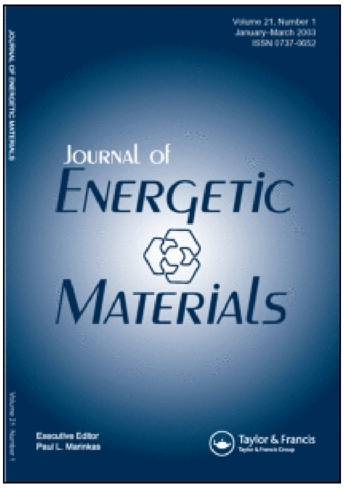


Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

Synthesis and properties of some trisubstituted trinitrobenzenes. TATB analogs

Michael Chaykovsky[a]; Horst G. Adolph[a]
[a] Energetic Materials Division, Naval Surface Warfare Center, Silver Spring, MD

To cite this Article Chaykovsky, Michael and Adolph, Horst G.(1990) 'Synthesis and properties of some trisubstituted trinitrobenzenes. TATB analogs', Journal of Energetic Materials, 8: 5, 392 — 414

To link to this Article: DOI: 10.1080/07370659008225431

URL: http://dx.doi.org/10.1080/07370659008225431

SYNTHESIS AND PROPERTIES OF SOME TRISUBSTITUTED TRINITROBENZENES. TATB ANALOGS

Michael Chaykovsky and Horst G. Adolph

Energetic Materials Division
Naval Surface Warfare Center
White Oak, Silver Spring, MD 20903-5000

ABSTRACT

The preparation of a number of trisubstituted trinitrobenzene derivatives which are structurally related to TATB is described. These compounds were designed to have diversified properties and were characterized with respect to their density and impact sensitivity. Some observations on sensitivity trends in these TATB analogs are discussed.

INTRODUCTION

The unique structure of 1,3,5-Triaminotrinitrobenzene[1-3] (TATB) confers properties which include a high density (1.935 g/cm^3), high thermal stability, a heat of detonation comparable to TNT, and an extremely low impact sensitivity (>320cm; 2.5kg drop weight). As part of a broad program on the determination of

Journal of Energetic Materials Vol. 8, 416-441 (1990)
Published in 1990 by Dowden, Brodman & Devine, Inc.

structure-property relationship in energetic materials, the object of this work was the synthesis and characterization of trisubstituted trinitrobenzenes which are structurally analogous to TATB. The compounds were designed to permit an elucidation of the effects of structural changes in the TATB molecule on impact sensitivity and density, as well as other properties of interest such as chemical and thermal stability.

The starting material for the preparation of these compounds was 1,3,5-trifluorotrinitrobenzene (TFTNB) because of its great reactivity toward aromatic nucleophilic substitution.[4] Displacement reactions of fluorine in TFTNB and its mono- and disubstituted derivatives were conducted with various N, O, and C nucleophiles to prepare a variety of trisubstituted trinitrobenzenes.

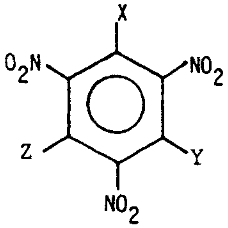
SYNTHESIS AND PROPERTIES OF TRISUBSTITUTED TRINITROBENZENES

TFTNB and its Mono- and Diamino Derivatives

1,3,5-Trifluorotrinitrobenzene (1) was prepared by the one-pot direct nitration of sym- trifluorobenzene.[5] The amino derivative, difluoropicramide, (2, DFP), and the diamino derivative, fluorodiaminotrinitrobenzene (3, F-DATB)[6] were prepared from 1 by published procedures.[4] Table 1 lists the properties of these compounds, which were used to synthesize the other compounds in this report.

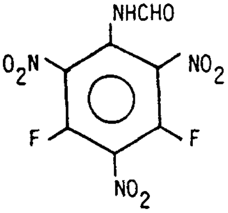
TABLE 1

Properties of TFTNB and Amino Derivatives

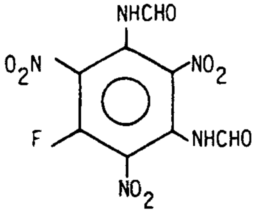


Compound No.	Substituents	M.P. (°C)	D (g/cm^3)[7]	I.S. H_{50} (cm)[8]
1 (TFTNB)	X,Y,Z-F	82	2.00	-
2 (DFP)	X,Y-F; Z-NH_2	118	1.939	62
3 (F-DATB)	X-F; Y,Z-NH_2	223	1.946[9]	176

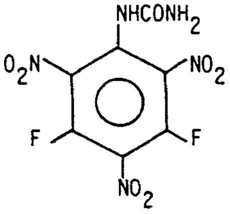
TFTNB reacted with formamide, in refluxing tetrahydrofuran, to give a moderate yield of the formamido derivative (4) which was separated by chromatography from a small amount of the diformamido derivative (5). Similarly, finely powdered urea slowly reacted with TFTNB at ambient temperature in tetrahydrofuran to give the ureido derivative (6).



