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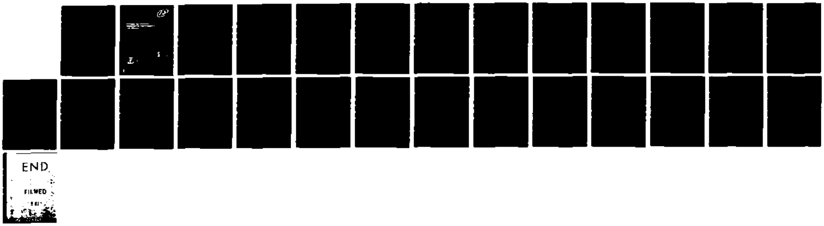

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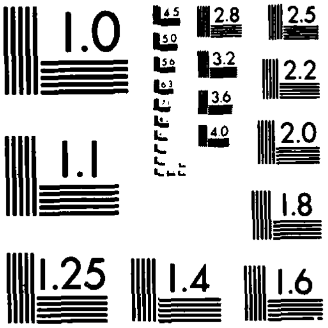

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SYNTHESIS AND PROPERTIES OF TRISUBSTITUTED TRINITROBENZENES. TATB ANALOGS

BY MICHAEL CHAYKOVSKY,
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RESEARCH AND TECHNOLOGY DEPARTMENT

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A series of trisubstituted trinitrobenzene derivatives structurally related to TATB, with diversified physical properties, were synthesized and evaluated with respect to stability, impact sensitivity, and density. Several compounds showed improved sensitivity-performance characteristics relative to standard explosives.

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FOREWORD

Explosive charges which are both highly energetic and insensitive are one of the goals of the Navy's explosive development effort. Both compositional and ingredient properties can greatly affect the balance of performance and sensitivity characteristics. In this work a study had been made of the effects of changes in molecular structure on sensitivity and crystal density of a series of polynitroaromatic compounds to provide guidance for the design and synthesis of insensitive explosives more powerful than TATB. This work was performed under Task SF33-337-691.

Approved by:

J. F. PROCTOR, Head
Energetic Materials Division

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INTRODUCTION

1,3,5-Triaminotrinitrobenzene[1,2] (TATB) is an energetic material which has found a wide range of use in explosive devices. Its unique structure confers properties which include a high density (1.94 g/cm^3), high thermal stability, a heat of detonation comparible to TNT, and an extremely low impact sensitivity (>320cm; 2.5kg drop weight).

The object of this work was the synthesis and initial characterization of trisubstituted trinitrobenzenes, many of which are structurally analogous to TATB. Most of the structures 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, and chemical energy (heat of detonation). In addition, it was hoped that new compounds with properties of interest for explosive applications would be found.

The starting material for the preparation of these compounds was 1,3,5-trifluorotrinitrobenzene (TFTNB) because of its great reactivity toward aromatic nucleophilic substitution. TFTNB was converted into the amino derivative difluoropicramide (DFP), and the fluorodiamino derivative (F-DATB), both of which also served as routine starting materials.

---

[1] Jackson, C. L., Wing, J. F., Am. Chem. J., 1888, 10, 287.

[2] Taylor, F. Jr., "Synthesis of New High Explosives. II. Derivatives of 1,3,5-Tribromo-2,4,6-Trinitrobenzene," NAVORD Report 4405 (1956).

RESULTS AND DISCUSSION

TFTNB and Amino Derivatives

1,3,5-Trifluorotrinitrobenzene (TFTNB, 2) was prepared[3] in this laboratory by the direct nitration of *sym*-trifluorobenzene (1) with potassium nitrate in 30% fuming sulfuric acid at 153-156°C for 72 hours (Scheme I). Although these conditions are rather severe, the reaction is fairly clean and the desired product is produced in 54% yield.

Some of the chemistry of TFTNB has been published recently.[4] Its reaction with acetamide in dimethylformamide at 85°C results in the replacement of one of the fluorines to give the acetamido derivative (3), which upon treatment with concentrated sulfuric acid, and then water, yields difluoropicramide (4) in almost quantitative yield. TFTNB reacts rapidly with two equivalents of *t*-butylamine in methylene chloride to give the disubstituted derivative (5), which solvolyzes in trifluoroacetic acid to yield F-DATB (6). Improved preparations for these compounds are given in the Experimental section of this report.

