hydrogen, near CO_2-balanced explosives. In the course of its synthesis, an improved procedure for the synthesis of 1,3,5-trifluorotrinitrobenzene was developed. An unusual cation effect was discovered in the arylation of the dinitromethide anion which may have general application in the control of ambident polynitroalkyl anions.

II. DISCUSSION

The recent report by Eremenko[1] and co-workers of the synthesis of picrylfluorodinitromethane prompted the synthesis of this material in our laboratory in order to determine its properties. On the basis of a measurement of its density, it seemed possible that the analogous F-picryldinitromethane (FPDNM), as yet unreported, would have a density greater than 2.00 if the



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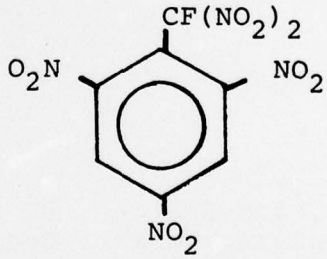

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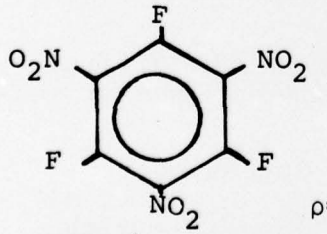
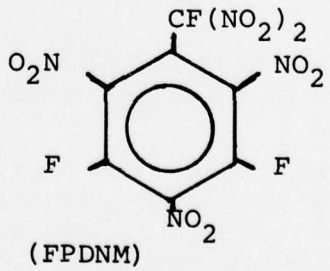


ρ=2.00

(TFTNB)

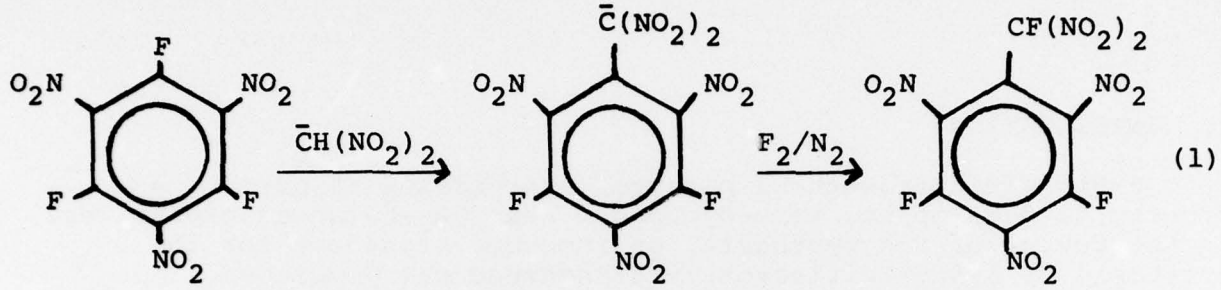


(FPDNM)

[1] Eremenko, L. T., et al., "Aqueous Fluorination of Substituted Aryldinitromethyl Anions," Izv. Akad. Nauk SSSR, Ser. Khim, 1973, p. 1424.

replacement of F in TFTNB with $CF(NO_2)_2$ had an effect comparable to the replacement of H with $CF(NO_2)_2$ in trinitrobenzene.

The synthesis of FPDNM was carried out with the use of TFTNB as starting material.



(1)

The preparation of TFTNB by KF displacement on 2,4,6-trichloronitrobenzene followed by a two-step nitration of the resultant trifluoro compound has been described in the literature.[2] An attractive alternative route[3] is a one-step nitration of 1,3,5-trifluorobenzene.[4] This procedure was found to be feasible and gave a 60% yield of TFTNB.[5]