4



5

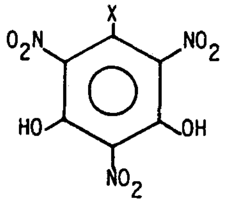


6

Styphnic Acid Derivatives

Difluoropicramide (DFP) and compounds 4 and 6 were hydrolyzed to the substituted styphnic acids (7), (8) and (9), respectively. Some properties are reported in Table 2.

TABLE 2
Properties of Styphnic Acid Derivatives



Compound No.	X	M.P. (°C)	D $(g/cm^3)^{10}$	I.S.; H_{50} $(cm)^8$
7	$-NH_2$	234	(1.88)	32.4
8	-NHCHO	174	(1.71)	73.8
9	$-NHCONH_2$	164	(1.81)	35.9

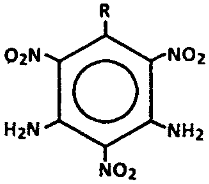
Derivatives of F-DATB

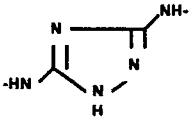
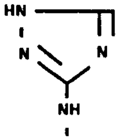
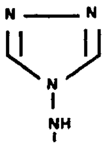
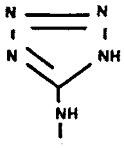
Table 3 lists the properties of F-DATB derivatives which were prepared by direct displacement of fluorine, except for compound 10, which was prepared from TFTNB.

TFTNB reacted with excess formamide in refluxing p-dioxane to give 10 in 31% yield, rather than the triformamido derivative. The details of this transformation are not known, since 10 was the only product isolated. The NMR spectrum of 10 in acetone shows a mixture of isomers due to hindered rotation about the carbon-

TABLE 3

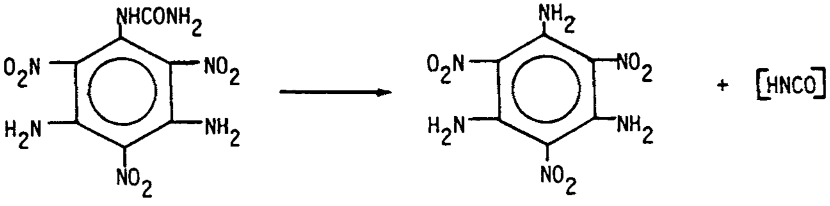
PROPERTIES OF F-DATB DERIVATIVES



COMPOUND NO.	R	M.P. (^{0}C)	D (g/cm^3)[10]	I.S. H_{50} (cm)[8]
10	-NHCHO	229	(1.83)	226
11	-NHCONH$_2$	>350	(1.90)	>320
12	-NHC(NH$_2$) = N-NO$_2$	184	(1.65)	46.6
13	-NH(CH$_2$)$_2$NH-	305	(1.80)	189
14		295	(1.79)	112
15		>340	(1.82)	118
16		232	(1.76)	55.4
17		230	(1.83)	30.8

nitrogen bond in the formamido group.[11] Reaction with gaseous ammonia or hydrolysis under acidic or basic conditions converted 10 into TATB.

Urea reacted readily with F-DATB in DMF at 90°C to give the ureido derivative (11), which exhibits properties similar to TATB. This compound is of interest because the ureido group may act as an energy-sink via conversion into an amino group with loss of HNCO. This conversion is seen in the mass spectrum of 11, which shows no mass ion for 11, but is qualitatively similar to the spectrum of TATB.



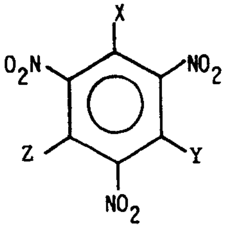
11

Nitroguanidine did not react with F-DATB. However, sodium nitroguanidide reacted to give 12. Ethylenediamine and 3,5-diamino-1,2,4-triazole each reacted with two equivalents of F-DATB to give the bis-derivatives 13 and 14, respectively. Both were isolated as fine powders which were difficult to crystallize. The heterocyclic derivatives (15), (16), and (17) were prepared by the reaction of F-DATB with the corresponding heterocyclic amines.

Fluorodinitroethoxy and Fluorodinitroethylamino Derivatives of F-DATB, DFP and TFTNB

Both fluorodinitroethanol[12] and fluorodinitroethylamine[13] reacted with each of the starting compounds (F-DATB, DFP and TFTNB) to give the fluorodinitroethoxy and fluorodinitroethylamino derivatives listed in Table 4. In all of these reactions, nucleophilic displacement of fluorine occurred smoothly and completely, in the presence of base, to yield the products 18 - 23 as crystalline solids.