Table 1 lists the physical properties of TFTNB and its amino derivatives. Although TFTNB and DFP have high densities, they are probably unsuitable as explosives because of their susceptibility to hydrolysis. F-DATB[5] is not readily hydrolyzed by atmospheric moisture and its properties of a high density and moderate impact sensitivity make it a candidate for further evaluation as an explosive.

---

[3] Koppes, W. M., Adolph, H. G., Sitzmann, M. E.,"Process for the Preparation of 1,3,5-Trifluoro-2,3,6-Trinitrobenzene," U. S. Patent 4,173,591, 1979.

[4] Koppes, W. M., Lawrence, G. W., Sitzmann, M. E., Adolph, H. G., "Reaction of 1,3,5-Trifluorotrinitrobenzene with Nucleophiles," *J. Chem. Soc.*, (*Perkin I*), 1981, 1815.

[5] Sitzmann, M. E., Lawrence, G. W., Adolph, H. G., Chaykovsky, M.,"1,3-Diamino-5-Fluorotrinitrobenzene and Method of Preparation," U. S. Patent applied for.

SCHEME I. SYNTHESIS OF TFTNB AND AMINO DERIVATIVES

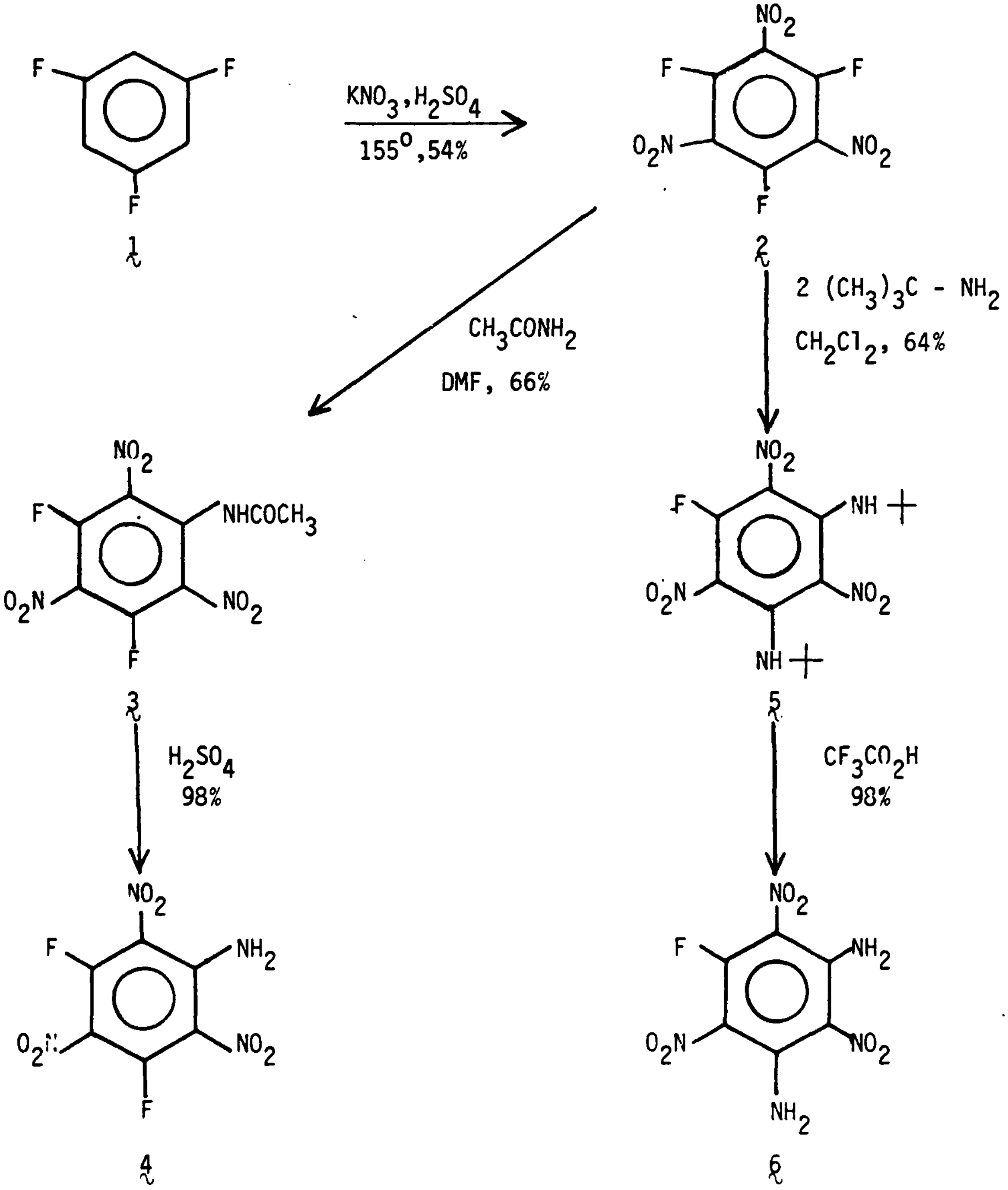


TABLE 1. PHYSICAL PROPERTIES OF TFTNB AND AMINO DERIVATIVES

Compound No.	Compound	M.P. (^{o}C)	ρo (g/cm^3)*	I.S. (H_{50}cm)**
2	TFTNB	82	2.00	-
4	DFP	118	1.939	62
6	F-DATB	223	1.946[6]	176

* X-ray diffraction values. The value for compound **2** was determined by J. Holden NSWC, White Oak; values for compounds **4** and **6** by H. Ammon and collaborators, Chemistry Department, University of Maryland, College Park.

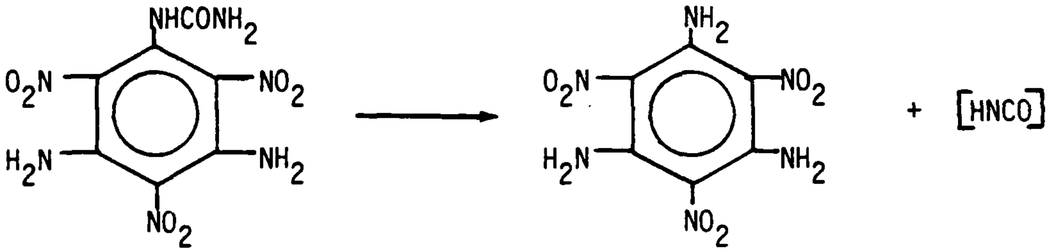
**Impact sensitivities throughout this report were determined by W. Hogge, Naval Weapons Station, Yorktown, VA., using the Bruceton method, NOL machine, type 12 tools, 2.5 kg weight, 35 ± 2 mgs, 5/0 sandpaper, 25 trials. TNT, 110; Expl. D, 110; Tritonal, 121; Comp A-3, 47.9; RDX, 24.2 cm.

Derivatives of F-DATB