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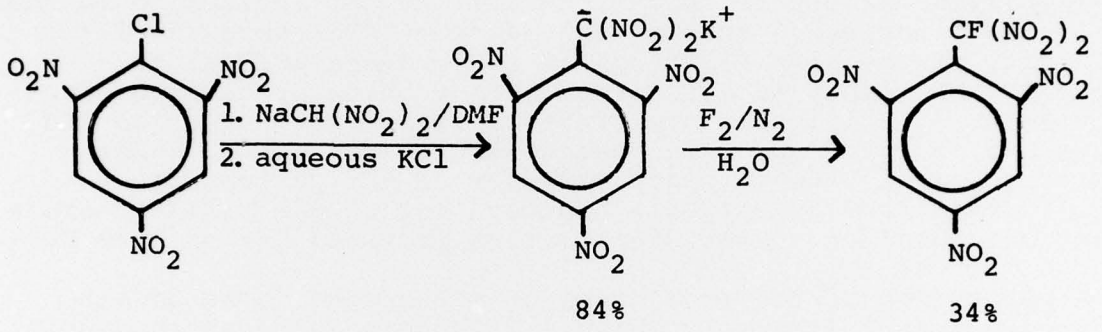
[2]Shaw, III, G. C. and Seaton, D. L., "The Synthesis of Some Fluorine - Containing Trinitrobenzenes," J. Org. Chem., Vol. 26, 1961, p. 5227.

[3]An alternative route to TFTNB was sought because of the difficulties in purification and low overall yield obtained in the procedure of reference 2.

[4]Available from PCR, Inc. and Fairfield Chemical Company or by reaction of KF with 1,3,5-trichlorobenzene: Shiley, R. H. et al, "Fluorination of 1,2,3-, 1,2,4-, and 1,3,5-Trihalobenzenes with Potassium Fluoride in Dimethyl Sulfone," J. Fluorine Chem., Vol. 2, 1972/1973, p. 19.

[5]An invention disclosure for this procedure has been filed with the NSWC/WOL Patent Counsel under Navy Case Number 62,269.

The reaction of picryl chloride with $Na^+CH(NO_2)^-_2$ and aqueous fluorination of the resultant picryldinitromethide anion were found to proceed as described in the literature[1] to give picrylfluorodinitromethane. The parallel synthesis of FPDNM from TFTNB (Equation (1)), however, required modification of conditions and reagents because of the effects caused by replacement of chlorine with fluorine in the displacement reaction and replacement of hydrogen with fluorine in the fluorination reaction.



(2)

In the reaction of TFTNB with $NaCH(NO_2)_2$ in DMF, the flourine was displaced with the oxygen of the anion to give on workup the potassium 3,5-difluoropicrate salt.[6] Only a trace of the desired C-attack product was observed. This type of leaving group effect has been reported in the reaction of nitrite ion with 2,4-dinitrohalobenzenes. In the case of ArF, O-attack was favored by at least 10:1 over N-attack; whereas in the case of ArCl, displacement occurred mainly by N-attack.[7]

In an attempt to obtain a more favorable balance of C- versus O-arylation for the dinitromethyl anion, the effect of changing the cation to lithium was investigated.[8] The effect on the

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[6] This picrate salt was also isolated (69% yield) from the reaction of TFTNB with $LiNO_2$ as a result of oxygen attack by the nitrite ion.

[7] Broxton, T. J., et al., "Aromatic Nucleophilic Substitution Reactions of Ambident Nucleophiles. II. Reactions of Nitrite Ion with Nitrohalobenzenes," J. Org. Chem., Vol 40, 1975, p. 2037.

[8] For a survey of conditions for preferential alkylation of ambident anions see: le Noble, W. J., "Conditions for the Alkylation of Ambident Anions," Synthesis, No. 1, 1970, p. 1.

ambident behavior of the anion was larger than expected. The yield of the desired C-arylation product went from essentially zero to 43%. The cation effect is generally not large in the alkylation of ambident anions and, moreover, a modest effect might have been anticipated in making only one jump in the alkali metal series. A cation effect peculiar to a gem-dinitro anion is suggested here which may have application to ambident anion control in a variety of reactions with polynitroalkyl anions.[9]

The aqueous fluorination procedure used for the potassium picryldinitromethane salt (Equation (2)) was not applicable in the case of its fluorinated analog derived from TFTNB because of the sensitivity of the ring fluorines in the product (FPDNM) to hydrolysis. Attempts to circumvent this problem by fluorination of potassium 3,5-difluoropicryldinitromethane in a H_2O/Freon 113 mixture and in dry CH_3CN were unsuccessful. The use of a 25% sulfuric acid solution in place of water as a fluorination medium[10] did retard hydrolysis, however, and an 84% yield of crude product was obtained. Recrystallization provided 61% of pure FPDNM.