TABLE 4
Properties of Fluorodinitroethoxy and Fluorodinitroethylamino Derivatives of F-DATB, DFP and TFTNB



Compound No.	Substituents	M.P. (°C)	D $(g/cm^3)^{10}$	I.S. H_{50} (cm)[8]
18	$X{-}CF(NO_2)_2CH_2O{-}$; $Y,Z{-}NH_2$	190	(1.82)	56.8
19	$X,Y{-}CF(NO_2)_2CH_2O{-}$; $Z{-}NH_2$	140	(1.79)	30.0
20	$X,Y,Z{-}CF(NO_2)_2CH_2O{-}$	170	(1.77)	14.9
21	$X{-}CF(NO_2)_2CH_2NH{-}$;$Y,Z{-}NH_2$	198	(1.82)	49.3
22	$X,Y{-}CF(NO_2)_2CH_2NH{-}$; $Z{-}NH_2$	145	(1.81)	21.2
23	$X,Y,Z{-}CF(NO_2)_2CH_2NH{-}$	182	(1.75)	22.0

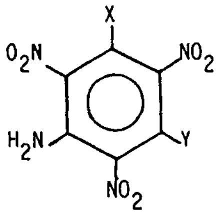
Cyano, Carboxamido and Carboxy Derivatives of F-DATB and DFP

The reaction of potassium cyanide with TFTNB and its amino derivatives F-DATB and DFP results in the formation of complex reaction mixtures of no practical synthetic value. However, cyanotrimethylsilane reacts with F-DATB and DFP in refluxing nitromethane to give the nitrile (24) and the dinitrile (25) respectively in good yields (Table 5). The syntheses of these compounds were reported in an earlier communication.[14] Under a variety of conditions, TFTNB also reacted with cyanotrimethylsilane, but, in each case, the result was a complex mixture from which no sym-tricyanotrinitrobenzene could be isolated. Some high melting silicon containing solids were isolated which were formed probably by further reaction of the cyanotrimethylsilane with the nitrile groups.[15]

The aromatic nitriles 24 and 25 were hydrolyzed by concentrated sulfuric acid to the amides 26 and 27 respectively, and hot 70% aqueous sulfuric acid converted both 24 and 26 to the carboxylic acid (28). Table 5 lists some properties of these compounds.

TABLE 5

Properties of Cyano, Carboxamido, and Carboxy Derivatives of F-DATB and DFP



Compound No.	Substituents	M.P. (°C)	D(g/cm^3)[10]	I.S.; H_{50} (cm)[8]
24	X–CN;Y–NH_2	221	(1.83)	184
25	X,Y–CN	179	(1.76)	92.9
26	X–$CONH_2$;Y–NH_2	290	1.887[16]	221
27	X,Y–$CONH_2$	>340	(1.85)	168
28	X–CO_2H;Y–NH_2	~240	1.863[17]	>320

DISCUSSION

Sensitivity Trends in TATB Analogs

The impact sensitivities of the new compounds reported here are to be examined in more detail in a broader context. However, some preliminary observations can be made.

The uniform increase in sensitivity on replacing a single amino group in TATB with a variety of groups of different steric requirements and energy content is obvious. The ureido (compound

11) and carboxyl (compound 28) groups are the sole exceptions. In the case of 11, this may be due to the endothermic decomposition of this material (possibly by loss of HNCO, see above) near 230°C, as was determined by differential scanning calorimetry. Diaminotrinitrobenzoic acid (28) also decomposes near 230°C (loss of CO_2), but exothermally, and the reason for its relative insensitivity is not obvious. Note that a similar increase in sensitivity is not observed for the styphnic acids 7 and 8 listed in Table 2, nor is there a decrease in sensitivity on introducing an amino group into styphnic acid (32 vs 43cm).[18]

Compound 13, in which two TATB molecules are linked via an ethylene group, is significantly more sensitive than TATB despite its lower oxygen balance and the absence of any obvious trigger linkages. On the other hand, the high sensitivity of the azole-linked TATBs may be due to the weak N-N linkages present in the heterocyclic rings.

The strong sensitization by the fluorodinitroethoxy and fluorodinitroethylamino substituents is noteworthy. This must be a manifestation of contributions by the additional energetic groups to the initiation processes.

EXPERIMENTAL

Infrared (IR) spectra were taken on a Perkin-Elmer Model 283 recording spectrophotometer. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian XL-200 instrument (TMS referenced). Mass spectra were determined using a Finnigan Model 4000, GC EI-CI instrument. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee. Melting points were determined on a Thomas-Hoover capillary apparatus and are uncorrected.

3,5-Difluorotrinitro-N-formylaniline (4) and 5-Fluorotrinitro-N,N'-diformyl-1,3-benzenediamine (5)

A solution of 1 (2.67g, 0.01 mol) and formamide (4.53g, 0.10 mol, 4 mL) in THF (20 mL) was refluxed for 3 h. TLC (Brinkman MN silica gel; 20% $CH_3CN-C_6H_6$) showed the presence of a major and minor component at R_f 0.71 and 0.40 respectively, in addition to lesser amounts of other substances. The solution was evaporated to dryness and the residue was dissolved in ether, washed with H_2O, dried ($MgSO_4$), and evaporated. The residue was chromatographed on silica gel 60 (60g, Merck EM, 70-230 mesh) using 20% $CH_3CN-C_6H_6$ as eluent. The major component was isolated and recrystallized from benzene to give 4 (1.2g, 41%): mp 179-180°C dec; IR (KBr) 1725 (sh) cm^{-1} and 1700 (C=O), 1620, 1555, 1480; mass spectrum (CI, CH_4) m/z 265 (M+1-CO, 100), 293 (M+1, 81), 321 ($M+C_2H_5$, 13), 333 ($M+C_3H_5$, 6.6); ^1H NMR (Me_2SO - d_6) δ 8.36 (s, CH), 11.63 (br s, NH).