Table 2 lists the physical properties of F-DATB derivatives which were prepared by direct displacement of fluorine, except for compound **7**, which was prepared from TFTNB. Compounds **10** and **11** are bis-derivatives.

TFTNB reacted with excess formamide in refluxing p-dioxane to give **7** in 31% yield, rather than the triformamido derivative. The details of this transformation are not known, since **7** was the only product isolated. Decarbonylation of the triformamido derivative or other intermediates probably occurs. The NMR spectrum of **7** in acetone shows a mixture of isomers due to hindered rotation about the carbon-nitrogen bond in the formamido group.[7] Reaction with gaseous ammonia or hydrolysis under acidic or basic conditions converted **7** into TATB.

Urea reacts readily with F-DATB in DMF at 90°C to give the ureido derivative (**8**), which exhibits properties similar to TATB. This compound is of interest because it may be even less sensitive than TATB. 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 **8**, which shows no mass ion for **8**, but which is qualitatively similar to the spectrum of TATB.



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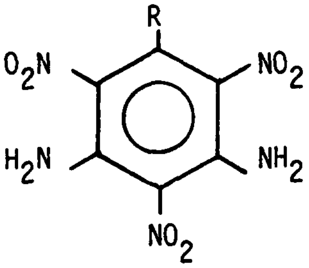
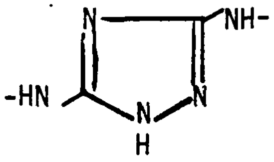
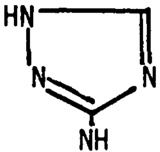
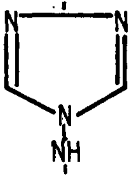
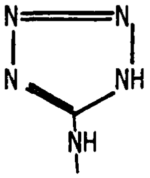
[6] Ammon, H. L., Bhattacharjee, S. K., Holden, J. R., "Crystallographic Studies of High Density Compounds: 5-Fluoro-2,4,6-Trinitro-1,3-Benzenediamine," Acta Cryst., 1982, B38, 1851.