A comparison of the properties of FPDNM with those of its 3,5-dihydro analog (Table 1) shows a favorable increase in density with fluorine substitution, as expected, but no enhancement of stability towards heat or impact. The instability of FPDNM can likely be attributed to a weakening of the C-N bond in the fluorodinitromethyl group due to steric crowding by the ortho nitro groups.[11] Of possible relevance to this hypothesis is the fact that the largest peak in the mass spectrum corresponds to loss of the two benzylic nitro groups.

The anticipated increase in density by replacement of a F in TFTNB with $CF(NO_2)_2$ did not occur, and indeed the density remained the same.

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[9] The cation effect is usually attributed to an association between the more electronegative atom in the ambident anion and the cation which increases in strength with a decrease in cation size. A special effect may be operative here because of the possibility of favorable steric factors for the formation of a six-membered ring involving the oxygens of the nitro groups and the lithium cation.

[10] This technique has previously been reported by Eremenko, L. T. and Oreshko, G. V., "Fluorination with Elemental Fluorine of Labile Polynitro Compounds. Adducts of the Michael Reaction," Izv. Akad. Nauk SSSR, Ser. Khim., 1969, p. 479.

[11] Kamlet, M. J., "Compounds Containing the Terminal Fluorodinitromethyl Group. I. Theoretical Background," NAVORD Report 6206, 23 Jan 1959.

TABLE 1. PHYSICAL PROPERTIES

	mp, °C	Density[a] g/cc	Impact[b] Sensitivity cm	Vacuum[c] Thermal Stability cc/g
Picrylfluorodinitromethane	130-131	1.87 (A)	13[d]	EC
1,3,5-Trifluorotrinitrobenzene	82.0-83.5	2.00 (B)	84[e]	0
F-Picryldinitromethane	71-72	1.98 (B)	8[d]	EC

(a) Density was determined by the flotation method (A) or from X-ray crystallographic data (B).

(b) Drop hammer test with type 12 tools (2.5 kg) on No. 5 sandpaper using 0.035 g samples per shot.

(c) Amount of gas released per gram of material during a 48 hour period at 100° in an evacuated system.[12] The symbol EC denotes a large release of gas which exceeded the capacity of the manometer tube.

(d) Value for RDX was 17 cm under the same conditions.

(e) Value for 1,3,5-trinitrobenzene (TNB) was 103 cm under the same conditions.[13] A value of 30 cm was more recently obtained for TFTNB as compared to values of 44 and 17 cm for TNB and RDX, respectively.

[12] Simmons, H. T. Sr., "The Vacuum Thermal Stability Test for Explosives," NOLTR 70-142, 28 Oct 1970.

[13] Schmidt-Collerus, J. J., et al, "Research on Fluorochemicals," Denver Research Institute, ASD Technical Documentary Report Number ASD-TDR-62-11, Jul 1962.

III. SUMMARY

A synthesis of FPDNM was developed which is parallel in approach to that of the previously reported picrylfluorodinitromethane. TFTNB was used as starting material and an improved synthesis of this compound was developed. In the first step of the FPDNM synthesis, arylation of the ambident dinitromethyl anion with TFTNB was found to be subject to a large cation effect. The use of sodium and lithium salts gave zero and 43% yields, respectively, of the desired C-arylation product.

TFTNB and FPDNM are of interest as examples of high density ($\rho \cong 2.00$), zero hydrogen explosives. While the utilization of FPDNM is restricted by its impact sensitivity and poor thermal stability, TFTNB has favorable physical properties and can now be synthesized on a large scale by nitration of TFB. TFTNB is a valuable intermediate in the synthesis of other zero hydrogen explosives by virtue of the ease of replacement of its fluorines in reaction with various anions.