Anal. Calcd for $C_7H_2F_2N_4O_7$: C, 28.78; H, 0.69; F, 13.01; N, 19.18. Found: C, 28.93; H, 0.74; F, 12.86; N, 18.91.

The minor component was recrystallized from 10% $CH_3CN-C_6H_6$ to give 5 (170 mg, 5.4%): mp 238-240°C dec; IR (KBr) 1695 cm^{-1} (C=O), 1605, 1555, 1490; mass spectrum (CI, CH_4) m/z 262 (M+1-2CO, 100), 318 (M+1, 34) 346 ($M+C_2H_5$, 9) 358 ($M+C_3H_5$, 6); ^1H NMR (Me_2SO-d_6) δ 8.26 (s, 2, 2CH), 11.33 (s, 2, 2NH).

Anal. Calcd for $C_8H_4FN_5O_8$: C, 30.29; H, 1.27; F, 5.99; N, 22.08. Found: C, 30.39; H, 1.50; F, 5.89; N, 22.07.

3,5-Difluorotrinitrophenylurea (6)

A mixture of 1 (2.67g, 10 mmol), powdered urea (600 mg, 10 mmol) and dry THF (50 mL) was stirred at room temperature for 17 h, then evaporated to dryness under vacuum. The residue was triturated with benzene (10 mL) and filtered to yield 6 (2.7g, 87.9%): mp 164-166°C dec. Recrystallization from 1,2-dichloroethane (charcoal) gave pale yellow needles: mp 175-176°C dec; IR (KBr) 1730 cm^{-1} (C=O); mass spectrum (CI, CH_4) m/z 265 (M+1-HNCO, 100).

Anal. Calcd for $C_7H_3F_2N_5O_7$: C, 27.37; H, 0.98; N, 22.80; F, 12.37. Found C, 27.40; H, 1.03; N, 22.75; F, 12.53.

5-Aminostyphnic Acid (7)

To a solution of 2 (1.58g, 6 mmol) in CH_3CN (100 mL) was added 1N aqueous $NaHCO_3$ (12 mL) and H_2O (30 mL). The solution was then refluxed for 1 h followed by evaporation under vacuum almost to dryness. Water (50 mL) was added and the solution adjusted to pH 0.1 with conc. HCl. The mixture was cooled in ice and the solid filtered to yield 7 (1.52g, 97.4%): mp 228-230°C dec. Recrystallization from H_2O gave brown-yellow needles: mp 233-234°C dec (lit.[19] mp 236-237°C dec); mass spectrum (CI, CH_4) m/z 261 (M+1, 100).

Anal. Calcd for $C_6H_4N_4O_8$: C, 27.70; H, 1.55; N, 21.54. Found: C, 27.72; H, 1.53; N, 21.43.

5-Formamidostyphnic Acid (8)

A mixture of 4 (2.34g, 8 mmol), $NaHCO_3$ (672 mg, 8 mmol), THF (80 mL), and H_2O (40 mL) was stirred at room temperature for 45 min, then evaporated under vacuum to 25 mL and adjusted to pH 0.5 with conc. HCl. The precipitated solid was filtered, washed with 1N HCl, dried, and recrystallized from benzene to give yellow needles (1.65g, 71.7%): mp 173-174°C dec. IR (KBr) 1725 (sh) cm^{-1} and 1700 (C=O), 1615, 1550, 1505. The ^1H NMR spectrum (acetone - d_6) showed a mixture of rotational isomers about the N-C=O bond. Sharp C-H singlets appeared at δ 8.35 and 8.37 (ratio ~1:5), a broad peak at 6.50 (OH) and broad overlapping peaks at 9.90 and 10.15 (NH).

Anal. Calcd for $C_7H_4N_4O_9$: C, 29.18; H, 1.40; N, 19.45. Found: C, 29.15; H, 1.29; N, 19.25.

5-Ureidostyphnic Acid (9)

A solution of 6 (3.07g, 10 mmol) in THF (100 mL) and H_2O (50 mL) was stirred at room temperature for 2 h, then concentrated under vacuum to 50 mL and adjusted to pH 0.1 with conc. HCl. The mixture was cooled in ice and filtered to give yellow crystals (2.3g, 75.9%): mp 158-160°C dec. A sample was dissolved in H_2O and precipitated with conc. HCl to give the analytical sample: mp 163-164°C dec; IR (KBr) 1725 (sh) cm^{-1} and 1690 (C=O), 1620, 1540; ^1H NMR (acetone - d_6) δ 6.42 (s, 2, OH), 7.82 (br s, 2, NH_2), 8.90 (br s, 1, NH).