[7] Pople, J. A., Schneider, W. G., Bernstein, H. J., "High-Resolution Nuclear Magnetic Resonance," (McGraw Hill: New York, 1959), p. 366.

TABLE 2. PHYSICAL PROPERTIES OF F-DATB DERIVATIVES



Compound No.	R	M.P.(^oC)	$\rho o(g/cm^3)$†	I.S.(H_{50}cm)
7	-NHCHO	229	(1.83)	226
8	$-NHCONH_2$	>350	(1.90)	>320
9	$-NHC(NH_2)=N-NO_2$	184	(1.65)	46.6
10	$-NH(CH_2)_2NH-$	305	(1.80)	189
11		295	(1.79)	112
12		>340	(1.82)	118
13		232	(1.76)	55.4
14		230	(1.83)	30.8

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† Values in parentheses are preliminary values determined on a Systems Science and Software (La Jolla, Calif.) 6102-12 gas pycnometer.

Nitroguanidine does not itself react with F-DATB. However, sodium nitroguanide reacts to give 9. Although nitroguanidine is a dense (1.77g/cm^3), insensitive compound, 9 was found to have a disappointingly low density and a rather high impact sensitivity. For this reason no nitroguanidine derivatives of DFP or TFTNB were prepared.

Ethylenediamine and 3,5-diamino-1,2,4-triazole each reacted with two equivalents of F-DATB to give the bis-derivatives 10 and 11 respectively. Both were isolated as fine powders which were difficult to crystallize. Unsuccessful attempts were made to oxidize the methylene groups of 10 to give the oxamide derivative, which might have shown a higher density in addition to having a better oxygen balance. Oxamide itself did not react with F-DATB under a variety of conditions.

The heterocyclic derivatives 12, 13, and 14 were prepared by the reaction of F-DATB with the corresponding heterocyclic amines. The triazole derivative 12 has physical properties which warrant its further evaluation as an explosive. Additional nitrogen-nitrogen linkages in the triazole 13 and the tetrazole 14 impart higher impact sensitivities to these derivatives.

Fluorodinitroethanol and Fluorodinitroethylamine Derivatives

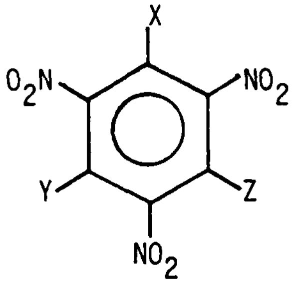
Fluorodinitroethanol[8] and fluorodinitroethylamine[9] derivatives of all three starting compounds (TFTNB, DFP and F-DATB) were prepared because of the energetic nature of these nitrated substituents, and because these series of compounds provide for direct structure-property comparisons. Both the alcohol and the amine reacted via nucleophilic displacement, in the presence of base, with each of the starting compounds to give the derivatives shown in Table 3. all of the derivatives are crystalline solids with moderately high densities. However, the introduction of even one of these substituents (compounds 15 and 18) increases the impact sensitivity rather dramatically relative to F-DATB (Table 1), and two or three substituents result in compounds (16, 17, 19, 20) which are very sensitive.

---

[8] Kamlet, M. J., Adolph, H. G., "Fluoronitroaliphatics. II. Fluoronitromethyl Compounds. Synthetic Approaches and General Properties," J. Org. Chem., 1968, 33, 3073.

[9] Adolph, H. G., Kamlet, M. J., "Fluoronitroaliphatics, IV. Some Reactions of 2-Fluoro-2,2-dinitroethanol," J. Org. Chem., 1969, 34, 45.

TABLE 3. PHYSICAL PROPERTIES OF FLUORODINITROETHANOL AND FLUORODINITROETHYLAMINE DERIVATIVES



Compound No.	Substituents	M.P.(°C)	ρ(g/cm^3)†	I.S.(H_{50}cm)
15	$X=CF(NO_2)_2CH_2O-;Y,Z=NH_2$	190	(1.82)	56.8
16	$X,Y=CF(NO_2)_2CH_2O-;\ Z=NH_2$	140	(1.79)	30.0
17	$X,Y,Z=CF(NO_2)_2CH_2O-$	170	(1.77)	14.9
18	$X=CF(NO_2)_2CH_2NH-;Y,Z=NH_2$	198	(1.82)	49.3
19	$X,Y=CF(NO_2)_2CH_2NH-;\ Z=NH_2$	145	(1.81)	21.2
20	$X,Y,Z=CF(NO_2)_2CH_2NH-$	182	(1.75)	22.0

† See footnote in Table 2.