IV. EXPERIMENTAL[14]

A. Preparation of 1,3,5-Trifluorotrinitrobenzene

A procedure filed for patent review under Navy Case Number 62,269 was used to prepare TFTNB from TFB in 50-60% yields. The recrystallized (CCl_4) material had mp 82-83.5° (lit[2] mp 87°).[15] Treatment of TFTNB with water has been reported[2] to result in complete hydrolysis of the fluorines to give trinitrophloroglucinol. In a test on its sensitivity to atmospheric moisture, 30 mg samples of TFTNB evenly spread over 2 x 2 cm surface were exposed for 20 days to humidities of 15, 52, and 79% which were maintained by saturated salt solutions. In the 79% R. H. sample only, there was a light yellow color developed on the surface of the solid and, although the bulk melting point remained unchanged, there remained a few specks of unmelted solid at 84°.

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[14] The fluoroaromatic compounds described in this report are sensitive to moisture. Solvents used in reactions and crystallizations were dried with 4A molecular sieves.

[15] The crystals from CCl_4 were found on occasion to retain as much as 5% by weight solvent, which was not easily removed under vacuum. These crystals melted at 82°-86°.

B. Reaction of Sodium Dinitromethane with Picryl Chloride. Preparation of Potassium Picryldinitromethane[16].

A solution of 6.20 g (0.025 mol) picryl chloride in 10 ml DMF was added dropwise to a stirred mixture of sodium dinitromethane[17] (7.00 g, 0.055 mol) and 35 ml DMF at 0°. The temperature was maintained at 15° - 25° during the addition. The mixture was stirred for 16 hours at room temperature then poured into a stirred solution of 18.0 g (0.24 mol) of KCl in 125 ml H_2O. After 2 hours in an ice bath the solution was filtered to give an orange precipitate which was washed with H_2O (2 x 25 ml) and CH_3OH (2 x 20 ml). The dry salt weighed 7.47 g, representing an 84% yield of potassium picryldinitromethane. This material changed from orange to brown to black during heating from 210° - 256° with an explosion point of 257°. It had $\lambda_{max}^{H_2O}$ 368.

Analysis

Calculated:	C, 23.67; H, 0.57; N, 19.71
Found:	C, 23.50; H, 0.58; N, 18.51

C. Reaction of Potassium Picryldinitromethane with Fluorine. Preparation of Picrylfluorodinitromethane.

The crude product obtained in 34% yield from the fluorination of potassium picryldinitromethane according to the procedure of Eremenko, et al,[1] was recrystallized from CH_2Cl_2 to give white needles with mp 130° - 131° (lit.[1] mp 131°) and $\lambda_{max}^{CH_3OH}$ 268 (ε = 26,000). The mass spectrum (70 ev) gave no parent ion. The highest mass occurred at m/e 243 which corresponds to P-2(NO_2).

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[16] Prepared by L. Lee of this Center using a modified procedure of Tselinskii, I. V. and Kolesetskaya, G. I. "Anions of Dinitromethyl Compounds. XXXIV. Synthesis of Aryldinitromethanes by the Reaction of the Sodium Derivative of Dinitromethane with Activated Aryl Halides," Zh. Obshch. Khim., Vol. 9, 1973, p. 2471.

[17] Obtained in 57% yield as a yellow solid from the procedure of Tselinskii, I. V. and Krylov, V. K., "Anions of Dinitromethyl Compounds. XXXIV. Synthesis of N-Substituted Dinitroacetamides," Zh. Obshch. Khim., Vol. 9, No. 12, 1973, p. 2474.

D. Reaction of TFTNB with Sodium Dinitromethane. Preparation of 3,5-Difluoropicric Acid.

A solution of 1.34 g (5.02 mmol) of TFTNB in 2 ml DMF[18] was added dropwise from a syringe over a 7 minute period to a stirred 0° solution of 1.28 g (10.00 mmol) of $NaCH(NO_2)_2$ in 6 ml DMF contained in a septum-capped vial. The dark red solution was stirred for 30 minutes at 0° then poured into 25 ml of a 10% KCl solution. This homogeneous orange mixture was cooled with an ice/salt bath to -15°. Some gas evolved from the solution on standing. After 1 hour some yellow precipitate began to form. The mixture was filtered after 2 hours at -11° to -15° to give a yellow solid which dissolved when washed with H_2O, leaving only a trace amount of orange residue.