Anal. Calcd for $C_7H_5N_5O_9$: C, 27.73; H, 1.66; N, 23.10. Found: C, 27.74; H, 1.55; N, 22.99.

N-Formyltrinitro-1,3,5-benzenetriamine (10)

A solution of 1 (5.34g, 0.02 mol) and formamide (9.06g, 0.2 mol, 8 mL) in p-dioxane (40 mL) was refluxed for 17 h. The solvent was evaporated and the residue was triturated with H_2O (60 mL). Filtration gave a deep-yellow solid (3.7g) which was heated in boiling CH_3CN (250 mL), filtered to remove insoluble matter, and the filtrate concentrated to 75 mL, treated with charcoal and filtered. The cooled solution yielded 10 (1.75g, 30.6%) as deep-yellow crystals: mp 220-224°C dec. Recrystallization from CH_3CN gave the analytical sample: mp 228-229°C dec; IR (KBr) 1718 cm^{-1} (C=O), 1600, 1495, 1440, 1360; mass spectrum (E.I.) 67 (100), 240 ($M-NO_2$, 90), 258 (M-CO, 10), 286 (M, 1). The ^1H NMR spectrum (acetone - d_6) showed a mixture of rotational isomers about the N-C=O bond. Sharp CH singlets appeared at δ 7.33 and 8.36 (ratio ~1:3) and broad NH and NH_2 peaks at 8.72, 9.56, and 10.25. This compound was converted almost quantitatively into TATB by NH_3 gas (in THF), and by acidic (HCl, THF) or basic (K_2CO_3, H_2O, THF) hydrolysis.

Anal. Calcd for $C_7H_6N_6O_7$: C, 29.38, H, 2.11; N, 29.37. Found: C, 29.18; H, 2.40; N, 29.53.

5-Ureidotrinitro-1,3-benzenediamine (11)

A solution of 3 (1.57g, 6 mmol) and urea (1.80g, 30 mmol) in dry DMF (30 mL) was heated for 1 h at 90°C. A yellow precipitate formed after about 5 min. The mixture was cooled, poured into cold H_2O (150 mL) and the solid filtered. Trituration of the solid with warm DMF-H_2O (1:1, 100 mL), filtration and drying gave 11 (1.67g, 92.3%): mp > 350°C dec; IR (KBr) 1730 cm^{-1} (C=O); mass spectrum (CI, CH_4), m/z 259 (M+1-HNCO, 100).

Anal. Calcd for $C_7H_7N_7O_7$: C, 27.91; H, 2.34; N, 32.56. Found: C, 27.65; H, 2.32; N, 32.31.

5-(2-Nitroguanidino)-trinitro-1,3-benzenediamine (12)

Sodium hydride (576 mg of 50% oil dispersion, 12 mmol) was placed in a reaction flask, washed once with hexane (10 mL) by decantation and then dried with a stream of dry nitrogen. Dry DMF (15 mL) was then added with stirring, followed by nitroguanidine (1.46g, 14 mmol), in portions, during vigorous evolution of hydrogen. After 15 min, the flask was cooled in ice and a solution of 3 (2.61g, 10 mmol) in DMF (10 mL) was added over 5 min. After 30 min, H_2O (120 mL) was added to the red solution and the mixture adjusted to pH 1 with conc. HCl. The precipitated solid was filtered, washed with H_2O and dried to give 3.05g of crude orange product. Recrystallization from CH_3CN afforded 12 (1.8g, 52.2%) as fine yellow crystals: mp 182-183°C dec.

Anal. Calcd for $C_7H_7N_9O_8$: C, 24.35; H, 2.04; N, 36.52. Found: C, 24.53; H, 2.13; N, 36.28.

1,2-Bis-(3,5-diaminotrinitroanilino)-ethane (13)

A mixture of 3 (1.57g, 6 mmol), ethylene diamine (180 mg, 3 mmol), $NaHCO_3$ (2.0g, 23.8 mmol) and 1,2-dichloroethane (100 mL) was refluxed for 1 h. The solvent was removed under vacuum and the solid residue was then stirred with H_2O (100 mL), filtered, washed with H_2O, and dried to give 13 (1.62g, 99.6%) as a yellow solid: mp 300-305°C dec.

Anal. Calcd for $C_{12}H_{14}N_{12}O_{12}$: C, 31.00; H, 2.60; N, 30.99. Found: C, 31.04; H, 2.73; N, 30.83.