Cyano, Carboxamido and Carboxy Derivatives

The reaction of potassium cyanide with TFTNB or its amino derivatives results in the formation of complex reaction mixtures of no practical synthetic value. However, cyanotrimethylsilane[10] reacts with F-DATB and DFP in refluxing nitromethane to give the nitrile (21) and the dinitrile (22) respectively in good yields (Table 4). 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 solids were isolated which were formed probably by further reaction of the cyanotrimethylsilane with nitrile groups to give silicon containing products.[10]

The aromatic nitriles 21 and 22 were hydrolyzed by concentrated sulfuric acid to the amides 23 and 24 respectively, and hot 70% aqueous sulfuric acid converted either 21 or 23 to the carboxylic acid (25). The physical properties of compounds 23, 24 and 25 make these candidates for further evaluation as explosives.

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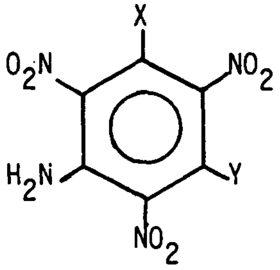
[10] Groutas, W. C., Felker, D., "Synthetic Applications of Cyanotrimethylsilane, Iodotrimethylsilane and Azidotrimethylsilane," Synthesis, 1980, 861.

TABLE 4. PHYSICAL PROPERTIES OF CYANO, CARBOXAMIDO, AND CARBOXY DERIVATIVES OF F-DATB AND DFP



Compound No.	Substituents	M.P.(°C)	$\rho o(g/cm^3)^\dagger$	I.S.(H_{50}cm)
21	X=CN;Y=NH_2	221	(1.83)	184
22	X,Y=CN	179	(1.76)	92.9
23	X=$CONH_2$;Y=NH_2	290	1.887*	221
24	X,Y=$CONH_2$	>340	(1.85)	168
25	X=CO_2H;Y=NH_2	∿240	1.863*	>320

†See footnote in Table 2.

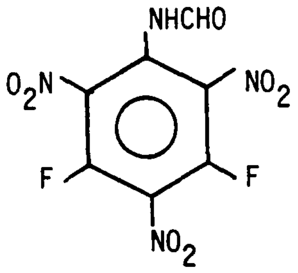
*X-ray diffraction value (Ref. 11 and unpublished data)

Formamido and Ureido Derivatives of TFTNB

As was discussed earlier, TFTNB reacts with excess formamide in refluxing dioxane to give compound 7 (Table 2). Under milder conditions, in refluxing tetrahydrofuran, the mono-and diformamido derivatives of TFTNB, compounds 26 and 27 can be isolated. Similarly, finely powdered urea slowly reacts with TFTNB at ambient temperature in tetrahydrofuran to give the monoureido derivative (28).

---

[11] Ammon, H. L., Bhattacharjee, S. K., "Crystallographic Studies of High-Density Organic Compounds: 3,5-Diamino-2,4,6-Trinitrobenzamide," Acta Cryst., 1982, B38, 2083.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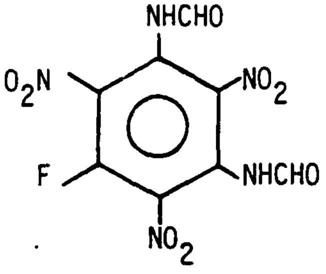
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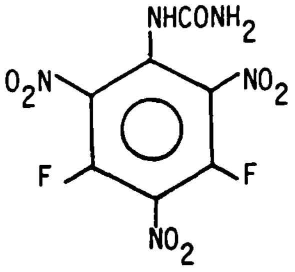
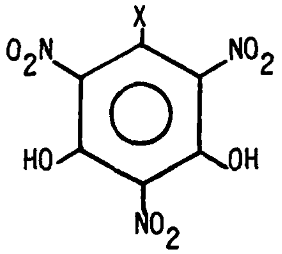

28

Hydroxy Derivatives

Difluoropicramide (DFP) and compounds 26 and 28 were hydrolyzed to the substituted styphnic acids (29), (30) and (31) respectively. The physical properties are reported in Table 5, along with those of diaminopicric acid (DAPA) for comparison. All of these hydroxylated compounds are much more sensitive than the corresponding amino compounds (TATB, 7, and 8). These acids, as their heavy metal salts, may be of interest for evaluation as primary explosives.