The trace amount of sparingly soluble orange solid is assumed to be the potassium salt of 3,5-difluoropicryldinitromethane (cf. Exp. B), while the water soluble yellow solid was identified as potassium 3,5-difluoropicrate, $\lambda_{max}^{H_2O}$ 345 (ε = 10,300). This material analyzed for 12.7% potassium as compared to 12.9% calculated and had a value of 97.8% of theoretical in the gravimetric analysis for 3,5-difluoropicrate ion precipitated as the tetraphenylarsonium salt. The picrate salt was converted to 3,5-difluoropicric acid by treatment with ethereal HCl. The phenol had mp 113° - 114° and showed a molecular ion at m/e 265 in the mass spectrum (70 ev).

E. Reaction of TFTNB with Lithium Dinitromethane. Preparation of Potassium 3,5-Difluoropicryldinitromethane.

A mixture of 6.01 g (47.0 mmol) $NaCH(NO_2)_2$, 2.00 g mmol) LiCl, and 26 ml DMF was stirred at room temperature for 3 hours in a N_2-flushed, septum-capped flask. Lumps caused by the precipitating NaCl were broken up by a stirring rod inserted through the septum. The unstirred mixture separated into an upper layer of light orange solution and a lower yellow layer of finely divided solid--presumably NaCl. This mixture was cooled to 0° with an ice bath and a solution of 6.27 g (23.5 mmol) TFTNB in 8 ml DMF[18] was added dropwise over 30 minutes[19] while the system was blanketed with N_2 with an N_2 bubbler. The red mixture was stirred an additional 30 minutes at 0° and then poured into a 10% KCl solution (10 g KCl, 0.134 mol,

[18] The TFTNB/DMF solution was prepared immediately before use since it was shown that dry DMF slowly reacts with TFTNB at room temperature.

[19] A slow addition was used because the reaction is exothermic and in order to minimize attack of the picryldinitromethide ion on TFTNB, a reaction which takes place slowly at room temperature.

in 90 ml H_2O). The resultant orange solution was cooled to -10° with an ice/MeOH bath. An orange precipitate was collected by filtration after 2 hours and washed with H_2O (4 x 5 ml) and Et_2O (4 x 5 ml). The salt was dried in vacuo to give 3.92 g (43%) of potassium 3,5-difluoropicryldinitromethane. The orange salt had a maximum solubility in H_2O of ca. 1% and showed $\lambda_{max}^{H_2O}$ 363.

F. Reaction of Potassium 3,5-Difluoropicryldinitromethane with Fluorine. Preparation of F-Picryldinitromethane.

A 300 ml, 3-necked flask equipped with a magnetic stirring bar, thermometer, and gas inlet tube (7 mm Teflon tubing immersed in solution) was charged with 3.00 g (7.67 mmol) of potassium 3,5-difluoropicryldinitromethane and a mixture of 50 ml conc. H_2SO_4 and 150 ml H_2O (25% acid solution). The salt was largely undissolved. The stirred solution was cooled to -10° with an ice/MeOH bath while a F_2/N_2 mixture ($\sim$1/5) was bubbled into the mixture until the color changed from orange to light yellow (1 hour). A light tan solid was collected by filtration and washed with cold water. The solid was dried in vacuo to give 2.40 g (84%) of crude F-picryldinitromethane. In a duplicate fluorination with 2.89 g (7.38 mmol) of salt, 2.30 g (84%) of product was obtained. The combined crude product (4.70 g) was heated with 50 ml CCl_4[20] to give 1.02 g of undissolved tan solid[21] and a clear filtrate from which 2.46 g of yellow crystals, mp 69° -71°, were obtained on cooling the solution to -5°. A second crop of 0.97 g from the mother liquor provided a total of 3.43 g (61%) of F-picryldinitromethane as yellow plates. A colorless material was obtained by several recrystallizations from CCl_4 with charcoal added, mp 71° - 72°[22]. The largest fragment in the mass spectrum (70 ev) corresponded to P-2(NO_2) at m/e 279.