3,5-Bis-(3,5-diaminotrinitroanilino)-1,2,4-triazole (14)

To a solution of 3,5-diamino-1,2,4-triazole (297 mg, 3 mmol) in DMF (20 mL) was added pyridine (491 mg, 3 mmol) followed by 3 (1.57g, 6 mmol). After stirring the deep red solution for 15 min at room temperature, H_2O (80 mL) was added, and the mixture was then adjusted to pH 2 with conc. HCl. The solid was filtered, washed with H_2O, and dried to give 14 (1.65g, 94.6%) as a rust-colored powder: mp 295-300°C dec (10°/min).

Anal. Calcd for $C_{14}H_{11}N_{15}O_{12}$: C, 28.92; H, 1.91; N, 36.14. Found: C, 28.99; H, 2.03; N, 34.72.

3-(3,5-Diaminotrinitroanilino)-1,2,4-triazole (15)

A mixture of 3 (1.57g, 6 mmol), 3-amino-1,2,4-triazole (1.008g, 12 mmol) and 1,2-dichloroethane (90 mL) was refluxed for 1 h, cooled, and the solid filtered. The yellow solid was then stirred with H_2O (50 mL), filtered, washed with H_2O, and dried to yield 15 (1.94g, quant.). The analytical sample was obtained by recrystallization from DMF-CH_3OH (charcoal): mp > 340°C dec; mass spectrum (CI, CH_4), m/z 326 (M+1, 100).

Anal. Calcd for $C_8H_7N_9O_6$: C, 29.54; H, 2.17; N, 38.77. Found: C, 29.65; H, 2.38; N, 37.61.

4-(3,5-Diaminotrinitroanilino)-1,2,4-triazole (16)

A mixture of 3 (1.57g, 6 mmol), 4-amino-1,2,4-triazole (1.26g, 15 mmol) and 1,2-dichloroethane (150 mL) was refluxed for 2 h, cooled, and the solid filtered. The yellow solid was then stirred with H_2O (100 mL), filtered, washed with H_2O, and dried to yield 16 (1.92g, 98.4%): mp 230-231°C dec. The analytical sample was obtained by recrystallization from DMF-CH_3CN (charcoal): mp 232°C dec.

Anal. Calcd for $C_8H_7N_9O_6$: C, 29.54; H, 2.17; N, 38.77. Found: C, 29.80; H, 2.25; N, 38.66.

5-(3,5-Diaminotrinitroanilino)-tetrazole (17)

A mixture of 3 (522 mg, 2 mmol), 5-aminotetrazole monohydrate (515 mg, 5 mmol) and 1,2-dichloroethane (30 mL) was refluxed for 5 h, cooled, and the solid filtered. The yellow solid was then stirred with H_2O (30 mL), filtered, washed with H_2O, and dried to yield 17 (600 mg, 92%). The analytical sample was obtained by recrystallization from DMF-MeOH. This compound decomposes violently (pops) between 215°C and 230°C (10°/min); mass spectrum (CI, CH_4) m/z 85 (100), 327 (M+1, 10).

Anal. Calcd for $C_7H_6N_{10}O_6$: C, 25.77; H, 1.85; N, 42.94. Found: C, 25.90; H, 1.86; N, 42.71.

5-(2-Fluoro-2,2-dinitroethoxy)-trinitro-1,3-benzenediamine (18)

A mixture of 3 (1.57g, 6 mmol), 2-fluoro-2,2-dinitroethanol (3.18g, 20.65 mmol, in 6 mL of CH_2Cl_2), $NaHCO_3$ (4.0g, 47.6 mmol), and 1,2-dichloroethane (100 mL) was refluxed for 3 h. The solvents were then evaporated under vacuum and the residue was triturated with H_2O (70 mL). Filtration afforded 2.35g of orange solid which was recrystallized from 1,2-dichloroethane-isopropyl ether to give pure <u>18</u> (1.6g, 67.5%): mp 187-188°C; ^1H NMR (Me_2SO - d_6) δ 5.43 (d, 2, CH_2, J=15 Hz), 8.60 (s, 4, $2NH_2$).

Anal. Calcd for $C_8H_6FN_7O_{11}$: C, 24.81; H, 1.53; N, 24.81; F, 4.81. Found: C, 24.66; H, 1.56; N, 24.69; F, 4.85.

3,5-Bis-(2-Fluoro-2,2,dinitroethoxy)-trinitroaniline (19)

A mixture of <u>2</u> (1.58g, 6 mmol), 2-fluoro-2,2-dinitroethanol (6.36g, 41.3 mmol, in 12 mL CH_2Cl_2), $NaHCO_3$ (4.0g, 47.6 mmol), and CH_2Cl_2 (100 mL) was refluxed for 5 h. The mixture was then washed with H_2O (2 x 50 mL), saturated salt solution (25 mL), dried (Na_2SO_4), and evaporated under vacuum to leave an orange solid which was recrystallized from 1,2-dichloroethane-isopropyl ether to yield <u>19</u> (2.4g, 75.2%): mp 132-136°C. Recrystallization from the same solvent mixture gave the analytical sample: mp 136-138°C; ^1H NMR (Me_2SO - d_6) δ 5.50 (d, 4, $2CH_2$, J=15 Hz), 7.92 (s, 2, NH_2).