TABLE 5. PHYSICAL PROPERTIES OF HYDROXY DERIVATIVES



Compound No.	X	M.P.(^{o}C)	$\rho o(g/cm^3)^{+}$	I.S.(H_{50}cm)
29	$-NH_2$	234	(1.88)	32.4
30	-NHCHO	174	(1.71)	73.8
31	$-NHCONH_2$	164	(1.81)	35.9
DAPA		282	1.890*	112

+See footnote in Table 2.

*X-ray diffraction value[12]

---

[12] Ammon, H. L., Bhattacharjee, S. K., "Crystallographic Studies of High-Density Organic Crystals: 3,5-Diamino-2,4,6-Trinitrophenol," Acta Cryst., 1981, B37, 2082.

SUMMARY AND CONCLUSIONS

This report describes the preparation of a number of trisubstituted trinitrobenzene derivatives which are structurally related to TATB. These compounds were designed to have diversified physical properties and were characterized with respect to their stability, density and impact sensitivity. Several of the compounds investigated show improved impact sensitivity-performance characteristics relative to the standard explosives TNT, comp B, comp A-3, and RDX as shown in Figure 1. These materials parallel to varying extents the important sensitivity characteristics of TATB, and warrant further evaluation to assess their utility as insensitive high explosives.

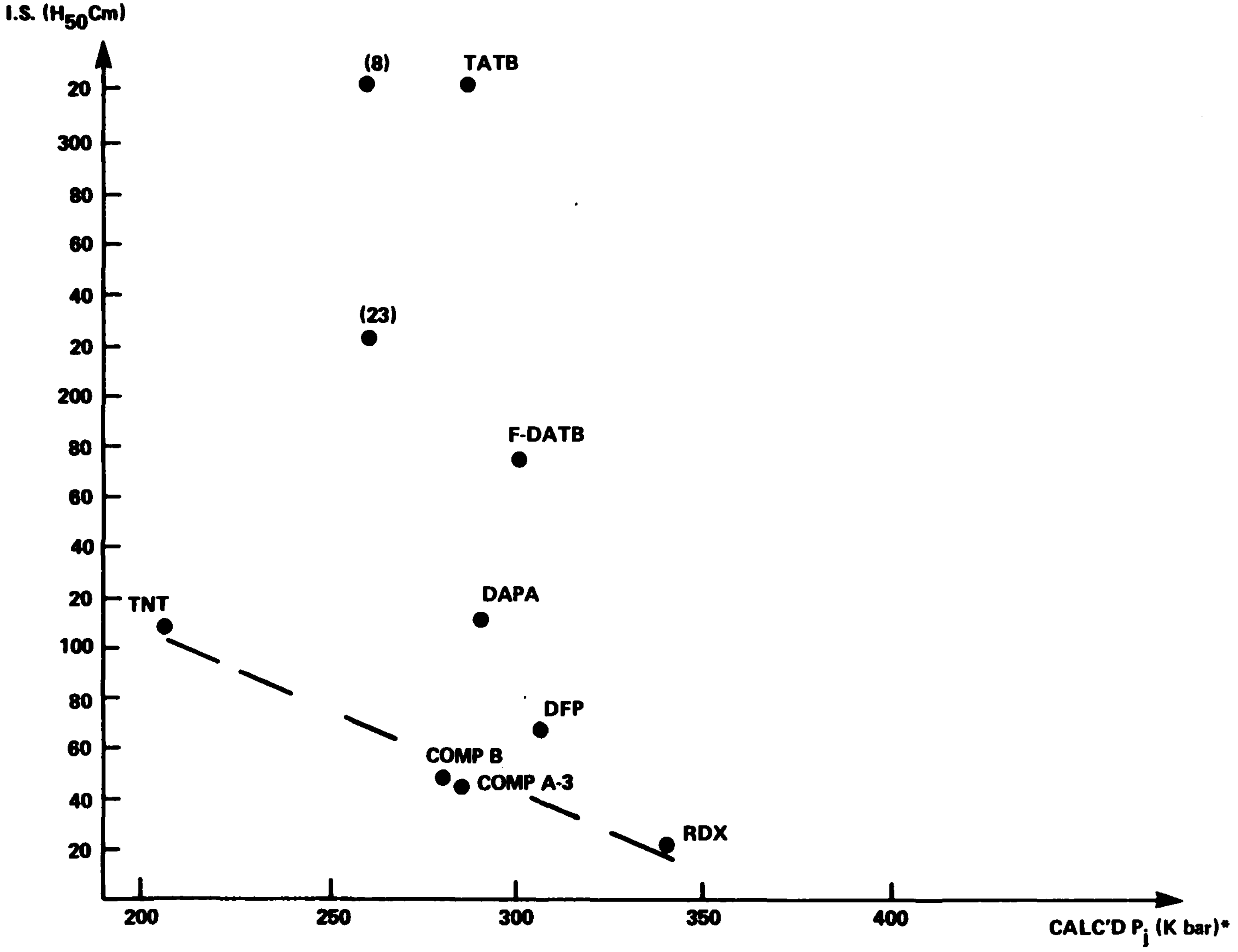


FIGURE 1. IMPACT SENSITIVITY–DETONATION PRESSURE RELATIONSHIPS

*(A) KAMLET, M. J., HURWITZ, H., J. CHEM. PHYS., 1968, 48, 3685.
(B) KAMLET, M. J., DICKINSON, C., J. CHEM. PHYS., 1968, 48, 43.

EXPERIMENTAL

Infrared(IR) spectra were taken on a Perkin-Elmer Model 283 recording spectrophotometer. ^{1}H 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, Tennesee. Melting points were determined on a Thomas-Hoover capillary apparatus and are uncorrected.

N-Acetyl-3,5-difluorotrinitroaniline (3)