Analysis

Calculated:	C, 22.65; F, 15.36; N, 18.87
Found:	C, 22.45; F, 15.60; N, 18.64

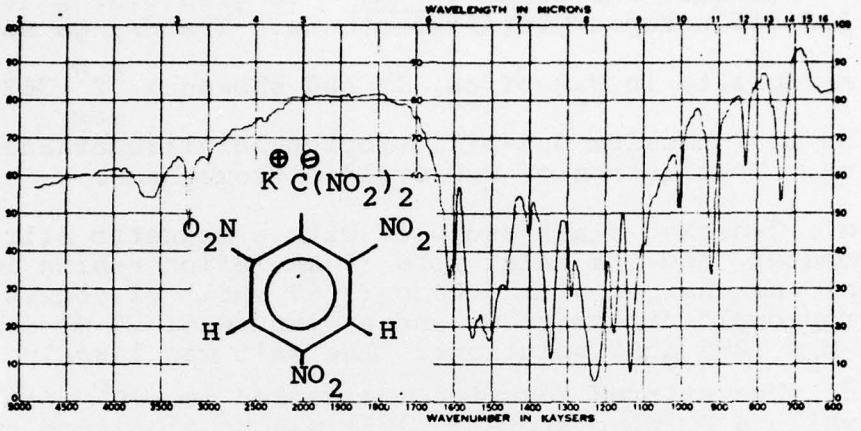
[20] Some decomposition occurred during this process as evidenced by brown fumes above the solution surface.

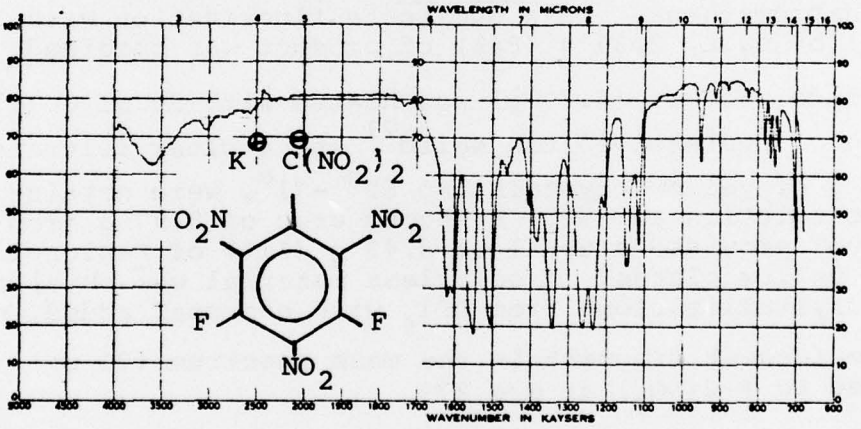
[21] The tan solid was soluble in water to give a light yellow, neutral solution. It was unchanged on heating to 200° and showed only a single strong absorption in the infrared at 765 cm^{-1}.

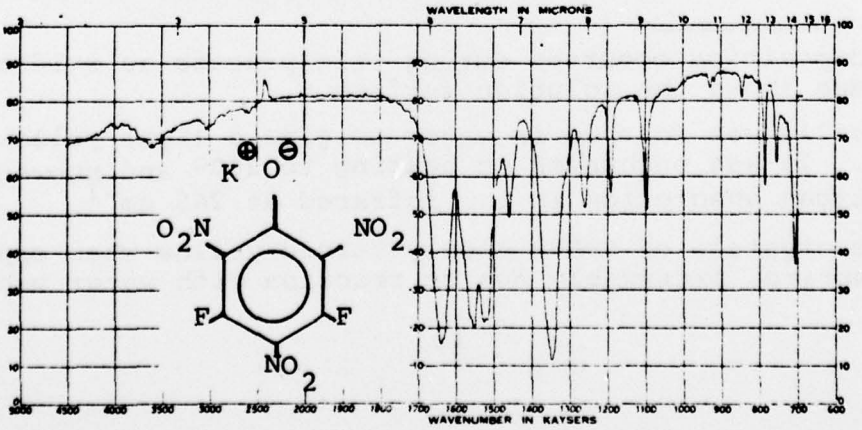
[22] The white crystals of FPDNM slowly turned yellow when exposed to the atmosphere, presumably due to reaction with water vapor.