Anal. Calcd for $C_{10}H_6F_2O_{16}$: C, 22.57; H, 1.14; N, 21.06; F, 7.14. Found: C, 22.78; H, 1.18; N, 20.92; F, 7.02.

1,3,5-Tris-(2-Fluoro-2,2-dinitroethoxy)-trinitrobenzene (20)

A mixture of <u>1</u> (1.07g, 4 mmol), 2-fluoro-2,2-dinitroethanol (6.36g, 41.3 mmol, in 12 mL CH_2Cl_2), $NaHCO_3$ (4.0g, 47.6 mmol), and CH_2Cl_2 (100 mL) was refluxed for 5 h. The mixture was then washed with H_2O (2 x 50 mL), saturated salt solution (25 mL), dried (Na_2SO_4) and evaporated under vacuum to leave a yellow oil which crystallized upon scratching. Recrystallization from 1,2-

dichloroethane-isopropyl ether gave yellow crystals of 20 (1.9g, 70.9%): mp 172-174°C; ^1H NMR (Me_2SO - d_6) δ 5.60 (d, 6, $3CH_2$, J=15 Hz).

Anal. Calcd for $C_{12}H_6F_3N_9O_{21}$: C, 21.53; H, 0.90; N, 18.84; F, 8.52. Found: C, 21.79; H, 0.90; N, 18.71; F, 8.65.

N-(2-Fluoro-2,2-dinitroethyl)-trinitro-1,3,5-benzenetriamine (21)

To a suspension of 3 (261 mg, 1 mmol) in CH_2Cl_2 (30 mL) was added pyridine (237 mg, 3 mmol), followed by a 2-fluoro-2,2-dinitroethylamine (4.59 mL of a 10% W:V CH_2Cl_2 solution, 3 mmol). The solid dissolved and after about 10 min, a precipitate appeared. After stirring at room temperature for 90 min, hexane (30 mL) was added and the solid filtered, then stirred with H_2O (30 mL), filtered again, and dried to give 21 (300 mg, 76.1%): mp 195°C dec. Recrystallization from 1,2-dichloroethane gave yellow crystals: mp 198°C dec; ^1H NMR (Me_2SO - d_6) δ 4.55 (d, 2, CH_2, J=14 Hz), 9.43 (s, 4, $2NH_2$).

Anal. Calcd for $C_8H_7FN_8O_{10}$: C, 24.37; H, 1.79; N, 28.43; F, 4.87. Found: C, 24.47; H, 1.71; N, 28.23; F, 4.82.

N,N'-Bis(2-fluoro-2,2-dinitroethyl)-trinitro-1,3,5-benzenetriamine (22)

To a solution of 2 (1.58g, 6 mmol) in CH_2Cl_2 (100 mL) was added $NaHCO_3$ (4.0g, 47.6 mmol) followed by 2-fluoro-2,2-dinitroethylamine (36.7 mL of a 10% W:V CH_2Cl_2 solution, 24 mmol). After stirring at room temperature for 3 h, the mixture was filtered and the pale yellow filtrate was then washed with H_2O (25 mL), 2N HCl (2 x 25 mL), H_2O (25 mL), saturated salt solution

(25 mL), dried (Na_2SO_4), and evaporated under vacuum to leave a yellow solid. Trituration with ether (15 mL) and filtering gave 22 (2.3g, 72.3%): mp 137-141°C dec. Recrystallization from 1,2-dichloroethane-isopropyl ether gave yellow crystals: mp 143-145°C dec. ^1H NMR (Me_2SO - d_6) δ 4.90 (d, 4, $2CH_2$, J=14 Hz), 9.70 (s, 2, NH_2).

Anal. Calcd for $C_{10}H_8F_2N_{10}O_{14}$: C, 22.65; H, 1.52; N, 26.42; F, 7.17. Found: C, 22.48; H, 1.48; N, 26.10; F, 7.28.

N,N',N"-Tris-(2-fluoro-2,2-dinitroethyl)-trinitro-1,3,5-benzenetriamine (23)

To a solution of 1 (1.60g, 6 mmol) in CH_2Cl_2 (100 mL) was added 2-fluoro-2,2-dinitroethylamine (55.1 mL of a 10% W:V CH_2Cl_2 solution, 36 mmol) followed by $NaHCO_3$ (6.0g, 71.4 mmol). After stirring at room temperature for 4 h, hexane (100 mL) was added and the mixture of solids was filtered. The solids were extracted with hot 1,2-dichloroethane (300 mL), treated with charcoal, filtered, and the filtrate was concentrated to 50 mL. Refrigeration overnight deposited 2.5g of yellow solid: mp 172-175°C. Recrystallization from 1,2-dichloroethane gave crystalline 23 (2.0g, 50%): mp 181-182°C. ^1H NMR (Me_2SO - d_6) δ 4.87 (d, 6, $3CH_2$, J=14 Hz).