A solution of 2 (10.68g, 40 mmol) and acetamide (2.48g, 48 mmol, dried over P_2O_5) in DMF (40 mL) was heated at 85° for 3 h and then poured onto a mixture of ice and H_2O (250 mL). The solid was filtered, dried over P_2O_5, and recrystallized from 1,2-dichloroethane to yield 3 (8.1g, 66.1%) as almost colorless crystals: mp 180-184°C. This material was suitable for hydrolysis to 4.

N, N'-Di-tert-butyl-5-fluorotrinitro-1,3-benzenediamine (5)

A solution of 2-amino-2-methylpropane (4.39g, 60 mmol) in CH_2Cl_2 (200 mL) was added dropwise over 2 h to a stirred mixture of 2 (8.01g, 30 mmol), $NaHCO_3$ (20g, 238 mmol) and CH_2Cl_2 (400 mL) at 0°C. After stirring for an additional 1 h at room temperature, the mixture was filtered and the filtrate was evaporated under vacuum to remove the solvent. The residue was dissolved in benzene (25 mL), placed onto a column of silica gel 60 (200g, EM reagent, 70-230 mesh) and rapidly eluted with benzene. Fractions were not saved until a major yellow band was eluted, which moved down the column fairly rapidly. These fractions were combined, evaporated under vacuum, and the residue was recrystallized twice from hexane (2 x 150 mL) to yield yellow prisms of 5 (7.15g, 63.8%): mp 120-123°C. Another recrystallization gave the analytical sample: mp 126-127°C; mass spectrum (EI) m/z 373 (M, 100) ^{1}H NMR ($CDCl_3$) δ 1.20 (s, 18, $6CH_3$), 5.30 (s, 2, 2NH).

Anal. Calcd for $C_{14}H_{20}FN_5O_6$: C, 45.04; H, 5.40; N, 18.76; F, 5.09. Found: C, 45.24; H, 5.47; N, 18.76; F, 4.95.

5-Fluorotrinitro-1,3-benzenediamine (6)

A suspension of 5 (5.0g, 13.4 mmol) in trifluoroacetic acid (30 mL) was stirred at room temperature for 5 h. Hexane (50 mL) was added and the solid filtered to yield 6 (3.5g, 100%): mp 220-222°C. Recrystallization from 1,2-dichloroethane gave yellow prisms: mp 222-223°C.