TABLE 2

INFRARED SPECTRA







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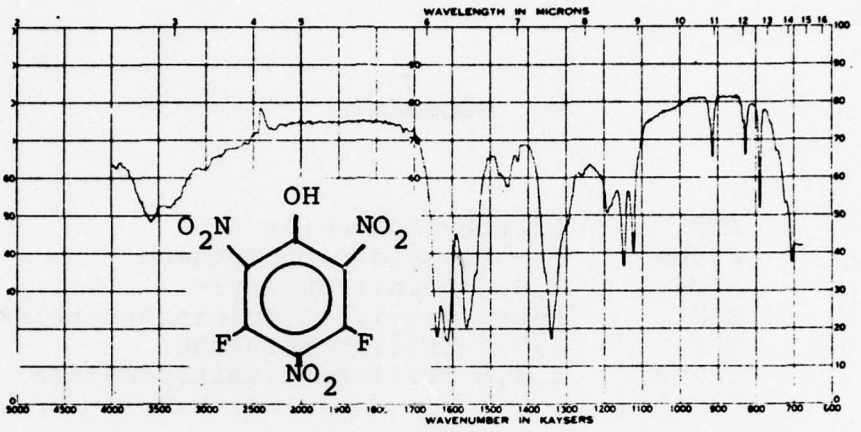

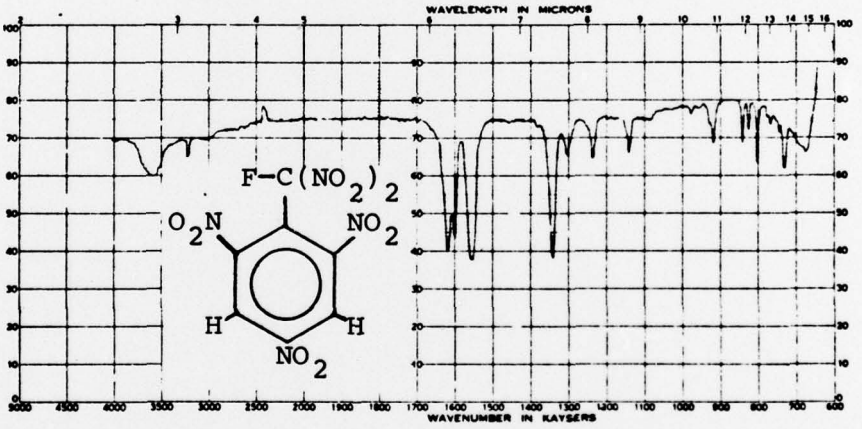

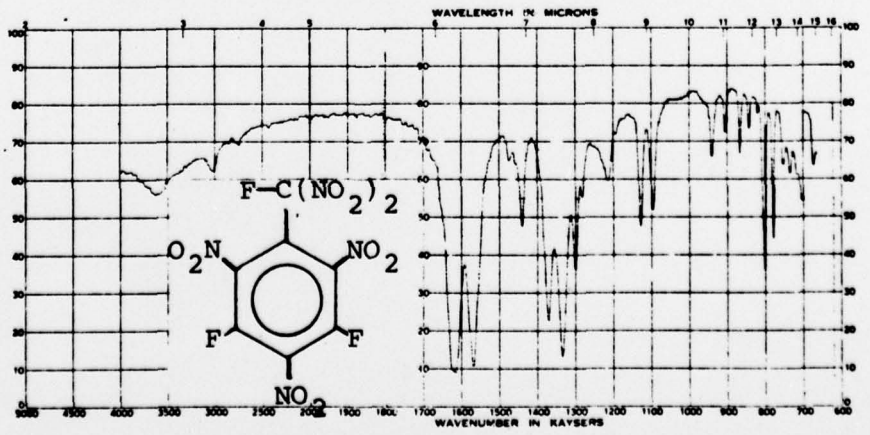

GLOSSARY

DMF	Dimethylformamide
FPDNM	F - Picryldinitromethane
Picryl	2,4,6-Trinitrophenyl-
RDX	Hexahydro-1,3,5-trinitro-s-triazine
TFB	1,3,5-Trifluorobenzene
TFTNB	1,3,5-Trifluorotrinitrobenzene

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