Anal. Calcd for $C_{12}H_9F_3N_{12}O_{18}$: C, 21.63; H, 1.36; N, 25.23; F, 8.55. Found: C, 21.69; H, 1.31; N, 25.11; F, 8.55.

3,5-Diaminotrinitrobenzamide (26)

A mixture of 24 (2.68g, 10 mmol)[14] and conc. H_2SO_4 (20 mL) was stirred at room temperature for 2 h, during which time the solid dissolved. The solution was then poured onto a mixture of ice and H_2O (150 mL) and the precipitated solid was filtered, washed with H_2O, and dried to give <u>26</u> (2.8g, 97.9%): mp 289-290°C dec. Recrystallization from CH_3NO_2 gave deep yellow crystals: mp 290-291°C dec.

Anal. Calcd for $C_7H_6N_6O_7$: C, 29.38; H, 2.11; N, 29.37. Found: C, 29.28; H, 2.11; N, 29.18.

5-Aminotrinitroisophthalamide (27)

Similarly, <u>25</u> was hydrolyzed[14] to yield <u>27</u> (99.7%) as a yellow solid: mp >340°C dec. The analytical sample was obtained by recrystallization from DMF-H_2O.

Anal. Calcd for $C_8H_6N_6O_8$: C, 30.58; H, 1.93; N, 26.75. Found: C, 30.70; H, 1.97; N, 26.64.

3,5-Diaminotrinitrobenzoic Acid (28)

A solution of <u>24</u> (1.34g, 5 mmol) in sulfuric acid (30 mL) and H_2O (15 mL) was refluxed for 90 min, cooled, and then poured onto a mixture of ice and H_2O (250 mL). The solid was filtered, washed with H_2O, and dried to give <u>28</u> (1.33g, 92.7%). Recrystallization from CH_3CN gave yellow needles: mp 240-245 (loss of CO_2) and 280-282°C dec; mass spectrum (EI, CH_4) m/z 244 ($M+1-CO_2$, 100), 272 ($M+C_2H_5-CO_2$, 9.2), 284 ($M+C_3H_5-CO_2$, 4.5).

Anal. Calcd for $C_7H_5N_5O_8$: C, 29.28; H, 1.76; N, 24.39. Found: C, 29.33; H, 184; N, 24.16.

ACKNOWLEDGMENT

This work was performed as part of the explosives project within the Office of Naval Technology Block Program for Explosives and Undersea Warheads (PE 62314).

REFERENCES AND NOTES

1. C. L. Jackson and J. F. Wing, Am. Chem. J. 10, 287 (1888).
2. F. Taylor, Jr., NAVORD Report 4405 (1956).
3. D. G. Ott and T. M. Benzinger, J. Energ. Mat. 5, 343 (1987), and references cited therein.
4. W. M. Koppes, G. W. Lawrence, M. E.Sitzmann and H. G. Adolph, J. Chem. Soc. Perkin Trans. 1, 1815 (1981).
5. W. M. Koppes, H. G. Adolph and M. E. Sitzmann, U. S. Patent 4,173,591 (1979).
6. M. E. Sitzmann, G. W. Lawrence, H. G. Adolph and M. Chaykovsky, U. S. Patent applied for.
7. X-ray diffraction values. The value for compound 1 was determined by J. Holden, NSWC, White Oak; values for compounds 2 and 3 by H. Ammon and collaborators, Chemistry Department, University of Maryland, College Park.
8. Impact sensitivities throughout this report were determined by W. Hogge, Naval Weapons Station, Yorktown, VA., using the Bruceton method, NOL machine, type 12 tools, 2.5 kg weight, 35 ± 2 mgs, 5/0 sandpaper, 25 trials. TNT, 110; Expl. D, 110; Tritonal, 121; Comp A-3, 47.9; RDX, 24.2 cm.

9. H. L. Ammon, S. K. Bhattacharjee and J. R. Holden, Acta Cryst. B38, 1851 (1982).

10. Values in parentheses were determined on a Systems Science and Software (La Jolla, Calif.) 6102-12 gas pycnometer.

11. J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw Hill, New York, 1959, p. 366.

12. M. J. Kamlet and H. G. Adolph, J. Org. Chem. 33, 3073 (1968).

13. H. G. Adolph and M. J. Kamlet, J. Org. Chem. 34, 45 (1969).

14. M. Chaykovsky and H. G. Adolph, Synth. Comm. 16 205 (1986), and Naval Surface Weapons Center Technical Report 83-22, March 1983.

15. W. C. Groutas and D. Felker, Synthesis 861 (1980).

16. X-ray diffraction value. H. L. Ammon and S. K. Bhattacharjee, Acta Cryst. B38, 2083 (1982).

17. X-ray diffraction value. H. L. Ammon and S. M. Prasad, Acta Cryst. C41, 921 (1985).

18. M. J. Kamlet and H. G. Adolph, Propellants, Explos. 4, 30 (1979).

19. B. Flursheim and E. L. Holmes, J. Chem. Soc. 3041 (1928).