N-Formyltrinitro-1,3,5-benzenetriamine (7)

A solution of 2 (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 7 (1.75g, 30.6%) as deep-yellow crystals: mp 220-224°C dec. Recrystallization 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 $\sim$ 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 (8)

A solution of 6 (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 8 (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 (9)

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 6 (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 9 (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 (10)

A mixture of 6 (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 10 (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 (11)

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 6 (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 11 (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 (12)

A mixture of 6 (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 12 (1.94g, quant.). The analytical sample was obtained by recrystallization from DMF-CH_3OH (charcoal): mp > 300°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 (13)

A mixture of 6 (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 13 (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 (14)

A mixture of 6 (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 14 (600mg, 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 (15)

A mixture of 6 (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 15 (1.6g, 67.5%): mp 187-188°C; 'H 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 (16)

A mixture of 4 (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 extracted 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 16 (2.4g, 75.2%): mp 132-136°C. Recrystallization gave the analytical sample: mp 136-138°C; 'H 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 (17)

A mixture of 2 (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 extracted 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 17 (1.9g, 70.9%): mp 172-174°C; 'H NMR (Me_2SO - d_6) δ5.60 (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 (18)

To a suspension of 6 (261 mg, 1 mmol) in CH_2Cl_2 (30 mL) was added pyridine (237 mg, 3 mmol), followed by 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 18 (300 mg, 76.1%) : mp 195°C dec. Recrystallization from 1,2-dichloroethane gave yellow crystals: mp 198°C dec; 'H 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 (19)

To a solution of 4 (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 19 (2.3g, 72.3%): mp 137-141°C dec. Recrystallization from 1,2-dichloroethane-isopropyl ether gave yellow crystals: mp 143-145°C dec. 'H 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 (20)

To a solution of 2 (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 were 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 20 (2.0g, 50%): mp 181-182°C. 'H 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-Diaminotrinitrobenzonitrile (21)

A solution of 6 (5.22g, 20 mmol) and cyanotrimethylsilane (4.96g, 50 mmol) in CH_3NO_2 (100 mL) was refluxed for 2 h and then evaporated under vacuum to leave a solid residue. Recrystallization from CH_3CN (100 mL) gave 21 (4.4g, 82%) as orange-brown crystals: mp 212-217°C dec. Recrystallization gave the analytical sample: mp 220-221°C dec; mass spectrum (CI, CH_4) m/z 269 (M+1, 100).

Anal. Calcd for $C_7H_4N_6O_6$: C, 31.35; H, 1.50; N, 31.34. Found: C, 31.39; H, 1.74; N, 31.19.

5-Aminotrinitroisophthalonitrile (22)

A solution of 4 (5.28g, 20 mmol) and cyanotrimethylsilane (9.92g, 0.1 mol) in CH_3NO_2 (100 mL) was refluxed for 2 h and then evaporated under vacuum to leave a solid residue. The solid was dissolved in hot benzene (200 mL), treated with charcoal, filtered, and the filtrate refrigerated overnight to yield bright orange crystals (solvate complex) which changed to yellow upon drying for several hours in an oven at 80°C. The yield of 22 was 4.65g (83.7%); mp 170-173°C dec. Recrystallization gave the analytical sample: mp 178-179°C dec; mass spectrum (CI, CH_4) m/z 279 (M+1, 100).

Anal. Calcd for $C_8H_2N_6O_6$: C, 34.54; H, 0.72; N, 30.22. Found: C, 34.47; H, 0.69; N, 30.15.

3,5-Diaminotrinitrobenzamide (23)

A mixture of 21 (2.68g, 10 mmol) 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 23 (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 (24)

Similarly, 22 was hydrolyzed to yield 24 (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 (25)

A solution of 21 (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 25 (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, 1.84; N, 24.16.

3,5-Difluorotrinitro-N-formylaniline (26) and 5-Fluorotrinitro-N,N'-diformyl-1,3-benzenediamine (27)

A solution of 2 (2.67g, 0.01 mol) and formamide (4.53g, 0.10 mol, 4 mL) in THF (20 mL) was refluxed for 3 h. TLC (Brinkmann 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 26 (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); 'H 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 27 (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); 'H 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 (28)

A mixture of 2 (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 28 (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 29

To a solution of 4 (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 29 (1.52g, 97.4%): mp 228-230°C dec. Recrystillization from H_2O gave brown-yellow needles: mp 233-234°C dec (lit.[13] 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 (30)

A mixture of 26 (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 'H NMR spectrum (acetone - d_6) showed a mixture of rotational isomer 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.

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[13] Flürscheim, B., Holmes, E. L., J. Chem. Soc., 1928, 3041.

5-Ureidostyphnic Acid (31)

A solution of 28 (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; 'H 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.

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